

# **Greenhouse Gas Measurement from Smallholder Production Systems**

## *Guidelines for Static Chamber Method*



RESEARCH PROGRAM ON  
Climate Change,  
Agriculture and  
Food Security



**CIMMYT**  
International Maize and Wheat Improvement Center

**Climate Change, Agriculture and Food Security (CCAFS)  
International Maize and Wheat Improvement Center (CIMMYT)  
Indian Council of Agricultural Research (ICAR)**



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## Foreword

Agriculture has to address three intertwined challenges simultaneously: ensuring food security through increased productivity and income, adapting to climate change and contributing to climate change mitigation. Agricultural activities and land-use changes contribute to about one-third of the total GHGs emissions and are the largest source of  $N_2O$ . However, agriculture also plays an important role as a carbon sink through its capacity to sequester and store carbon in soils and in plants and trees. Reducing agricultural emissions and increasing carbon sequestration in the soil and biomass has the potential to reduce agriculture's contribution to climate change. Therefore, quantification of GHG emissions from agricultural production system is necessary to identify management practices that provide opportunities to reduce GHGs emission yet providing greater resilience in production systems, food security and rural welfare. This will eventually help in guiding national planning for low-emissions development, generating and trading carbon credits, certifying sustainable agriculture practice, informing consumers' choices with regard to reducing their carbon footprints, assessing product supply chain and supporting farmers in adopting less carbon-intensive farming practices. Realizing these needs, greenhouse gas quantification from agro-ecosystem has been the subject of scientific investigation and many national and international organizations are involved in this. Indian Council of Agricultural Research is also heavily involved in strategic researches on climate change adaptation under the umbrella of National Initiative on Climate Resilient Agriculture (NICRA).

Among different methods of measuring GHG emission from agricultural production system, chamber based method is more common in smallholder production systems. This method is particularly suitable for GHG measurement from the production system of developing countries mainly because it is relatively inexpensive, versatile in field and the technology is very easy to adopt. This method can be used to develop emission factor of different production practices at field and farm level and also to refine and calibrate simulation models for large scale estimation contributing to national emission inventories. However, harmonization of the chamber based measurement protocol is important for inter-study comparisons and assessment of the reliability of results coming from different studies.

I am happy that a group of scientists from CIMMYT and ICAR has developed guidelines for static chamber based greenhouse gas measurement from smallholder production systems. I am sure this protocol will be immensely helpful to researchers of various national and international organizations engaged in monitoring of GHG emission from agriculture production systems. I take this opportunity to congratulate authors as well as CIMMYT, ICAR and CCAFS for timely bringing out this valuable guideline.

**Alok K. Sikka**

*Deputy Director General (NRM)*

March, 2014





## Executive Summary

Renewed interest in quantifying greenhouse gas emissions from soil has led to development and application of multitude of techniques. But, chamber-based flux measurement technique is most common and frequently used method for GHG flux measurement in smallholder production systems. Despite the apparent conceptual simplicity of chamber-based methods, chamber design, deployment, and data analyses can have marked effects on the quality of the flux data derived from chamber-based measurement. This also have implications on making comparisons of GHGs emissions from the studies by various researchers even within similar cropping systems and management practices. Therefore, harmonization of GHGs emission studies by chamber based method is necessary. This synthesis provides

standard guidelines to scientists involved in GHG quantification by using chamber based methods as well as to facilitate inter study comparison. As any methodology or protocol, chamber methodology has also gone rigorous modification, refinement and improvement over time. Further, type of materials used, dimension, place and time of deployment, sampling time and frequency and analysis method differs slightly from location to location based on the systems being studied, resources availability and so on. Efforts have been made to summarize minimum requirement but also highlighting the need of site-specific consideration. Adoption of harmonized methods that is sensitive and unbiased will result into less error and allows accurate interpolation and extrapolation over time and space.



## 1. Introduction

Globally, agriculture is directly responsible for 14% of annual greenhouse gas (GHG) emissions and induces an additional 17% emission through deforestation for additional land under agriculture; mostly in developing countries (Vermeulen *et al.*, 2012). Developing countries currently account for about three-quarters of direct emissions and are expected to be the most rapidly growing emission sources in the future (FAO 2011). It has been also reported that main agricultural GHGs - methane ( $\text{CH}_4$ ) and nitrous oxide ( $\text{N}_2\text{O}$ )-accounts for 10-12% of anthropogenic emissions globally (Smith *et al.*, 2008). Rapid population growth and shifting trends in dietary patterns towards more meat and dairy products will further lead to increased emissions unless production efficiencies and management are improved. Agriculture however, also plays an important role as a carbon sink through its capacity to sequester and store carbon in soils and in plants and trees. Reducing agricultural emissions and increasing carbon sequestration in the soil and biomass has the potential to reduce agriculture's contribution to climate change by 5.5-6.0 gigatons (Gt) of carbon dioxide equivalent ( $\text{CO}_2$  eq) per year (Olander *et al.*, 2013). Depending upon management practices, agricultural sector can be significant emitter to GHGs neutral. Therefore, quantification of GHG emissions from agricultural production system is necessary to identify management practices that provide opportunities to reduce GHGs emission yet providing greater resilience in production systems, food security and rural welfare. This will eventually help guiding national planning for low-emissions development, generating and trading carbon credits, certifying sustainable agriculture practice, informing consumers' choices with regard to reducing their carbon footprints, assessing product supply chain and supporting farmers in adopting less carbon-intensive farming practices (Olander *et al.*, 2013).

With these realizations, quantification of GHGs from agricultural production systems has been the subject of intensive scientific investigation for several years. This need has driven the development of different methods for quantifying exchanges of GHGs between landscape and atmosphere. Due to heterogeneity of agricultural production niches, different tools and techniques are suitable under different conditions. Although multitudes of approaches have been developed and tested under various production environment, they can broadly be classified into two main categories: Chamber and micrometeorological (Denmead, 2008). The chamber based measurement is still a dominant method suitable for small-holder farming condition due to its adaptability, portability, cost effectiveness and flexibility to diverse production environments. Further, the measurements from chambers are commonly used to develop, calibrate and validate empirical and process-based models to quantify the emission of gas at farm scale and beyond. Chambers are the tools most commonly used for measuring gas fluxes from the soil surface. Chamber techniques have been used to estimate soil respiration for more than eight decades and remain the most commonly used approach (Mosier *et al.*, 1995; Rochette and Eriksen-Hamel, 2008; Rochette and McGinn, 2004). Chamber permits measurement of very small flux, are relatively inexpensive to build & use and can be adapted to a wide range of field conditions and experimental objectives. More than 95% of the thousands of published emission studies ( $\text{N}_2\text{O}$  in particular) used chamber methods (Rochette, 2011). They are very useful for quantifying the impact of various treatments. The only limitation is that their coverage is limited over space and time. The key aspects of chamber methodology such as chamber design, dimension, sampling frequency, storage time and analytical procedure all have significant effect GHG emission result and hence have implications on making comparisons of GHGs

emissions from the studies conducted and being conducted by range of researchers across ecologies even within similar cropping systems and management practices. Therefore, developing standard guidelines for chamber based measurements is very critical in future GHG emission quantification studies.

## 2. Operating principle of chamber based method

The operating principle of chamber method is to restrict the volume of air with which gas exchange occurs so as to magnify changes in concentration of gas in the head space (Denmead, 2008). Chambers are classified as, flow through (open to the atmosphere) and non-flow through (closed chambers) (Rochette and Eriksen-Hamel, 2008). In a flow-through chamber, a constant flow of outside air is maintained through the headspace of the chamber and the difference in concentration between the air entering and leaving the headspace is measured whereas, in a closed chamber, there is no or a very small replacement of air in the headspace so that the gas concentration increases over time. This increase in concentration with time is considered as actual flux from soil. Literature on GHG emission measurement is dominated by the use of non-flow through, non-steady state chamber methodologies commonly known as static chambers (Bouwman *et al.*, 2002).

## 3. Chamber components, design and dimension

The chamber material and other components used in chamber construction such as seals, tubing, septa, and vents should neither react with any gases in question nor should they emit any contaminants. Commonly used materials for chamber and its components, include stainless steel, aluminium, polyvinyl chloride (PVC), polycarbonate, polyethylene or polymethyl

methacrylate (Plexiglas, acrylic sheet) (Clough *et al.*, 2012; Parkin and Venterea, 2010a). As long as basic requirements are met, it is recommended to fabricate chambers locally by utilizing local materials to make GHG quantification system cost-effective. For example, GHG measurement by employing chambers fabricated with locally available steel sheet and plastic pail (Fig. 1) gave satisfactory result in rice-wheat system of North-Western India (CIMMYT, unpublished data). Material should be white or coated with reflective material to minimize internal heating by solar radiation.

It is recommended to use paired chamber, in which the base/anchor of chamber is permanently placed in the soil and upper part of the chamber is placed and sealed onto the base at the time of gas sampling (Fig. 1). The anchor should be inserted sufficiently into the soil (at least 8 cm) to prevent lateral movement but its height above soil surface should be as close to the soil surface as possible i.e.  $\leq 5$  cm (Parkin and Venterea, 2010b). Chambers should be large enough to cover at least 175 cm<sup>2</sup> of the soil surface, and appropriate height to maximize flux detection and minimize perturbation of environmental variables. Chamber height may be increased to accommodate plants inside the chamber. As chamber height increases, the impact of environmental variables (temperature, humidity and gas concentration) is reduced but sensitivity is also reduced.

## 4. Chamber deployment

Temporal and spatial variability of fluxes are the large sources of uncertainties associated with flux estimates from static chamber method. Therefore care should be taken to choose appropriate size and number of chambers, to install them at right place as well as to take sample at right time of the day with acceptable frequency of sampling. Installation of chambers or chamber bases causes soil disturbance, which





**Fig. 1.** Base of the chamber permanently placed in the field (upper) and top of the chamber inserted and sealed onto the base (lower)

may impact gas emission. In general, anchors of the chambers are permanently installed in the place where measurement is to be taken so as to minimize soil disturbance and root damage. In cultivated systems, chamber anchors are typically removed prior to cultivation, planting and fertilizer application. Those anchors should be replaced back to its place at least 24 hours prior to flux measurement (Parkin and Venterea, 2010b). However, care should

be taken not to have significant microclimate effect within chamber area due to permanent placement of chambers. Placement of chamber plays very important role in flux determination in agricultural production systems. If the goal is to quantify net trace gas flux from a particular production system, then ideally, plants should be included inside chambers during flux determinations (Fig. 1). However, inclusion of plants may require increasing in

chamber height thereby reducing sensitivity. In such cases, closure period of the chamber may need to be extended. Chamber deployment duration is trade-off between minimal changes in the physical environment inside the chamber (shorter the duration better it is) and reliable estimate of flux (longer the duration, better it is). For chambers with a maximum height of 20 cm, Rochette *et al.* (2012) recommended deployment period of 30-40 minutes. In

general, chamber height to deployment time ratio should be  $\geq 40$  cm per hour (Rochette and Eriksen-Hamel, 2008). Headspace mixing, particularly around the crop canopy is another pre-requisite with the use of tall chamber to accommodate plants. Fans have been used to mix air in closed chamber headspaces to overcome possible bias from vertical gas concentration gradients ( Fig. 2; Jørgensen *et al.*, 2012). Parkin and Venterea (2010) used a



**Fig. 2.** Computer cabinet fan attached inside the chamber top (upper) for gas mixing. A 9V battery (lower) over the chamber top to supply power to operate computer fan while sampling



gas sampling manifold inside the chamber to draw headspace gas from four quadrants during sampling in order to overcome the occurrence of vertical gas concentration gradient. Parkin and Venterea (2010b) reported that mixing of headspace gas by pumping the syringe before sampling is not recommended as pumping may cause pressure perturbations and/or excess dilution of headspace gas by entry of outside air through the vent tube

In addition, row-cropping or raised bed planting may produce inter-row gradients in soil, water and nutrient contents resulting into differential GHG emission. This can be accounted for by an adequate chamber deployment pattern: e.g. by placing chambers both in row and inter-row space/furrow (Fig. 3). Alternatively, relatively larger chambers can be used to include both row and inter-row space/furrow: within a sing chamber (Fig. 3; Cai *et al.*, 2012).



**Fig. 3.** Deployment of chambers in crop row and in-between crop rows (upper, Photo source: USDA-ARS with permission) and a big chamber covering both row and inter-row space (lower)



Pressure gradients can occur when the chamber is placed on its base, and during the sampling of the chamber headspace due to cooling or warming of the chamber air (Davidson *et al.*, 2002) or wind driven turbulence (Rochette, 2011). If this happens, it is recommended to open the vent (should be provisioned in the chamber but at close to soil surface as possible) during chamber placement. However, care should be taken during windy period when wind may de-pressurize the chamber by pulling air out of the chamber headspace, leading to mass flow of soil gases, commonly known as *venturi* effect (Bain *et al.*, 2005). The chamber should have a sampling port to sample headspace gas (Fig. 4). It should be inert and can be made airtight by using butyl rubber septa.

Gas-tight seal between two components of chamber is another consideration to prevent gas leaking out of the chamber and external air into the chamber. This is commonly achieved by placing a rubber gasket between the chamber and its base (Parkin and Venterea, 2010a) or by using chamber base with built-in trough (Fig. 5) that holds water and acts as a seal between two components (Christiansen *et al.*, 2011).

## 5. Gas sampling and storage

In static chamber method, trace gas concentrations are determined by physically removing gas sample from the chamber headspace followed by its analysis in the



**Fig. 4.** Sapling port in locally fabricated chamber using butyl rubber septa (left inset) and motor-cycle valve (right inset)



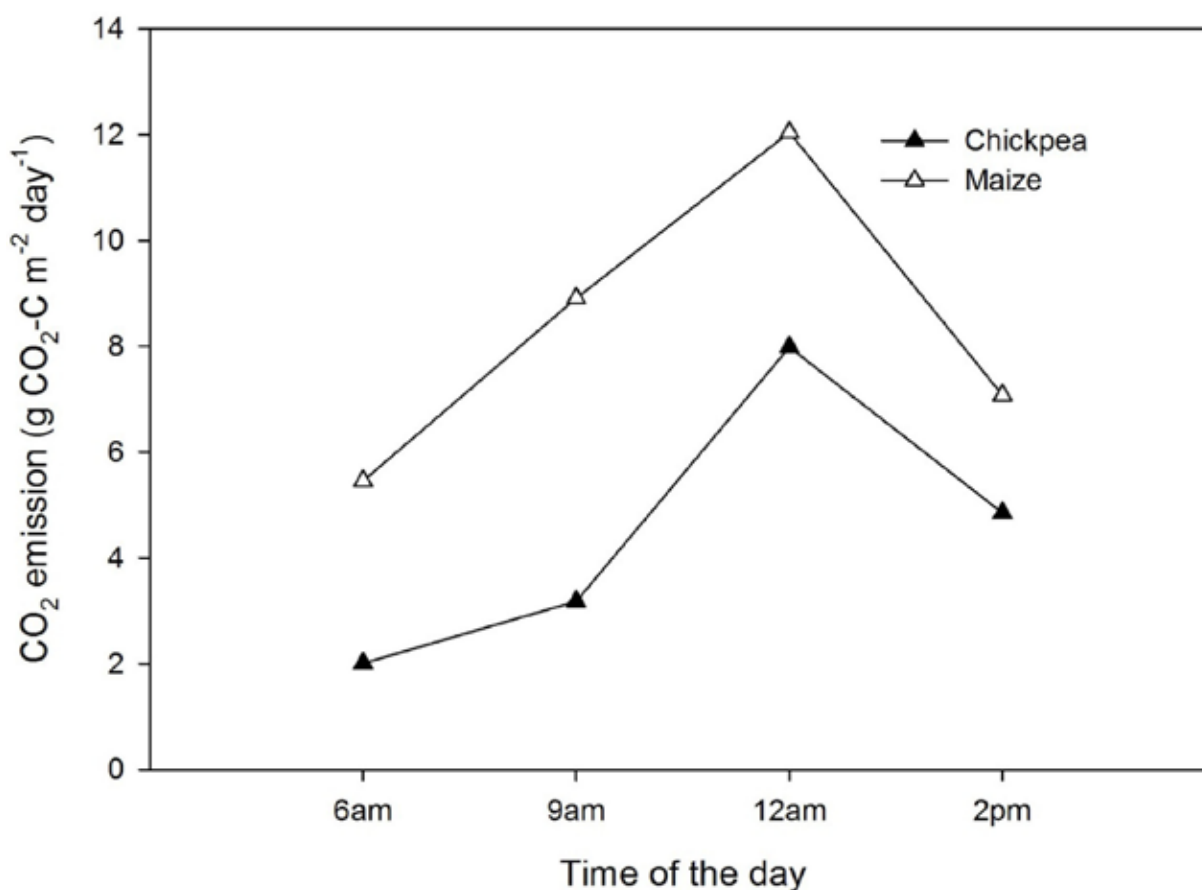
**Fig. 5.** Water trough on the anchor that seals two components of the pair chamber, Karnal, Haryana

laboratory. Therefore, gas sampling should be done following a rigorous methodology to minimize systematic bias in the flux estimate and to account for temporal and spatial variability of GHGs emission. As mentioned in previous sections, the base/anchor of the chamber should be permanently installed in the field or placed back into the field at least 24 h prior to sampling in the cases where it has to be removed during field operations. Walking around the chambers for gas sampling and other measurement can compact the soil which greatly influence production and diffusion of gas. Under very moist condition, it is advisable that chamber should be relocated periodically.

### 5.1. Time of the day to sample

The time of the day to take headspace sample depends on the objective of the research.

If the objective is to compare emission difference among the treatment in short-term, the sampling can be taken at the time when the emission is expected to be at peak. In Northwest India, maximum CO<sub>2</sub> emission from maize and chickpea field was observed between 9 am and 12 noon in the month of April (Fig. 6) (CIMMYT-DMR Unpublished data). But, if the objective is to estimate daily flux by using point-in-time measurement, headspace sampling should be taken at the time of day when the flux is believed to equal its daily mean. GHGs emission from the soil is mainly controlled by soil temperature (Livesley *et al.*, 2008) and therefore headspace sampling when temperature in plough layer is close to its daily mean is often indicative of the average daily flux (Laville *et al.*, 2011). Studies suggest that between 10 am and 12 noon reflects the daily



**Fig. 6.** Emission of CO<sub>2</sub> from Maize and Chickpea during different time of the day in April, DMR, New Delhi, India

average (Rochette *et al.*, 2012). However, it is recommended to conduct diurnal variation studies in each site and during different seasons to determine the best time of the day to sample. If possible, a plot with residue on surface may need to be sampled at different time of the day than a plot without residue as soil temperature is directly influenced by surface residue retention.

## 5.2. Accounting for spatial and temporal variability

Fluxes are determined by calculating the rate of change of trace gas concentration in the chamber headspace. Therefore, gas samples should be withdrawn at regular intervals during the chamber deployment. In general, higher the number of headspace gas samples collected

in each sampling campaign, better the flux estimate. However, the number of headspace samples to be collected depends on the number of chambers to be sampled, available resources and linear increase of headspace gases over time. Rochette (2011) proposed that four or more air samples should be taken in each deployment, to adequately assess the quality of the calculated flux. Sampling is performed by inserting a polypropylene syringe into the chamber septa and slowly removing a gas sample (5-50 ml based on the analytical method). The gas samples can be transferred to a previously evacuated glass vial sealed with butyl rubber septum for storage.

Emissions of GHGs from soils are extremely variable in time and space over which the emission results need to be integrated. Further,

environmental patterns (e.g. rainfall) and farm operation (e.g. tillage, fertilization, irrigation etc) influence the GHG emission very much. Nitrous oxide, in particular, is so episodic that most emission are observed during peaks that can last from few hours to few weeks after soil disturbance, rainfall and fertilization (Bouwman *et al.*, 2002). All these variabilities should be accounted for while taking sample for GHG analysis. Because limited resources usually restrict chamber numbers (to account spatial variability) and sampling frequency (to account temporal variability), the sampling strategies need to be optimized to minimize the uncertainty in flux estimate arising from limited temporal and spatial coverage. In general, it is advisable to sample at least once a week during normal growing season (Parkin, 2006). Apart from this regular interval, it is recommended to sample just before the events that would induce peak emissions such as tillage, fertilization and irrigation and continue sampling until such

event induced peak is expected. This ensures that interpolation of the pre- and post-event emissions is reliable and does not underestimate or overestimate the emission.

### 5.3. Storage of gas sample

If gas-tight syringes are used for sample collection, air sample can be stored in the syringe itself for short-term (Rochette and Bertrand, 2007), but this is an expensive option. Generally, air sample is transferred into a leak-proof, clean sample container which is non-reactive to the gases in question. The glass vials (exetainers) sealed with rubber septa are commonly used. The glass vials should be evacuated in advance of gas sampling. Evacuation can be done by using a vial evacuation manifold consisting of the pump, vacuum gauge, valve and needles (Fig. 7). As an alternative to evacuation, the vials can be flushed four times backward and forward with chamber headspace air just before sampling



*Fig. 7. Vial evacuation manifold*



and transferring headspace air sample into the vial (de Klein *et al.*, 2003). In order to avoid incursion of ambient air into the vials during storage, it is recommended to over-pressurize vials by inserting higher volume of air sample than the actual size of vial (Rochette and Bertrand, 2003). Once collected, the air sample must be stored until analysis. Analysis of the sample should be carried out as soon as possible to prevent contamination of sample due to leakage. However, with proper sealing, sample can be stored for longer period. Rochette and Bertrand (2003) stored 10 ppm N<sub>2</sub>O upto 126 days in containers sealed with butyl rubber without significant loss in N<sub>2</sub>O concentration.

## 6. Analysis of gas samples

Gas samples collected and stored in vials are generally analysed by using standard gas

chromatography. The sample from the vial is injected into Gas chromatograph (GC) through a sample injection valve which then enters into GC column. Injection of sample from vials to GC can be done manually or by having an automated system. Specific method of gas sample injection into the GC will depend upon the specific instrumentation and resources available at each location. Automated system increases the precision and accuracy but with manual system it is feasible to detect any problem immediately. It is recommended that sample's pressure is equilibrated to ambient atmospheric pressure just prior to GC analysis so that the sample volume equates the internal volume of the vial (Kelliher *et al.*, 2012).

Once the sample is injected in the GC column, it is separated and passed through detectors specific to the particular gas (Fig. 8). Nowadays,



**Fig. 8.** Thermal Conductivity Detector (TCD) Electron Capture Detector (ECD) and Flame Ionization Detector (FID)

most GCs come with all three detectors i.e. Thermal Conductivity Detector (TCD), Electrode Capture Detector (ECD) and Flame Ionization Detector (FID) for analysis of CO<sub>2</sub>, N<sub>2</sub>O and CH<sub>4</sub>, respectively from the same air samples. If the GC does not contain one of the detectors or if one is non-functional, then that particular gas concentration can be determined by using other alternative methods. For example, Pandey *et al.* (2012) determined CO<sub>2</sub> concentration by using a portable CO<sub>2</sub> analyser (Li-820, LI-COR Biosciences, USA) along with chamber whereas for N<sub>2</sub>O and CH<sub>4</sub> they transferred the gas in the vials and analysed using standard gas chromatograph.

Concentration of gases can be calculated through peak area of sample in relation to the peak area of the respective standard gases of known concentration (Fig. 9). To accurately measure the GHGs in question in an air sample, GC system must be calibrated by using standard gas of known concentration. Besides regular calibration, each batch of GC run should also include standards of known concentration for each gas in question along with the sample. In order to account for problems associated with GC drift it is recommended that samples from individual chambers be run in sequence i.e. sample of chamber 1 at zero time followed by the sample of same chamber at time 1 rather than segregating all the samples by time i.e. analyzing zero time samples from all chambers together.

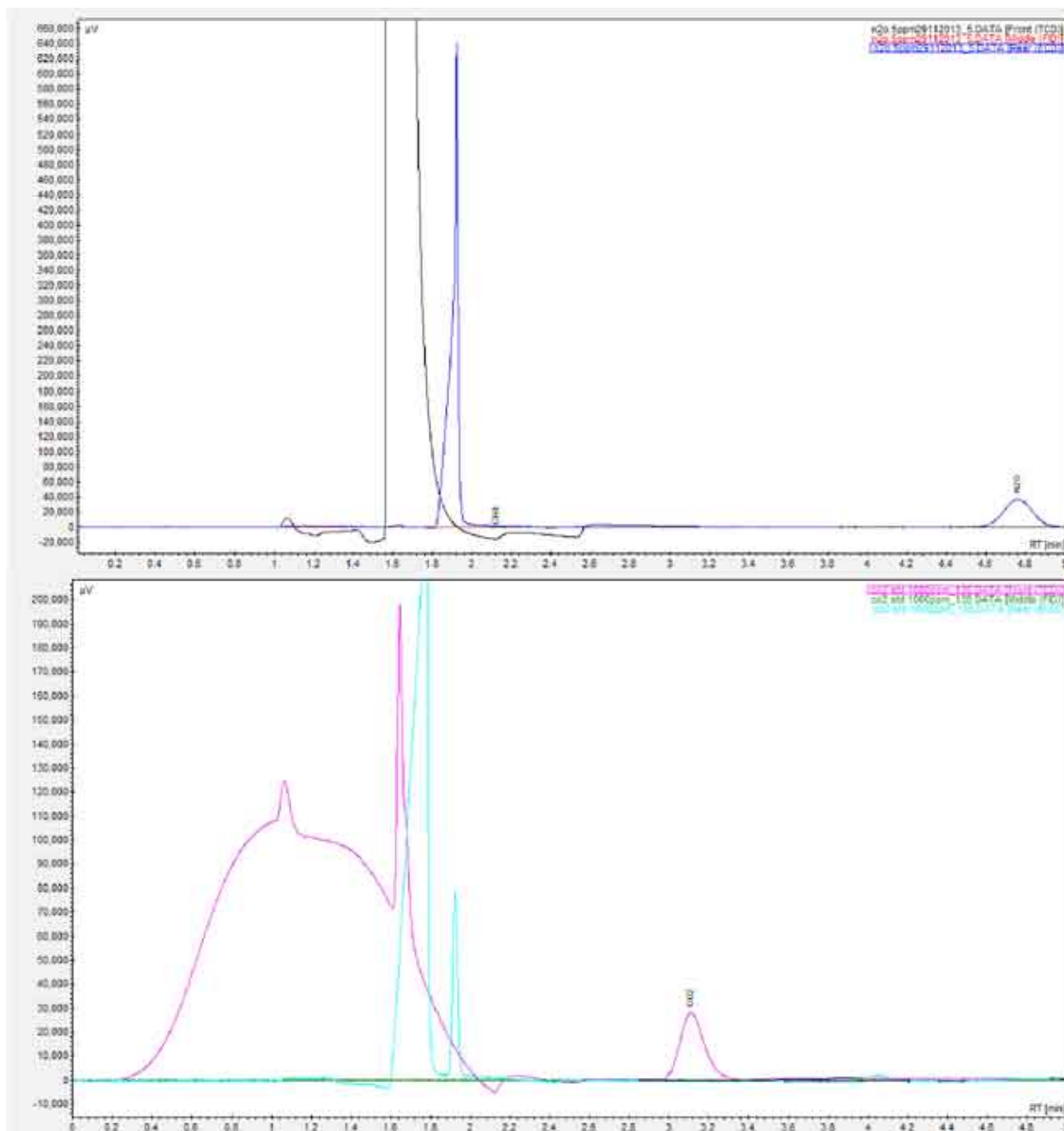
## 7. Calculation of flux

Flux calculation method can substantially alter the magnitude of flux estimates, as well as the sensitivity of detecting fluxes (Parkin *et al.*, 2012). Therefore, use of appropriate calculation method is very important for accurately transforming raw chamber headspace concentration data into flux value. Various flux calculation schemes differ in their

theoretical basis, numerical requirements and probably in their accuracy and precision.

GHG flux calculation in non-steady-state chambers is based on the accumulation of GHGs within chamber headspace over time. This is done by establishing relationship between chamber concentration (C) and time (t) after deployment. Therefore, volume of the chamber, area covered by chamber and gas sampling interval are important variables to consider while calculating fluxes of trace gas from their concentration obtained from GC analysis. If the rate of change of headspace trace gas concentration is constant (i.e. C vs. t is linear), then linear regression can be used to calculate the slope of the concentration vs. time data. Linear Regression (LR) approach is computationally simple and least sensitive to measurement error but being an empirical method and not accounting for diffusion-theory it is not suitable in the cases when gas concentration vs time relationship is curvilinear (Venterea *et al.*, 2012). Nevertheless, LR method is widely used in calculating flux from static chamber based measurement (Rochette and Eriksen-Hamel, 2008). Hutchinson and Mosier (1981) proposed an alternative method commonly known as HM algorithm based on steady-state diffusion theory but this method is restricted only to three equally-spaced measurements. Therefore, this method is no more used due to availability of improved non-linear methods even if data pattern requires adopting non-linear method. As an alternative to HM algorithm, Pedersen *et al.* (2010) have proposed a stochastic diffusion model known as extended HM model which is based on original HM algorithm but with extended applicability to account for lateral gas diffusion induced by chamber placement and/or gas leaks from imperfect seal. Quadratic regression (QR) method proposed by Wagner *et al.* (1997) can be fitted to data following non-linear patterns. Both extended HM and QR scheme can be





**Fig. 9.** Area under the curve (in  $\mu\text{V}$ ) obtained with 0.5 ppm  $\text{N}_2\text{O}$  (upper) and 1000 ppm  $\text{CO}_2$  (lower) standard gas in Gas Chromatograph

used with more than three sampling points and with any sampling interval. In fact, QR method should be used only when there are at least four or more than four sampling points. Livingston *et al.* (2006) developed a non-steady-state diffusive flux estimator (NDFE) reportedly derived from a more rigorous

theoretical basis which accounts for soil-gas production, diffusion and accumulation in a chamber under non-steady-state condition. However, it is computationally complicated lacks repeatability with same set of data. To overcome some of these limitations, Venterea (2010) developed chamber bias correction

(CBC) method in which flux is determined by using any of the conventional flux calculation schemes (LR, HM or QR) which is then multiplied by a theoretically-based correction factor. The correction factor in CBC method is calculated by using soil physical properties such as bulk density, water content and clay content as well as chamber height and chamber deployment period. The CBC method avoids the need for a non-linear regression program and therefore flux can be calculated using a conventional spreadsheet but requires additional soil data.

Therefore, the method employed for flux calculation depends on the type of data, measurement frequency used and associated bias as well as error. For example Venterea *et al.* (2009) demonstrated a trade-offs between bias and error with various flux calculation method, with LR having greater bias but less error compared with HM and QR methods. In many cases, combination of methods may be necessary to obtain the best overall precision and minimum bias.

As mentioned above, standard gases are used to calibrate GC and sample gas concentration is calculated using area under the curve for sample in relation to the area under the curve for standard gas. Since the units associated with the gas standards are typically ppm(v), gas concentration of sample calculated based on this relation will also be ppm(v) which needs to be converted to a mass basis by using ideal gas law as follows:

$$PV = nRT$$

where P = Pressure, V = Volume, n = number of moles of gas, R = the gas law constant and T = Temperature.

Determination of minimum detection limit (MDL) under each sampling and analytical condition is very important as field fluxes of trace gases, particularly N<sub>2</sub>O and CH<sub>4</sub> are low most of the

time. For the calculations employing regression methods, this can be done by calculating goodness-of-fit of regression procedure i.e. t-test of the slope of the regression line to assess if the flux is significantly different from zero (Rochette *et al.*, 2004). The MDL is a function of the sampling and analytical precision as well as the chamber volume and surface area. Sampling and analytical precision is determined by calculating the standard deviation of many standards on the gas chromatograph (n > 20) and the precision is calculated as ± 2SD. This along with information on the chamber volume, surface area, and chamber deployment time is used to compute the MDL as described below (Baker *et al.*, 2003).

$$MDL = \frac{2 \text{ SD } (\mu\text{L L}^{-1}) \times \text{Chamber Volume (L)}}{\text{Chamber Footprint (m}^2\text{)} \times \text{Deployment Time (min)}}$$

Units for the above computation of the MDL are  $\mu\text{L trace gas m}^{-2} \text{ min}^{-1}$ . To convert to  $\mu\text{Mol m}^{-2} \text{ min}^{-1}$  the universal gas law must be used.

## 8. Calculation of seasonal flux

In static chamber method, measurement taken in a point in time is used to calculate daily flux and then cumulative flux for the season or even year. Diurnal variation should be taken into consideration to estimate daily flux based on the measurement taken at particular time of the day. For this, it is recommended to measure the fluxes at times of the day that more closely correspond to the daily average temperature. Some authors (e.g. Smith *et al.*, 1998) suggested Q<sub>10</sub> temperature correction to account for diurnal variation assuming that temperature variations are mainly responsible for diurnal flux variation. However, care should be taken to account for the time lag between gas production in the soil profile and gas flux from the surface while determining the average soil temperature to be used for Q<sub>10</sub> flux correction.

Further, it is not possible to measure the flux everyday by using static chamber method and therefore it is necessary to estimate the flux during non-measurement dates to calculate seasonal/yearly cumulative flux. In general, higher the frequency of measurement, the more accurate the cumulative flux estimate will be. To calculate cumulative fluxes, the daily fluxes can be integrated using trapezoidal integration method (Venterea *et al.*, 2012). The simplest method to fill in the gaps for non-measurement dates is to interpolate the flux using flux taken before and after that particular date. In order to use this method, the expected flux during non-measurement dates should be similar to that of flux taken before and after that date. Therefore, it is recommended to measure the flux continuously during the period when amount of flux is expected to be higher than normal such as tillage, fertilizer application, irrigation, rainfall and thawing (if any). CO<sub>2</sub> fluxes for the non-measurement dates can also be estimated by establishing empirical relationship between temperature and respiration, and light and photosynthesis (Glenn *et al.*, 2010).

## 9. Key considerations

Major considerations while employing chamber based method for GHGs measurement from agro-ecosystems are summarized in following points.

- i. Chamber should be constructed using materials that are non-reactive to the GHGs studied.
- ii. Dimension of the chamber (area, height and base depth) should be decided based systems being studied aiming to minimize error due to poor sealing and perturbation but to maximize flux detection and area to be sampled and to prevent lateral flow of gas from soil profile to the chamber.
- iii. If height of the chamber needs to be increased to accommodate plants inside the chamber, closure period of the chamber need to be extended.
- iv. To minimize disturbance during chamber deployment, it is recommended to use pair chamber with anchor/base of the chamber permanently/semi-permanently installed in the soil.
- v. Headspace air should be well mixed before sampling to overcome the possible bias from vertical gas concentration gradients.
- vi. In row-cropping systems, inter-row gradients should be accounted for either by placing chambers in rows as well as inter-row space or by using large chambers that covers both row and inter-row space.
- vii. Pressure build-up inside the chamber may be an issue particularly while using small chambers. If so happens, it is recommended to open vent during chamber placement.
- viii. When using paired chamber, two components can be made air-tight using a rubber gasket or build-in water trough.
- ix. If the objective of the study is to estimate cumulative emissions, sampling should be done at the time of day when the flux is believed to equal its daily mean i.e. when the temperature in plough layer is close to its daily mean.
- x. In each deployment, four or more air samples should be taken to adequately assess the quality of the calculated flux.
- xi. Emission of GHGs from soil is extremely variable which is further influenced by environmental patterns and farm operation such as rainfall, tillage, fertilization, irrigation and so on. All these variabilities should be accounted for while taking sample for seasonal GHG analysis.
- xii. Air samples should be analyzed as soon as possible after collection but can be stored upto more months with proper sealing.

- xiii. Beside regular calibration of GC, each batch of run should also include standards of known concentration for each gas in question along with the sample.
- xiv. Appropriate flux calculation method should be chosen to transform headspace concentration data (obtained from GC) into flux depending of number of sampling point and rate of change in headspace gas concentration. Linear Regression is computationally simple and widely used method but non-linear methods should be used when gas concentration vs time relationship is curvilinear. In many cases, combination of methods may be necessary to obtain the best overall precision and minimum bias.
- xv. Determination of minimum detection limit (MDL) under each sampling and analytical condition is very important as field fluxes of trace gases are low most of the time.
- xvi. To calculate seasonal/annual flux, it is necessary to estimate the flux during non-measurement dates. The simplest method to estimate flux for non-measurement dates is to interpolate the flux using flux taken before and after that particular date.

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