

Two Different Enclosure-based Measurements Applications for Trace Gas Surface Emission and Sensitivity Analysis for Soil NO Emission by Using a Flow-through Dynamic System

Deug-Soo Kim

School of Civil and Environmental Engineering, Kunsan National University,
Kunsan, Jeonbuk 573-701, Korea

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지표 미량기체 방출에 대한 두 가지 다른 형태의 Enclosure 기반 측정 방법의 응용 및 Flow-through Dynamic System을 이용한 토양 NO 방출의 민감도 분석

김 득 수

군산대학교 토목환경공학부

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ABSTRACT

Rapid increases in the concentrations of greenhouse gases and many other chemically important trace gases have occurred over the last several centuries. For understanding the roles of these important gases in global change, it is essential to identify their sources and sinks, to characterize biogenic gas fluxes between the biosphere and atmosphere, and to understand the processes that control them. In this paper, enclosure-based measurements are described in a practical manner for field experiments. Theoretical reviews of mass balance equation in the enclosure and sensitivity of the flow-through dynamic flux chamber technique are presented; specifically for the case of NO flux measurements from soil surface. The physical system and theory behind the flow-through dynamic flux chamber method are examined. New calculation flux formula was introduced by considering NO chemical loss on chamber wall and uncertainties of the NO flux calculation were discussed.

Key words : Enclosure-based, Closed flux chamber technique, Flow-through dynamic chamber, Sensitivity analysis, Soil NO emission

I. INTRODUCTION

Matson and Harriss (1995) indicated that the change of atmospheric chemical compositions has been well-documented and the change is one of the most important ongoing human-caused global changes. They summarized most of evidences of rapid increases in the concentration of CO₂, CH₄, N₂O and a number of other radiatively and chemically important trace gases over

the last several centuries. Although numerous studies have been conducted and focused on the interactions between biosphere and atmosphere, the reasons for the increase and the consequences of changing atmospheric composition are not always understood. It is true that understanding the sources and sinks and the characteristics of biogenic gas fluxes between the biosphere and atmosphere, and the processes that control them, are essential.

There are a number of different measurement techniques to quantify emission from the source surface i.e., enclosure-based measurement and micrometeorological technique. Each technique has advantages and limitations and one can use one of these techniques depending on the scientific question being asked and the experimental conditions. The enclosure techniques are relatively inexpensive, and one is able to easily set up the measurement systems to a remote site because of their portability. The enclosure techniques are particularly useful to identify the spatial variations of sources and to develop practical relationships between the sources' characteristics and flux variations because both can be measured directly. However, the enclosure technique only covers small area surface measurement of flux and needs to extrapolate the results from the small scale in space and time to regional scale (e.g., Bartlett and Harriss, 1993; Matson and Harriss, 1988).

The purpose of this paper is to provide brief reviews on the function and the use of enclosure-based measurement systems applicable in gas exchange studies at the soil-atmosphere interface. Two different kinds of enclosure-based measurements are introduced: one is a closed chamber (static, non-steady state) system and the other is a flow-through chamber (dynamic, steady state) system. Their usefulness and an exemplary sensitivity of a flow-through system for soil NO flux calculation are discussed.

II. SAMPLING METHODS AND FLUX CALCULATIONS FOR THE ENCLOSURE TECHNIQUES

2.1. Closed chamber system (static chamber)

Closed chamber technique is applicable to measure the trace gas fluxes from soil surface into atmosphere. The chamber technique to estimate soil gas emissions has been reviewed extensively (e.g., Livingston and Hutchinson, 1995), and compared favorably to other approaches such as micrometeorological approach (i.e., gradient and eddy correlation methods) (e.g., Kaplan *et al.*, 1988; Smith *et al.*, 1997). Various designs of enclosure have been developed for flux measurements in agricultural fields (Reicosky *et al.*, 1990; IAEA, 1992; Hutchinson and Livingston, 1993).

Different shapes of chamber could be used for the enclosure, which are usually cylindrical, rectangular, and half-spherical. Matthias *et al.* (1978) investigated the effect of closed chamber geometry on soil gas

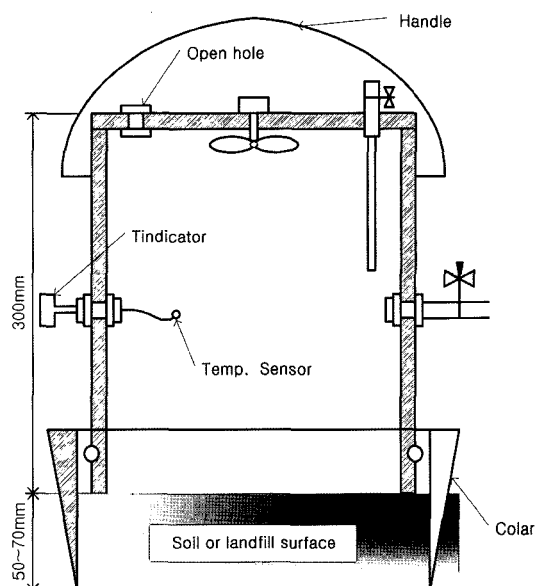


Fig. 1. Example of a schematic of closed chamber for flux measurement.

exchange rates using a two-dimensional molecular diffusion model. According to their results, height of a closed chamber if the cross sectional area is constant, should be small enough that a change in the enclosed trace gas concentration can be measured over as short a time as logistically possible, yet large enough to minimize disturbance of the enclosed surface (Livingston and Hutchinson, 1995). Enclosure basal areas are most common on the order of 700–900 cm², and the selection of appropriate basal area is largely defined by the scale of the questions addressed by the research objectives and sampling location of each study (Livingston and Hutchinson, 1995).

In Fig. 1, for example, the chamber is open bottom fluorinated ethylene propylene (FEP) Teflon-lined cylinder (diameter ~ 0.28 m, height ~ 0.3 m, and volume ~19 L) to prevent trace gas from loss by wall reaction. A three-way Luer fitting tube (1.5 mm internal diameter) on top of the chamber maintains an equilibrium gas pressure between the inside and outside of the chamber. In order to minimize and/or prevent from artificial disturbance by chamber displacement to the surface, it is more useful to make multiple-component enclosure. Usually the chamber is composed of two components, which are main-body and open-base (Fig. 1). This chamber's main-body fits onto a stainless steel metal ring (open-base), which is deployed into the soil to a

depth of ~ 0.1 m in advance of actual observation (several hours) (Kim *et al.*, 2002). A motor-driven Teflon impeller (~ 0.15 m diameter) is installed inside the chamber. Experiment is conducted to determine if the mixing speed of the Teflon impeller altered soil gas flux measurements (Roelle *et al.*, 1999). Varying the speed between 20 and 100 revolutions per minute (rpm) did not produce any significant changes for the case of NO flux. Gas samples are collected into Teflon air bags (1L volume) through a sampling port (~ 4 mm inner diameter) with a Swagelock valve fitting on the chamber wall. If trace gas is not highly reactive, stainless needle with a three-way Luer fitting tube on the top of the chamber can be used to collect the gas samples with 50ml plastic syringe. Error in the measured flux may occur if the rate of air sample withdrawal is not compensated by pressure venting (Livingston and Hutchinson, 1995). The error, however, is assumed to be negligible because of relatively small sample volume (~1L) compared to the inside chamber volume (~19L). To calculate soil gas flux, two samples are collected from the chamber at 15 minutes interval (this time interval can be variable and may depend on chamber dimension and the kind of trace gases that are measured), after placing the chamber body on the base ring, which had been deployed into the soil well in advance

of the measurement. The sampling interval of 15 minutes is determined by the results from several sets of preliminary sampling tests with a chamber. Fig. 2 shows an example of linear increases of gas concentrations inside the chamber over the sampling interval which were examined throughout the field test at the soybean and green onion fields in May 2000. The gas fluxes were estimated by using the time rate of changes in the gas concentration. After finishing a daily measurement, the metal ring should be moved to another place within the area of 10 m radius and placed into the soil to a depth of ~0.1 m.

The static chamber system is most useful when a deployment of a continuous trace gas analyzer is not available at the field (e.g., gas chromatography system, tunable diode laser-spectrometer). To measure the rates of concentration gradient of enclosed air, the air samples from the enclosure are collected over a certain time period; and they are sent and analyzed in the laboratory.

After obtaining the average gas concentrations during the sampling interval, the soil gas flux is calculated by the following general formula derived from mass balance in the chamber (Smith *et al.*, 1997).

$$J_{gas} = \rho_{gas} \cdot \frac{V}{A} \cdot \frac{\Delta C}{\Delta t} \cdot \frac{273}{(273 + T)} \quad (1)$$

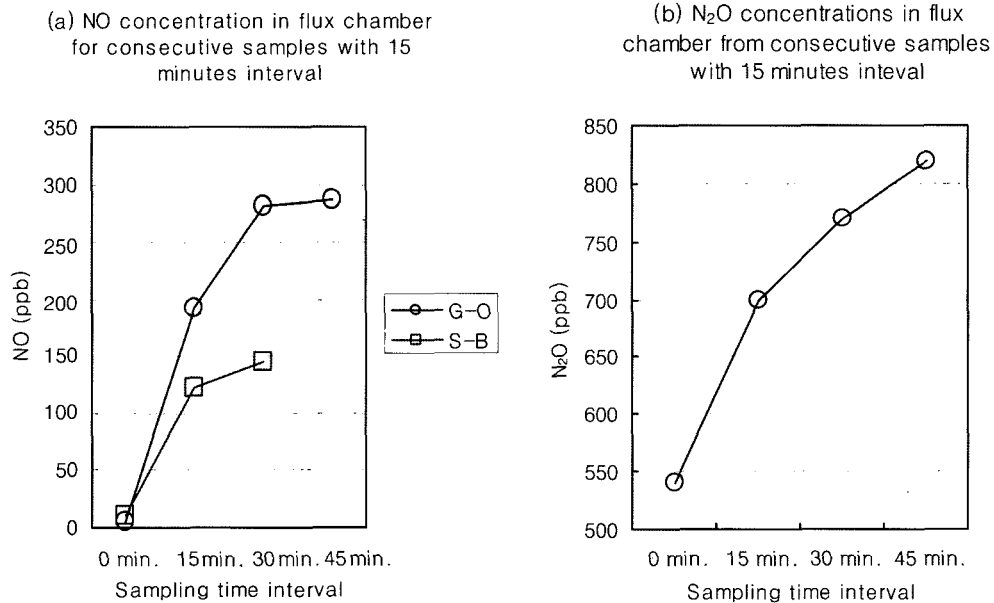


Fig. 2. Increase in (a) NO and (b) N₂O concentrations in chamber with sampling time interval at upland soils from chamber pre-test experiment (Kim, 2001).

where, J_{gas} is soil gas emissions, ρ_{gas} is gas density, V is chamber volume, A is the covered area by the static chamber, T is average internal chamber temperature during the 15 minutes sampling time interval, and $\Delta C/\Delta t$ is the rate of gas concentration increases with sampling time interval.

2.2. Flow-through enclosure system (dynamic and steady state system)

To review theoretical flux calculation method by flow-through enclosure technique, and examine sensitivity for chemically reactive trace gas emission such as nitric oxide (NO) by using the dynamic system, an example of a schematic of a flow-through flux chamber is illustrated in Fig. 3. The flow-through system is useful for measuring continuous trace gas flux from soil surface, in which sampling gases are continuously analyzed by real time analyzer *in situ*.

General descriptions of the chamber system for NO emission are as follows. The chamber lined with 5 mm thick fluorinated ethylene propylene (FEP) Teflon is used to measure NO flux from the soil. The translucent chamber (volume of ~24 L) fits gas-tight inside of a stainless steel metal ring, which is driven into the ground to a depth of ~0.1 m (see Fig. 3). Ambient air, which is used as a carrier gas, is pumped through chamber at a constant flow rate ($Q \text{ L min}^{-1}$). The air inside chamber is mixed by a motor-driven Teflon stirrer. Teflon tubing (1/

4 inch O.D.) is used to connect chamber and analytical instrumentations. Entire measurement system is coated by Teflon, or is composed of stainless steel to minimize further chemical reactions with the sample stream. Sample line connecting the chamber and instrumentation does not exceed 10 m, and sample residence time in the sample line is approximately less than 5 s. The size of the outlet port on the chamber ensures that there would be no substantial pressure differences between the outside atmosphere and the air within chamber. NO concentration in the sample and the ambient air are monitored by two separate NO chemiluminescent analyzers (e.g., TECO 42S, Thermo Environmental Instruments Inc.). The instruments are periodically calibrated (once a week in normal conditions) at the field site. Details of dynamic chamber technique for NO flux measurement had been discussed and published elsewhere by NC Air Quality research group (Kim *et al.*, 1994; Aneja *et al.*, 1995; Sullivan, 1995; Roelle, 1996).

NO flux can be calculated by considering the mass balance of NO in the chamber (Kaplan *et al.*, 1988; Kim *et al.*, 1994). The mass balance equation is given by

$$\frac{d[C]}{dt} = \left(\frac{Q[C]_0}{V} + \frac{J}{h} \right) - \left(\frac{L}{h} + \frac{Q}{V} \right) [C]_f \quad (2)$$

where

- h internal height of chamber [m],
- J emission flux per unit area [ppb m s^{-1}],

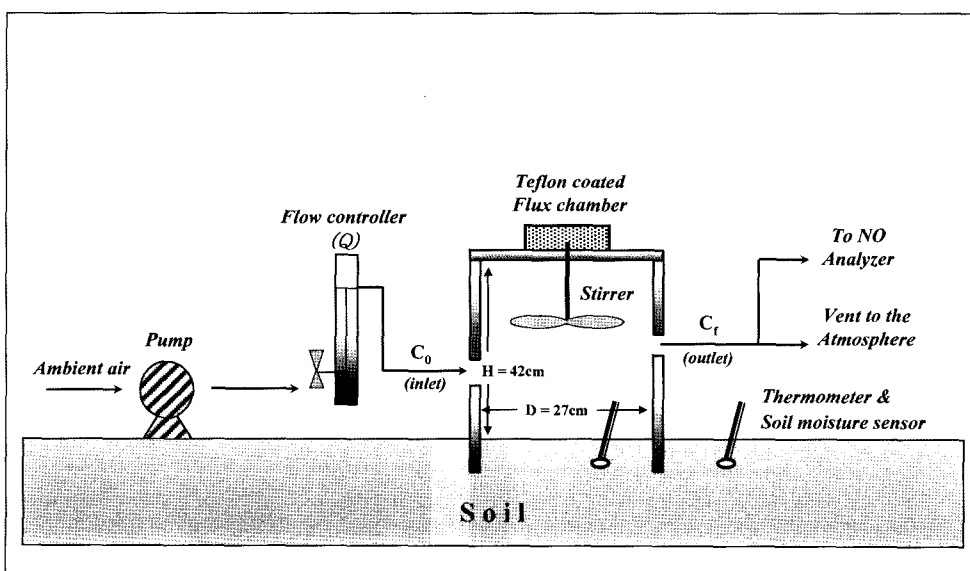


Fig. 3. A schematic of the flow-through dynamic flux chamber used for measuring the soil NO emission. All the internal surfaces of the chamber are coated with fluorinated ethylene propylene (FEP) Teflon (Kim, 2005).

- L wall loss in the chamber per unit area assumed to be a first-order reaction with NO [m s^{-1}],
 Q flow rate through the chamber [L min^{-1}],
 V volume of the chamber [m^3],
 $[C]_f$ NO concentration inside the chamber [ppb],
 $[C]_0$ NO concentration in ambient air near the ground [ppb].

If relatively non-reactive trace gases (e.g., CO_2 , CH_4 and N_2O) are dealt with measuring fluxes, loss by chemical reaction is negligible in equation (2). Assuming well-mixed condition inside the chamber, a general solution of the mass balance equation (2) can be derived for NO concentration in the chamber. The NO flux from soil is therefore determined as an equilibrium-state NO concentration, $[C]_{eq}$ in the chamber.

$$\frac{J}{h} = \left(\frac{L}{h} + \frac{Q}{V} \right) [C]_{eq} - \frac{Q[C]_{air}}{V} \quad (3)$$

where $[C]_{eq}$ is an equilibrium NO concentration in the flux chamber. When ambient NO concentrations near the ground, $[C]_{air}$, are observed to be less than 1 ppbv during the measurement (which is one or two orders of magnitude less than $[C]_{air}$), the last term in equation (3) could be neglected from flux calculation.

In equation (3), L represents the total loss term (e.g., by chamber wall reaction with NO and by chemical reactions of NO with oxidants entering the chamber such as ozone, proxy radicals (Kim *et al.*, 1994; Aneja *et al.*, 1995)). The L here has been determined empirically based on eight experiments through day and night (Kaplan *et al.*, 1988; Kim *et al.*, 1994). The total loss in the chamber has been estimated to be 0.83 mm s^{-1} with a constant flow rate, which agreed well with the previous results (Roelle, 1996).

III. SENSITIVITY ANALYSIS OF SOIL NO GAS EMISSION USING FLOW-THROUGH ENCLOSURE SYSTEM

There are a few theoretical reviews of the flow-through dynamic flux chamber technique in which the simple steady state solution of the NO mass balance equation maintaining inside the flux chamber was determined (Kaplan *et al.*, 1988). In order to solve for the steady state solution of the equation (2), it is important to understand both the physical system and theory behind the flow-through dynamic flux chamber method.

To simplify the solution, the final formula for the calculation of the soil NO flux with field measurement data has been derived under the several assumptions as well as state condition. For instance, the effects of the chemical reaction of NO with other reactive species on soil emission are generally ignored in the flux calculation. However, during the measurement near the ground, chemical reactions may be crucial to the flux change since the presence of primary reactants (oxidant species) such as ozone (O_3) and hydroxyl peroxide (HO_2) near the ground still exist and change the NO concentration inside the chamber by oxidation. This will increase the uncertainty of the NO flux calculation without considering the chemical reactions of NO near the surface. Therefore, it is critical to examine whether soil NO emission without considering the chemical loss reaction of NO is valid or not.

Hereafter the theory behind the flow-through enclosure method is examined and reviewed. And the new calculation flux formula is introduced by considering the most important chemical reactions using NO chemistry and the uncertainties accompanied with are also discussed.

3.1. Mass balance equation with chemical loss in the flux chamber

Considering chemical reactions of NO near ground, the mass balance equation for NO inside chamber (Kim *et al.*, 1994; Kaplan *et al.*, 1988) is given by equation (4) which only add chemical loss or production term, R into equation (2);

$$\frac{d[C]}{dt} = \left(\frac{Q[C]_0}{V} + \frac{JA}{V} \right) - \left(\frac{LA}{V} + \frac{Q}{V} \right) [C]_f + R \quad (4)$$

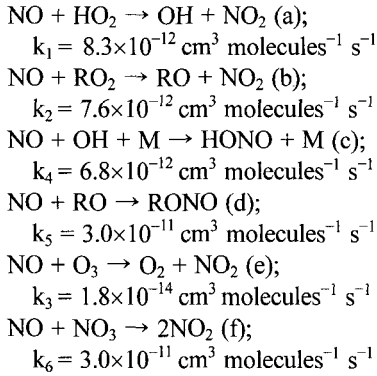
where

- A soil surface area in the chamber [m^2],
 $[C]$ NO concentration in the chamber [ppb],
 $[C]_0$ ambient NO concentration (at the inlet) [ppb],
 $[C]_f$ NO concentration at the outlet [ppb],
 R chemical loss (or production) by chemical reactions in the chamber [ppb s^{-1}].

Assuming a well-mixed chamber, the NO concentration at the outlet of the chamber, $[C]_f$, is close to the concentration inside, $[C]$ so that $[C] \approx [C]_f$.

In order to solve the mass balance equation (4) for soil NO emission, the chemical loss rate, R , in the mass balance equation should be considered. The following important chemical reactions relating with NO chemis-

try in the atmosphere might be considered for the flux calculation (Pitts and Pitts, 1986);



Therefore, the loss of NO through these chemical reactions inside the chamber may affect soil NO emission. Therefore, the chemical loss term in the mass balance equation (4) remains to improve accuracy of the estimation. Total loss of NO by chemical reactions can be written as follows;

$$R = - \left(\sum_{i=1}^n k_i R S_i \right) [C] \quad (5)$$

where n is the number of chemical reactions involving NO, k_i is the corresponding reaction rates for the reaction (a) through (f), $R S_i$ is the concentrations of the reactant species in the reactions, and $[C]$ is the concentration of NO in the chamber. The mass balance equation (4) now becomes;

$$\frac{d[C]}{dt} = \left(\frac{J}{h} + \frac{Q[C]_0}{V} \right) - \left(\frac{Q}{V} + \frac{L}{h} + \sum_{i=1}^n k_i R S_i \right) [C] \quad (6)$$

The solution for the NO concentration at a given time, $C(t)$ of the mass balance equation (6) is given by

$$C(t) = \left([C]_0 - \frac{\beta}{\alpha} \right) e^{-\alpha t} + \frac{\beta}{\alpha} \quad (7)$$

where $\alpha = \frac{Q}{V} + \frac{L}{h} + \sum_{i=1}^n k_i R S_i$ and $\beta = \frac{J}{h} + \frac{Q[C]_0}{V}$ are assumed to be independent with time. Note that regardless of α , the value of coefficient of exponential term, $C(t)$ approaches $\frac{\beta}{\alpha}$ as t approaches ∞ . It means that NO concentration in the chamber, $C(t)$, approaches a constant value of $\frac{\beta}{\alpha}$ with time. After a certain length of time, NO concentration in the chamber will reach the constant value ($[C]_{eq} \equiv \frac{\beta}{\alpha}$), so called an equilibrium state (or steady state). This result gives us an idea, if $[C_0] > \frac{\beta}{\alpha}$, mathematically NO concentration in the chamber $C(t)$ decrease with time; while $C(t)$ increases with time if $[C_0] < \frac{\beta}{\alpha}$. At the equilibrium state, there are

no formation and no destruction of NO. It means that the rate of NO formation equals the rate of destruction at this concentration ($[C]_{eq}$). Physically, this behavior means that soils will act as a source or sink for atmospheric NO depending on the ambient level of NO near the surface. The concentration $[C]_{eq}$ is sometimes called the NO compensation point (Johansson and Granat, 1984; Kaplan *et al.*, 1988; Conrad, 1994). α is a parameter which depends both on the transfer resistance in soil and air and losses in the chamber due to chemical reactions. The NO equilibrium mixing ratio is determined mathematically by the balance between soil emission of NO into the chamber and dilution by the flow through the chamber.

3.2. NO flux calculation and sensitivity of chemical reactions to the flux

Solving the equation (7) for the flux of soil NO, J becomes as time approaches infinity:

$$J = h \left\{ \left(\frac{Q}{V} + \frac{L}{h} + \sum_{i=1}^n k_i R S_i \right) C(\infty) - \frac{Q}{V} [C]_0 \right\} \quad (8)$$

In equation (8), $C(\infty)$ is to be the equilibrium concentration of NO in the chamber; $C(\infty) \approx [C]_{eq}$. The solution for the flux could be called a steady state and is given by

$$J = h \left\{ \frac{Q}{V} ([C]_{eq} - [C]_0) + \left(\frac{L}{h} + \sum_{i=1}^n k_i R S_i \right) [C]_{eq} \right\} \quad (9)$$

If the losses by chamber wall and chemical reactions are neglected, J simply becomes

$$J = h \left\{ \frac{Q}{V} ([C]_{eq} - [C]_0) \right\} \quad (10)$$

This simple steady state solution, which is the same as equation (3), under assumptions of no chemical losses and no uptake by the chamber wall, has been used to calculate emission flux of NO from soils in most field studies (Johansson and Granat, 1984; Williams *et al.*, 1987; Parrish *et al.*, 1987; Johansson and Sanhueza, 1988; Johansson *et al.*, 1988; Slemr and Seiler, 1991; Shepherd *et al.*, 1991; Davidson *et al.*, 1991; Williams and Fehsenfeld, 1987). To examine the significance of the chemical loss terms, the NO flux calculations have to be compared with and without the chemical reaction terms. It could possibly underestimate soil NO flux without considering chemical loss reactions and uptake by wall. This may result in significant errors of natural NO emission inventories over large scale areas for the model estimation. For

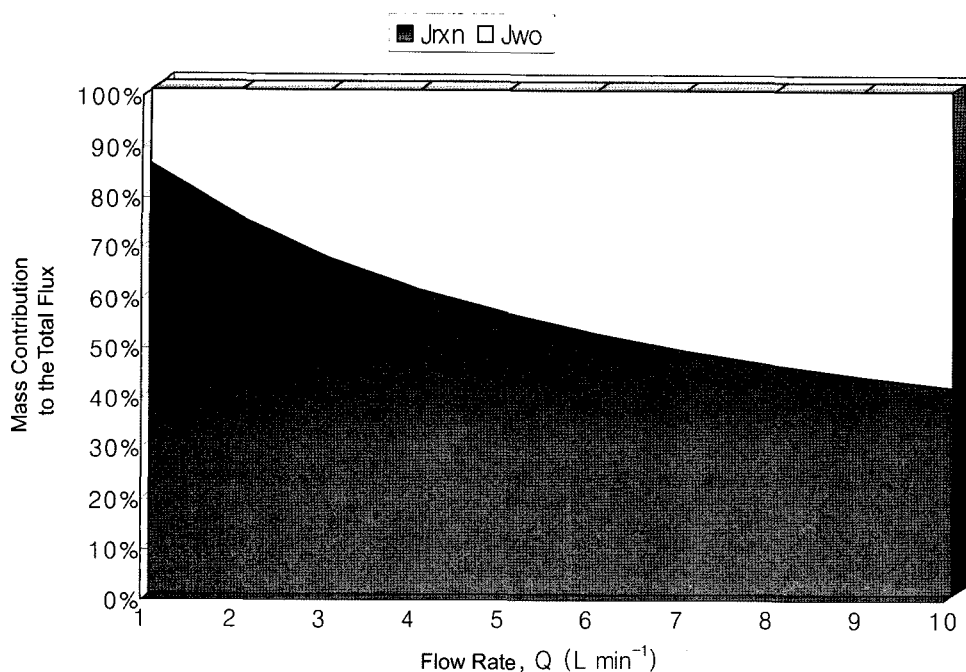


Fig. 4. Effects of chemical loss of NO on the total NO flux from soils. Total is sum of fluxes with (J_{rxn}) and without (J_{wo}) loss effects. Ratio J_{rxn}/J_{total} indicates the error in total NO flux from soils (Kim, 2005).

this reason, it is important to correct the soil NO emission data, especially for use in a photochemistry modeling study on a regional scale.

Kim (2005) conducted sensitivity analysis of the chemical loss effects on the NO flux calculation at given initial and field conditions ($[NO]_0 = 0.2$ ppbv, $[O_3] = 5$ ppbv, $J_{NO} = 3 \text{ ng m}^{-2}\text{s}^{-1}$, and $V=27.6 \text{ L}$, $h=0.47 \text{ m}$) resulted from a rural grassland field NO flux experiments such as SOS (Southern Oxidant Study) site SONIA (Southeastern Oxidant of Nitrogen Intensive Analysis) in Candor, North Carolina during summer season. Fig. 4 shows the flux calculated with and without loss terms as a function of flow rate from the results (Kim, 2005). J_{rxn} decreases with increase in flow rate. This is mainly due to the lower equilibrium concentration in the chamber as Q increases. On the other hand, J_{NO} increases with increase in flow rate. The range of the error (J_{rxn}/J_{NO}) varies from 85% to 42% as the flow rate increases from 1 to 10 L min^{-1} . The result suggests that the error level is lessened by increase in flow rate. The analysis shows, when loss effects are neglected in flow through chamber method, a significant error in total soil NO flux could be resulted. Therefore, it is suggested that NO flux from soils calculated without consideration of chemical loss reactions of NO in the

chamber should be corrected by addition of J_{rxn} .

IV. SUMMARY

The methodologies for measuring gas emissions from soil surface have been discussed. There are two different kinds of enclosure-based measurements: closed static system and flow-through dynamic systems. These are simple to operate, relatively low in cost, and especially useful for addressing research objectives served by discrete observations in space and time. Flux calculation methods for these two different systems were also addressed and their differences were discussed.

The flow-through flux chamber method has been used in field measurements of NOx flux from soils. In many cases, however, chemical reactions and wall loss inside chamber have not been thoroughly considered in the process of flux calculation at the field experiments. It is necessary to understand the physical and mathematical background of the flow-through dynamic flux chamber system in order to specify the flux sensitivity by these loss effects.

The sensitivity of the chemical loss on the NO flux was examined as a function of flow rate and the given

set of initial conditions. The results revealed that the equilibrium concentration does not significantly change when $Q \geq 10 \text{ L min}^{-1}$. Significant error in total soil NO flux could be resulted when loss effects are neglected in flow through chamber method. It is suggested that NO flux from soils calculated without consideration of chemical loss reactions of NO in the chamber should be corrected by considering their chemical reactions.

적 요

지난 수 세기 동안 온실기체와 기타 화학적으로 중요한 미량기체들이 급격하게 증가하였다. 이러한 주요 기체가 기후 변화에 미치는 영향을 이해하기 위해서는 각 기체들의 흡원과 발원을 규명하고, 생물권과 대기권 사이에서 발생하는 생물 기원 기체 플럭스들을 특성화 하며, 주요 기체를 조절하는 프로세스들을 이해해야 한다. 본 논문에서는 야외 실험을 위한 실용적 방법인 enclosure 기반의 관측법을 소개한다. 특히, 토양표면에서 방출되는 일산화질소 플럭스에 대한 enclosure 내에서의 질량수지 방정식과 flow-through dynamic 플럭스 챔버 기법의 민감도를 제시하고 flow-through dynamic 플럭스 챔버 방법의 물리적인 시스템과 이론을 소개한다. 또한 챔버 벽에서 발생하는 일산화질소의 손실을 고려하므로써 새로운 플럭스 계산식을 소개하였고 그 계산식의 불확실성을 논의하였다.

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