Chapter 12
Measurement of Methane Fluxes from Terrestrial Landscapes Using Static, Non-steady State Enclosures

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Abstract Wetlands are a dominant natural source of atmospheric methane (CH_4), a potent greenhouse gas whose concentration in the atmosphere has doubled over the past 150 years. Evaluating the impacts of CH_4 emissions on global climate and developing policies to mitigate those impacts requires a quantifiable and predictive understanding of natural CH_4 processing. Developing field sampling campaigns that quantify CH_4 flux in landscapes with prominent wetland features is a vital first step to developing that understanding. This chapter describes a field sampling approach that relies on static chambers to capture the CH_4 emitted from saturated soils and laboratory analyses of sequential samples to quantify CH_4 fluxes. Ultimately, by relating CH_4 fluxes from intensively sampled field sites to more easily measured ecosystem properties (e.g., temperature, water table, and productivity), models may be developed to predict CH_4 fluxes at larger landscape and regional scales.

Keywords Methane, saturated soils, static chamber, water table, wetland

12.1 Introduction

Atmospheric concentrations of methane (CH_4), the second-most abundant anthropogenic greenhouse gas, have doubled in the last 150 years (Wahlen 1993). Although atmospheric concentration of CH_4 is approximately 200 times less than that of carbon dioxide (CO_2), on a per-molecule basis, CH_4 is 25 times more effective

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at trapping heat than CO_2. The rapid rise of atmospheric CH_4 coupled with its heat trapping properties highlight the importance of understanding CH_4 sources and sinks to help predict and manage the effects of CH_4 on the global climate system.

The net methane flux from terrestrial soils is comprised of competing microbial processes: methanogenesis (CH_4 production) and methanotrophy (CH_4 oxidation, or consumption). Methanogenesis is an anaerobic carbon mineralization pathway. Wetland soils, typically low in oxygen and often high in organic carbon, are the largest natural source for atmospheric methane (Schelsinger 1997). CH_4 produced in anoxic, saturated soils may be consumed in overlying unsaturated soils, affecting the net flux to the atmosphere. Additionally, dry upland soils can consume CH_4 that diffuses into soil from the ambient atmosphere (Born et al. 1990, Striegl et al. 1992). Given the importance of CH_4 in the carbon budget of some ecosystems and its strength as a greenhouse gas, it is considered an important component of the North American Carbon Program (Wofsy and Harriss 2002).

The processes influencing soil CH_4 fluxes are highly variable in space and time creating large uncertainty in the flux of CH_4 from terrestrial landscapes to the atmosphere. A hierarchical, scaled approach to improving our estimates of CH_4 fluxes from these landscapes is a high priority of the North American Carbon Program. This chapter describes a static-chamber approach to measuring CH_4 fluxes that is appropriate for spatially intensive sampling campaigns in landscapes with significant wetland components.

12.2 Measurement of Methane

Chamber-based approaches to trace gas measurement (e.g., such as those described by Bradford and Ryan in the previous chapter) offer the advantages of operational simplicity, portability, and low cost. An enclosure or chamber is placed over the soil to create a headspace of air, which can be sampled repeatedly over a short period of time (20–60 minutes). Samples are analyzed for target gas species, whose fluxes can be calculated based on the change in concentration over the duration of deployment. Unlike the infrared gas analyzers used to measure CO_2, portable instrumentation for providing instantaneous measurements of CH_4 in the field is not readily available, so gas samples must be stored and transported to a suitably equipped laboratory to measure CH_4 concentration.

12.2.1 Chamber Design and Deployment

Livingston and Hutchinson (1995) discuss factors to consider regarding the design, construction and deployment of chambers for measuring trace gas fluxes. For measuring CH_4 fluxes, the most commonly used technique utilizes a static vented enclosure system with two components: collars that are permanently installed in the

ground and a portable chamber that fits over the collars. The use of permanently installed collars helps to create a tight seal with the soil surface while minimizing the disturbance effects of collar installation during periods of gas flux measurement. Chamber design and deployment described here is based upon approaches discussed in Livingston and Hutchinson (1995) and Holland et al. (1999). Here, chamber dimensions and design closely conform to those used for CO_2 measurements (Bradford and Ryan, Chapter 11) to take advantage of gas flux collars that were previously installed for that purpose. The primary difference between the chambers is that these static chambers contain no line hook-up to pumps, but rather, are designed for syringe sampling.

12.2.1.1 Materials

1. Permanently installed collars made of 10-in. diameter, schedule 40 PVC pipe, cut to 12.5 cm in length, with one edge beveled on a routing table.
2. Chamber components
   (a) Chamber top, made from 10-in. diameter, schedule 40, PVC cap. This should be light in color to minimize chamber heating during deployment (e.g., PlasticTrends part #D16010).
   (b) Vent, 1/4 in. stainless steel Swagelock fitting with 12 cm of plastic tubing (Livingston and Hutchinson (1995) discuss the optimum dimensions of vents as a function of chamber size and wind-speed).
   (c) Sample port, with either septum or valve, to accept syringe needle or luer-tip.
   (d) Thermocouple wire to monitor change in chamber air temperature during deployment period and thermocouple reader.
   (e) Inner PVC lip, made from 2 cm section of 10 -diameter PVC pipe, attached with PVC sealant to the inside of the cap, 2.5 cm from the base, with a self-adhesive closed cell foam gasket pressed to the lip bottom. During deployment, the gasket helps to create a seal against the PVC collar.
3. A plastic syringe (20 or 30 mL volume) with stopcock fitting and needle for sampling (25 gauge needles are commonly used). Extra syringes and needles are helpful to have with you in the field.
4. One 9-mL headspace vial with a septa and aluminum crimp-seal is needed for each sample taken. Exact vial dimensions may depend on the autosampler of the gas chromatagraph being used for the laboratory analysis. Vials should be sealed prior to visiting the field site. There are different strategies for preparing the vials. Vials can be sealed with laboratory air, provided that CH_4 concentration is low. Alternatively, vials can be flushed with nitrogen or evacuated with a vacuum pump. Because lab air may be variable in CH_4 content and evacuated vials may allow air to seep in prior to use, the nitrogen flushing approach may yield more consistently prepared vials. If the background gas in sealed vials is laboratory air, extra vials should be prepared as blanks to determine the

background concentration. Additionally, vials prepared in the lab to contain known concentrations of CH_4 should be taken to the field to evaluate potential leakage related to storage and transport.

An alternative approach to using vials for sample storage is to store the sample in the original syringe that is used to draw the sample from the chamber, sealing the sample with the stopcock. This approach eliminates possible errors in transferring gas samples to headspace vials, and eliminates time needed to prepare vials. If the available gas chromatograph makes use of an autosampler, this approach is not possible.

12.2.1.2 Collar Installation

1. Collars should be installed at least one week prior to sampling to minimize anomalies caused by soil disturbance.
2. Position collar on top of soil in desired location.
3. With long bread knife or saw or similar tool, cut around the edge of the collar
4. Press collar 5–10 cm into the soil until secure, leaving enough of the collar above the surface to enable the chamber to sit on the collar (~3 cm). In some cases, using a hammer to drive collars into the soil may expedite this operation, but this is not recommending for organic soils, where hammering can cause considerable compaction.
5. The depth from the collar top to the soil surface should be noted so that the actual volume of the enclosure can be calculated. Microtopographic variation in the soil may necessitate using the mean depth of multiple measurements.

Note: In organic or wet soils, the pressure on the soil from walking or standing near the collar can alter gas fluxes. Building boardwalks or platforms to stand on during sampling can help to minimize this disturbance.

12.2.1.3 Deployment

1. Measure and record the ambient air temperature.
2. Place the chamber on top of the collar to be measured so that the chamber gasket sits on the rim of the collar. Ground vegetation that interferes with the chamber seal should be tucked inside the chamber.
3. With a syringe, draw the initial sample (time = 0) and inject the sample into storage vials. The volume of sample injected should over-pressurize the vials to minimize leakage into the vial during sample storage. For 9-mL headspace vials, 15-mL injections of sample are typical. If using evacuated vials, experiment to evaluate the maximum sample volume that you can consistently inject to over pressurize the vial, and use that volume.
4. Sample the chamber again at 10, 20, and 30 minutes, injecting samples into new vials.

5. Depending on the proximity of other collars and the number of chambers available, simultaneous sampling of multiple chambers may be possible.
6. When the last sample is drawn, measure the chamber air temperature with the thermocouple reader and record.
7. Return samples to laboratory for analysis as soon as possible.

Figures 12.1 and 12.2 illustrate chamber design and deployment.

12.2.2 Laboratory Analysis

Vials should be analyzed for CH_4 using a gas chromatograph (GC) with a flame ionization detector (FID). There is a diversity of possible GC configurations for measuring CH_4 and they will not be covered here. Crill et al. (1995) and Holland et al. (1999) provide relevant information for configuring a GC to analyze CH_4.

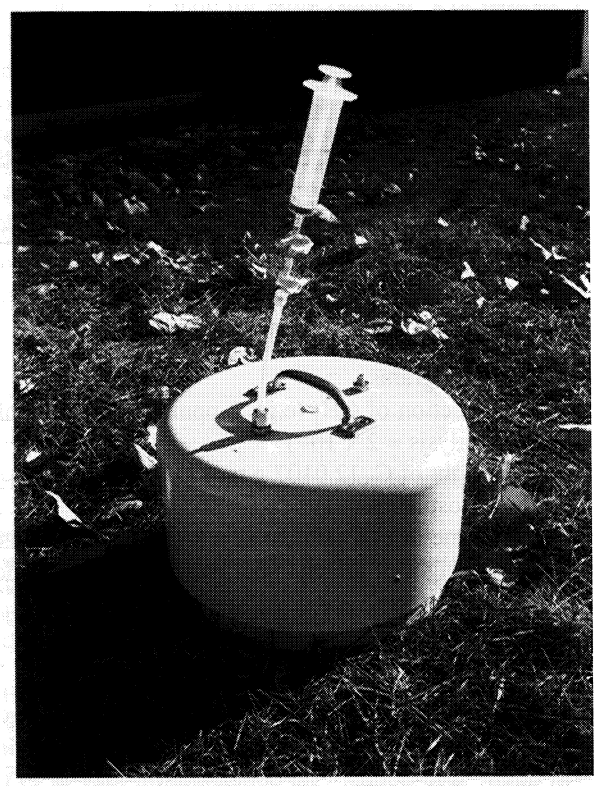

Fig. 12.1 Gas sampling chamber positioned on collar with syringe equipped with stopcocks attached to 1/4″ bev-a-line tubing sample port. A 1/4″ diameter Swagelok fitting (on the right) serves as a vent

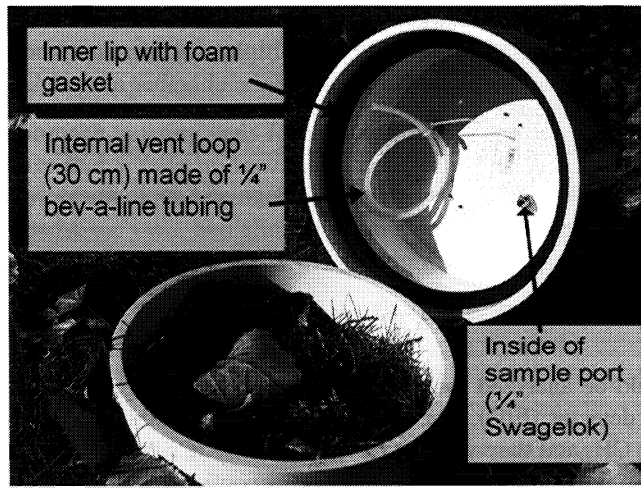

Fig. 12.2 Underside of gas sampling chamber adjacent to collar

12.2.3 Calculations

Flux calculations are based on the change in chamber CH_4 concentration over time. Concentrations, as measured by gas chromatography and adjusted as necessary for dilution in the headspace vial, can be converted into mass using the Ideal Gas Law:

$$m_{CH4} = (C_{CH4} \times M \times P \times V) / (R \times T) \quad (12.1)$$

where

m_{CH4} = mass of CH_4-C in grams
C_{CH4} = concentration fraction of CH_4 (e.g., 2 ppm CH_4 as determined by chromatographic analysis = 2 x 10^{-6})
M is the molecular weight of C, 12.0107 g mol^{-1}
P is the pressure in atmospheres (~1)
V is the enclosure volume in L. Calculate as π x r^2 x D, where r is the chamber radius and D is the height of the chamber cap plus the mean depth from the collar rim to the soil surface.
T is the chamber air temperature when the gas was sampled.
R is the universal gas constant, 0.0820575 L atm K^{-1} mol^{-1}

For each collar, the mass of CH_4 should be plotted versus time to evaluate linearity of methane production. The rate of production (mass per time) is the slope of the best fit line through these points. The concentration may level off over time, causing a deviation from linearity. Such deviations are commonly attributed to artificial effects that stem from limitations of enclosures, and are typically discarded from the regression.

Calculate flux, the movement of mass through an area per unit time per unit time as:

$$f = a / A \tag{12.2}$$

where

a = the slope of the best fit line described above and
A = the cross-sectional area of the collars.

12.3 Scaling CH_4 Fluxes

Measurements of CH_4 fluxes from wetland soils typically have high variability both spatially (i.e., collar to collar) and temporally (i.e., within collar). The number of chamber measurements needed to characterize seasonal or annual fluxes with confidence can be high (e.g., 50–100 individual collars per site; Holland et al. 1999). The labor required to carry out this degree of sampling is seldom available for individual sites, and is unrealistic for large landscapes or regions. Ultimately, seasonal and annual estimates of landscape- and regional-scale CH_4 fluxes may need to rely on modeling or remote sensing approaches that link methane fluxes to other ecosystem properties or processes that are more easily measured. Soil temperature, water table depth, and the spatial extent, community structure, and net primary productivity of wetland ecosystems have been used in regional methane flux models (e.g., Potter 1997, Potter et al. 2006). CH_4 flux datasets generated from intensive sampling campaigns and coupled with other data on ecosystem properties and processes should be highly valuable for developing and fine-tuning models of CH_4 flux at larger scales.

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