# Chapter 4

# Quantifying Greenhouse Gas Emissions from Managed and Natural Soils

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## Abstract

Standard methods for quantifying GHG emissions from soils tend to use either micrometeorological or chamber based measurements approaches. The latter is the most widely used technique, since it can be applied at low costs and without power supply at remote sites to allow measurement of GHG exchanges between soils and the atmosphere for field trials. Instrumentation for micrometeorological measurements meanwhile is costly, requires power supply and a minimum of 1 ha homogeneous, flat terrain. In this chapter therefore we mainly discuss the closed chamber methodology for quantifying soil GHG fluxes. We provide detailed guidance on existing measurement protocols and make recommendations for selecting field sites, performing the measurements and strategies to overcome spatial variability of fluxes, and provide knowledge on potential sources of errors that should be avoided. As a specific example for chamber based GHG measurements we discuss sampling and measurement strategies for GHG emissions from rice paddies.

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## 4.1 Introduction

Microbial processes in soils, sediments and organic wastes such as manure are a major source of atmospheric greenhouse gases (GHG). These processes create spatially as well as temporally heterogeneous sources or sinks. Consequently, a thorough understanding of the underlying processes and a quantification of spatio-temporal dynamics of sinks and sources are the bases for a) developing GHG inventories at global, national and regional scales, b) identifying regional hotspots and c) developing strategies for mitigating GHG emissions from terrestrial, specifically agricultural, systems.

At the ecosystem scale, biosphere-atmosphere fluxes of $CO_2$, $CH_4$, and $N_2O$ are bi-directional, i.e. what is observed is a net flux of production and consumption processes (e.g. $CO_2$: photosynthesis and autotrophic and heterotrophic respiration; $CH_4$: methanogenesis and methane oxidation; $N_2O$: nitrification and denitrification as source processes and denitrification as a sink process). The same is true for soil-atmosphere exchange processes, though, with regard to $CO_2$, often only respiratory fluxes are measured.

Approximately 2/3 of all $N_2O$ emissions are linked to soil and manure management (Fowler et al. 2009; IPCC, 2013). For $CH_4$ as well, soils and organic wastes strongly influence atmospheric $CH_4$ concentrations. It is estimated that wetland and paddy soils represent approximately 1/3 of all sources for atmospheric $CH_4$ (Fowler et al. 2009). On the other hand well-aerated soils of natural and semi-natural ecosystems – and to a lesser extent soils of agro-ecosystems - are sinks for atmospheric $CH_4$; removing approximately 20-45 TG $yr^{-1}$ of $CH_4$ from the atmosphere (Dutaur and Verchot, 2007), which corresponds to approximately 6-8% of all sinks for atmospheric $CH_4$ (Fowler et al. 2009). For $CO_2$, soils are a major source due to autotrophic (plant root) and heterotrophic (microbial and soil fauna breakdown of organic matter) respiration. However, at the ecosystem scale, soils can act as net sinks as well as sources for $CO_2$, since at this scale plant primary production ($CO_2$ fixation from the atmosphere by photosynthesis), litter input to soils as well as respiratory fluxes are considered. It is well established that soils to a depth of 1 m globally store approximately 3 times the amount of carbon currently found in the atmosphere (Batjes, 1996; IPCC, 2013). Thus, land use and land management changes, as well as changes in climate affect plant primary production and fluxes of litter to the soil and soil organic matter mineralization dynamics. This can either result in a mobilization of soil C and N stocks, or, with adequate management, turn soils into C sinks. The latter is an essential process for removal of atmospheric $CO_2$ and climate protection and has been called the “recarbonization” of our terrestrial ecosystems (Lal, 2009).

Due to the mostly microbiological origin of soil, sediment and organic waste GHG emissions, changes in environmental conditions directly affect the exchange of GHG between terrestrial systems and the atmosphere (Butterbach-Bahl and Dannenmann, 2011). Changes in

temperature affect enzyme activities, while changes in redox conditions - as influenced by soil aeration fluctuations as a consequence of changes in soil moisture – can favor sequentially different microbial processes. For example, field irrigation and water logging as a standard management for rice paddies, results in anaerobic soil conditions, thereby slowing down and stopping aerobic decomposition processes, while sequentially initializing a series of microbial processes that use other elements and compounds than oxygen as an electron acceptor: first $NO_3^-$ (denitrification), followed by $SO_4^-$ and $Fe^{3+}$ and $Mn^{3+/4+}$ reduction, before finally $CH_4$ is produced as a product of organic matter degradation under strictly anaerobic conditions by methanogens (Conrad, 1996).

Environmental conditions not only change naturally across days, seasons and years as a consequence diurnal and seasonal temperature rainfall regimes, but also due to management of agricultural (forest with regard to plantations) land, as was explained above with the example of flooding of paddy fields. Changes in environmental conditions affect the activity of the microbial community as well as that of plants, and consequently, the associated GHG production and consumption processes. Thus, GHG emissions from soils show a rather pronounced temporal variability on short (diurnal) and longer (days to weeks and years) timescales (e.g. Luo et al. 2012). Moreover, environmental conditions also change on spatial scales because soil conditions, plant cover, land management and thus, nutrient availability, soil aeration and microbial community composition, also change across microscale (e.g. soil matrix) to landscape and continental scales. As a result, GHG fluxes also vary considerably across spatial scales, making it necessary to develop a solid sampling strategy to target measurement sites, i.e. determine which sites are representative for the landscape one would like to work in, for estimating GHG fluxes and develop strategies to mitigate those emissions. Targeting (Chap. 2 of these guidelines) is a cornerstone to allow meaningful upscaling to landscape and higher spatial scales. But targeting already starts at the measurement site, since decisions have to be made where (and when) to place chambers for flux measurements (Fig. 1a).

This chapter does not aim to provide a cookbook of how to measure soil and manure GHG fluxes. Plenty of work has been published on this topic, filling bookshelves and libraries (see e.g. Table 1). Here, we will provide guidance to the relevant literature and highlight potential problems that might come up when designing a GHG measurement program (Fig. 1) rather than be specific and explain the sampling procedures in detail. We also provide examples how to overcome problems in the context of GHG measurements for smallholder systems.

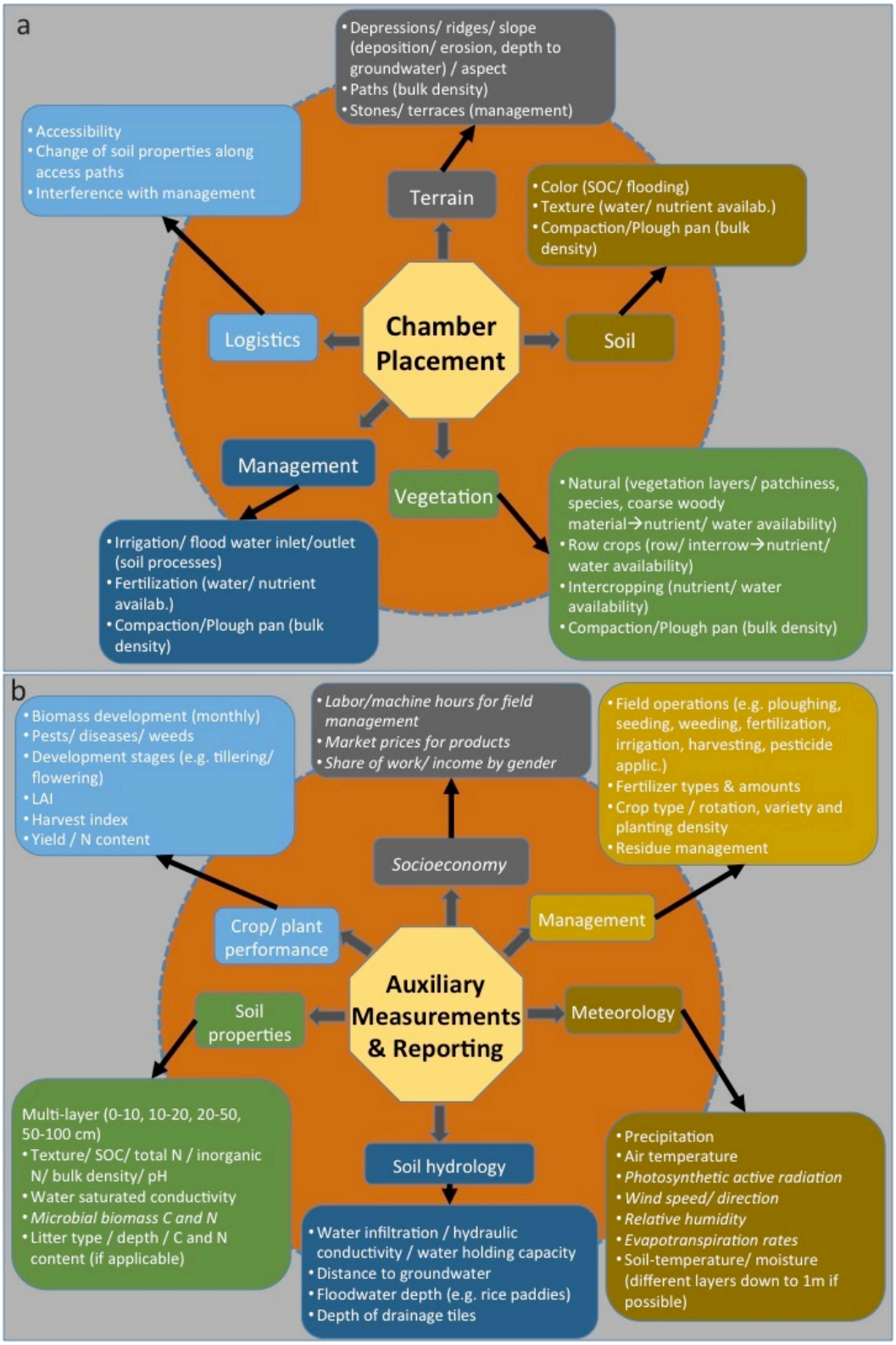


**Figure 1** General recommendations for a) chamber placement, b) measurement of auxiliary parameters (italics indicate additional measurements/ parameters which might be worthwhile to observe)

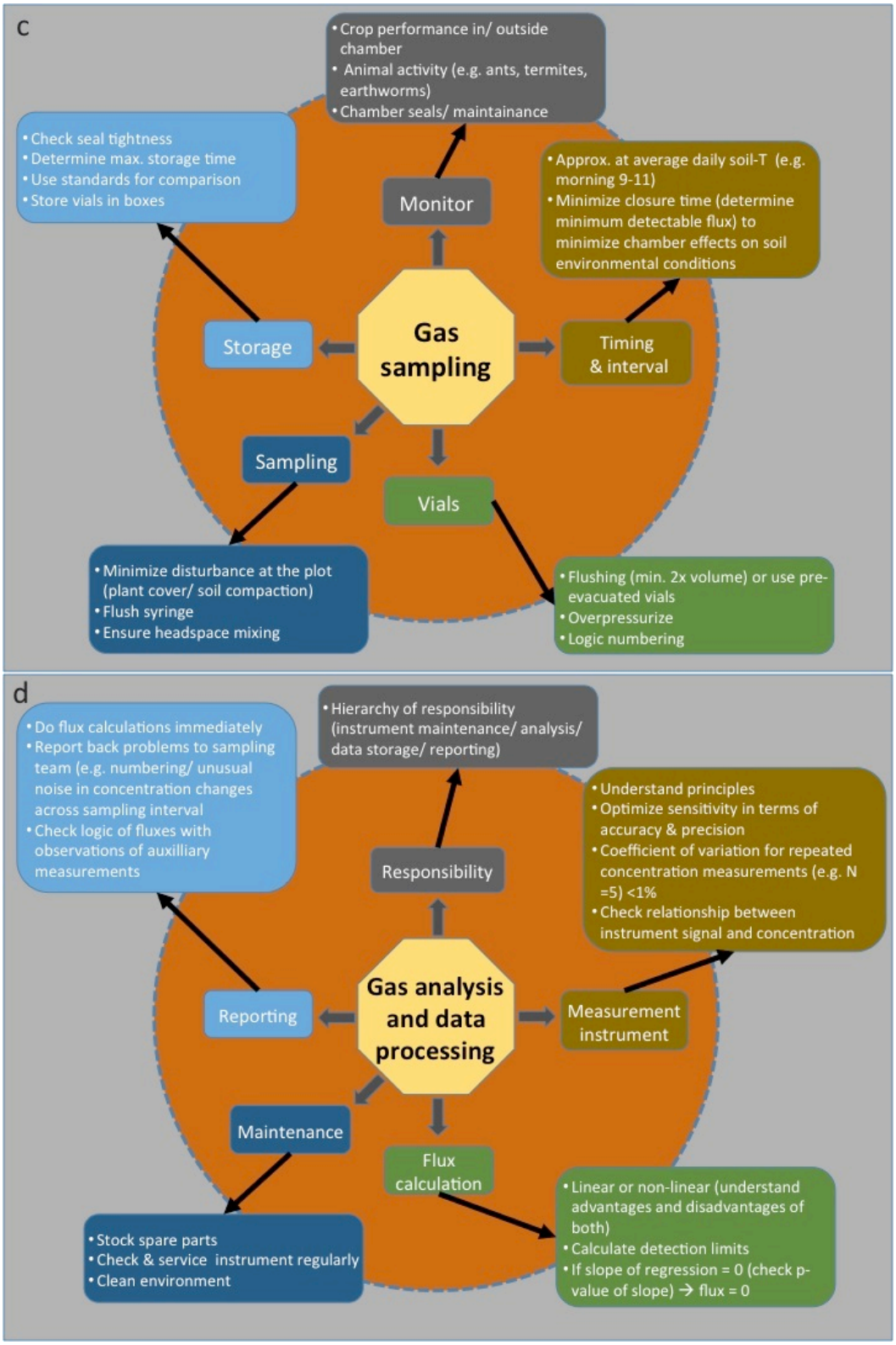


**Figure 4.1** General recommendations for c) gas sampling and d) gas concentration measurements for static chamber soil GHG flux measurements

## 4.2 What technique is most suitable for measuring biosphere-atmosphere exchange processes of GHGs?

The two most commonly used techniques for measuring fluxes between terrestrial ecosystems and the atmosphere are: a) enclosure based (chamber) measurements (manual or automated), and b) micro meteorological measurements (e.g. eddy covariance or gradient methods) or a combination of both (Denmead, 2008). The choice of the measurement technique itself is largely driven by resource investment, demand and by the research question.

### 4.2.1 Micro-Meteorological Measurements

Use of micro-meteorological techniques requires homogenous fields with a significant fetch (>1 hectare) that should not be influenced by buildings, trees, slopes etc. Land use, land management, vegetation and soil properties should be homogenous for the direct fetch area, but also for the wider area. Typically these techniques are applied in flat terrain with large, homogenous land use, such as pasture, grassland, maize or wheat mono-crops, forests, or tree plantations. Capital costs of micro-meteorological measurements of GHG fluxes are high, since the required sensors (3-d wind field, fast-response gas analyzers) plus auxiliary instruments (meteorological station, mast, etc.) for flux measurements at one site, for $CO_2$ and energy fluxes only, cost around 60,000-80,000 USD Adding other components, such as $CH_4$ (open path sensors are available) and $N_2O$ (requiring laser spectroscopy instruments), requires a significant additional investment in instruments (starting from 30,000-40,000 USD per gas). Energy supply for the instruments (if not only focused on open path $CO_2/H_2O/CH_4$ technology) is another constraint that should be considered. The two most prominent global networks for multi-site and multi-species observations of biosphere-atmosphere-exchange of GHG's using micro-meteorological methodologies at least for $CO_2$ fluxes are the National Ecological Observatory Network (NEON) in the USA (http://neoninc.org/) and the Integrated Carbon Observation Network (ICOS) in Europe (http://www.icos-infrastructure.eu/?q=node/17). Both networks offer information, processing tools for calculating fluxes and experts for providing support for designing, establishing and running micrometeorological measurements.

Micro-meteorological techniques for assessing GHG exchange are not recommended for smallholder systems due to the complexity of land uses and land management, small-scale gradients in soil fertility, and complex crop rotations with intercropping (Chikowo et al. 2014).

Some literature for a first reading on micro-meteorological techniques is listed in Table 1.

### 4.2.2 Chamber Measurements

This technique allows measurements of GHG fluxes at fine scales, with chambers usually covering soil areas <1 $m^2$, and are thus much better suited for smallholder farming systems. They can be operated manually or automatically (Breuer et al. 2000). Chamber measurements

are rather simple and therefore the most common approach for GHG measurements since they allow gas samples to be stored for future analysis and, with the exception of automated systems, they do not require power supply at the site. In contrast with micrometeorological approaches, chambers are suitable for exploring treatment effects (e.g. fertilizer and crop trials) or effects of land use, land cover or topography on GHG exchange. However, care must be used in order to obtain accurate data, since installation of the chamber disturbs environmental conditions and measured fluxes might not necessarily reflect fluxes at adjacent sites if some precautions are not considered (see section 5.2.1 below).

There are two types of chambers: dynamic and static chambers. For dynamic chambers the headspace air is exchanged at a high rate (>1-2 times the chambers volume per minute) and fluxes are calculated from the difference in gas concentrations at the inlet and outlet of the chambers multiplied by the gas volume flux, thereby considering the area which is covered by the chamber (Butterbach-Bahl et al. 1997). Static chambers are gas-tight, without forced exchange of the headspace gas volume, and are usually vented to allow pressure equalization between the chamber's headspace and the ambient air pressure (e.g. Xu et al. 2006). The volume of the "vent tube" should be greater than the gas volume taken at each sampling time.

Two situations call for using dynamic chambers: first, when measuring reactive gas fluxes such as soil NO emissions, and when there is a need to minimize the bias of changes in headspace air concentrations on the flux (Butterbach-Bahl et al. 1997). The second point is important, as significant deviations of chamber headspace gas concentrations from ambient air concentrations affect the exchange process between soils and the atmosphere itself, since the flux at the soil-atmosphere interface is the result of simultaneous production and consumption processes. For example, if $N_2O$ concentration in the chamber headspace is much higher than atmospheric concentrations, microbial consumption processes are stimulated. Moreover, since emissions are mainly driven by diffusion and gas concentration gradients, significant increases/decreases in headspace concentrations of the gas of interest will slow down/accelerate the diffusive flux. Both mechanisms finally result in a deviation of the flux magnitude from undisturbed conditions (Hutchinson and Mosier 1981). It is important to be aware of this, though for practical reasons it is partly unavoidable because the precision of the analytical instruments used for gas flux measurements, such as electron capture detectors and gas chromatography, is insufficient to allow for dynamic chamber measurements. However, there are methods to cope with this problem, such as using non-linear instead of linear models to calculate fluxes as measured with static chamber technique (e.g. Kroon et al. 2008; Table 1), using quantum cascade lasers in the field (fast box; Hensen et al. 2006) and in general by minimizing chamber closure time as much as possible. Chamber closure time is affected not only by the magnitude of the gas flux but also by the chamber height. Therefore, in agricultural systems where plants need to be included for representative measurements, it is suggested to

use chambers which can be extended by sections according to plant growth (Barton et al. 2007).

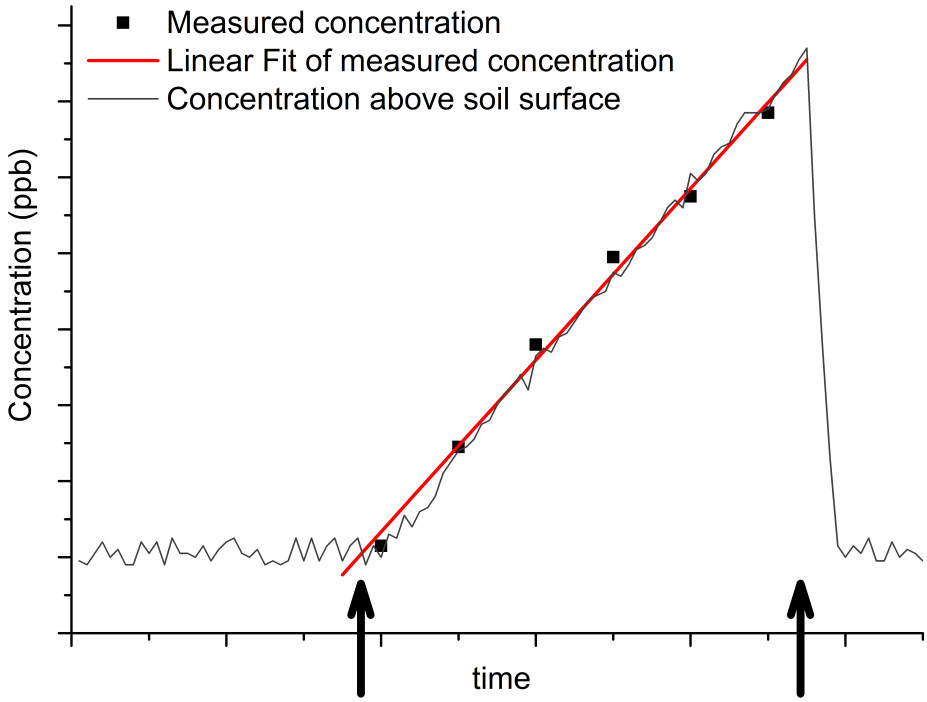


**Figure 4.2** Theoretical evolution of the concentration of a gas being emitted from the soil upon use of a static chamber. Concentration of the gas above the soil surface (black line) remains at a relatively constant level; at the moment when the chamber is closed (left arrow), the concentration in its headspace begins to rise. Along the closing period of the chamber, several gas samples are taken (black squares) and subsequently the concentration is determined, e.g. by use of gas chromatography. Right after opening the chamber (right arrow) concentration above soil surface returns to atmospheric background levels. Soil GHG emissions are most commonly calculated from the linear increase of the headspace gas concentration during the chamber closing period (red line), the volume of the chamber, the area of the soil covered by the chamber, as well as air temperature, air pressure and molecular weight of the molecule under investigation (see e.g. Butterbach-Bahl et al. 2011). It should be noted, that changes in gas concentration upon chamber closure can significantly deviate from linearity, showing e.g. saturation effects. In all cases it should be tested if non-linear flux calculation methods to not fit better observed changes in chamber headspace concentrations with time (see e.g. Pedersen et al. 2010).

Static chamber are usually mounted on a frame – which should be inserted (approximately 0.02-0.15 m) at least a week before first flux measurements to overcome initial disturbances of soil environmental conditions due to the insertion of the frame. Once the chamber is closed gas-tight on the frame, headspace concentrations start to change, either increasing if the soil is

a net source (e.g. for $CO_2$ - Fig. 2), or decreasing if the soil is functioning as a net sink (e.g. $CH_4$ uptake by upland soils). For accurate calculation of gas flux a minimum of four gas samples from the chamber headspace across the sampling interval (e.g. 0, 10, 20, 30 min following closure) is recommended (Rochette 2011).

Gas flux measurements with static and dynamic chambers have often been described and Table 1 provides an overview of recommended literature, while Fig. 1 indicates important considerations when using chamber methodology. Static chambers can not only be used for measurement of soil $N_2O$ and $CH_4$ and $CO_2$ respiratory fluxes, but also for measuring net ecosystem exchange of carbon dioxide. The latter requires the use of transparent chambers and consideration of corrections for photosynthetic active radiation and temperature inside and outside the chamber (Wang et al. 2013).

***Chambers and changes in environmental conditions*** Closing a chamber gas-tight from the surrounding environment immediately affects a number of boundary conditions. The pressure inside the chamber might differ from the outside, because when chambers are gas-tight and exposed to sunlight, the temperature of the headspace air increases so that air pressure insight the chamber increases too. Both factors affect the gas exchange between the soil and the air. Thus, chambers should be heat insulated and opaque (except for the determination of net ecosystem respiration; see. Zheng et al. 2008) and a vent should be used (see Hutchinson and Livingston, 2001) to equilibrate pressure differences between ambient and headspace air. Upon chamber closure of transparent non-insulated chambers exposed to direct sunlight headspace temperature might increase by 10-20 °C within 20 min. Insulated chambers will also show a slight increase in soil headspace temperature. This affects microbial as well as plant respiratory activity. Therefore, minimizing closure times is necessary not only to minimize the effects of changing headspace gas concentrations on diffusive fluxes as described above, but to minimize temperature changes as well as (Table 1). One should therefore calculate the minimum flux that can be detected with the analytical instrument to be used and adjust the closure time accordingly. If possible, limit closure time to a maximum of 30-45 min. If automated chamber systems are used, change positions weekly or at 2-week intervals to minimize effects on soil environmental conditions, in particular soil moisture. Chambers have been shown to reduce soil moisture even if they open automatically during rainfall, (Yao et al. 2009).

***Chambers and spatial variability of GHG fluxes*** Soil environmental conditions change on a small scale due to differences in a) bulk density resulting from machine use or livestock grazing, b) texture as a consequence of soil genesis, c) management (rows, interrows, cropping), d) temperature (plant shading), e) soil moisture (e.g. groundwater distances or as an effect of texture differences), f) soil organic carbon (heterogenous distribution of harvest residues) or g) rooting depth and distribution (with effects on soil microbial diversity, activity and distribution)

(see Fig. 1a). For example, urine or feces dropping by livestock on rangeland or manure application to cropland has been shown to increase spatial and temporal variability of fluxes, since at plot scale not every patch responds equally to increased availability of substrate for microbial N and C turnover processes due to small scale differences in soil properties, soil environmental conditions and microbial activity and diversity. Overcoming spatial variability effects on GHG fluxes is a major challenge, specifically for highly diverse smallholder systems. The problem can be addressed by proper sampling design (Fig. 1) (see e.g. Davidson et al. 2002) or by using the gas pooling technique (Arias-Navarro et al. 2013) (Fig. 3).

Proper sampling design in this context requires firstly that the landscape should be stratified into a number of separate categories. This stratification needs to include geophysical information as well as management activities. Also, in order to understand the drivers of the management decisions, it is critical to collect the political and socio-economic climate of the various farms. The sampling approach can then concentrate measurement activities on emission hotspot and leverage points to capture heterogeneity and account for the diversity and complexity of farming activities (Rosenstock et al. 2013)

The gas pooling technique is similar to what is usually done for soil or water analyses. The principal idea of gas pooling is to generate a composite air sample out of the headspace of several chambers (Fig. 3). The chamber headspace is sampled at least 4 times across the closure period as is usually done, but gas samples at time 0, 10, 20, or 30 min are combined for several chambers for each individual sampling time (Arias-Navarro et al. 2013). As a consequence, information on the spatial variability is lost, but can be regained if on some sampling days fluxes of the chambers are measured individually. This technique allows installation of a significantly higher number of chambers without increasing the amount of gas samples to be analyzed.

**Table 4.1** Literature overview on published protocols and recommendations for soil-atmosphere GHG measurements with emphasis on the static chamber methodology (*recommended reading)

| Topic | Specialization | Methods | Highlight | Reference |
|---|---|---|---|---|
| *General overviews on methodology* | | | | |
| Measuring biosphere-atmosphere exchange of $CH_4$ and $N_2O$ | Overview on measuring techniques | Theoretical and practical information on measurements | Very good overview on measuring techniques | Denmead 2008* |
| Rice paddies/ wetlands/uplands | $CH_4$ flux measurement methods | Overview of techniques | Overview on $CH_4$ measuring techniques (micromet, chambers) | Schütz and Seiler 1992 |
| $CH_4$ and $N_2O$ fluxes from livestock systems | Review | Description of approaches and underlying mechanisms | Review, incl. processes, methodology | Kebreab et al. 2006 |
| Overview on measuring techniques with focus on static chambers flux measurements | Overview on techniques | Provides practical guidance on measuring soil GHG fluxes | Overview on methodologies and short-comes | Butterbach-Bahl et al. 2011 |
| Quality assurance for static chamber measurements | Quality assurance | Minimum set of criteria for static chamber design and deployment methodology | Confidence in the absolute flux values reported in about 60% of the studies was estimated to be very low due to poor methodologies or incomplete reporting | Rochette and Eriksen-Hamel 2007* |
| Micrometeorological measurements of $N_2O$, $CO_2$, $CH_4$ | Micro-meteorology | Description of procedures | Theory and application of micrometeorological measurements of GHG fluxes from agricultural fields | Pattey et al. 2006 |
| *Chamber measurement protocols* | | | | |
| Protocol for soil $N_2O$ flux measurements | Detailed description of all steps for soil gas flux measurements | Static chamber, focus on $N_2O$ | Detailed step by step description of procedures | De Klein and Harvey 2012* |
| Protocol for measurements of $N_2O$ and $CH_4$ fluxes from agricultural sources | Wide range of different techniques | Good overview about micro-meteorological and chamber techniques, incl. techniques to measure CH4 emissions from ruminants | Standard text book on method to measure agricultural GHG fluxes for reference | IAEA 1992 |
| Protocol for chamber | Focus on chamber | Provides overview on | Standard protocol for the USDA-ARS GRACEnet | Parkin and Venterea |

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| measurements | based flux measurements of $N_2O$, $CH_4$, $CO_2$ | calculations and practical recommendations for measurements | project | 2010* |
| Protocol for chamber measurements in rice paddies | $CH_4$ fluxes from rice paddies | Sampling times and dates across the rice growing season | Simplified measuring protocol for $CH_4$ fluxes from rice paddies to minimize number of measurements | Buendia et al. 1998 |
| Protocol for soil $N_2O$ flux measurements | Description of protocols for $N_2O$ measurements | Overview on static chamber methodology with focus on $N_2O$ | Discusses potential errors when installing static chambers and provides minimum requirements for using these chambers | Rochette 2011 |
| Common practices for manual GHG sampling | Literature review on protocols as being practised | Static closed chamber | Most widely used methodological features of manual GHG sampling identified | Sander et al. 2014b |
| Protocol for gas pooling technique for static chamber measurements | Gas pooling technique | Overcoming spatial heterogeneity with static chambers | Pooling of gas samples across individual chambers is an acceptable approach to integrate spatial heterogeneity | Arias-Navarro et al. 2013 |
| *Flux calculation for static chamber technique* | | | | |
| Flux calculation | Non-linear versus linear calculation methods for soil $N_2O$ fluxes | Static chamber | Linear calculation schemes are likely more robust to relative differences in fluxes | Venterea et al. 2009* |
| Flux calculation | Diffusion model | Static chamber | Common measurement practices and flux calculations underestimate emission rates by 15-25% under most circumstances. Error dependent on chamber height, soil air porosity and flux calculation method | Livingston et al. 2005* |
| Flux calculation | Flux correction for static chamber measurements of $N_2O$ and $CO_2$ fluxes | Static chambers | Correction scheme for estimating the magnitude of flux underestimation arising from chamber deployment | Venterea et al. 2010 |
| Flux calculation | Flux correction | Static chambers | The systematic error due to linear regression is of the same order as the estimated uncertainty due to temporal variation | Kroon et al. 2008 |
| Flux calculation | Flux correction | Static chamber | Linear versus non-linear, provides link to free R software download for flux calculation | Pedersen et al. 2010* |
| Flux calculation | Flux correction | Static chambers | Significant underestimation of soil $CO_2$ flux strength if linear regression is applied | Kutzbach et al. 2007 |
| Flux calculation | Theoretical evaluation | Static chamber | Measurement and simulation of measuring errors | Hutchinson and Rochette 2003 |
| Static chamber $N_2O$ | Headspace $N_2O$ | Changes in soil gas | Increased headspace concentration of $N_2O$ | Conen and Smith 2000 |

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| fluxes | increase | concentrations upon chamber closure | reduced effective efflux of $N_2O$ from the soil | |
| *Chamber design and comparison of methods* | | | | |
| Comparison of chamber designs and flux calculation | Linear versus non-linear flux calculation | Static chamber comparison | Increasing chamber height, area and volume significantly reduces flux underestimation | Pihlatie et al. 2012 |
| Chamber measurements of $N_2O$ fluxes from soils | Focus on soil $N_2O$ fluxes | Closed and dynamic chambers | Comparison of different chamber types (sizes) with eddy covariance fluxes | Smith et al. 1996 |
| Static chamber design | Soil $N_2O$ fluxes | Recommendations for chamber and vent design and flux calculation method | Vent dimension effects N2O fluxes. One of the first papers on chamber design, flux calculations and venting | Hutchinson and Mosier 1981 |
| *Venting of static chambers* | | | | |
| Venting of closed chambers | Comparison of vented versus non-vented chambers | Closed chamber $N_2O$ fluxes | Venting can create larger errors than the ones it is supposed to overcome | Conen and Smith 1998 |
| Venting of closed chambers | Comparison of vented versus non-vented chambers | Closed chamber $CO_2$ fluxes for forest soils | Increases of $CO_2$ fluxes exceeding a factor of 2 in response to wind events for vented chambers | Bain et al. 2005 |
| Venting of closed chambers | Vent design | Closed chambers | Presenting a new vent design to avoid overestimation of $CO_2$ fluxes under windy conditions due to the Venturi effect | Xu et al. 2006 |
| Venting of closed chambers | Vent design and seals | Closed chambers | Discussion on the necessity of vents and of appropriate flux calculation | Hutchinson and Livingston 2001 |
| *Chambers and small scale variability of fluxes* | | | | |
| Chambers and small scale heterogeneity of soil properties | Effect of soil physical characteristics on fluxes | Flux calculation methods in dependence of soil properties | Re-iterates effects of non-steady soil conditions on errors while measuring fluxes with chambers | Venterea and Baker 2008 |
| Static chamber measurements of soil $CO_2$ fluxes | Spatial heterogeneity, flux calculation | Frequency of sampling and number of chambers for overcoming spatial heterogeneity | Means of eight randomly chosen flux measurements from a population of 36 measurements made with 300 cm2 diameter chamber were within 25% of full population mean 98% of the time and were within 10% of the full population mean 70% of the time | Davidson et al. 2002 |
| Protocol for gas pooling technique for static chamber measurements | Gas pooling technique | Overcoming spatial heterogeneity with static chambers | Pooling of gas samples across individual chambers is an acceptable approach to integrate spatial heterogeneity | Arias-Navarro et al. 2013 |
| *Timing of measurements, sampling frequency and cumulative fluxes* | | | | |

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| Sampling frequency and $N_2O$ flux estimates | Comparison of auto-chambers with replicated manual chambers | Evaluating the importance of sampling time | Auto-chambers are useful if significant diurnal fluctuations in temperature are expected and for better quantifying fertilization emission pulses | Smith and Dobbie 2001 |
| Sampling frequency and $N_2O$ flux estimates | Automated measuring system | Effect of sampling frequency on estimates of cumulative fluxes | Sampling once every 21d yielded estimates within -40% to +60% of the actual cumulative flux | Parkin 2008 |
| Sampling frequency and $N_2O$ flux estimates | Automated measuring system | Evaluation of effects of sampling frequency on flux estimates | Low frequency measurements might lead to annual estimates which differ widely from continuous, automated flux measurements (e.g. 1 week = -5 - +20%) | Liu et al. 2010 |
| Static chamber measurements | Comparison of flux estimates by automated and manual chambers | Chamber effects on soil environmental conditions | Seasonal cumulative $N_2O$ and $CH_4$ fluxes as measured by manual chambers on daily basis were overestimated 18% and 31%, since diurnal variation in fluxes were not accounted for. On the other side, automated chambers reduced soil moisture. To avoid this, change of chamber positions is recommended | Yao et al. 2009 |
| $CH_4$ and $N_2O$ flux measurements from manure slurry storage system | Comparison of continuous and non-continuous flux measurements | Recommendations of sampling intervals and timing of measurements | For $CH_4$, sampling between 1800 and 0800h at intervals <7d yielded ±10% deviation for $N_2O$ was 50% when sampling at 2000h | Wood et al. 2013 |

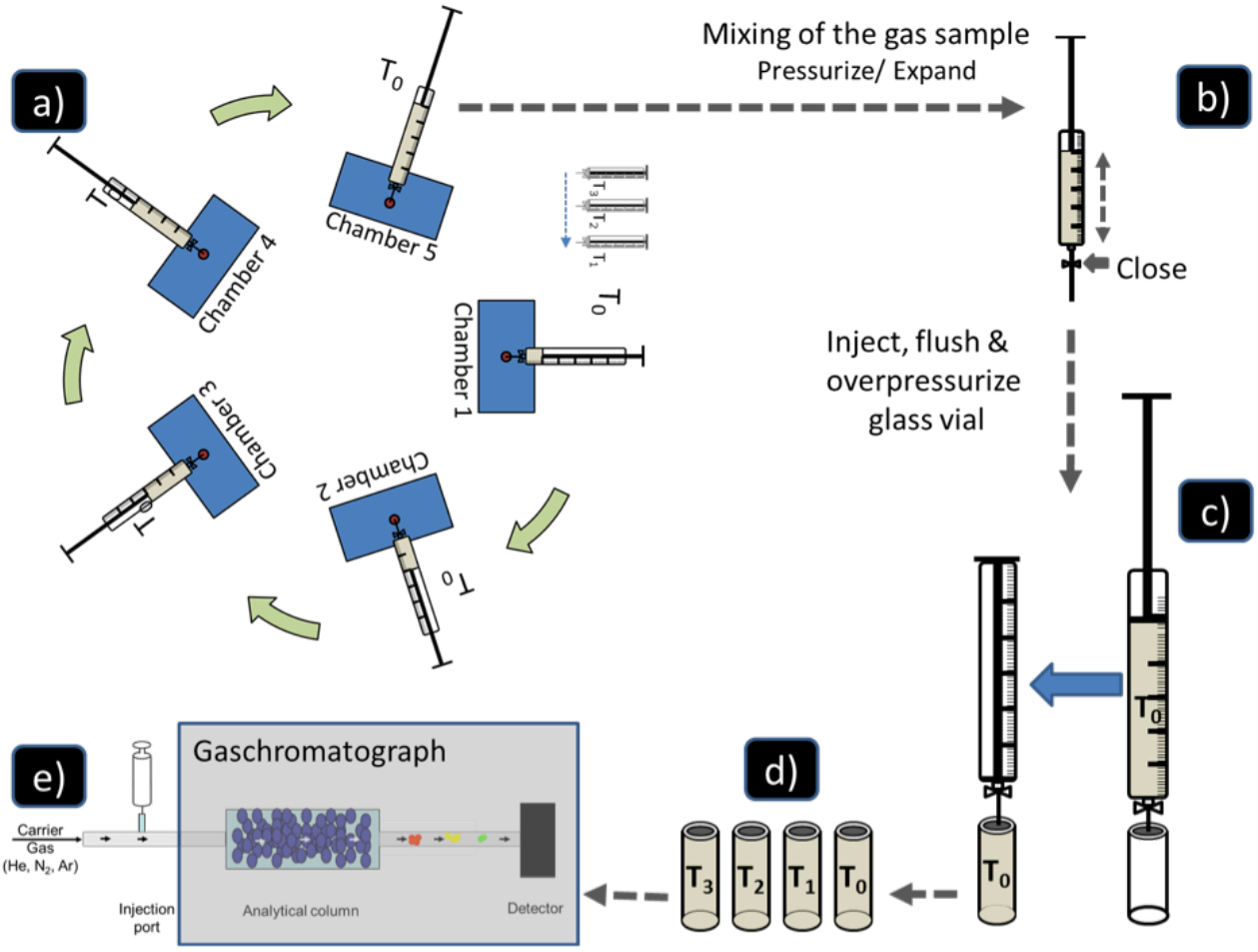


**Figure 4.3** The concept of gas pooling. a) Gas pooling across chambers for a given sampling time, b) gas sample mixing within the syringe, c) transfer of the gas sample to a vial, d) 4 vials for four sampling times and 5 chambers, e) air sample analysis via gas chromatography (for further details see Arias-Navarro et al. 2013)

## 4.3 Measurement of GHG fluxes in rice paddies

Due to its importance as a source for atmospheric $CH_4$ we specifically discuss measurements of GHG fluxes in rice paddies in more detail. Unlike other field crops, rice is usually grown in flooded fields. The standing water creates anaerobic conditions in the soil that allows growth of a certain class of microorganisms (*methanogenic archaea*) that use simple carbon compounds (e.g. $CO_2$ or acetate) as electron donors and produce methane in anaerobic respiration. Methane oxidation, on the other hand, does occur but only in the uppermost mm of flooded paddy soil or in the rhizosphere – due to radial $O_2$ losses of rice roots (Butterbach-Bahl et al. 1997) - and during un-flooded periods. Since methanogenic archaea are extremely sensitive to oxygen and immediately stop $CH_4$ production while stimulating $CH_4$ oxidation, drainage of rice fields is an attractive mitigation option.

Methane is the most important GHG in rice production systems and has some implications on the chamber design and sampling time. Nitrous oxide emissions are generally low in flooded fields but increase with drainage. However, this increase in $N_2O$ emissions does not off-set the mitigation effect that dry field conditions have on $CH_4$ emissions (Sander et al. 2014a).

Overall, requirements for GHG measurements of flooded rice production systems (dominated by $CH_4$ emissions) are partly different from measurement at upland systems, which has some important implications on the chamber design and general sampling procedure (Table 2).

### 4.3.1 Rice chamber design and general procedure

*(see also Table 2)*

Methane that is produced in the soil has three different emission pathways to the atmosphere: 1) diffusion through the water layer, 2) ebullition (bubbling) and 3) transport through the arenchyma of the rice plants. The largest share of emitted methane (up to 90%) is in fact transported through the rice plant itself (Wassmann et al. 1996; Butterbach-Bahl et al. 1997), which makes it indispensable to include rice plants into the closed chamber (→ chamber height >1m). This also applies to any measurements of wetland GHG fluxes, since plant-mediated transport is of critical importance here as well). The chamber base (the part of the chamber that remains in the soil during the whole growing season) should be installed at least one day (better a week or more) before the start of the sampling campaign and should not be higher than ~20cm (with 10 cm below and 10 cm above soil surface) in order to minimize an effect on plant growth. To account for variability within the field, each chamber should include at least 4 rice plants or 4 'hills' in a transplanted system and an area of average plant density in a seeded system, resulting in a chamber area of $\geqslant 0.16 m^2$. Note that due to the flooded field conditions, the chamber base in rice systems should have holes (~2cm above soil surface) to allow water exchange between the chamber inside and the field. This hole or holes must be closed before sampling in case irrigation water level falls and the hole(s) is above the water layer.

Movement in the wet paddy soil can potentially cause gas bubbles to evolve and impede undisturbed gas sampling. Therefore, installation of boardwalks in the field is highly recommended. Exposure to high air temperatures and high solar radiation often characterize rice paddies and so it is in particular crucial to ensure that the plants inside the chambers are not damaged by heat stress during sampling. Therefore, the chamber material should be reflective or white or the chamber should be equipped with proper insulation. Since the gas volume in the closed chamber changes due to temperature increase and samples being taken, chambers should have a vent to allow equilibration with outside air pressure.

### 4.3.2 Time of day of sampling

Methane emissions typically follow a distinct diurnal variation following changes in soil temperature (Neue et al. 1997), i.e. low emissions during night time that increase after sunrise, peak around noon to early afternoon and decrease again thereafter. Therefore the timing of gas sampling is of great importance in order to measure as close as possible at a time representing a daily average flux rather than at times leading to over or underestimation of fluxes. Minamikawa et al. (2012) found that methane fluxes around 10 a.m. were closest to the daily mean $CH_4$ flux in temperate regions. Similar assumptions are likely valid for tropical and subtropical regions. However, we recommend measuring region-

specific diurnal emission patterns at least three times during the growing season of rice and based on the observed diurnal patter to decide on the best sampling time. Alternatively, measuring diurnal soil temperature profiles at 5-cm depth can provide reasonable estimations of the time of day with mean methane emission as soil temperature and $CH_4$ flux are closely related.

**Table 2** Overview of recommended minimum requirements for closed chamber sampling in rice paddy and for measurements of field GHG fluxes from upland arable fields

| Feature | Minimum requirement/ recommendation | |
|---|---|---|
| | **Rice paddy** | **Arable field** |
| Chamber dimension | 4 rice hills included, ≥0.16m$^2$, >1m height *or* extendable, chamber base ~20cm high | Height 10-40 cm (flexible height if possible), insertion depth 5-20 cm, minimum area 0.04 m$^2$. Include plants as long as possible, consider row/ interrow effects |
| Chamber material | Reflective *or* white *and/or* insulated | Opaque, insolated (use transparent material only if NEE should be measured) |
| Chamber equipment | Thermometer, fan, sampling port, hole f. irrigation water, vent | Thermometer, fan, vent |
| Frequency | Once per week *or* elaborated flexible schedule. | Once per week, following the first 10 days after fertilization or re-wetting of dried soils if possible daily measurements |
| Length of measuring period | One year | One year |
| Spatial replicates | At least 3, possibly use gas pooling technique | At least 3, possibly use gas pooling technique |
| Time of day | At time of approx. average daily soil temperature (often mid morning). Record diurnal flux variation from time to time | record diurnal flux variation |
| Closure time | As short as possible, as long as necessary, In hot environments 20-30min, not more than 45min | As short as possible, as long as necessary, In hot environments 20-30min, not more than 45min |
| Number of gas samples for flux calculation | ≥4 per deployment | ≥4 per deployment |

These recommendations have been synthesized from prior chamber measurement protocols (see Table 1) and amended or modified on basis of expert judgments. For further details see also Fig. 1.

### 4.3.3 Sampling frequency

The precision of cumulative seasonal GHG emissions largely depends on the sampling frequency. Minamikawa et al. (2012) found that sampling once a week for flooded rice in temperate regions results to an accurate estimation of total emissions. Buendia et al. (1998) proposed a more flexible sampling schedule of 10-day intervals in the beginning of the growing season, 20-day intervals in the middle and 7-day intervals at the end of the season in tropic environments and came up with similarly accurate seasonal emission estimates.

It is important to note that more frequent sampling is necessary during dry periods of rice cultivation as methane emissions from paddy soils with a high clay content show a sharp peak when drainage is applied (Lu et al. 2000) and nitrous oxide emissions increase during

dry periods (Jiao et al. 2006). In order to have complete flux information of an area, some gas samples should also be taken between two cropping seasons.

## 4.4 Analytical Instruments Used for Chamber Measurements

When using the static chamber approach, several analytical instruments can be used for determining GHG concentrations in the sample air, either directly in the field or, following storage of headspace gas samples in vials or gas-tight syringes, at a later time in the laboratory. The latter always requires that the gas-tightness of the vials/ syringes is tested regularly.

### 4.4.1 Gas chromatography

Instruments used for gas sample analysis rely on different operational principles. Gas chromatography (GC) is the most commonly used analytical technique when determining GHG concentrations in gas samples from chambers (e.g. Keller et al 1986; Kiese and Butterbach-Bahl K 2002; Kelliher et al. 2012). Usually, 1-3 ml of air sample is injected into the gas chromatograph and the different compounds are separated on an analytical column (e.g. Hayesep N for $N_2O$, 3 m, 1/8") for detection with various detectors. For $N_2O$ commonly a $^{63}Ni$ electron capture detector (ECD) is used. Please note that the ECD should be operated at between 330-350°C, since the $N_2O$ sensitivity is highest and the cross-sensitivity to $CO_2$ is lowest in this range. However, there is still a cross-sensitivity to $CO_2$ if $N_2$ is used as sole carrier and purge gas (Zheng et al. Wang et al. 2010). No cross sensitivity exits if Argon/$CH_4$ is used as carrier gas or if the ECD cell is purged with a gas mixture of 5% $CO_2$ in $N_2$ (Wang et al. 2010). Another possibility to eliminate the cross-sensitivity of $N_2O$ and $CO_2$ is to use a pre-column filled with Ascarite (coated NaOH), which scrapes the $CO_2$ from the gas-stream. However, pre-columns need to be changed frequently (approximately 2 week intervals) due to saturation and capturing of air sample moisture.

Another critical point is that if gas chromatographs with ECD are used for concentration measurements, the signal to concentration ratio might deviate from a linear response if – in the case of $N_2O$ – sample air concentrations are significantly >700 ppbv. Therefore, a check of the linearity of the signal to concentration ratio should be done for each instrument and gas under consideration.

For $CH_4$ a flame ionization detector (FID) is normally used and, if a methanizer is introduced before the detector, $CO_2$ can also be measured with a FID (or more standard: use of a thermal conductivity detector for $CO_2$).

### 4.4.2 Spectroscopic Methods

Spectroscopic methods are becoming more and more prominent for measuring GHG fluxes between soils and the atmosphere by static chamber technique. A specific example is the photo-acoustic spectroscopy (PAS), with instruments being miniaturized to make them suitable for direct field use, e.g. allowing direct measurements of changes in chamber headspace $N_2O$, $CH_4$ or $CO_2$ concentration with time following chamber closure (e.g. Leytem et al 2011). PAS technique, as every spectroscopic method, is based on the principle that

GHGs absorb light at a specific wavelength, here in the infrared spectra. The absorption is thereby directly linked to the concentration (Beer-Lambert law) and in the case of PAS, the absorption of the light or energy is converted to an acoustic signal, which is measured by a microphone. For chamber measurements in the field, the PAS instrument is usually connected to the chamber in a closed loop so that the air from the apparatus exhaust is returned to the chamber avoiding under-pressure or dilution.

PAS instruments are becoming popular as an alternative to GC-technique due to portability, low maintenance, and ease-of-operation (Iqbal et al 2012). In principle, commercially available PAS instruments, such as INNOVA (Lumasense Technologies) require only a yearly calibration only and are “plug-and-play” instruments ready to be used in the field. However, because GHGs and water vapor have multiple absorption bands across the measuring spectra, such instruments are prone to interferences. Recently, Rosenstock et al. (2013) showed that for INNOVA instruments $N_2O$ concentration measurements were non-linearly affected by water content and $CO_2$. Comparable results were already reported by Flechard et al. (2005), though only a few researchers have noted the problems that might be associated with the use of PAS. The manufacturers claim that the INNOVA software accounts for cross interferences, but corrections do not seem to work sufficiently while testing several instruments (Rosenstock et al. 2013). Furthermore, there is also evidence that ambient air temperature affects the electronics and thus, the reliability of measured GHG concentrations (Rosenstock et al 2013), when using PAS under field conditions. Specifically for $N_2O$, measured concentrations varied up to 100% depending on environmental conditions (Rosenstock et al. 2013). Also the precision and accuracy of $CH_4$ measurements seems to be rather low, with deviations in concentration of nearly 400 % for calibration gases (Rosenstock et al. 2013). As it stands now, it is advisable to question the use of INNOVA instruments for $CH_4$ as well as for $N_2O$ measurements in particular by using the instrument for simultaneous measurements of multiple gas species.

Other techniques may include tunable diode lasers (TDL), quantum cascade lasers (QCL), Fourier transform infrared spectroscopy (FTIR) or cavity ring-down spectroscopy (CRDS). Instruments using these spectroscopic techniques usually operate under high vacuum and, thus, a continuous air flow through the instrument is required. Therefore, instruments need to be at the study site and physically connected to chambers. Though these instruments are still quite expensive (e.g. compared to GC) they are becoming more and more robust and suitable for field applications. However, a constant (use of UPS is suggested) mains power supply is still needed and checks for cross-sensitivity should be a standard procedure in the laboratory.

### 4.4.3 Auxiliary Measurements

As described earlier in this chapter, spatio-temporal patterns of GHG fluxes are closely linked to changes in environmental conditions (see also Fig. 1). Therefore, GHG flux measurements are rather useless if environmental parameters such as soil and vegetation properties and management are not monitored at the same time, since these factors significantly affect

fluxes. This necessarily also includes the quantification of soil C and N stocks, as for example application of animal manure to arable fields and rangeland has been shown to significantly increase soil carbon stocks (Maillard and Angers, 2014), which needs to be considered when calculating the GHG balance of a given system. Moreover, since GHG flux measurements are expensive and can't be repeated everywhere, models need to be developed, tested and finally used for estimating fluxes at landscape, regional and global scale as well as for exploring mitigation options at multi-year scales or for predicting climate change feedbacks on biosphere-atmosphere exchange processes. Comprehensive datasets, including both flux measurements and detailed information on soil and vegetation properties and management are prerequisites for model development and testing. Surprisingly such datasets are still scarce, because either flux measurements do not meet required measuring standards or the needed auxiliary measurements and site information are not monitored or reported.

Since responsibilities for GHG flux and auxiliary measurements are often split between collaborators, there is a need to clarify personal responsibility of data provision prior to the start of measurements. Rochette and Eriksen-Hamel (2007) reviewed published $N_2O$ flux data and developed a minimum set of criteria for chamber design and methodology. According to their evaluation of 365 studies, there was low to very low confidence in reported flux values in about 60% of the studies due to poor methodologies or incomplete reporting. Thus, it is necessary to improve not only the quality of flux measurements, but also the reporting of soil and vegetation properties and management. See Fig. 1 for suggested variables for measurement.

## 4.5 Conclusions

For the quantification of biosphere-atmosphere exchange processes of GHGs micro-meteorological or chamber based techniques can be used. In view of the diversity and patchiness of landuses and land management associated with smallholder agriculture, chamber based methods, specifically the closed (static) chamber approach, is recommended. Overcoming spatial and temporal variability's of fluxes remain an issue, and should be addressed by a well designed sampling scheme including landscape targeting of measuring sites (see Rufino et al. this book), targeting of chamber placement at field and plot scale (Fig. 1), running of at least 3-5 replicates per plot to address small-scale variability (and possibly use of the gas pooling technique, Fig. 3), flux measurements in weekly intervals over a period of at least one year and detailed documentation of environmental conditions and field activities (Fig. 1). This all will ensure that data can finally be used for modeling and upscaling. Quality control and quality assurance remains an issue at all steps, also with regard to gas analytics. Probably the most efficient way for a researcher to familiarize themselves with gas flux measurement techniques is a longer stay with a recognized research group.

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