AN ABSTRACT OF THE THESIS OF

Stephan Mark Nay for the degree of Master of Science in Forest Science presented on November 2, 1994. Title: Evaluating Methods for Measuring Soil-CO_2-Efflux in Artificial, Controlled and Natural Ecosystems.

Signature redacted for privacy.

Abstract approved: _____

Bernard T. Bormann and Kermit Cromack Jr.

Chamber methods for measuring soil-CO_2-efflux were evaluated in an artificial, controlled and natural ecosystems. The artificial ecosystem was designed to simulate a soil surface and to maintain a constant and measurable CO_2 efflux based on Fick's law of diffusion and to provide the most fundamental test of chamber methods. A static-chamber with absorbent and a dynamic-chamber with an infrared gas analyzer (IRGA) were the methods evaluated. The chamber methods were evaluated at four efflux rates in 24-h trials. The range of effluxes tested, 0 to 0.77 g CO_2 m^{-2} h^{-1}, includes most of the values reported in the literature. The static-chamber method greatly overestimated a zero efflux, overestimated intermediate effluxes by 25 percent, and underestimated the highest rate by 57 percent. The dynamic-chamber method underestimated all rates by 15 percent. Alteration of the CO_2 concentration in the headspace of the static-chamber suggests that absorption rates were not in equilibrium with the surface efflux.

Controlled ecosystems were also used to evaluate the dynamic-chamber-IRGA method for monitoring soil-CO_2-efflux over an eight month period; this represented a more complex system than the artificial ecosystem. The controlled ecosystems consisted of ten box-lysimeters, with soils of various

carbon contents and no plants. The change in soil carbon over and eight month period was compared to soil-CO_2-efflux for the same period. In nine of the ten controlled ecosystems no statistical differences ($\alpha = 0.05$) were observed between soil-CO_2-efflux and soil-C loss. A difference was observed in the ecosystem with the highest soil-C loss. Processes producing non-CO_2 carbon gases and an inadequate sampling of CO_2 efflux early in the experiment may explain the discrepancy. Otherwise the results of this experiment were consistent with the artificial ecosystem experiment.

Soil-CO_2-efflux was also measured in various forest stands in Oregon, Washington and Alaska during summer months. Rates were measured with the dynamic-chamber-IRGA method and ranged from 0.43 to 2.87 g C m^{-2} h^{-1} with the highest rates corresponding to the most northerly sites. Rates I measured were 1.5 to 4.0 times that of comparable data in other studies that used static-chamber-absorbent methods.

Evaluating Methods for Measuring Soil-CO_2-Efflux in Artificial, Controlled and Natural Ecosystems

by

Stephan Mark Nay

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

Completed November 2, 1994
Commencement June 1995

Master of Science thesis of Stephan Mark Nay presented on November 2, 1994

APPROVED:

Signature redacted for privacy.

Co-Major Professor, representing Forest Science

Signature redacted for privacy.

Co-Major Professor, representing Forest Science

Signature redacted for privacy.

Head of Department of Forest Science

Signature redacted for privacy.

Dean of Graduate School

I understand that my thesis will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my thesis to any reader upon request.

Signature redacted for privacy.

Stephan Mark Nay, Author

ACKNOWLEDGMENTS

I am highly grateful to the funding provided by USDA Forest Service, Pacific Northwest Research Station, Long-Term Ecosystem Productivity Program. I am also very thankful to have a supportive supervisor in my workplace; without Dr. Bernard Bormann's support this endeavor would not have been possible.

I would like to thank my committee members Dr. Bernard Bormann, Dr. Kermit Cromack and Dr. Larry Boersma for their help in all aspects of this project and all the many things that I have learned from them. Beyond committee members, Dr. Kim Mattson, Dr. Jeffrey Borchers, Dr. Henri Spaltenstein and Dr. Janice Thies provided useful comments on my study proposal and engaged me in many thought provoking discussions. Dr. Mattson and Dr. Bormann were contributing authors of the manuscript "Biases of Chamber Methods for Measuring Soil CO_2 Efflux Demonstrated with a Lab Apparatus" which was accepted for publication in *Ecology*. Martha Brookes also provided helpful comments on the *Ecology* manuscript.

Dr. Thomas Sabin provided statistical consultation. Carol Glassman assisted and provided a lab and equipment to analyze soil for carbon. Dr. John Bahm also assisted and provided a lab and equipment to analyze soil water samples for organic carbon. Dr. Mattson provided gas chromatography equipment and instruction for its use. Fellow graduate students and co-workers, who are not without names but are many, were also a valuable source of help.

Lastly and mostly I want to thank my loving wife Barbara for her help and unwavering commitment during this effort. Much of the time and energy that I have devoted to this pursuit has come at her expense.

CONTRIBUTION OF AUTHORS

Chapter 2 of this thesis (An Artificial Ecosystem Experiment) has been accepted for publication in *Ecology* under the title 'Biases of chamber methods for measuring soil CO_2 efflux demonstrated with a laboratory apparatus'. This article will appear in the December 1994 issue. I am the first author of this article. The idea of the experiment was mine and I took the lead on constructing the apparatus, conducting the experiment, analyzing the data and writing the manuscript. Kim Mattson and Bernard T. Bormann were contributors in this work assisting with the experimental design, data collection and writing. Mattson's encouragement to do the experiment and his expertise with gas chromatography were particularly helpful.

TABLE OF CONTENTS

TABLE OF CONTENTS (Continued)

LIST OF FIGURES

LIST OF TABLES

Evaluating Methods for Measuring Soil-CO_2-Efflux in Artificial, Controlled and Natural Ecosystems

1. INTRODUCTION

The measurement of soil-CO_2-efflux *in situ* is problematic despite the fact that various techniques have been employed for at least 70 years. Lundegårdh (1927) used a chamber he termed a "respiration bell" to make measurements of soil-CO_2-efflux. Despite this history, chamber methods today are varied and lack standardization (Anderson 1982, Cropper et al. 1985, Nakayama 1990). This makes it difficult to interpret results quantitatively and to make comparisons between studies. As a result, there is a great need to compare methods against reference systems with known fluxes. Nakayama (1990), in his review of soil-CO_2-efflux measurement methods, suggests the use of a refence system; but knows of no instances where one has been used.

In this thesis research, I approach the problem of evaluating methods in three parts. The first is to test the methods in an artificial ecosystem, where the basic principles of diffusion are used to produce effluxes of CO_2 from the surface of a porous medium. The second part is to test the methods in a controlled ecosystem of intermediate complexity between the artificial ecosystem and the field conditions of a natural ecosystem. The controlled ecosystems in this experiment are contained by box-lysimeters. The controlled ecosystem experiment uses the change in soil carbon as a check of the soil-CO_2-efflux measurements. The third part is to make field measurements to assess of the practicality of the methods, provide pre-sampling information for future research, and serve as a basis for analyzing some of the existing literature.

Considering that the infra-red gas analyzer (IRGA) is one of the most accurate analytical tools available for measuring CO_2 concentrations, and has

been made a portable instrument since the mid-80's by several manufacturers, a dynamic-chamber-IRGA method seemed a logical method to examine. A static-chamber-absorbent method is also examined due to its popularity and historical use.

Gas Diffusion

Soil respiration is considered to be the CO_2 and other volatile C compounds given off by soil animals and microbes (heterotrophs) as well as plant roots (autotrophs) through metabolic activity. However, what is observed at the soil surface as soil-CO_2-efflux can be influenced by two major factors: (1) the rate at which CO_2 is being produced and (2) the rate at which it is able to be transported out of the soil.

The main process by which CO_2 is transported out of the soil and into the atmosphere is diffusion. The process of gas diffusion in free air is described by Fick's law of diffusion:

$$J = D \bullet \frac{dC}{dx} \qquad (1)$$

where J is a flux (mass per area and time), D is a diffusion constant, dC is a gas concentration gradient and dx is a distance. The diffusion constant for CO_2 in free air (deJong and Schappert, 1972) is

$$D_0^{CO_2} = 0.139 \bullet \frac{cm^2}{s} \bullet \left(\frac{T}{273\ K}\right)^2 \qquad (2)$$

and T is temperature in Kelvin (K).

This expression can then be modified for diffusion of gas through a porous medium, such as a soil, by the addition of a tortuosity factor (ξ). Jury et al. (1991) states that the Millington-Quirk equation is based in theoretical terms and has worked well for a variety of soils; it is as follows:

$$\xi = \frac{a^{3.33}}{\phi^2} \quad (3)$$

where tortuosity is a function of soil air content (a) and soil porosity (ϕ). Combining soil tortuosity with Fick's law we obtain an equation that largely describes the vertical transport of CO_2 in the soil:

$$J_s^{CO_2} = -D_0^{CO_2} \bullet \xi_s \bullet \frac{dC}{dz} = -D_s^{CO_2} \bullet \frac{dC}{dz} \quad (4)$$

where dz refers to the change in depth in soil. While this equation does not account for all the fates of CO_2, it does provide the basis for an understanding of the factors that control the rates of soil-CO_2-efflux. The concentration of CO_2 in ambient air is approximately 350 to 400 uL L^{-1} at the soil surface and at a depth of 50 cm it may be as high as 50,000 uL L^{-1} (Elliott and McCalla, 1972 and Buyanovsky and Wagner, 1983) thus providing the gradient necessary for the transport of CO_2 out of the soil and into the atmosphere. Other processes that can influence the transport of CO_2 include sorption, and dissolution in H_2O which are accounted for in a more sophisticated model proposed by Boersma and Ouyang (1991).

Methods for Measuring Soil-CO_2-Efflux *In Situ*

There are a wide range of methods which have been used to measure soil-CO_2-efflux *in situ*. These methods can be divided into the three broad categories: microclimatological, profile concentration, and chamber methods and are briefly discussed here.

Microclimatological methods have been used to measure soil-CO_2-efflux (Nakayama 1990) and are reviewed by Verma (1990). The microclimatological methods consist of the eddy correlation as well as two gradient-based methods: the Bowen ration-energy balance method and the aerodynamic method. The

microclimatological approach as a whole has the advantage of being non-disturbing to the site yet has practical limitations for use in forests and mountainous terrain. For example the gradient-based methods require large homogeneous surfaces; thus at their current state of development are not particularly suitable for work in forest ecosystems. The eddy-correlation method has some potential for use in forest ecosystems, but may be limited to slopes less than 20 percent (Verma 1990). These methods are typically used to account for net fluxes of CO_2 from the ecosystems being examined and are essentially measures of net ecosystem production. To actually measure soil-CO_2-efflux these methods need to be applied over bare ground; or require an accounting of photosynthesis and aboveground autotrophic respiration. The eddy-correlation method however has been used by Baldocchi et al. (1986) to make direct estimates of soil-CO_2-efflux in a deciduous forest.

The *profile concentration method* uses samples of the soil atmosphere at various depths and Equation (4) or a similar equation to model gas flux. This method was compared with four other methods for estimating soil-CO_2-efflux by de Jong et al. (1979) and was found to give the highest estimates. Mattson (1994) compared the profile method to a static-chamber method and found both methods gave comparable results at lower rates (<0.3g CO_2 m^{-2} h^{-1}), but that the profile method gave higher estimates at higher rates. Procedures for the profile gradient methods are described by Rolston (1986a) as are the major errors and uncertainties, which largely relate to the variability of the soil-gas diffusivity and concentration gradients. This approach does not appear to have been used extensively.

Chamber methods comprise of placing a vessel onto a soil surface in order to capture soil-CO_2-efflux. Throughout this thesis, the word `chamber'

only refers to the devices affixed to the soil surface for this purpose. Chamber techniques date back to at least the 1920's (Anderson 1982 and Nakayama 1990) and are by far the most extensively used type of methodology for estimating soil-CO_2-efflux. Chamber methods can be divided into two sub-groups: static and dynamic. Static-chambers have no air flow, whereas dynamic-chambers do. The static-chamber methods in general are the oldest, simplest, least expensive and most common.

Static-chamber methods work in two ways. One approach allows the CO_2 from the soil to build up in the headspace of the chamber. A sample of the chamber atmosphere is then taken (usually with a syringe) at different times and then analyzed for CO_2 concentration. The change in concentration over the change in time (dC/dt) is then used to calculate the flux ($J_s^{co_2}$) according to the following equation:

$$J_s^{co_2} = \frac{dC}{dt} \bullet \frac{V}{A} \qquad (5)$$

where *dC* is the change in concentration of the headspace of the chamber, *dt* is the change in time, *V* is the chamber volume, and *A* is the sampling area of the chamber. If the chamber is a cylinder then *V/A* reduces to chamber height. Since gas concentrations are typically measured on a volume bases (*V/V*), we use the ideal gas law

$$PV = nRT \qquad (6)$$

to convert volume to mass, where *P* is pressure (J m^{-2}), *n* is moles, *R* is the universal gas constant equal to 8.314 J mol^{-1} K^{-1} and *T* is temperature in Kelvin.

A gas constant specific to CO_2 mass (R_{co_2}) can be derived by dividing the universal gas constant by the molecular weight of CO_2 which yields

0.189 J g^{-1} K^{-1}. The ideal gas law can then be rewritten for the specific purpose converting CO_2 volumetric concentrations to mass as follows:

$$M = \frac{P}{R_{co_2} T} \bullet V \tag{7}$$

If we combine Equation (5) with equation (7) we obtain the following equation which produces a CO_2 flux rate in mass per area and time.

$$J_s^{co_2} = \frac{P}{R_{co_2} T} \bullet \frac{dC}{dt} \bullet \frac{V}{A} \tag{8}$$

The other static-chamber method, *static-chamber-absorbent method*, uses alkali absorption; where a chemical base is placed inside a chamber and absorbs the CO_2 as it enters the chamber. Then, either by acid titration (for liquid base solutions) or by gravimetric analysis (for solid bases), the quantity of CO_2 absorbed for a given time frame is determined. The liquid bases usually used consist of solutions of NaOH or KOH, while the most commonly used solid base is soda lime (a mixture of variable proportions of NaOH, CaO and/or $Ca(OH)_2$).

There are a number of potential sources of error associated with the use of an alkali absorption technique; these relate to the efficacy of the alkali to absorb the CO_2, and the alteration of the boundary layer conditions of the soil surface by the static chamber. The effectiveness of the alkali can be influenced by a number of factors; which include the amount of alkali surface exposure, the temperature, and the water vapor pressure (Anderson 1982). If the rate at which the alkali absorbs CO_2 is less than the efflux from the soil surface, the result would be an increase in the CO_2 concentration inside the chamber. Subsequently, this would result in a reduction of the gradient between the atmosphere above and below the soil surface and produce a lower efflux rate. Because the alkali materials must be handled in the field and then transported to

a laboratory for analysis, there is an additional potential source of error. Of the 40 studies cited in the synthesis article by Schlesinger (1977), the static-chamber with absorbent was used 21 times. This approach is still commonly used today (Joshi et al. 1991, Carlyle and Than 1988, Grahammer et al. 1991, Raich et al. 1990).

Dynamic-chamber methods are designed to have air-flow pass through the chamber and a gas analysis device either in an open- or closed-loop design. The most common gas analysis device used with the dynamic-chamber is the IRGA. The use of alkali absorbent has also been incorporated into a dynamic-chamber method in a design proposed by Freijer and Bouten (1991).

With *open-dynamic-chamber methods*, a comparison is made between the CO_2 concentration in the air stream leaving the chamber versus the CO_2 concentration of the ambient air stream entering the chamber. Kanemasu et al. (1974) points out serious potential problems with the use of open-dynamic-chambers. They found that if flow through the chamber was generated by applying a negative pressure, then observed efflux rates were approximately a magnitude greater than when a positive pressure was used. Therefore any use of an open-dynamic-chamber should balance air pressures of incoming and outgoing airstreams.

A typical *closed-dynamic-chamber method*, has air-flow circulating through both a chamber and an IRGA (Norman et al. 1992) Thus, with this closed-loop system, the pressure problems associated with an open-dynamic-chamber are alleviated. The calculations for $J_s^{CO_2}$ are basically the same as the static-chamber without absorbent (Equation 8) with the change in concentration of CO_2 over the change in time (dC/dt) being used to calculate the flux rate. One difference is that V in this case includes the volume of the chamber, the

IRGA and the tubing. Another difference is that the time step (*dt*) with the dynamic-chamber and IRGA is seconds as opposed to hours or days with the static-chamber methods. In this thesis, a dynamic-chamber and IRGA in a closed loop is the only configuratation used and is refered to as the *dynamic-chamber-IRGA method.*

When the CO_2 concentration in a chamber increases, the gradient between the air and the soil is reduced. If the reduction in the gradient is sufficient, then an underestimate of the efflux should result. There are at least three possible ways to adjust for this alteration of the environment: (1) correct with a formula (Hutchinson and Mosier, 1981), (2) use a chamber height that keeps dC/dt relatively small (see Equation 8), or (3) lower the CO_2 concentration of the chamber atmosphere to below ambient and measure *dC/dt* at concentrations comparable to ambient.

The artificial lowering of the CO_2 concentration in the chamber atmosphere, a protocol used by Norman (1992) and Rochette et al. (1991) working with a dynamic-chamber-IRGA method, is achieved by passing the returning air stream through a soda lime tube in order to scrub out CO_2. The returning air becomes CO_2-free and thereby dilutes the chamber CO_2 concentration. One could argue, that if there is an increase in the soil storage of CO_2 from an increase in the chamber CO_2 concentration, then a reduction in the chamber CO_2 concentration should cause a depletion of CO_2 in the soil profile (a mining effect). Freijer and Bouten (1991) however found that the effect of their dynamic absorption chamber on the natural conditions of the CO_2 profile in the soil was minimal. Still, the degree to which the chamber CO_2 concentration can be lowered without severely impacting the soil profile atmosphere warrants further study.

There are a large number of studies which compare different methods of measuring soil-CO_2-efflux *in situ* (de Jong et al. 1979, Edwards 1982, Cropper et al. 1985, Freijer and Bouten 1991, Norman et al. 1992, Rochette et al. 1992 and Nakadai et al. 1993); their conclusions, however, differ. It can be difficult to compare the results from these types of studies. One problem is that it is not possible to make direct comparisons by applying two or more methods simultaneously to the same piece of ground at the same time. Another problem is in determining which method is providing the best estimate if true rates are not known. Yet another problem is in ascertaining what element of a particular method is responsible for the difference in the observed rate. There are many subtleties within any given method which conceivably could have large impacts.

Calculating Net Primary Production Using Soil-CO_2-Efflux

The main goal of this research is to evaluate methods for measuring soil-CO_2-efflux. A tool that can accurately measure soil-CO_2-efflux at the stand level should be of great value for calculating carbon budgets of ecosystems. Accurately estimating soil-CO_2-efflux may prove to be critical in the evaluation of ecosystem net primary production (NPP), particularly on sites which need to be monitored long-term and with minimal destructive sampling.

The Long-Term Ecosystem Productivity (LTEP) Program at the USDA Forest Service, Pacific Northwest Research Station is currently initiating long-term ecological studies to evaluate factors influencing site productivity. Integrated Research Sites (IRS) are now being laid out on six national forests in Oregon and Washington with plans for the studies to be monitored over a 200-yr period. Net primary production (NPP) is the proposed measure of site productivity in the LTEP program. Integrated Research Sites in the LTEP

program are scheduled for harvest treatments to begin in 1994, therefore there is a relative urgency to develop the methods related to calculation of NPP.

Calculating total ecosystem NPP is difficult at best, and is particularly challenging when the belowground components are included. Also, since NPP is not considered constant through time for a particular site, it will need to be monitored frequently during the course of the experiment. The methods involved in calculating NPP not only need to be accurate but need to be non-disruptive to the processes being studied.

Net primary production is defined by the following equation:

$$NPP = GPP - R_a \tag{9}$$

where *GPP* is gross primary production (or the total amount photosynthate produced) and R_a is autotrophic respiration (respiration of green plants). Net ecosystem production (*NEP*) represents the change in carbon stored in the ecosystem thus:

$$NEP = \Delta B = GPP - R_t \tag{10}$$

where ΔB is the change in biomass (live or dead) and R_t is total ecosystem respiration. R_t consists of both autotrophic respiration and heterotrophic respiration (respiration of decomposers and consumers), so that:

$$R_t = R_a + R_h. \tag{11}$$

By rearrangement and substitution, we obtain the following NPP equation:

$$NPP = \Delta B + R_h. \tag{12}$$

Heterotrophic respiration (R_h) can arbitrarily be divided into two components: aboveground heterotrophic respiration (R_{ha}) which is largely attributed to the respiration of herbivores, and belowground heterotrophic respiration (R_{hb}) which is largely attributed to decomposition processes within the soil. R_{ha} in general is believed to be a relatively small number (< 2 % NPP)

in most forest ecosystems (Schlesinger 1991, Richards 1987) and unless there is conspicuous herbivory such as insect defoliation, R_{ha} can probably be neglected in calculating NPP. Thus we assume that

$$R_h = R_{hb}. \tag{13}$$

When soil-CO_2-efflux ($J_s^{CO_2}$) is measured we make the following assumption:

$$J_s^{CO_2} = R_S \tag{14}$$

where R_S is total soil respiration. Thus, it is assumed that for practical purposes R_S is in equilibrium with $J_s^{CO_2}$ and that anaerobic respiration which produces CH_4 is insignificant. R_S itself consists of two major components: belowground heterotrophic respiration (R_{hb}) and belowground autotrophic respiration (R_{ab}).

$$R_S = R_{hb} + R_{ab} \tag{15}$$

Since R_{ab} is not included in the calculation of *NPP* (Equation 12) the fractionation of R_S is necessary for complete evaluation of *NPP* with the measurement formula as follows:

$$NPP = \Delta B + J_s^{CO_2}\left(\frac{R_{hb}}{R_S}\right) \tag{16}$$

Work done by other investigators regarding R_{ab} or root respiration include Singh and Shekhar (1986), Ewel et al. (1987b), Cropper and Gholz (1991), Joshi et al. (1991) Sprugel and Benecke (1991) and Cheng et al. (1993). Measuring total soil-CO_2-efflux with accurate partitioning coefficients will provide the best estimates of R_{hb}. Without partitioning coefficients, values for soil-CO_2-efflux estimate the upper limit for R_{hb}. By measuring litterfall we can further confine the possibilities for R_{hb} if we assume that litterfall rates are in equilibrium with their decomposition processes.

While the aboveground portion of NPP has been studied fairly extensively, studies of belowground productivity are few (Vogt et al. 1986a, Raich and Nadelhoffer 1989). Although relatively little work has been done on belowground productivity, it is considered to be substantial and is estimated to be between 30 and 70 percent of total NPP for forest ecosystems (Grier et al. 1989). Also not well known is how belowground NPP relates to the aboveground NPP (Raich and Nadelhoffer 1989). There is some evidence that this relationship is not constant and that the proportion of carbon allocated belowground increases as site quality decreases (Grier et al. 1989) The estimation of changes in root biomass and the production of root detritus can be prone to large experimental error (Vogt et al. 1986b, Lauenroth et al. 1986); furthermore it requires extensive repeated destructive sampling of the belowground ecosystem by soil coring. Destructive sampling however, is undesirable because it prevents researchers from making repeated measurements of the same sample area through time. Therefore, an alternative non-destructive approach for assessing belowground carbon cycling is needed.

Soil respiration represents a major flux in the carbon cycle and is thought to be second only to GPP, and equal to or greater than NPP at the global scale (Raich and Schlesinger 1992). Therefore, because of the magnitude of R_S, both accurate estimates of soil-CO_2-efflux and the relative contributions of autotrophic and heterotrophic respiration are essential in evaluating NPP as described in Equation (16).

Some researchers have also considered estimates of soil respiration as an actual index of NPP (Grier et al. 1989, Raich and Schlesinger 1992). Investigators Schlesinger (1977) and Singh and Gupta (1977) suggest that the

difference in soil-CO_2-efflux and litterfall should be equal to belowground carbon allocation for steady-state communities.

Soil-CO_2-efflux measurements are of interest to those working at global or microbiological scales. Soil-CO_2-efflux data from various studies have been used in synthesis studies of global carbon fluxes (Schlesinger 1977, Raich and Nadelhoffer 1989, and Raich and Schlesinger 1992). Mircrobiologists have used soil-CO_2-efflux as an indicator of microbial activity and to detect the influences of herbicides and pesticides on soil organisms (Nakayama 1990). Investigators Neilson and Pepper (1990) have used soil-CO_2-efflux as an indicator of changes in soil aeration.

Spatial and Temporal Variation

The decomposition of soil organic matter is strongly influenced by a number of factors; it has been demonstrated by Fogel and Cromack (1977) to vary with changes along a climatic gradient of moisture and temperature. Grahammer et al. (1991) found that they could account for 85 to 93 percent of the variation in the soil-CO_2-efflux measurements of a grassland by measuring volumetric water content. Bunnel et al. (1977) were able to account for 71 to 96 percent of the variability in microbial respiration using the abiotic factors: moisture, temperature and O_2. Models, using only moisture and temperature to predict soil-CO_2-efflux in forests, have been developed and are able to account for 75 to 90 percent of the variability detected in soil-CO_2-efflux measurements (Schlentner and Van Cleve 1985, Carlye and Than 1988, and Reiners 1968). Mathes and Schriefer (1985) however, found no statistical significance for soil moisture in explaining variation, yet did find a strong correlation with soil temperature.

Spatial variability in soil-CO_2-efflux appears to be high. Cropper et al. (1985) determined that 15 sample points were needed to be within 10 percent of the mean, with 90 percent confidence, in a 28-yr old southern pine plantation. Raich et al. (1990) calculated similar numbers for a 80-yr old pine forest in Harvard Forest, MA. Both of these investigators were using a static-chamber and absorbent method. However, Rochette et al. (1991), working in an agricultural field using a dynamic-chamber-IRGA method (much like what is used in this study), found that between 33 and 190 sample points were needed to be within 10 percent of the mean, with 95 percent confidence. These estimates were for times of the year when peak soil-CO_2-rates occurred. Spatial correlation in agricultural fields has been found to take place at scales of less than a half meter (Nakayama 1990 and Rochette et al. 1991).

Seasonal patterns have also been observed in investigations of soil-CO_2-efflux; these often coincide with changes in moisture, temperature and/or photosynthate production. Seasonal differences have been observed by a number of investigators (Joshi et al. 1991, Garrett et al. 1978, Rochette et al. 1991, Gordon et al. 1987) with highest rates occurring during the summer months. In Joshi et al's. (1991) study in the Central Himalayas, this high rate also corresponded with the rainy season. Kursor (1989) found soil profile concentrations of forests in Panama to nearly double during the two month course of the rainy season.

Information on diurnal variation of soil-CO_2-efflux is less extensive than for seasonal variation. In a grassland study, Grahammer et al. (1991) generally found higher rates during the day which were attributed to photosynthate production. On the other hand, Garrett et al. (1978) found little diurnal change in soil-CO_2-efflux in an Oak-Hickory forest, despite their observance of significant

diurnal differences of ambient CO_2 concentrations in the air above the soil surface.

2. AN ARTIFICIAL ECOSYSTEM EXPERIMENT

Introduction

Investigators have historically measured soil CO_2 efflux as an indicator of soil microbial and root activity and more recently in calculations of carbon budgets. The most common methods estimate CO_2 efflux by placing a chamber over the soil surface and quantifying the amount of CO_2 entering the chamber per unit area of soil per unit time. Schlesinger (1977), Anderson (1982), Rolston (1986a), Raich and Nadelhoffer (1989), and Nakayama (1990) have reviewed various chamber methods. No single method is established as a standard (Anderson 1982, Nakayama 1990, and Norman et al. 1992), partly because methods are not compared to known effluxes (Nakayama 1990). Past comparisons have only shown a method to be higher or lower than another method.

This study compared the responses of two commonly used chamber methods to known effluxes from the surface of a simulated soil. Our known effluxes are based on calculations using Fick's law of diffusion. The two methods we tested were a static-chamber method with soda lime as a CO_2 absorbent and a dynamic-chamber method consisting of an infrared gas analyzer in a closed air-circulation loop. Because the absorption rate of alkali materials used in static chambers is thought to be a source of bias (Nakadai et al. 1993, and Freijer and Bouten 1991), we were also interested in how the soda lime absorbent affected the headspace CO_2 concentration of the static chambers.

Methods

The apparatus for testing the two methods (Figure 2.1) consisted of a CO_2 generator, a diffusion box, and a diaphragm pump to circulate air between the two. Carbon dioxide was generated in a flask of 0.5 M HCl by continuous additions of 0.3 M $NaHCO_3$ solution at a controlled rate ranging from 0 to 30 ml h^{-1}. The diffusion box, constructed of 0.5-cm-thick Plexiglas, had inside dimensions of 75 X 75 X 40 cm. Air with CO_2 from the generator was introduced into the bottom half of the box (footspace) through a plenum and mixed with two fans. Above the footspace, an 18-cm-thick layer of polyurethane foam provided a porous medium through which the CO_2 diffused. We used a water manometer to test for overpressure of the footspace; none was detected. Lab air temperatures ranged from 21 to 29°C and relative humidity ranged from 21 to 55 percent.

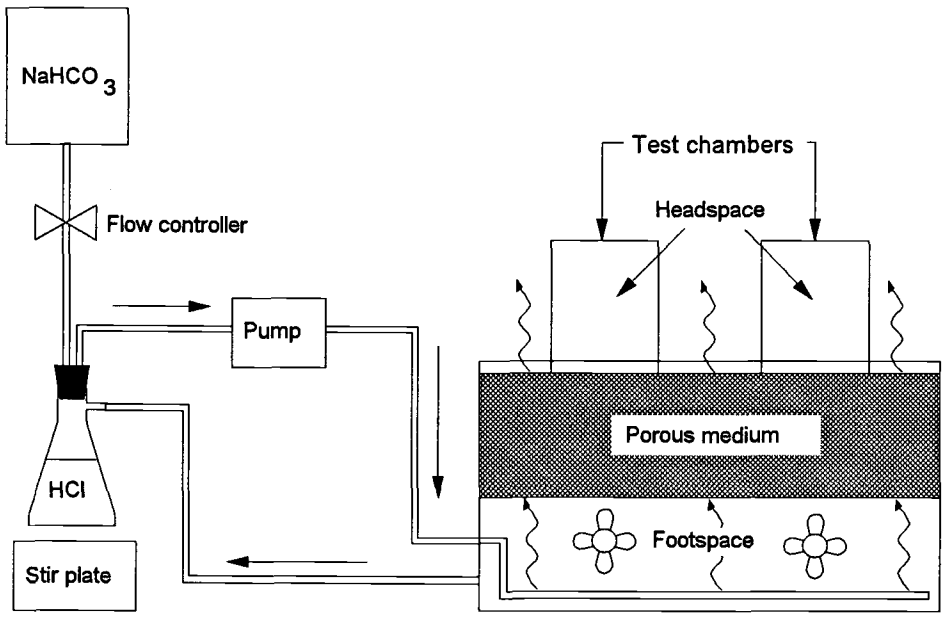

Figure 2.1. Laboratory apparatus for testing chamber methods to measure soil-CO_2-efflux.

Four different efflux rates ranging from 0 to 0.77 g CO_2 m^{-2} h^{-1} were achieved in trials lasting 24 h. This range of effluxes is similar to those reported for soils globally (Raich and Schlesinger 1992). The efflux of CO_2 (J) from the surface of the foam was calculated based on Fick's law of diffusion:

$$J = -D_S \frac{dC}{dz} \qquad (17)$$

where DS is the diffusivity of CO_2 in the foam and dC/dz is the CO_2 concentration gradient through the foam. Diffusivity of the foam was determined at 25°C to be 0.099 cm^2 s^{-1} (SE = 0.002 cm^2 s^{-1}, n = 3) by using methods described by Rolston (1986b). The CO_2 gradient was calculated as the difference in CO_2 concentration between the top and bottom surfaces of the foam divided by the foam thickness. DS was corrected for minor variations in air temperature by using the equation: $DS = 0.083(T/273K)^2$, where 0.083 cm^2 s^{-1} is the foam diffusivity adjusted to 273 K and T is air temperature in K.

Air samples were collected with a 0.5-ml syringe at the top foam surface and through a septum in the footspace and the CO_2 concentrations were determined by gas chromatography (GC-8A fitted with a Porapak Q column and a thermal conductivity detector, Shimadzu Corp., Kyoto, Japan). These samples were taken at about 30- to 60-min intervals. Throughout the trials, the footspace CO_2 concentration was regulated by minor adjustments to the flow rate of $NaHCO_3$ solution.

The *static-chamber method*, based on Edwards (1982), estimated CO_2 entering the chamber by the mass increase of the soda lime absorbent. Three polyvinyl chloride (PVC) chambers 21 cm in diameter by 20 cm in height were used in each trial. Soda lime (60 g, 6 -12 mesh) was contained in tins 8 cm in diameter by 5 cm in height and set directly on the foam surface inside a collar. Five-cm-tall collars made of the same PVC material as the chambers were

inserted into the foam to a depth of 2.5 cm. Static chambers were affixed to the collars and sealed with duct tape. We used three blanks in each trial to account for weight change from handling of the soda lime. The headspace concentrations of CO_2 in the static chambers were also monitored during a trial by taking five to eight syringe samples through a rubber septum in the top of each of the chambers.

The *dynamic-chamber method*, based on Norman et al. (1992), used an infrared gas analyzer (LI-6200, Li-Cor, Inc., Lincoln, NE) to monitor changes in the CO_2 concentration of air circulating to and from the dynamic chamber. Our dynamic chamber was of the same dimensions and materials as our static chambers. Before each sampling, the chamber was allowed to equilibrate with the ambient air by resting on its side. After equilibration, the chamber was affixed to a collar, also the same as the static chambers, and sealed with a closed-cell foam-rubber gasket. The rate of CO_2 concentration buildup was then measured for 78 s. Three locations on the foam surface were sampled about eight times over the course of each trial except during the highest efflux when two locations were sampled.

Results and Discussion

Both the static- and dynamic- chamber methods exhibited biases when compared to the calculated efflux based on Fick's law of diffusion. The static-chamber method greatly overestimated the zero efflux, overestimated the two intermediate effluxes of 0.12 and 0.24 g CO_2 m^{-2} h^{-1} by about 25 percent, and underestimated the highest efflux of 0.77 g CO_2 m^{-2} hr^{-1} by 57 percent. The dynamic chamber method consistently underestimated all effluxes above zero by 15 percent. (Figure 2.2)

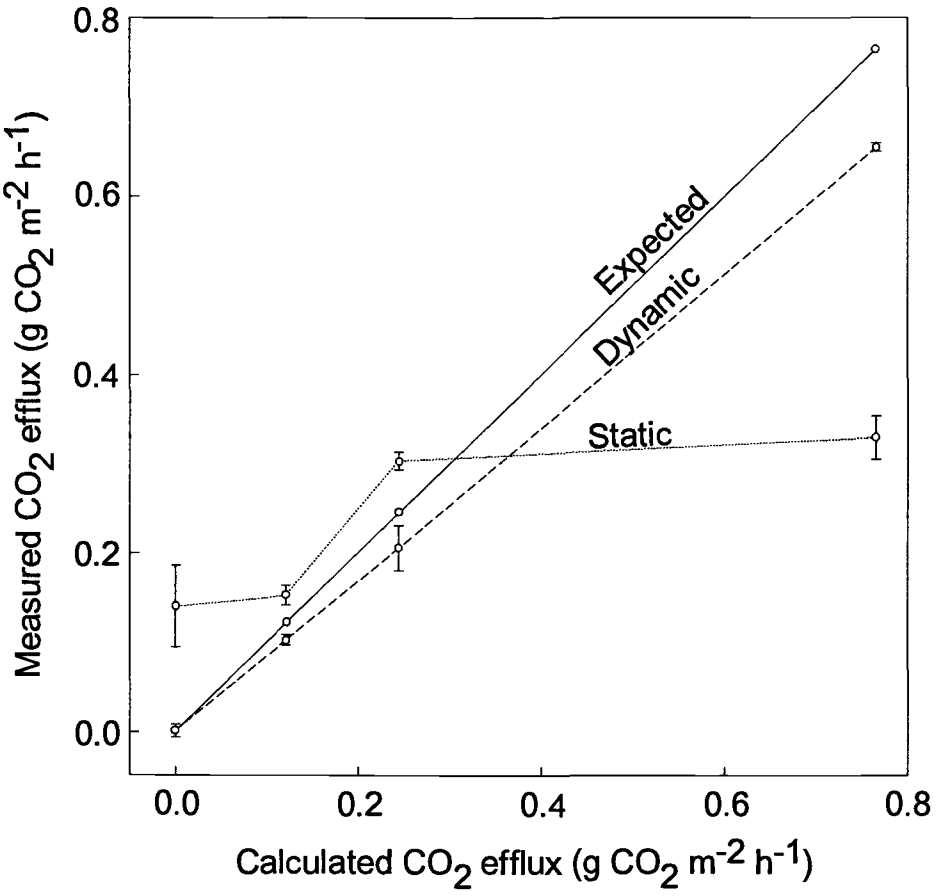

Figure 2.2. CO_2 efflux measured by chamber method compared with CO_2 efflux calculated by Fick's law, with ± 1 SE for chamber method estimates (some SE's obscured by data points).

The average headspace CO_2 concentrations of the static chambers differed from the ambient air by -180, -60, +15, and +450 µmol/mol during the 0, 0.12, 0.24, and 0.77 g CO_2 m^{-2} h^{-1} trials, respectively. The three greatest differences were statistically significant (ANOVA, $\alpha = 0.05$). No significant differences were found among headspace concentrations within a trial. The headspace concentration of the dynamic chamber changed on average from the ambient air by +36 µL L^{-1} in the 0.77 g CO_2 m^{-2} hr^{-1} trial and was proportionally less for the other trials.

Our study demonstrates that both overestimates and underestimates of efflux result from the use of a static-chamber method with soda lime absorbent. The corresponding increase in the headspace CO_2 concentration in our highest efflux trial likely also reduced the CO_2 gradient in the foam directly below the chamber and altered a portion of the diffusion path of CO_2 away from the chamber. In the two lowest efflux trials, the reduced concentration in the headspace had an opposite effect. The CO_2 gradient was increased, thus enhancing the diffusion of CO_2 from the foam and surrounding air into the static chamber. The underestimate by the dynamic chamber may be a result of our using a linear rather than a nonlinear model to estimate efflux from the rate of change in the headspace CO_2 concentration (Hutchinson and Livingston 1993).

The bias for the static method observed in this study may be more pronounced than the bias in field studies because of differences in diffusivities between the foam and natural soils. The diffusivity of our foam was 60% of the diffusivity of free air whereas the diffusivity of soils typically range from 2 to 50% of free air (Glinski and Stepniewski 1985). Given two soils with the same CO_2 efflux, the soil with the higher diffusivity will have a lower CO_2 gradient. With a lower gradient, changes in headspace CO_2 concentrations will have a larger effect on the gradient and consequently on the measured efflux. In field studies (Cropper et al. 1985, Ewel et al. 1987a, Norman et al. 1992, and Rochette et al. 1992) comparing static to dynamic methods of measuring CO_2 efflux, when the dynamic measures exceed 0.2 g CO_2 m^{-2} hr^{-1}, the static method estimates diverge from the dynamic estimates. This point of divergence is similar to what we observed by using foam.

Our results should raise a certain degree of caution about using any chamber methods that have not been calibrated against known effluxes,

especially in calculating carbon budgets where accurate measurements are essential. Any use of the static-chamber method ought to be particularly scrutinized. Although disagreement exists about the accuracy of static-chamber methods with alkali absorbents, these techniques--if applied carefully--are believed to allow accurate relative comparisons of in situ soils (Anderson 1982). This assumption may not be valid. Depending on the range of effluxes, true differences in soil CO_2 efflux could be nearly impossible to detect with the static-chamber method. For this technique to be effective for relative comparisons, the sensitivity range must be wide enough to capture the true range of effluxes being measured. At a minimum, the air in the static-chamber headspace should be sampled to determine if the CO_2 concentration has been significantly altered from ambient conditions.

The apparatus we introduce in this study is a much simplified model of a natural soil. Future work should proceed from this point to incorporate more of the complexity of a natural system. Our approach has the advantages of providing a known CO_2 efflux, not being limited to the existing conditions of field studies, and isolating confounding factors of the environment and chamber design that influence results.

3. A CONTROLLED ECOSYSTEM EXPERIMENT

Introduction

The goal of this experiment was to determine if monitoring of soil-CO_2-efflux with the dynamic-chamber-IRGA method could account for changes in the carbon content of a soil ecosystem. The soil ecosystems in the box-lysimeters studied in this experiment differ from natural systems by having finite boundries, less heterogeneous soils and no plants. By working with a system with defined boundaries (box-lysimeter), accounting for inputs and outputs is greatly enhanced . By excluding plants from the ecosystem, no additions of carbon to the soil should occur. By working with soils that have been well mixed ,sampling errors should be greatly reduced. If the soil-CO_2-efflux is adequately monitored and then results of monitoring should not differ from the change in soil carbon. The ecosystems contained in the box-lysimeters represent a higher degree of complexity that the artificial ecosystem that was examined in Chapter 2. While controlled these are real ecosystems and are of lesser complexity, due to soil mixing and the exclusion of plants, than the field conditions where the methods need to be employed.

A number of other experiments were also conducted in conjunction with the box-lysimeters. Other experiments examined the effects of using chamber fans, spatial variation and comparisons the dynamic-chamber-IRGA method and the static-chamber-absorbent method.

Methods

Box-Lysimeter Construction

Ten box-lysimeters (152 X 152 X 70 cm, Figure 3.1) were constructed within a concrete nursery bed structure at the Forestry Research Lab on the campus of Oregon State University. Within the concrete structure, the ten box-lysimeters were delineated by plywood dividers. At the same time ten smaller boxes (0. 75 X 0.30 X 0.70 m) were also constructed. The small boxes contained some of the same soil mixture used to fill the experimental boxes. This extra soil material from the small boxes was used to refill holes created from soil coring in the box-lysimeters.

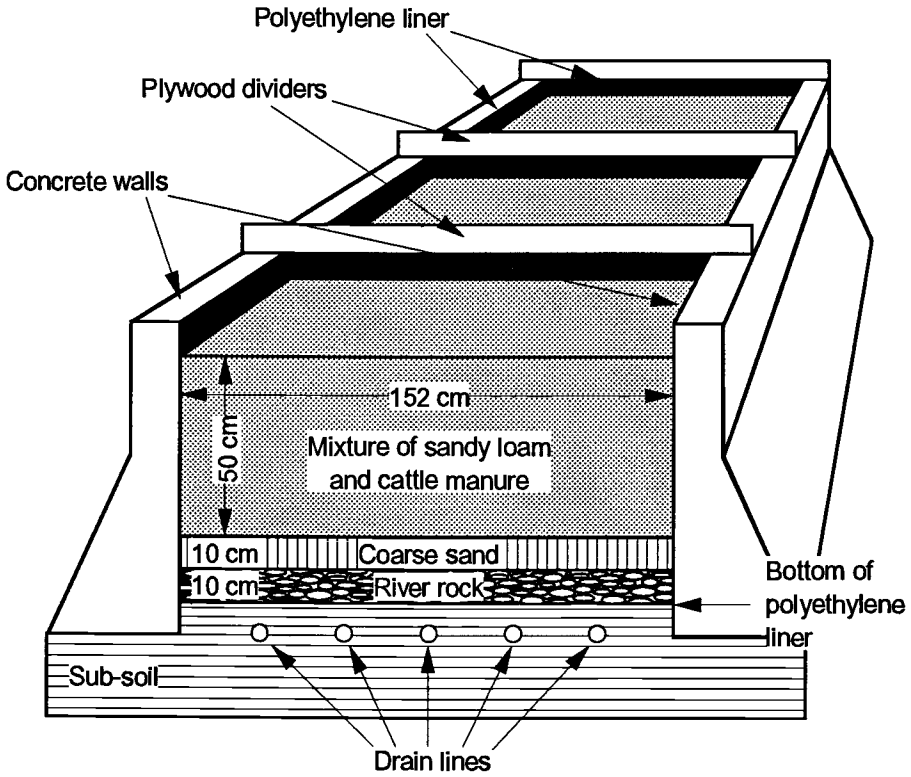

Figure 3.1. Box-lysimeters diagram.

The box-lysimeters were lined with 0.15 mm thick (6 mil) polyethylene and fitted with a 10 cm diameter drain. The drain was located in the center of each box and plumbed to a catchment area. All boxes had a 10 cm layer of coarse river rock overlaid with a 10 cm layer of coarse sand. Above the coarse sand was 50 cm of soil comprised of various mixtures of mineral and organic matter.

Soils for each of the box-lysimeters were individually mixed and consisted of a sandy loam / loamy sand (USDA textural classification) from a local river bottom, and cattle manure from the OSU dairy farm. Liquids were extracted from the manure at the dairy farm. The manure was approximately four weeks old at the time of mixing with the mineral matter. Soils were mixed on a volumetric basis. Both mineral matter and manure were passed through a 2.5 cm sieve to remove rocks and break up large aggregate material. The soil materials were mixed by turning with a front-end-loader tractor. The scoop of the front-end-loader also served as a measurement device.

Five nominal volumetric mixture ratios of manure to mineral soil of 2:1, 1:1, 1:2, 1:3, and 1:4 were made. Each nominal mixture type was used to fill two boxes. Two boxes filled with the same mixture type however were not necessarily true replicates. The mixture ratios were not precise and simply served as targets to insure that an array of mixtures were produced. The ten box-lysimeters are essentially ten independent experiments.

Construction of box-lysimeters took three days, while mixing and filling with soils took an additional three days. Each box was filled with approximately 60 cm of the soil mixture and allowed to sit for at least five days. After this period the excess soil above 50 cm was removed and placed in the appropriate small box of extra material. The boxes sat undisturbed for an additional nine

days before extracting initial-soil-cores which delineated the beginning of the monitoring experiment.

Weeding was done throughout the experiment to prevent additions of organic matter to the soil. An 80% shade cloth was used in the latter parts of the experiment to help keep weeds to a minimum. Plants provide a source of C to the soil. The design of this experiment was to only account for C leaving the ecosystem; any additions of C would confound results of the experiment.

Core Sampling

A sampling area of 137 X 137 cm was designated within each of the boxes. (Figure 3.2) This sampling area was then further subdivided into 36 sub-sampling cells used for locating sampling points for various activities including soil coring, soil-CO_2-efflux monitoring and soil moisture measurements. Records were kept of the type of sampling that occurred within a sub-sampling cell, in order to exclude cells from incompatible sampling activities. For example cells that had initial soil coring were excluded from soil-CO_2-efflux monitoring and other soil sampling.

Ten soil cores were extracted from the center of ten randomly selected sub-sampling cells. The soil corer was a 5 cm diameter piece of electrical conduit with a tee handle. The cutting edge of the corer was sharpened. A twisting motion was used for inserting the corer into the soil until contact with the underlying coarse-sand layer was made; the soil core was then extracted. The coring produced a hole with a well defined edge and an unobstructed view to the coarse-sand layer; this gave me the impression of having obtained a complete and representative sample of the soil. Soil from the appropriate small box of extra soil was then used to refill holes to as near as possible the same initial

conditions. Initial coring delineating the beginning of the experiment was done May 19 and 20, 1992.

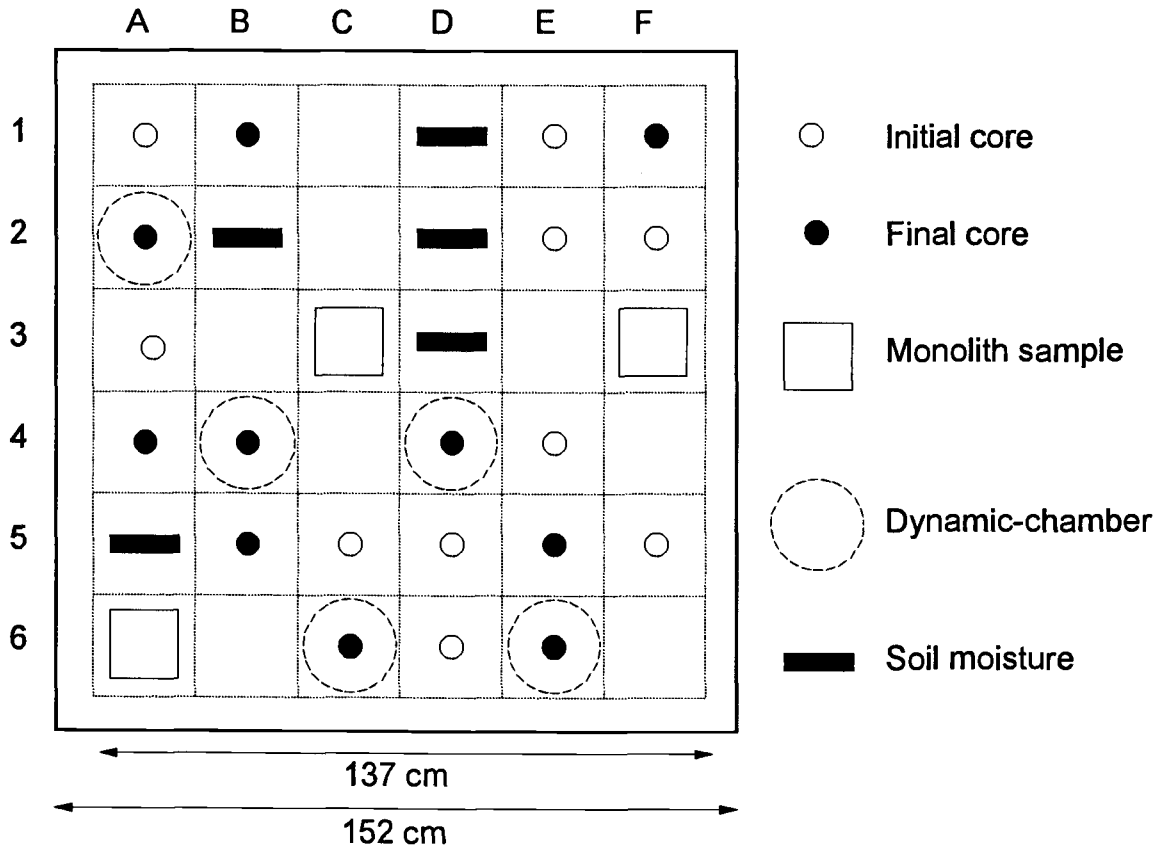

Figure 3.2. Box-lysimeter sampling grid with an example layout of sampling activities for a single box.

Soil core samples were placed in an oven the same day as they were extracted and dried at 70°C for a minimum of 72 h after which they were weighed, bagged and labeled for storage. At the end of the experiment a second set of ten cores were extracted from each of the box-lysimeters; these were dried, weighed, bagged and labeled in the same manner as the initial cores. The final cores were taken from a separate set of randomly selected sub-

sampling cells. All soil analyses were done after the conclusion of the experiment.

The original intent of the experimental design was to compare the carbon content of the initial cores to the final cores to determine the change over time. However, a preliminary analysis of oven dry weights revealed that the final cores actually weighed on average 22 percent more than the initial cores. This suggested that despite the appearance of having obtained complete and representative samples, this coring method did not work as presumed.

A possible explanation for the incomplete samples of the coring was that the material became compacted in the end of the corer and was then forced to the outside of the corer. The problem may have been more pronounced in the beginning of the experiment than the end, since the organic matter was more fibrous in the beginning and thus more difficult to cut, whereas at the end of the experiment the organic matter was more decomposed.

Monolith Sampling

Because of the sampling problems with the soil corer, an extended soil sampling regime was designed to correct the biases of the original core sampling. Correcting the biases of the core sampling required the assumption that while the organic matter(OM) changed with time, the mineral matter(MM) did not. By combining an accurate measurement of the mineral content of the soil with OM:MM ratios, the initial and final carbon contents of the soils could be determined.

A new soil sampling device (soil monolith sampler) was devised to sample a larger portion of the soil. The soil monolith samples provided the data to calculate mineral content per unit area and the soil cores provided the OM:MM

ratios at the beginning and end of the experiment. The soil-monolith sampler had a square sampling area of 218 cm^2. The larger sampler has the advantage of a reduced edge effect thus less friction from the sides when inserting into the soil. The monolith sampler also featured a serrated and sharpened cutting edge. Inserting the monolith sampler required that it be pounded into the soil.

To asses the efficacy of the monolith sampler, a small study was conducted in two of the small boxes of extra soils. The extra soils used for this experiment had the same soil mixture as did Boxes 8 and 9. Three samples were taken with the monolith soil sampler from each of these two boxes of extra soil. The remaining soil in the extra boxes was then excavated. The monolith sampling estimate was compared to the total mass of soil from the extra box. The result was that the soil-monolith sampling estimated approximately 91 percent of the mineral mass it was thought to have sampled, therefore a correction factor of 1.1 was used to adjust monolith sample weights.

Monolith sampling in the box-lysimeters had a sample size of three. These samples were randomly located in sampling cells which had not previously been cored or sampled for soil moisture. As with the core samples, the monolith samples were immediately placed in an oven and dried at 70°C for 72 h.

Soil Analysis

Soil samples were ground with a 20 cm disc pulverizer (Bico Inc., Burbank, California) to less than 425 µm (40-mesh). Loss on ignition (LOI) was used to determine organic matter content and was equal to the mass loss of a crucible with 1 to 5 g of ground soil after baking at 450 °C for 4 h. A portion of the soil-core samples from Box 10 were ground to less than 250 µm (60-mesh).

The finer ground samples were then analyzed in a C, N and S analyzer (NA1500 Series 2, Carlo-Erba Instruments, Milan, Italy) to determine a ratio of C:OM. The initial-core-samples had a mean C:OM ratio of 0.528 (SE = ±0.018), while the final-core-samples had a mean C:OM ratio of 0.489 (SE = ±0.016).

Calculation of Soil Carbon Loss

The calculation for change in soil carbon relies on the assumption that mineral matter mass (*MM*) in the soil was constant through time. The calculations are as follows:

$$\left[\left(\frac{C_0}{OM_0} x \frac{OM_0}{MM_0}\right) - \left(\frac{C_{244}}{OM_{244}} x \frac{OM_{244}}{MM_{244}}\right)\right] x \frac{MM_{333}}{BS_{333}} x \frac{BS_{333}}{A} = \frac{dC}{dt}\frac{1}{A} \qquad (18)$$

where the subscripts refer to sampling times by the day of the experiment (*0* = initial, *244* = final, and *333* = post final (monolith sampling)). *BS* is bulk soil mass, *C* is carbon mass, and *OM* is organic matter mass. The monolith sampling determined the *BS* per area, and LOI determined the relationships between *BS*, *MM*, and *OM*. A combination of LOI and carbon analysis were used to determine the relationship between *C* and *OM*.

All of the components of Equation (18) are means of multiple samples, and therefore have a variance associated with each component in the equation. The variance of a product is a computable statistic, however the calculation of a confidence interval is extremely complicated if at all possible by traditional statistical methods. Therefore, statistical bootstraping methods (Efron and Tibshirani 1986) were used to calculate a 95 percent confidence interval for carbon loss in each box. Bootstraping methods rely on computer-intensive calculations where repeated random samples of the existing sampling data was done for each of the components in Equation (18) to produce a distribution of

outcomes for the product of Equation (18). This distribution of outcomes was then used to determine a 95 percent confidence for the mean product.

Soil-CO_2-Efflux Monitoring

Soil-CO_2-efflux measurements were performed with the dynamic-chamber-IRGA method with largely the same protocol for measurements described in the artificial ecosystem experiment (Chapter 2). Exceptions to the Chapter 2 protocol are that collars were not used, that the dynamic-chamber had fans, and that the dynamic-chamber height was increased to 60 cm for much of the experiment.

Two preliminary experiments were conducted to compare results obtained with and without collars and with and without fans in conjunction with the dynamic-chamber and IRGA. These experiments were conducted on the box-lysimeter soils at the beginning of the monitoring experiment. The test of collar versus no-collar was done on three of the boxes with five replicates. In all three trials no differences in soil-CO_2-efflux were seen between measurements obtained with or without collars ($\alpha = 0.05$).

The test of the fan effect was conducted in a single trial on a single box-lysimeter soil. Ten soil-CO_2-efflux measurements were made with the dynamic-chamber fans off; these measurements were made in ten separate sample cells. The measurements were then repeated with the chamber fans on. Again no difference in soil-CO_2-efflux was detected between these two methods ($\alpha = 0.05$). The effect of the fans was that soil-CO_2-efflux measurements tended to be less variable with the chamber fans on (CV = 0.28) versus with chamber fans off (CV = 0.37).

The increase in chamber height to 60 cm was necessary to accommodate the high soil-CO_2-efflux observed early in the experiment. A taller chamber reduces the rate at which the CO_2 concentrations increase with time and as a result, there is less deviation from ambient CO_2 concentrations. For the most part, CO_2 concentrations in the dynamic-chamber did not rise above 600 $\mu L\ L^{-1}$ within a sampling run. The IRGA had an upper detection range of 1100 $\mu L\ L^{-1}$ CO_2. With a chamber height of only 20 cm, in the beginning of the experiment, it was easy to overrun the range of the IRGA.

The sampling scheme for monitoring soil-CO_2-efflux consisted of five randomly selected cells in the sampling grid. Cells that were used to obtain initial-soil-cores were excluded from soil-CO_2-efflux monitoring. The distribution of the five monitoring cells differed for each box-lysimeter. Soil-CO_2-efflux samples were repeatedly done about every two weeks from the same sample cells. Calculations of carbon loss by soil-CO_2-efflux consisted of integrating the monitoring data from each sample cell over the course of the experiment. The 95 percent confidence intervals were then based on the variation of the five integrated values per box.

Results and Discussion

Soil Carbon Loss

The mass loss of carbon based on soil analysis and Equation 18 ranged from 2.2 to 17.7 kg C m^{-2} over the 244 days (0.67 yr) of the experiment. Soils data used to calculate soil carbon loss according to Equation 18 are listed in Appendix A, Table A.1. Mass loss as a percent of the initial contents ranged from 17 to 53 percent, with the lowest percent loss occurring in the box

containing the lowest initial carbon (17.2 kg m^{-2}) and the highest percent loss occurring in the box with the highest initial carbon (33.3 kg m^{-2}). The relationship between the initial C content and mass loss of C were linearly related and are shown in Figure 3.3.

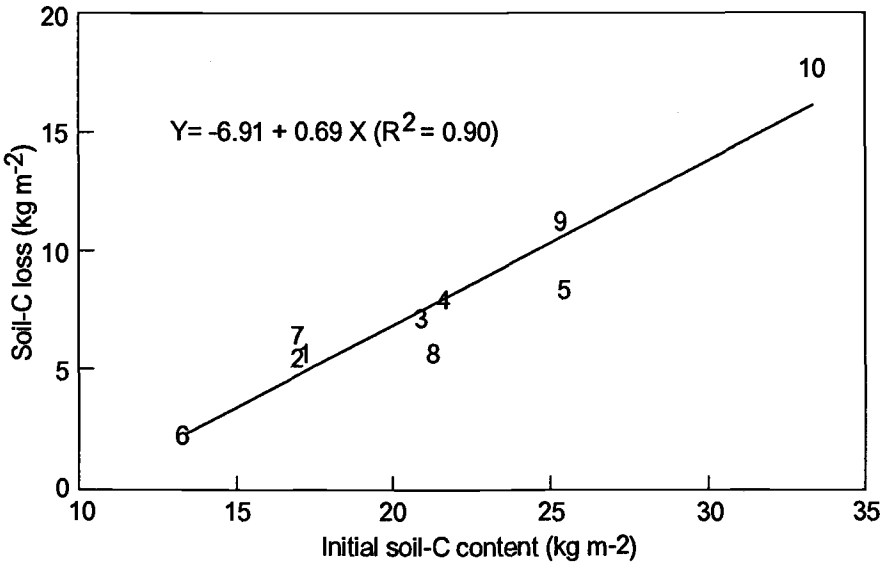

Figure 3.3. Soil-C loss after 244 days vs initial soil-C content of the ten box-lysimeters, numbers refer to box identification.

Decomposition of soil organic matter in ecological research is often expressed in the form of a decay function. Using a first order decay function as follows:

$$k = \ln\left(\frac{C_t}{C_0}\right) \Big/ t \qquad (19)$$

where C_t is the carbon content at time t in years and C_0 is the initial carbon content and k is the decay constant, k ranged from 0.27 to 1.12. The decay constant for the remaining eight boxes varied between 0.46 and 0.87; the average for all ten boxes was 0.65.

It appears that the decay rates observed in this experiment are reasonable. Approximately two-thirds of a green manure will decompose in a year when mixed with soils (Richards 1987, Brady 1990) which yields a decay constant of about 1.1. Green manures are more decomposable than farm yard manures when mixed into the soil (Russell 1973). Sommerfeldt et al. (1988) report that 35 to 45 percent of an application of one to two year old feed lot manure added to a soil, will remain after the first year of decomposition for applications of 3 to 18 kg m^{-2} of wet manure. These decay rates correspond to decay constants (k) of 0.8 to 1.0 with the decay rates accelerating with the amount of manure added. This same pattern of increased decay rates with increased amounts of manure was observed in this experiment.

Consideration was given to the possibility that carbon could have left the box-lysimeters through means other than CO_2 efflux. Other carbon effluxes examined were losses through soil water leachate, as organic or inorganic carbon, or from the soil surface as methane or other volatile compounds.

The soil water outflow was measured for Boxes 1 through 5. Soil water outflow of the box-lysimeters during the first month was not examined for carbon content due to contamination by an algal bloom in the catchment containers. The initial outflow not examined was no more than 10 liters m^{-2}. No outflow was observed between mid-June and mid-October. From mid-October until the end of the experiment (January) soil water collections were made in accordance with rainfall events. The total outflow ranged from 24 liters m^{-2} for Box 5 to 148 liters m^{-2} for Box 1, boxes with higher organic matter tended to have lower outflow.

Carbon loss as dissolved and suspended organic carbon or total organic carbon (TOC) was determined for water samples for each soil water collection through analysis in a carbon analyzer (Dohrmann Carbon Analyzer, Model DC-

80). Inorganic carbon was purged from the water samples through acidification (0.5 ml 4M H_2SO_4 / 50 ml H_2O) prior to the analysis. The total estimates of organic carbon lost in soil water outflow ranged from 2.7 g C m^{-2} for Box 5 to 10.2 g C m^{-2} for Box 3 and represented at most 0.14 percent of the C mass loss for the five boxes analyzed.

Carbon loss as dissolved inorganic carbon (DIC) was estimated by modeling of the soil atmosphere. Carbon dioxide will dissolve into H_2O in accordance with Henry's Law:

$$p = X^*K_H \qquad (20)$$

where p is the partial pressure of a gas, X is the mole fraction of the gas in solution and K_H is a Henrys law constant. Equation 20 and the average soil-CO_2-efflux measured after September (when outflow of soil H_2O occurred) were used to estimate the CO_2 concentration at -50 cm. The estimates for the CO_2 concentration in the soil atmosphere at -50 cm ranged from approximately 1.7 (Box 5) to 3.8 (Box 10) percent. These estimates for CO_2 concentration were then applied to the Henry's Law equation and multiplied by the outflow of soil H_2O. The results of this analysis also indicate that this potential loss of soil carbon was inconsequential being at the most 0.02 percent of the total carbon loss.

The final potential loss of carbon considered are the products of anaerobic respiration either from methanogenesis or fermentation. Unfortunately no estimates of methane efflux were measured in this experiment and therefore we must rely on the physical characteristics of the soils and the literature for this analysis. Methanogenesis is an anaerobic process and grazing animals contain populations of the microbes for carrying out the process, thus it

is likely that the soils used in this experiment were well equipped to produce methane.

The porosity of the soils in this experiment were high ranging from 58 to 76 percent of the soil volume. Porosity was calculated from bulk density and the assumptions that the particle density of mineral matter was 2.65 g cm^{-3} (Brady, 1990) and that the particle density of the organic matter was 1.0 g cm^{-3}. Brady, (1990) states that the particle density of soil organic matter generally averages between 1.1 and 1.4 g cm^{-3}. Since the organic matter in these soils was particularly fresh, 1.0 g cm^{-3} seemed reasonable. The soil water content measured with time domain reflectometry (IRAMS Soil Moisture Analyazer, CPN Corporation, Martinez, California) generally averaged around 20 percent, thus leaving air-filled porosities of 38 to 56 percent. Soil with an air-filled porosity above 25 percent is considered to be well aerated (Glinski and Stepniewski 1985).

Though the general condition of the soils were well aerated, this does not necessarily preclude the possibility of methangenesis from occurring; these soils could still contain anaerobic microsites. In the beginning of this experiment soil-CO_2-effluxes on the order of 10 g CO_2 m^{-2} h^{-1} were measured. When I calculate CO_2 concentrations at -50 cm based on this order of efflux using Equation 4 I obtain CO_2 concentrations of 29 percent at -50 cm. While stochiometrically it does not seem likely that these concentrations of CO_2 could actually be realized, it does suggest a high likelihood that the atmosphere at depth in these soils were becoming anaerobic.

Various aerobic soils such as peatland, tundra, temperate forest, grasslands and deserts have been demonstrated to oxidize methane and are often considered to be sinks for atmospheric methane (Hütsch et al. 1991). In

an experiment conducted at the Rothamsted Experimental Station, it was demonstrated that soil cores taken from soils amended with farm yard manure could oxidize methane at rate of 1.28 *u*g C m^{-2} h^{-1} (Hütsch et al. 1991). In fact their study focused on the reduced ability of soils to be a sink for CH_4 when amended with inorganic nitrogen rather than through additions of organic matter. Therefore if CH_4 were produced in the box-lysimeters, it would seem likely that some if not all would have been oxidized before leaving the soil surface.

Fermentation is another anaerobic process that likely occurred in the box lysimeters which would have produced both ethanol and CO_2. Very little if any soil water was observed to flow out of the boxes with the higher organic matter content in the beginning months of this experiment. Therefore any carbon in the form of ethanol would likely have been volatilized as ethanol vapor and been undetected in the soil-CO_2-efflux measurements or further oxidized to CO_2 which would have been detected. It is difficult to find rates of ethanol production and oxidation in the literature that would be applicable to this case.

Other non-methane organic compounds can be emitted from the soil. However Hanson and Hoffman (1994) found that non-methane organic compounds were one to two magnitudes less than CO_2 efflux from cores take from a forest floor. Abdul-Kareem and McRae (1984) report concentrations of up to 6 $\mu L\ L^{-1}$ for ethane and 0.2 $\mu L\ L^{-1}$ for ethylene in mounded topsoil with an organic matter content of approximately 3 percent. Again these concentrations are several magnitudes less than that of CO_2 in the soil atmosphere and thus it appears these gases fluxes would also be small in comparison to soil-CO_2-efflux. On the other hand the soil in these two studies are not exactly analogous to the soils in the box-lysimeters. The chemistry of the organic matter in a forest is likely much different than that of cattle manure and the organic matter content

of the soils in both these studies is a magnitude less than the highest organic matter amendment to the box-lysimeter soils.

Soil-CO_2-Efflux

The soil-CO_2-efflux rates observed in this experiment were quite high in comparison to what would typically be found in the field, particularly in the beginning of the experiment when rates were ten-fold larger than I observed in the field (Figure 3.4 and Table 4.1). The highest initial rates corresponded with soils with the highest initial organic matter. Soil-CO_2-efflux declined dramatically over the course of the experiment; the last measurements being only about five percent of the first measurements(Figure 3.4). The drop in soil-CO_2-efflux rates seen in the second sampling appears to be attributed to a corresponding decline in temperature. Other drops in efflux rates are unexplained. Soil temperature data collected at the time of soil-CO_2-efflux sampling is displayed in Appendix C, Table A.3.

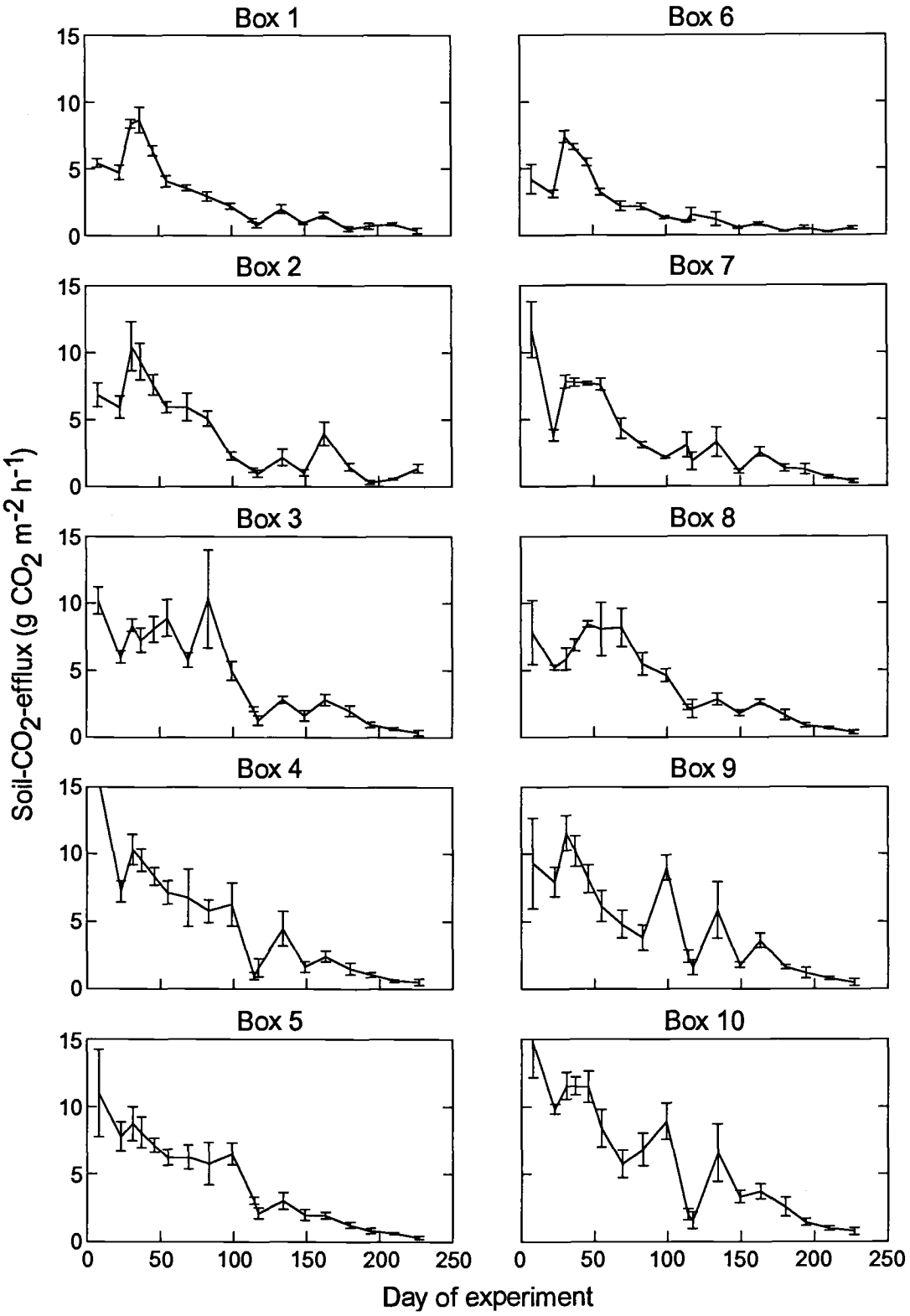

Figure 3.4. Mean soil-CO_2 effluxes (± 1 SE, n = 5) by day of experiment for the box-lysimeters, using the dynamic-chamber-IRGA method.

Soil Carbon Loss Versus Soil-CO_2-Efflux

Estimates of soil-CO_2-efflux and soil carbon change were not significantly different ($\alpha = 0.05$) for 9 out of 10 of the box lysimeters (Figure 3.5). Box 10, which had the highest carbon mass loss and highest initial carbon content, did produce significantly different estimates. Overall the confidence intervals for the estimates of soil-CO_2-efflux were nearly half the estimates of the change in soil carbon. The lower variation in soil-CO_2-efflux estimates may be due to the fact that the dynamic-chamber sampled a larger area than the sampling methods used in the soil analysis. Sampling by the dynamic-chamber covered an area 8.6 times as large as the soil cores and 2.7 times as large as the monolith samples.

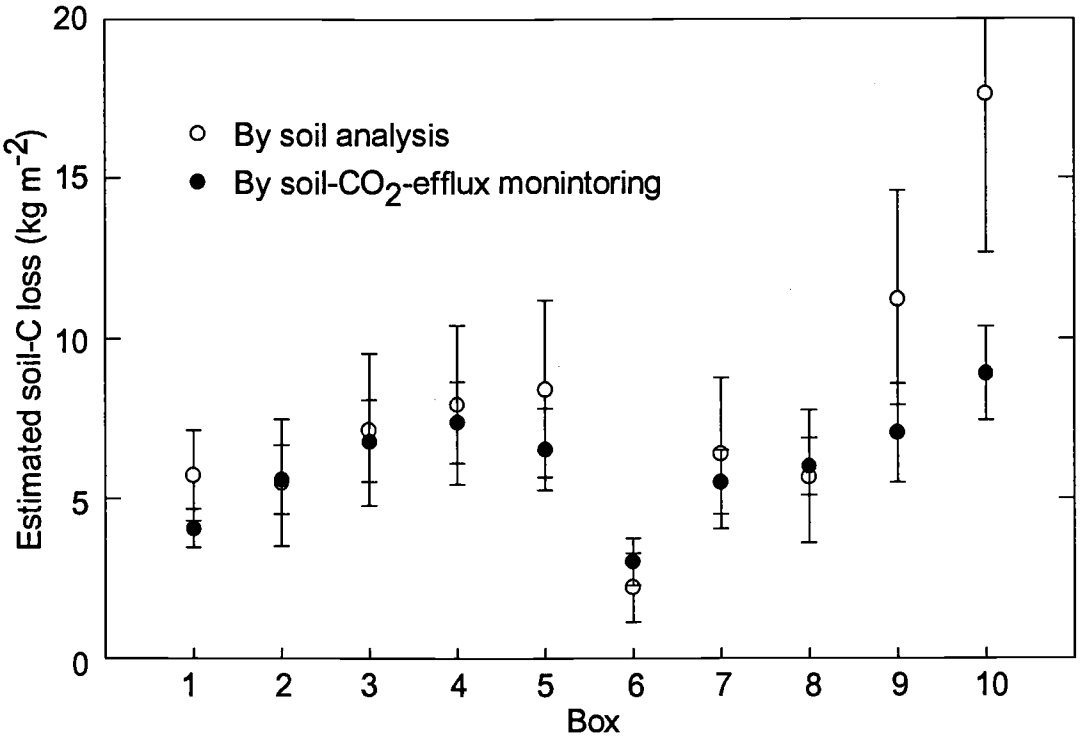

Figure 3.5. Mean soil-C loss (± 95 percent confidence interval) by soil analysis and by soil-CO_2-efflux monitoring

There is an unexplained carbon loss in Box 10. Loss in soil water outflow as TOC and DIC were considered to be insignificant. Experimental error associate with either the analysis of soil carbon or the measurement of soil-CO_2-efflux, or both are potential error sources. Production of ethanol and other volatile carbon compounds are also possible sources for error.

A number of sensitivity analysis of the soils data were conducted; however, no satisfactory explanation was found to account for the large discrepancy between soil-CO_2-efflux measurements and the change in soil carbon. Quality control steps were taken, such as reweighing all samples to confirm weights and randomly repeating loss on ignition analysis on approximately 10 percent of the samples. The performance of the IRGA was examined to determine if the IRGA had a different response pattern at high flux rates than at lower rates. Specifically I looked to see if there was declining rate of dC/dt within a sample run of the dynamic-chamber and IRGA at higher effluxes; again nothing was revealed.

The final consideration is that the soil-CO_2-efflux sampling was inadequate at the beginning of the experiment when the highest soil-CO_2-efflux rates occurred. The first measurements of CO_2 efflux took place nine days after the beginning of the experiment and, on average, accounted for approximately 15 percent of the total CO_2 efflux for the entire experiment. Rates then declined rapidly with the following eight measurements each representing, on average, seven to eight percent of the total. Thus it is likely that the integrated value which was calculated for the first measurement period, underrepresented the actual soil-CO_2-efflux in the beginning of the experiment. Since it appears that with higher concentrations of cattle manure, yield higher decomposition rates (Hütsch et al.1991) we might expect that my underestimate of soil-CO_2-efflux to

be more pronounced in the box with the highest cattle manure amendment. It is difficult to surmise that this could completely explain the all of the unaccounted for carbon loss in Box 10.

The best explanation I can make of the large discrepancy seen in Box 10 is that the error has a combination of sources. The most likely sources are non-CO_2 carbon gas fluxes and an undersampling of soil-CO_2-efflux at the beginning of the experiment. The soil temperature of Box 10 (measured at -10 cm) in the beginning of this experiment was 39°C; this was 10°C higher than the maximum soil temperature measured at the Hyslop weather station (10 km north of Corvallis) for the same day and depth. Box 10 also had the highest temperatures of all the box-lysimeters with the range being 7°C. After the first month of the experiment, soil temperatures in general declined and the soil temperatures for Box 10 came in alignment with the rest of the boxes. The soil temperature data indicates that whatever processes that went undetected in the soils (particularly Box 10), occurred early on in the experiment. Soil temperature data for the box-lysimeters and the Hyslop weather station can be found in Appendix C, Table A.3.

The discrepancy between the soil-CO_2-efflux and the change in soil carbon appears to be related to the amount of change in soil carbon. While soil-CO_2-efflux and change in soil carbon for Box 9 (second largest carbon loss) was not statistically significant (α =0.05), it does seem to follow the same trend as Box 10 (Figure 3.6) The lack of statistical significance is likely due to the high variation and low statistical power of the experiment. If Boxes 9 and 10 are excluded, a liner regression model of soil-CO_2-efflux versus soil carbon loss has a slope of 0.90 with an R^2 of 0.67. The slope of this line is not statistically different (α =0.05) from a slope of 1.0 which would represent one-to-one

relationship of soil-CO_2 efflux and soil carbon loss. The slope of this regression line is also not significantly different (α =0.05) from a 0.85 slope that was observed in the artificial ecosystem experiment (Chapter 2) with the dynamic-chamber-IRGA method. Despite the discrepancies with Boxes 9 and 10, the results of this experiment are consistent with the results of the artificial ecosystem experiment. The dynamic-chamber-IRGA method appears to give reasonable but slightly conservative estimates of soil-CO_2-efflux.

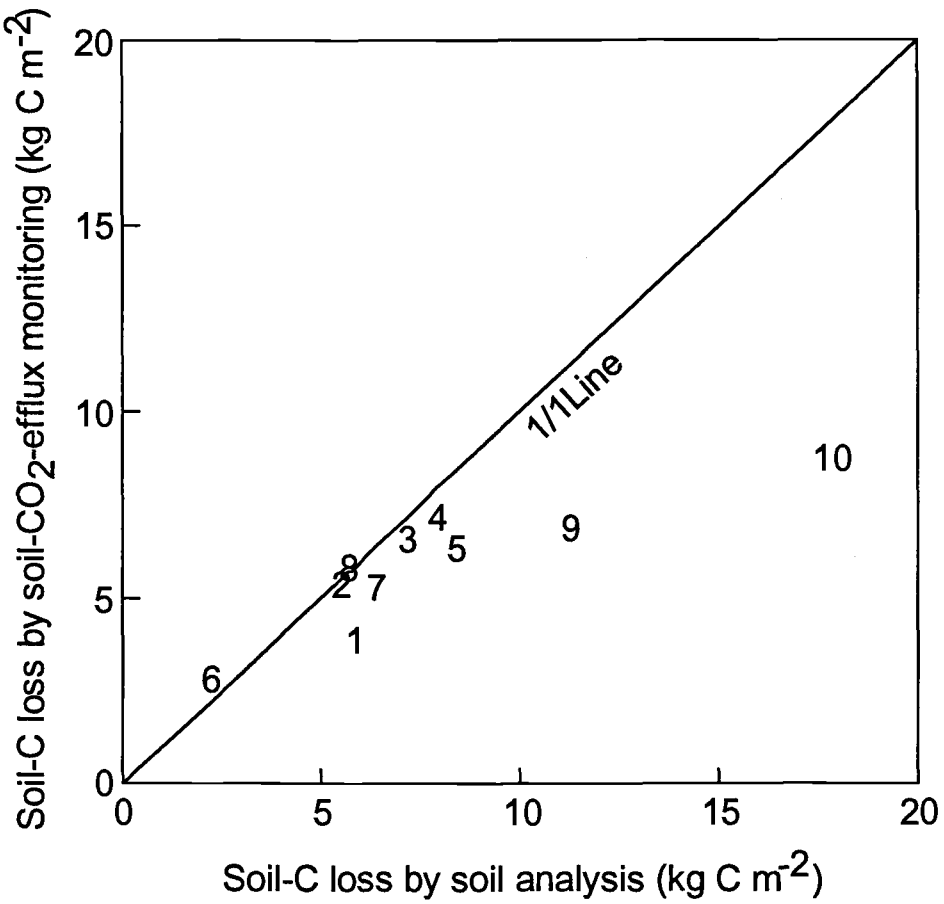

Figure 3.6. Soil-CO_2-efflux monitoring vs soil analysis to estimate soil-C loss.

Spatial Variation

While the soils in the box-lysimeters were sieved and well mixed to be as uniform as possible, I still observed a high degrees of spatial variability. Figure 3.7 illustrates the spatial variation detected with dynamic-chamber-IRGA method throughout the surface of one box-lysimeter. In this case, every sample cell was sampled with the dynamic-chamber-IRGA method within a 3 h period. The surface plot seen in Figure 3.7 is a linearly interpolated mesh of the 36 measurements. The mean soil-CO_2-efflux in this experiment was 2.46 g CO_2 m^{-2} h^{-1}, with a standard error of 0.11 g CO_2 m^{-2} h^{-1} and a coefficient of variation of 27 percent.

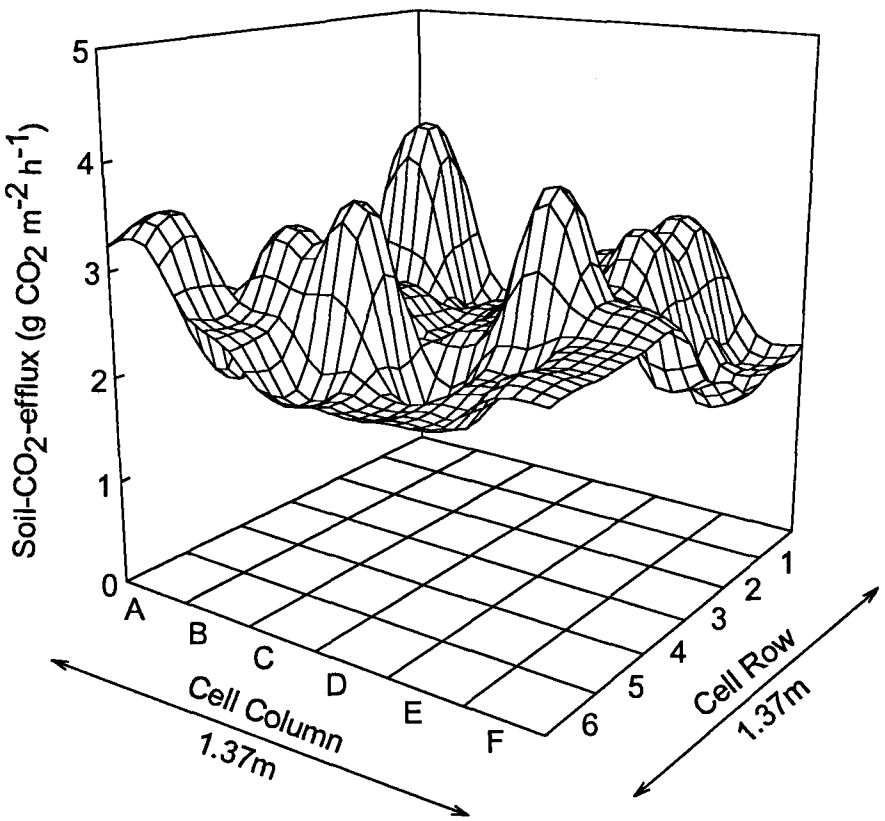

Figure 3.7. Soil-CO_2-efflux of 36 sample cells from a single box-lysimeter in an interpolated mesh plot (Box 3, 11/6/92).

In another experiment examining spatial variation, each cell in a single row of one box was repeatedly sampled 10 times during a 4 h period. The results of this experiment are illustrated in Figure 3.8 and demonstrates two points. First, that the dynamic-chamber-IRGA method produces repeatable results and second, that spatial variability even under these ideal conditions is very high.

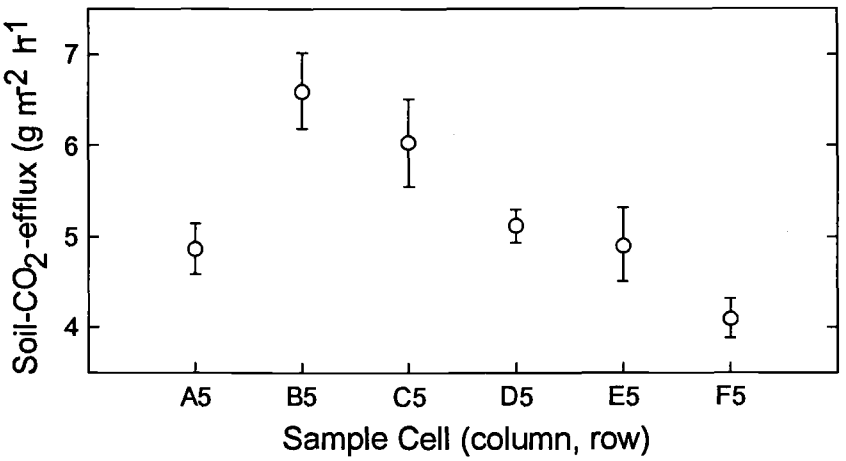

Figure 3.8. Mean soil-CO_2-efflux (± 95 percent confidence interval) for Box 8 on 8/4/92 by sample cell in a single row, n = 10

In a similar experiment, the dynamic chamber-IRGA method was used to monitor soil-CO_2-efflux in ten randomly selected sample cells over a 24 h period. The same ten sample cells were repeatedly measured every two hours. In Figure 3.9 the data is grouped by time of sample; here we see that there are no statistical differences (α= 0.5) over the 24 h of this experiment. However, if we reorganize the data and group by spatial location (Figure 3.10), we see that the variation at a particular spatial location throughout the 24 h is quite small and that the variation between locations is quite high with statistically significant differences between spatial locations (α= 0.5). The high variability observed in

this experiment also corresponds with the high variability that is reported by Rochette et al. (1991) in which they conclude that spatial patterns of variability in soil-CO_2-efflux for an agricultural soil occurred at distances less than 0.15 m.

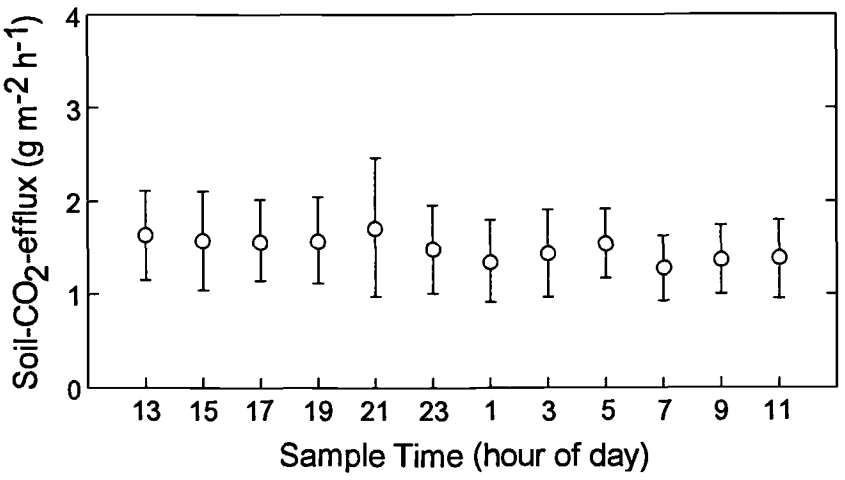

Figure 3.9. Mean soil-CO_2-efflux (± 95 percent confidence interval) for Box 2 on 9/28/92 and 9/29/92 by hour of day, n = 10.

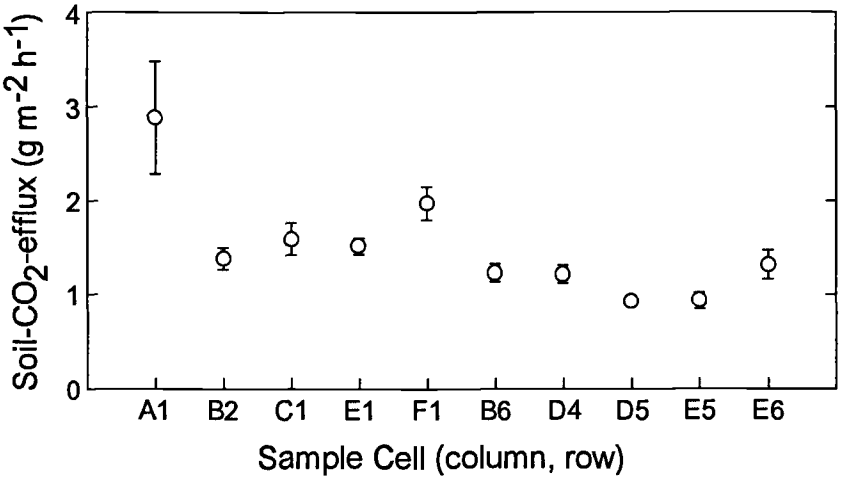

Figure 3.10. Mean soil-CO_2-efflux (± 95 percent confidence interval) for Box 2 on 9/28/92 and 9/29/92 by sample cell, n = 12.

Dynamic- and Static-Methods Compared

A final experiment done in conjunction with the box-lysimeter experiment was a comparison between the static-chamber-absorbent and the dynamic-chamber-IRGA methods. The absorbent used in this experiment was soda lime (60 g 1.7-3.4 mm granules) the same as used in the artificial ecosystem experiment. Four trials were conducted each lasting 24 h. Five static-chamber-absorbent measurements were compared to the mean of five dynamic-chamber-IRGA results from five spatial locations. Spatial locations sampled with the dynamic-chamber-IRGA method were repeatedly measured six to eight times during the 24 h period. In all trials the results obtained with the dynamic-chamber were significantly greater ($\alpha = 0.05$), with the mean dynamic-chamber-IRGA results being 2.5 to 6.3 times as great as the results obtained with the static-chamber (Figure 3.11). The stand error of the measurements made with the dynamic-chamber-IRGA method averaged four times that of static-chamber-absorbent method. This difference in variation by methods could explain the low estimates of sampling points needed as reported by Cropper et al. (1985) and Raich et al. (1990) and the high estimates reported by Rochette et al. (1991). The mean soil-CO_2-effluxes for the four trials as measured with dynamic-chamber ranged from 1.50 to 2.75 g CO_2 m^{-2} h^{-1}.

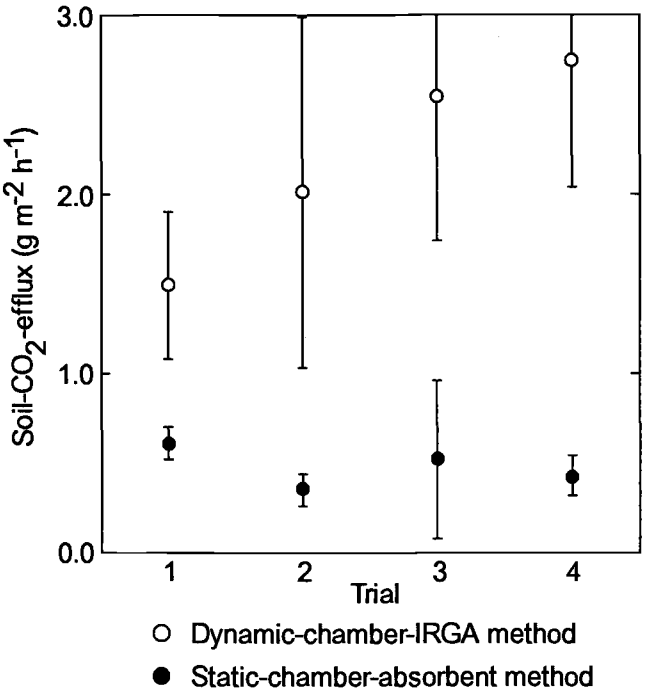

Figure 3.11. Mean soil-CO_2-efflux (± 95 percent confidence interval) by the dynamic-chamber-IRGA method and by static-chamber-absorbent method, n=5.

4. SOIL-CO_2-EFFLUX IN FORESTS OF THE PACIFIC NORTHWEST AND ALASKA

Introduction

Measurements of soil-CO_2-efflux were made in the field using the dynamic-chamber-IRGA method. Potential sites for work to be done in conjunction with the Long-Term Ecosystem Productivity program (Oregon and Washington) were examined as well as two sites in Alaska. This data provides presampling information that should be useful in determining the amount of sampling needed for future work. Direct comparisons between the use of the dynamic-chamber-IRGA and static-chamber-absorbent methods were not done in this field study. Raich and Schlesingers's (1992) synthesis article of global soil respiration, we lists two studies where soil-CO_2-efflux was monitored for a least one full year (Vogt et al., 1980 and Schlentner and Van Cleve, 1985) in this region. These two studies plus a more recent study by Mattson (1994) used static-chamber-absorbent methods; thus some indirect comparisons of methods for the field can be derived.

Methods

A single transect 30 to 40 meters long was established at each site with sampling points located at one meter intervals. The protocol for making measurements with the dynamic-chamber-IRGA method was the same as in all previous experiments described in this thesis. Collars were not used in any of the transect measurements. The dynamic chamber (PVC, 21 cm diameter and 6.9 L) used in the Alaska transects was the same chamber used in the artificial and controlled ecosystem experiments (Chapters 2 and 3). The dynamic-

chamber used for the Oregon and Washington sites was a stainless steel bowl (17.5 cm diameter and 1.37 L). Fans were used in conjunction with the PVC chamber on the Alaska transects but not when using the stainless steel chamber. Soil temperatures were also measured at each of the sampling points at a depth of 10 cm. All transects were sampled between June 18 and August 17. The Oregon and Washington sites were sampled during the summer of 1991 and the Alaska sites in the summer of 1994.

Results and Discussion

A list of the sites, their geographical location, a brief description and results of the measurements are located in Table 4.1. The spatial variation detected from the measurement was high with coefficients of variation ranging from 41 to 110 percent. The estimated number of sampling points needed to be within 10 percent of the mean 95 percent of the time ranged from 69 to 475. Using similar dynamic-chamber-IRGA methods and transect spacing as those which I used, Rochette et al. (1991) reported coefficients of variation of 25 to 69 percent for an agricultural field, thus the variation I observed in the forest does not seem that surprising. Temporal variation was not examined in this work, however spatial variation alone will provide daunting challenges in future work to characterize stand level soil-CO2-efflux for these ecosystems.

The Chena site had the highest rates of 2.87 g CO_2 m^{-2} h^{-1} and was the most northerly sites measured. The Juneau site had the second highest rates of 1.65 g CO_2 m^{-2} h^{-1} and was the second most northerly site. The Oregon and Washington sites ranged from 0.43 to 1.03 g CO_2 m^{-2} h^{-1} with no particular pattern related to latitude. Soil temperatures ranged from 8 to 25 °C amongst all the sites, however no corresponding pattern of soil-CO_2-efflux was observed.

Schlentner and Van Cleve (1985) report on soil-CO_2-efflux measurements for two growing seasons in four different forest types in the vicinity of Fairbanks, Alaska. The four forest types that they examined were aspen (*Populus tremuloides* Michx.), white birch (*Betula papyrifera* Marsh.) , black spruce (*Picea mariana* (Mill.) B.S.P.) and white spruce (*Picea glauca* (Moench) Voss). Static chambers with soda lime were used in Schlentner and Van Cleve's study. The highest rates they report occurred in or near July with peak values ranging from 0.53 to 0.66 g CO_2 m^{-2} h^{-1} with the highest rates occurring in the white birch stand . I also located a transect in the same general location and in a similar white birch stand as that described by Schlentner and Van Cleve. However the soil-CO_2-efflux rates I measured with the dynamic-chamber-IRGA method were over four times as great as that of Schlentner and Van Cleve. My measurements were made in late June.

Vogt et al. (1980) also report on soil-CO_2-efflux measurements for two growing seasons in four different forest types in western Washington (47°23'N and 121°56'W). The four forest types they examined were red alder (*Alnus rubra* Bong.), Douglas-fir (*Pseduotsuga menziesesii* Mirb.), western hemlock (*Tsuga heterophylla* Raf.) and Pacific silver fir (*Abies amabilis* Dougl.). Static chambers with KOH solution were used in the Vogt et al. study. The highest rates they report occurred in the western hemlock stand and ranged from 0.33 to 0.42 g CO_2 m^{-2} h^{-1} during the summer and autumn months. While I did not make measurements in the same general location I did make measurements in a western hemlock stand near Forks, Washington (Forks 1) and a mixed conifer stand near Wenatchee, Washington (Wenatchee) that were of the same approximate latitude as Vogt et al. (1980); I measured 50 percent higher efflux rates in both cases.

The Umatilla site had the lowest rates I measured in all my transects and was roughly equal to the highest of all the measurements by Vogt et al. (1980). Mattson (1994) also monitored soil-CO_2-efflux in a 40-yr old Douglas-fir and western hemlock stand in western Oregon (44°45'N and 122°35'W) for over two years. Similar to the Vogt et al. study the highest rates that Mattson reports using a static-chamber-absorbent method are about 0.46 g CO_2 m^{-2} h^{-1}. The absorbent that Mattson used was a NaOH solution.

The two sites near Forks (Forks 1 and 2) were the closest in proximity, soils and geomorphology and provided the best case to look at a possible treatment effect on soil-CO_2-efflux. The soils at the clearcut site (Forks 2) had a 3°C higher temperature (measured at -10 cm) and 25 percent higher mean soil-CO_2-efflux. While the differences in these two sites were not statistically significant ($\alpha = 0.05$) it does appear that we could see a treatment effect with more intensive sampling. To detect a significant difference ($\alpha = 0.05$ and $\beta = 0.05$), I estimated that the number of samples needed is about 232.

Table 4.1. Soil-CO_2-efflux transect data from forests of Oregon, Washington and Alaska.

Site	Latitude	Longitude	Elev. (m)	Over-story Age (yrs)	Forest Type	n	Soil Temp 10 cm (°C)	Soil-CO_2 Efflux (g CO_2 m^{-2} h^{-1})	CV	95%CI	n for 95%CI <0.05$\bar{X}$	n for 95%CI <0.10$\bar{X}$
Chena	64°52'N	146°46'W	215	unk	white birch/ white spruce	40	8	2.87	0.42	0.39	275	69
Juneau	58°22'N	134°34'W	50	160	western hemlock/ Sitka spruce	40	10	1.65	0.54	0.29	451	113
Forks 1	48°05'N	124°15'W	200	70-80	western hemlock/ Sitka spruce	39	13	0.62	0.50	0.10	381	95
Forks 2	48°05'N	124°15'W	200	15	western hemlock/ Sitka spruce	31	16	0.80	0.80	0.24	983	246
Wenatchee	47°03'N	121°15'W	1220	70-90	Douglas-fir/ mixed conifer	40	17	0.61	0.47	0.09	334	83
Umatilla	45°50'N	117°55'W	1280	200	Douglas-fir/ mixed conifer	40	8	0.43	0.41	0.06	252	63
Siuslaw	44°23'N	123°52'W	275	80-100	Douglas-fir/ western hemlock	31	14	0.48	0.63	0.11	618	154
Willamette	44°04'N	122°25'W	550	60	Douglas-fir/ western hemlock	34	24	0.58	1.11	0.23	1900	475
Siskiyou	42°19'N	124°10'W	915	100	Douglas fir/ mixed hardwoods	40	25	1.03	0.76	0.25	881	220

5. CONCLUSIONS AND SUMMARY

The dynamic-chamber-IRGA method consistently underestimated by 15 percent a calculated CO_2 efflux based on Fick's Law of diffusion in the artificial ecosystem experiment (Chapter 2). When the dynamic-chamber-IRGA method was used to monitor soil-CO_2-efflux for eight months in controlled ecosystems (box-lysimeters) to estimate the change in soil carbon (Chapter 3) the results were consistent with the artificial ecosystem experiment. While the 15 percent error of the dynamic-chamber-IRGA method has not been accounted for, the consistency in which the dynamic-chamber and IRGA has performed indicates that this tool has the potential to accurately measuring soil-CO_2-efflux. Some obstacles still remain with this method in order to quantify soil-CO_2-efflux of a stand-scale ecosystem. The dynamic-chamber-IRGA method as was used in this work can only measure one parcel of ground at a time. Indications from the controlled ecosystem experiment (Chapter 3) and the field transect study (Chapter 4) are that spatial variability is high. If the dynamic-chamber-IRGA method is going to be used in future studies as was done in this thesis, then hundreds of samples will be needed to make precise estimates of soil-CO_2-efflux. Temporal variation in the field still needs to be examined.

When the static-chamber-absorbent method was compared to a calculated efflux based on Fick's law of diffusion the static-chamber method performed inconsistently. At a high efflux rate of 0.77 g CO_2 m^{-2} h^{-1} the static-chamber-absorbent method greatly underestimated and at a zero efflux overestimated. When this method was compared to the dynamic-chamber-IRGA method in four trials on the box-lysimeter soils, the static-chamber-absorbent method estimates were less than half that of the dynamic-chamber-IRGA method. Other investigators have observed similar relationships between these

two methods as what I observed in this thesis work. (Cropper et al. 1985, Ewel et al. 1987a, Norman et al. 1992, and Rochette et al. 1992). The direct comparison that I make in this thesis work, the direct comparison from various other studies, as well as the indirect comparisons I make from my field measurements to other field studies are illustrated in Figure 5.1. From these many comparisons we can see a pattern of responses. Based on the evidence that the dynamic-chamber-IRGA method produces estimates consistent with soil-CO_2-efflux rates, I can only conclude that the efficacy of the static chamber with absorbent diminishes greatly as efflux rates increase.

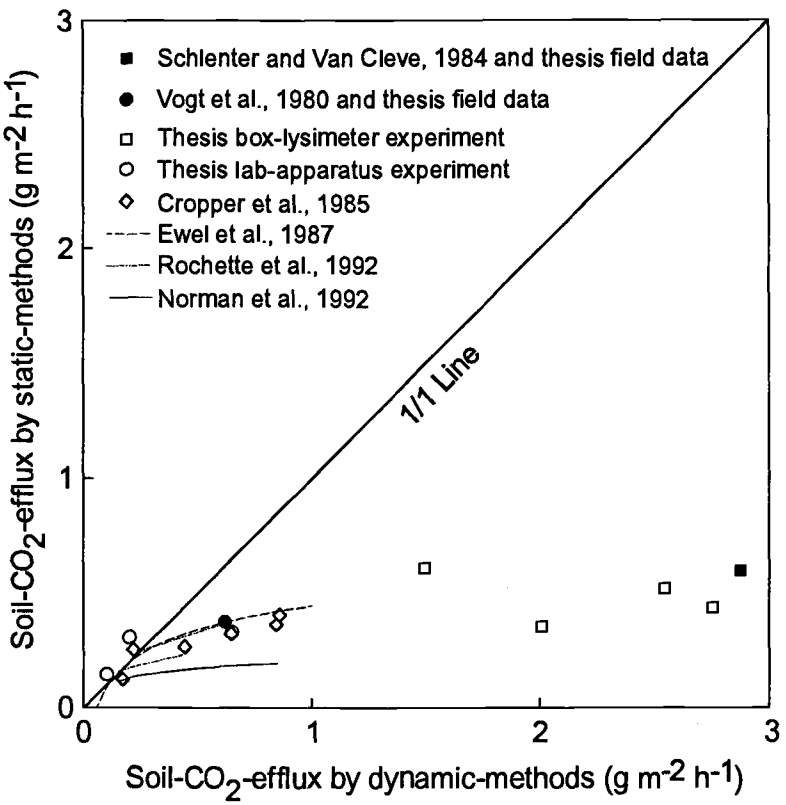

Figure 5.1. Soil-CO_2-efflux by static-chamber-absorbent methods vs the dynamic-chamber-IRGA methods from several studies.

Based on this analysis it would also seem logical to conclude that much of the reported rates for soil-CO_2-efflux are underestimates since the use of static chambers with absorbent has been so prevalent. Likewise, synthesis of case studies into global trends for soil-CO_2-efflux rates (Schlesinger, 1977, Raich and Naddelhoffer, 1989 and Raich and Schlesinger, 1992) maybe greatly underestimating actual rates. Raich and Schlesinger (1992) estimate the global soil respiration rate to be 68 Pg C yr^{-1} and state that a small change in soil respiration rates could easily rival the 5 Pg C yr^{-1} of atmospheric CO_2 loading from fossil fuel burning. It would seem that the biases associated with the static-chamber methods could just as easily be of the same magnitude as fossil fuel burning.

While there are general trends in how the static-chamber-absorbent method performs, it may be tempting to correct existing data; this however could be a tedious and challenging process. Since the bias with the static-chamber methods vary with efflux rates, individual sample values would have to be adjusted rather than mean values. Corrections at higher rates would be less reliable due to the decrease in sensitivity of the static-chamber with absorbent. Also attention needs to be given to design variations within a given method. For example, researchers Nakadai et al. (1993) concluded that the use of a static-chamber with alkali absorbents results in over-estimates of soil-CO_2-efflux when compared to a dynamic-chamber and IRGA. However, Nakadai et al. used a sponge soaked with KOH solution in their study which likely resulted in an increased amount of surface area for CO_2 absorption. It appears that this design modification had a large effect on the performance of this method.

While the dynamic-chamber-IRGA method as used in this thesis appears to work well several questions remain. For example, is the 15 percent underestimate observed in the artificial ecosystem experiment unique to the

equipment and procedures employed in this thesis research, or can a correction of this method be used universally. The use of an IRGA for measuring soil-CO_2-efflux in the field also has some practical limitations. The costs of acquiring (approximately $10,000) an IRGA can be prohibitive in many instances. The need for many samples and the limitation of having to make measurements in a serial manner is another drawback. Thus, there is still a need for further development of methods for soil-CO_2-efflux measurement.

Three ideas for future development of chamber methods are the inclusion of a chamber fan in the static-chamber-absorbent method, larger diameter dynamic-chambers with the IRGA, and an automated system of multiple dynamic-chambers also with the IRGA. Freijer and Bouten (1991) introduce the idea of a dynamic-chamber with a soda-lime trap to alleviate the problems of high headspace concentrations of CO_2. The use of a fan in conjunction with the static-chamber may be a simpler solution to achieve the same results with less expense. A larger diameter dynamic-chamber may be able to integrate much of the spatial variability and thus reduce the number of samples needed at a given site. The use of an automated system of in-place dynamic-chambers would be of great benefit for studying temporal variability and reducing the tedium of making many serial measurements.

The artificial and controlled ecosystem experiments of this thesis may represent the first attempts to evaluate soil-CO_2-efflux measurement methods by comparison to reference fluxes based in simple theoretical principles; Fick's law in the first case (Chapter 2) and conservation of mass in the second (Chapter 3). Of these two approaches, development of the lab-apparatus used in the artificial ecosystem experiment would seem preferable for future work. The lab-apparatus could easily be improved to also include conservation of mass as a further check to confirm efflux rates based on Fick's law. Actual soil could be

used to better simulate field conditions. The main advantages of the lab-apparatus relate to the control of the environment and to the short time needed to conduct a trial.

The box-lysimeter experiment took months of monitoring and quite extensive soil analysis to complete a single trial. The results of the soil analysis actually produced an imprecise target for comparison of the monitoring data. Despite the problems with the box-lysimeter experiment it did demonstrate that the dynamic-chamber-IRGA method gave reasonable estimates for an actual ecosystem albeit a somewhat simplified ecosystem. Several other noteworthy points were also brought to light with this experiment. First, despite the appearance of having homogenized the soils by mixing, a high degree of variation was expressed in both soil analysis and in soil-CO_2-efflux monitoring. Second, the importance of evaluating methods for quantifying ecosystem processes was further demonstrated through the problems experienced with the soil cores. Finally, by looking for convergence between two methods, a box-lysimeter experiment allows for other processes that *a priori* are not apparent to be exposed.

BIBLIOGRAPHY

Abdul-Kareem, A.W. and S.G. McGrae. 1984. The effects on topsoil of long-term storage in stockpiles. Plant and Soil **76**:357-363.

Anderson, J.P.E. 1982. Soil respiration. Pages 831-871 *in* A. L. Page, R. H. Miller, and D. R. Keeney, editors. Agronomy Monograph 9: Methods of soil analysis, Part 2. Chemical and biological properties, 2nd edition. American Society of Agronomy, Inc., and Soil Science Society of America, Inc., Madison, Wisconsin, USA.

Baldocchi, D.D., S.B. Verma, D.R. Matt, and D.E. Anderson. 1986. Eddy-correlation measurements from the floor of a deciduous forest. Journal of Applied Ecology **23**:967-975.

Boersma L. and Y. Ouyang. 1993. Dynamic mathematical model for oxygen and carbon dioxide exchange between soil and atmosphere. *in* T.S. Vinson and T.P. Kolchugina, editors, Proceedings of the international workshop on carbon cycling in boreal forest and sub-Arctic ecosystems: biospheric responses and feedbacks to global climate change. U.S. Environmental Protection Agency, Environmental Research Lab, Corvallis Oregon EPA/600/R-93/084 87-99.

Brady, N.C. 1990. The nature and properties of soils. Macmillian Publishing Company. New York, NY.

Bunnell, F.L., D.E.N. Tait, P.W. Flanagan, and K. Van Cleve. 1977. Microbial respiration and substrate weight Loss - I. Soil Biology and Biochemistry **9**:33-40.

Buyanovsky, G.A. and G.H. Wagner. 1983. Annual cycles of carbon dioxide level in soil air. Soil Science Society of America Journal **47**:1139-1145.

Caryle, J.C., and U.B. Than. 1988. Abiotic controls of soil respiration beneath an eighteen-year-old *Pinus radiata* stand in south-eastern Australia. Journal of Ecology **76**:654-662.

Cheng, W., and D.C. Coleman, C.R. Carroll and C.A. Hoffman. 1993. *In situ* measurement of root respiration and soluble C concentration in the rhizosphere. Soil Biology and Biochemistry. **25**:1189-1196.

Cropper, W.P., Jr., K.C. Ewel, and J.W. Raich. 1985. The measurement of soil CO_2 evolution *in situ*. Pedobiologia **28**:35-40.

Cropper, W.P., Jr. and H.L. Gholz. 1990. *In situ* needle and fine root respiration in mature slash pine (*Pinus elliottii*) trees. Canadian Journal of Forestry Research **21**:1589-1595.

de Jong, E., R.E. Redmann, and E. A. Ripley. 1979. A comparison of methods to measure soil respiration. Soil Science **127**:300-306.

Edwards, N.T. 1982. The use of soda-lime for measuring respiration rates in terrestrial systems. Pedobiologia **23**:321-330.

Efron, B. and R. Tibshirani. 1986. Bootstrap methods for standard errors, confidence intervals, and other measures of statistical accuracy. Statistical Science **1**:54-77

Elliott, L.F. and T.M. McCalla. 1972. The composition of the soil atmosphere beneath a beef cattle feedlot and a cropped field. Soil Science Society of America Journal **36**:69-70

Ewel, K.C., W.P. Cropper and H.L. Gholz. 1987a. Soil CO_2 Evolution in Florida slash pine plantations. I. Changes through time. Canadian Journal of Forest Research **17**:325-329.

Ewel, K.C., W.P. Cropper and H.L. Gholz. 1987b. Soil CO_2 Evolution in Florida slash pine plantations. II. Importance of root respiration. Canadian Journal of Forest Research **17**:325-329.

Fogel, R., and K.J. Cromack. 1977. Effect of habitat and substrate quality on Douglas-fir decomposition in western Oregon. Canadian Journal of Botany **55**:1632-1640.

Freijer, J.I., and W. Bouten. 1991. A Comparison of field methods for measuring soil carbon dioxide evolution: experiments and simulation. Plant and Soil **135**:133-142.

Garrett, H.E., G.S. Cox, and J.E. Roberts. 1978. Spatial and temporal variations in carbon dioxide concentrations in an oak-hickory forest ravine. Forest Science **24**:180-190.

Glinski, J., and W. Stepniewski. 1985. Soil aeration and its role for plants. CRC Press Inc., Boca Raton, FL.

Gordon, A.M., R.E. Schlentner, and K. Van Cleve. 1987. Seasonal patterns of soil CO_2 respiration and CO_2 evolution following harvesting in the white spruce forests of interior Alaska. Canadian Journal of Forest Research **17**:304-310.

Grahammer, K., M.D. Jawson, and J. Skopp. 1991. Day and night soil respiration CO_2 from a grassland. Soil Biology and Biochemistry **23**:77-81.

Grier, C.C., K.M. Lee, N.M. Nadkarni, G.O. Klock, and P.J. Edgerton. 1989. Productivity of forests of the United States and its relation to soil and site factors and management practices: A review. U.S. Forest Service, Pacific Northwest Research Station; PNW-GTR-222.

Hanson, P.J., and W.A. Hoffman. 1994. Emissions of Non-Methane Organic Componds and Carbon Dioxide from Forest Floor Cores. Soil Science Society of America Journal **58**:552-555.

Hutchinson G.L., and G.P. Livingston. 1993. Use of chamber systems to measure trace gas fluxes. Pages 63-78. *in* L. A. Harper, A. R. Mosier, J. M. Duxbury, and D. E. Rolston, editors. Agricultural ecosystem effects on trace gases and global climate change. ASA Special Publication 55. American Society of Agronomy, Crop Science Society of America, and Soil Science Society of America. Madison, Wisconsin, USA.

Hutchinson, G.L., and A.R. Mosier. 1981. Improved soil cover method for field measurement of nitrous oxide fluxes. Soil Science Society of America Journal **45**:311-316.

Hütsch B.W., C.P. Webster, and D.S. Powlson. 1991. Long-term effects of nitrogen fertilization on methane oxidatation in soil of the Broadbalk Wheat Experiment. Soil Biology and Biochemistry **25**:1307-1315

Joshi, M., G.S. Mer, S.P. Singh, and Y.S. Rawat. 1991. Seasonal pattern of total respiration in undisturbed and disturbed ecosystems of central Himalaya. Biology and Fertility of Soils **11**:267-272.

Jury, W.A., W.R. Gardener, and W.H. Gardener. 1991. Soil Physics, Fifth Edition. John Wiley & Sons, Inc., New York.

Kanemasu, E.T., W.L. Powers, and J.W. Sij. 1974. Field chamber measurements of CO_2 flux from soil surface. Soil Science **118**:233-237.

Kursar, T.A. 1989. Evaluation of soil respiration and soil CO_2 concentration in a lowland moist forest in Panama. Plant and Soil **113**:21-29.

Lauenroth, W.K., H.W. Hunt, D.M. Swift, and J.S. Singh. 1986. Reply to Vogt et al. Ecology **67**:580-582.

Lundegardh, H. 1927. Carbon dioxide evolution of soil and crop growth. Soil Science **23**:417-453.

Mathes, K., and T. Schriefer. 1985. Soil respiration during secondary succession: Influence of Temperature and Moisture. Soil Biology and Biochemistry **17**:205-211.

Mattson, K. 1994. CO_2 efflux from coniferous forest soils: comparison of measurement methods and effects of added nitrogen. Advances in Soil Science *in press*.

Nakadai. T., H. Koizumi, Y. Usami, M. Satoh, and T. Oikawa. 1993. Examination of the methods for measuring soil respiration in cultivated land: effect of carbon dioxide concentration on soil respiration. Ecological Research **8**:65-71.

Nakayama, F.S. 1990. Soil respiration. Remotes Sensing Reviews **5**:311-321.

Neilson, J.W., and I.L. Pepper. 1990. Soil respiration as an index of soil aeration. Soil Science Society of America Journal **54**:428-432.

Norman, J.M., R. Garcia, and S.B. Verma 1992. Soil surface CO_2 fluxes and the carbon budget of a grassland. Journal of Geophysical Research **97:**18,845-18,853.

Raich, J.W., and K.J. Nadelhoffer. 1989. Belowground carbon allocation in forest ecosystems: global trends. Ecology **70**:1346-1354.

Raich, J.W., R.D. Bowden, and P.A. Steudler. 1990. Comparison of two static chamber techniques for determining carbon dioxide efflux from forest soils. Soil Science Society of America Journal **54**:1754-1757.

Raich J.W., and W.H. Schlesinger. 1992. The global carbon dioxide flux in soil respiration and its relationship to vegetation and climate. Tellus **44B:**81-99.

Reiners, W.A. 1968. Carbon dioxide evolution from the floor of three Minnesota forests. Ecology **49**:471-483.

Richards, B.N. 1987. The microboiology of terrestrial ecosystems. Longman Scientific and Technical, Longman Group UK Ltd. and John Wiley and Sons, Inc. New York, NY.

Rochette P., E.G. Gregorich, and R.L. Desjardin. 1992. Comparison of static and dynamic closed chambers for measurement of soil respiration under field conditions. Canadian Journal of Soil Science **72**:605-609.

Rochette, P., R.L. Desjardins, and E. Pattey. 1991. Spatial and temporal variability of soil respiration in agricultural fields. Canadian Journal of Soil Science **71**:189-196.

Rolston, D. E. 1986a. Gas flux. Pages 1103-1119 *in* A. Klute, editor. Agronomy Monograph 9: Methods of soil analysis, Part 1. Physical and mineralogical methods, 2nd edition. American Society of Agronomy, Inc., and Soil Science Society of America, Inc., Madison, Wisconsin, USA.

Rolston, D. E. 1986b. Gas diffusivity. Pages 1089-1102 *in* A. Klute, editor. Agronomy Monograph 9: Methods of soil analysis, Part 1. Physical and mineralogical methods, 2nd edition. American Society of Agronomy, Inc., and Soil Science Society of America, Inc., Madison, Wisconsin, USA.

Russell, E.W. 1973. Soil conditions and plant growth. Longman Group Limited. New York, NY.

Schlentner, R. E., and K. Van Cleve. 1985. Relationships between CO_2 evolution from soil, substrate temperature, and substrate moisture in four mature forest types in interior Alaska. Canadian Journal of Forest Research **15**:97-106.

Schlesinger, W.H. 1977. Carbon balance in terrestrial detritus. Annual Review of Ecology and Systematics **8**:51-81.

Singh, J.S., and S.R. Gupta. 1977. Plant decomposition and soil respiration in terrestrial ecosystems. The Botanical Review **43**:449-528.

Singh, K.P., and C. Shekhar. 1986. Seasonal pattern of total soil respiration, its fractionation and soil carbon balance in a wheat-maize rotation cropland at Varanasi. Pedobiologia **29**:305-318.

Sommerfeldt, T.G., C. Chang and T. Entz. 1988. Long-term annual manure applications increase soil organic matter and nitrogen and decrease carbon to nitrogen ration. Soil Science Society of America Journal **52**:1668-1672

Sprugel, D.G., and U. Benecke. 1991. Woody-tissue respiration and photosynthesis. Pages 329-355. *in* J. P. Lassie and T. M. Hinckley, editors. Methods and Approaches in Tree Ecophysiology. CRC Press, Roca Raton, Florida.

Verma, S.B. 1990. Micrometerological methods for measuring surface fluxes of mass and energy. Remotes Sensing Reviews **5**:99-115.

Vogt, K.A., R.L. Edmonds, G.C. Antos and D.J. Vogt. 1980. Relationship between CO_2 evolution, ATP concentrations and decomposition in four forest ecosystems in western Washington. Oikos **35**:72-79.

Vogt, K.A., C.C. Grier, and D.J. Vogt. 1986a. Production, turnover and nutrient dynamics of above and belowground detritus of world forests. Pages 303-377 *in* A. MacFadyen and E. D. Ford, editors. Advances in Ecological Research. Volume 15. Academic Press, Harcourt Brace Jovanich Publishers, London.

Vogt, K.A., C.C. Grier, S.T. Gower, D.G. Sprugel, and D.J. Vogt. 1986b. Overestimation of net root production: a real or imaginary problem? Ecology **67**:577-579.

APPENDICES

Appendix A. Soils Data for Box-Lysimeters

Table A.1 Soils data for box-lysimeters.

Item	Units	Box 1	Box 2	Box 3	Box 4	Box 5	Box 6	Box 7	Box 8	Box 9	Box 10
Soil carbon, t=0	kg m^{-2}	17.2	17.0	21.0	21.7	25.5	13.4	17.0	21.4	25.4	33.3
Soil carbon, t=244	kg m^{-2}	11.5	11.6	13.8	13.8	17.0	11.1	10.6	15.7	14.1	15.7
Soil thickness, t=244	cm	45.5	43.7	41.5	41.9	41.2	43.8	42.7	40.3	39.0	38.1
Bulk density, t=0	g cm^{-3}	1.00	0.74	0.60	0.55	0.51	0.97	0.73	0.65	0.46	0.45
Bulk density, t=244	g cm^{-3}	1.08	0.83	0.69	0.63	0.58	1.10	0.83	0.79	0.54	0.51
Porosity, t=0	m^3 m^{-3}	0.58	0.68	0.73	0.74	0.75	0.60	0.68	0.70	0.77	0.75
Porosity, t=244	m^3 m^{-3}	0.56	0.65	0.70	0.72	0.73	0.55	0.65	0.65	0.75	0.76
Decay constant (k)	yr^{-1}	0.60	0.58	0.62	0.68	0.60	0.27	0.70	0.46	0.87	1.12
Mineral matter	g cm^{-2}	46.7	33.7	25.9	23.4	20.5	45.9	33.5	28.6	18.2	16.2
Mean Soil H_2O, prior 9/30	m^3 m^{-3}	0.16	0.16	0.20	0.17	0.18	0.16	0.21	0.18	0.18	0.19
Mean Soil H_2O, after 9/30	m^3 m^{-3}	0.22	0.23	0.27	0.23	0.26	0.23	0.27	0.25	0.25	0.26
H_2O out after 9/30	L m^{-2}	148	110	115	88	24	NA	NA	NA	NA	NA
Dissolved inorganic C out after 9/30	g m^{-2}	1.20	1.07	0.97	0.76	0.15	NA	NA	NA	NA	NA
Total organic C out after 9/30	g m^{-2}	6.45	4.77	10.18	6.90	2.76	NA	NA	NA	NA	NA

t = time in day of the experiment.

Appendix B. Soil Carbon Loss Data for Box-Lysimeters

Table A.2. Data for estimating soil carbon loss in box-lysimeters.

Item	Units	n	Statistic	Box 1	Box 2	Box 3	Box 4	Box 5	Box 6	Box 7	Box 8	Box 9	Box 10
Soil-C loss estimated by soil-CO_2-efflux monitoring													
$\frac{dC}{dt}\frac{1}{A}$	$\frac{\text{kg C}}{244\ \text{d}}\frac{1}{\text{m}^2}$	NA	mean	4.07	5.60	6.80	7.39	6.54	3.02	5.51	6.00	7.05	8.91
			SE	0.22	0.39	0.46	0.46	0.46	0.27	0.36	0.32	0.56	0.53
Soil-C loss estimated by soil analysis													
$\frac{dC}{dt}\frac{1}{A}$	$\frac{\text{kg C}}{244\ \text{d}}\frac{1}{\text{m}^2}$	NA	mean	5.77	5.54	7.21	7.99	8.48	2.23	6.45	5.73	11.32	17.75
			SE	0.72	1.01	1.21	1.27	1.41	0.54	1.20	1.06	1.70	2.53
Soils analysis data used to calculate soil-C loss (see Equation 18)													
$\frac{C_0}{OM_0}$	g g^{-1}	10	mean	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.528
			SE	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.018
$\frac{OM_0}{MM_0}$	g g^{-1}	10	mean	0.070	0.096	0.153	0.176	0.235	0.055	0.096	0.142	0.264	0.389
			SE	0.002	0.004	0.008	0.007	0.009	0.001	0.007	0.005	0.012	0.014
$\frac{C_{244}}{OM_{244}}$	g g^{-1}	10	mean	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.489
			SE	NA	NA	NA	NA	NA	NA	NA	NA	NA	0.016
$\frac{OM_{244}}{MM_{244}}$	g g^{-1}	10	mean	0.050	0.070	0.109	0.120	0.170	0.050	0.065	0.112	0.159	0.198
			SE	0.007	0.003	0.003	0.006	0.007	0.001	0.003	0.004	0.010	0.019
$\frac{MM_{333}}{BS_{333}}$	g g^{-1}	10	mean	0.955	0.932	0.900	0.901	0.873	0.956	0.939	0.920	0.867	0.847
			SE	0.004	0.006	0.010	0.023	0.030	0.005	0.008	0.019	0.033	0.050
$\frac{BS_{333}}{A}$	kg m^{-2}	3	mean	493	365	290	261	236	483	359	313	211	193
			SE	24	25	11	32	43	29	6	15	41	50

C = carbon, *t* = time, *A* = area, *OM* = organic matter, *MM* = mineral matter, *BS* = bulk soil, and subscripts = day of experiment

Appendix C. Soil Temperature Data for Box-Lysimeters

Table A.3. Soil temperature for box-lysimeters and Hyslop weather station in °C and at -10 cm.

Date	Box 1	Box 2	Box 3	Box 4	Box 5	Box 6	Box 7	Box 8	Box 9	Box 10	Hyslop max	Hyslop min
05/31/92	32.0	32.5	35.6	36.0	36.9	34.9	35.9	36.1	36.5	38.9	29.4	20.6
06/15/92	19.0	20.8	22.8	24.3	24.3	22.0	22.4	23.0	25.6	26.1	22.2	16.1
06/23/92	31.5	31.8	32.3	33.3	32.3	32.1	32.5	31.9	33.2	33.4	33.3	25.0
06/29/92	23.4	NA	25.8	NA	26.8	25.0	NA	25.8	NA	26.8	26.1	21.1
07/17/92	32.3	31.9	34.0	33.5	31.7	33.1	34.5	34.2	33.5	33.4	32.8	22.2
07/31/92	30.1	30.1	32.5	32.9	31.1	31.9	32.2	33.3	31.9	31.9	33.9	23.3
08/14/92	26.2	26.9	28.6	28.3	27.4	26.8	27.2	28.0	27.6	27.9	32.2	22.8
08/30/92	22.3	22.6	25.0	25.9	25.5	23.4	23.2	24.2	27.2	26.8	28.3	20.0
09/14/92	14.9	15.4	16.9	17.6	17.2	15.8	16.7	17.2	18.3	17.6	22.8	15.6
09/17/92	15.5	16.9	17.1	18.6	17.7	14.6	15.9	16.5	16.9	16.7	21.7	16.1
10/19/92	13.6	13.6	13.8	13.9	13.7	13.7	13.8	13.9	14.0	14.0	15.6	13.3
11/02/92	11.5	11.8	11.8	11.9	11.8	11.8	12.0	12.1	12.0	12.3	13.3	11.7
12/03/92	2.1	2.7	2.8	2.9	2.9	2.5	2.5	2.8	2.9	3.1	6.1	4.4
12/19/92	2.5	2.5	2.7	2.7	2.6	2.8	2.7	2.6	2.5	2.7	2.8	2.2
01/05/93	2.4	2.6	2.7	2.8	2.8	2.8	2.7	2.8	2.8	2.8	3.9	2.2

The Hyslop weather station is located 8 km northeast of box-lysimeter site.

Appendix D. List of Variables

a	soil air space
dt	change in time
dC	change in CO_2 concentration (*u*L L^{-1}), change in C mass
dx	change is space, distance
dz	change in height
k	decay constant
n	moles
t	time
A	area
B	biomass
BS	bulk soil mass
D	diffusivity of a gas
$D_0^{CO_2}$	diffusivity of CO_2 in free air (0.139 cm^2 s^{-1} * $(K/273)^2$)
$D_s^{CO_2}$	diffusivity of CO_2 in soil
GPP	gross primary production
$J_s^{CO_2}$	soil-CO_2 efflux (g CO_2 m^{-2} h^{-1})
K_H	Henry's law constant
MM	mineral matter mass
NEP	net ecosystem production
NPP	net primary production
OM	organic matter mass
P	air pressure
R	universal gas constant (8.314 J mol^{-1} K^{-1})
R_a	autotrophic respiration
R_{ab}	autotrophic respiration belowground
R_{co_2}	CO_2 gas constant (0.189 J g^{-1} K^{-1})
R_h	heterotrophic respiration
R_{ha}	hererotrophic respiration aboveground
R_s	soil respiration

Appendix D. List of Variables (Continued)

R_t	total ecosystem respiration
T	temperature
V	volume
X	molar fraction
ξ_s	soil tortuosity factor
p	partial pressure of gas
ϕ	soil porosity