

Sensitivity Study of the Flow-through Dynamic Flux Chamber Technique for the Soil NO Emissions

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Abstract

A mathematical sensitivity analysis of the flow-through dynamic flux chamber technique, which has been utilized usually for various trace gas flux measurement from soil and water surface, was performed in an effort to provide physical and mathematical understandings of parameters essential for the NO flux calculation. The mass balance equation including chemical reactions was analytically solved for the soil NO flux under the steady state condition. The equilibrium concentration inside the chamber, C_{eq} , was found to be determined mainly by the balance between the soil flux and dilution of the gas concentration inside the chamber by introducing the ambient air. Surface deposition NO occurs inside the chamber when the C_{eq} is greater than the ambient NO concentration (C_0) introducing to the chamber; NO emission from the soil occurs when the C_{eq} is less than the ambient NO concentration.

A sensitivity analysis of the significance of the chemical reactions of NO with the reactive species (i.e. HO_2 , CH_3O_2 , O_3) on the NO flux from soils was performed. The result of the analysis suggests that the NO flux calculated in the absence of chemical reactions and wall loss could be in error ranges from 40 to 85% to the total flux.

Key words : Sensitivity analysis, Flux measurement, Flux chamber technique, Flow-through dynamic chamber, Soil NO emission

1. INTRODUCTION

It is essential to understand the tropospheric chemistry of the oxides of nitrogen ($NO_x = NO + NO_2$) in relation with the production of photochemical oxidants and its spatial budget because NO_x is the precursor specie and essential in the photochemical formation of ozone in the urban and rural atmos-

phere. Moreover, the atmospheric concentration of hydroxyl (OH) radical is mainly regulated by NO_x concentration and the temporal and spatial distribution of OH has been shown to be sensitive to the level of NO_x in the atmosphere (Kim *et al.*, 1994; Liu *et al.*, 1987).

In urban areas, oxides of nitrogen are emitted into the atmosphere primarily by anthropogenic sectors, such as combustion of fossil fuels and biomass burning (Logan, 1983). However, in rural areas soils may be a significant source for the atmospheric

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NO_x. Yienger and Levy (1995) have reported, based on their empirical model results that soil emissions can account for up to 75% of the total NO_x budget. Land use by mankind is having a significant impact on global soil NO_x emission. NO_x emission from soils also exhibit highly spatial and temporal variabilities because there are many variables controlling the NO_x emission from soils, such as soil moisture contents, soil temperature and soil N contents (Kim, 1997a, b; Johansson and Sanhueza, 1988; Johansson *et al.*, 1988; Anderson and Levine, 1987; Williams *et al.*, 1987; Slemr and Seiler, 1984). NO_x emitted from soils are produced by nitrification, the oxidation of organic nitrogen and (or) ammonia to nitrate, and also produced during denitrification of nitrate. The more nitrogen that is being cycled through the system, the greater quantity is converted into these gases and emitted from the soils (Smith *et al.*, 1998). Kim and Kim (2002) have reported that soil N content and soil NO emission increased significantly after applying N fertilizer to agricultural field, and suggested that cultivated land could be larger source than any other anthropogenic source, attributed to the use of synthetic nitrogen fertilizers. Anthropogenic sources are generally confined to small geographic areas and can be well quantified. On the other hand, natural sources of NO_x, principally lightning and emission from soils (including agricultural fields), are more wide spread and less intense making quantitative estimation much more difficult (Kim *et al.*, 2002; Kroeze and Mosier, 2000; Williams *et al.*, 1992). There is a recognized need for improved understanding of the factors responsible for high variability observed in measurements of NO soil emissions in order to reduce uncertainties in global budgeting efforts (Davison and Kinglerlee, 1997; Matson, 1997; Kim *et al.*, 1995; Kim and Aneja, 1994).

For the photochemical modeling study it is important to make a good estimation of NO_x emission from soil because of the source significance of biogenic soil including agricultural sectors, especially over the large rural areas. Therefore the great number of field measurements data sets of NO soil emission over various soil characteristics and loca-

tions are desirable for the regional basis photochemical modeling, and it is crucial to improve the NO emission input data for obtaining appropriate model results. In order to make highly qualified emission data sets, the soil NO flux measurement technique has to be fully understood with sound scientific background and carefully conducted at the field sites.

Several techniques have been utilized to measure the NO emission flux from soils including flow-through dynamic flux chamber method, gradient method and eddy correlation methods. Many published studies of NO_x soil flux measurements (Kim *et al.*, 2002; Kim, 2001; Li *et al.*, 1999; Roelle *et al.*, 1999; Kim, 1997a, b; Kim *et al.*, 1995; Kim and Aneja, 1994; Kim *et al.*, 1994; Johansson and Sanhueza, 1988; Anderson and Levine, 1987; Parrish *et al.*, 1987; Williams *et al.*, 1987; Slemr and Seiler, 1984) have relied on the flow-through chamber technique. Inter-comparison analysis between the flow-through dynamic chamber method and gradient methods indicates that the results from chamber method agree well those from gradient method (Kaplan *et al.*, 1988; Parrish *et al.*, 1987).

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 it is important to understand both the physical system and theory behind the flow-through dynamic flux chamber method. To simplified 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, in the real atmosphere near the ground chemical reactions in the flux chamber may be crucial since the presence of primary reactants (oxidant species) such as ozone (O₃) and hydroxyl peroxide (HO₂) near the ground still exist and change the NO concentration inside the cham-

ber by oxidation. This will make 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 calculated without considering the chemical loss reaction of NO is valid with certain uncertainty or not. In this paper, the physical system and theory behind the flow-through dynamic flux chamber method were examined and reviewed, and the new calculation flux formula introduced with considering the most important chemical reactions and discussed the uncertainties accompanied with.

2. SYSTEM OF THE FLOW-THROUGH DYNAMIC CHAMBER

A schematic of the dynamic flow-through flux chamber is illustrated in Fig. 1. General descriptions of the chamber system 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 ~10 cm (see Fig. 1). Ambient air, which is used as a carrier gas, is pumped through the chamber at a constant flow rate (Q L/min). The air inside the chamber is mixed by a motor-driven Teflon stirrer. Teflon tubing (1/4 inch O.D.) is used to connect the

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. It makes sure the size of the outlet port on the chamber ensures that there were no substantial pressure differences between the outside atmosphere and the air within the chamber. NO concentration in the sample and the ambient air are monitored by two separate NO chemiluminescent analyzers (TECO 42S, Thermo Environmental Instruments Inc.). The instruments are periodically calibrated (once a week in normal condition) at the field site.

3. FLUX CALCULATION METHODOLOGY

3.1 Mass balance equation with chemical loss in the flux chamber

Using the flow-through dynamic flux chamber (Fig. 1), ambient air is drawn through the chamber of volume, V , at a given flow rate, Q . The mass balance equation for NO inside chamber (Kim *et al.*, 1994; Kaplan *et al.*, 1988) is given by

$$\frac{d[C]}{dt} = \left(\frac{Q[C]_0}{V} + \frac{JA}{V} \right) - \left(\frac{LA}{V} + \frac{Q}{V} \right) [C]_f + R, \quad (1)$$

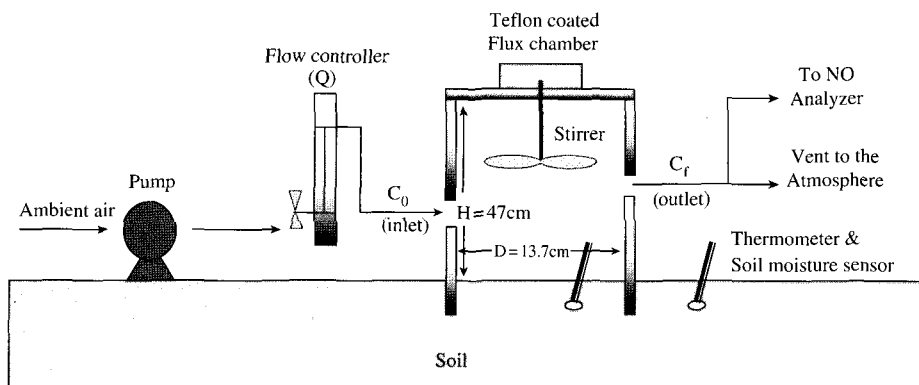


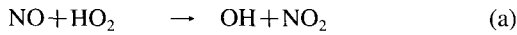
Fig. 1. A schematic of the flow-through dynamic flux chamber used for measuring the soil NO emission. The all internal surface of the chamber are coated with fluorinated ethylene propylene (FEP) Teflon.

where

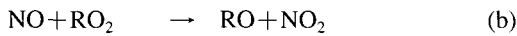
- A soil surface area in the chamber; m^{-2}
 V volume of the chamber; m^{-3}
 h inner height of the chamber ($= A/V$); m
 Q constant flow rate through the chamber; $m^3 s^{-1}$
 J NO emission rate; $ppb m s^{-1}$
 [C] NO concentration in the chamber; ppb
 [C]₀ ambient NO concentration (at the inlet); ppb
 [C]_f NO concentration at the outlet; ppb
 L wall loss rate in the chamber per unit area assumed first order in [C]; $m s^{-1}$
 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 equal to the concentration inside, [C] so that [C] ≈ [C]_f.

In order to solve the mass balance equation (1) 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 chemistry in the atmosphere might be considered for the flux calculation (Pitts and Pitts, 1986);



$$k_1 = 8.3 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$$



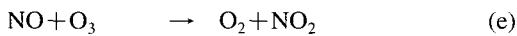
$$k_2 = 7.6 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$$



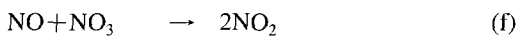
$$k_4 = 6.8 \times 10^{-12} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$$



$$k_5 = 3.0 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$$



$$k_3 = 1.8 \times 10^{-14} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$$



$$k_6 = 3.0 \times 10^{-11} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1}$$

Reaction (c) and (d) do not permanently remove NO from the atmosphere since photolysis of HONO and RONO reforms NO in the system. The first approximation could be made that only reaction (e) and (f) are considered while the others can be

neglected because the background concentration of O₃ and NO₃ are relatively higher than those of other radical species (i.e. HO₂, RO₂, OH, RO) under the rural atmosphere. Reaction (f) may be more important at night time because the NO₃ level during the night is higher than those during the day. Since O₃ and NO₃ concentrations near ground surface sharply decrease due to surface deposition on to the ground and vegetation, the destruction rate of NO by these chemical species may be also small near the surface where the flux measurement is made. However, a conservative assumption to include most important chemical reactions of NO could be accepted since measurable O₃ concentration (~10 ppb) has been found near surface, and vertical profiles of the radicals are almost constant in the troposphere (Warneck, 2000). 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 (1) remains to improve accuracy of the estimation.

Total loss of NO by chemical reactions can be written as follows;

$$R = - \left(\sum_{i=1}^n k_i RS_i \right) [C] \quad (2)$$

where n is the number of chemical reactions involving NO, k_i is the corresponding reaction rates for the reaction (a) through (f), RS_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 (1) now becomes;

$$\frac{d[C]}{dt} = \left(\frac{J}{h} + \frac{Q[C]_0}{V} \right) - \left(\frac{Q}{V} + \frac{L}{h} + \sum_{i=1}^n k_i RS_i \right) [C] \quad (3)$$

The solution for the NO concentration at a given time, C(t) of the mass balance equation (3) is given by

$$C(t) = \left([C]_0 - \frac{\beta}{\alpha} \right) e^{-\alpha t} + \frac{\beta}{\alpha} \quad (4)$$

where $\alpha = \frac{Q}{V} + \frac{L}{h} + \sum_{i=1}^n k_i RS_i$ 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 β/α with time. After a certain length of time, NO concentration in the chamber will reach the constant value ($C_{eq} \equiv \beta/\alpha$); so called an equilibrium state (or steady state). This result gives us an idea, if $C_0 > \beta/\alpha$, mathematically NO concentration in the chamber $C(t)$ decrease with time; while $C(t)$ increases with time if $C_0 < \beta/\alpha$. Fig. 2 shows the time change of the NO concentration in the chamber, $C(t)$ depending on the equilibrium concentration (C_{eq}). Based on the analytical solution, deposition of NO will then occur if the near ground ambient NO concentration is higher than the equilibrium value, $\beta/\alpha (= C_{eq})$; and emission from the surface will occur if it is below β/α . 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 (Conrad, 1994; Kaplan *et al.*, 1988; Johansson and Granat, 1984). The existence of NO compensation point has frequently been observed in the field (Kaplan *et al.*, 1988; Johansson and Granat, 1984; Slemr and Seiler, 1984). Slemr and Seiler (1991) reported that NO_2 emission flux from soils in field conditions has only been observed at atmospheric mixing ratio of NO_2 ranging below ~ 16 ppb.

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

The solution of mass balance equation (4) can be rewritten as follows:

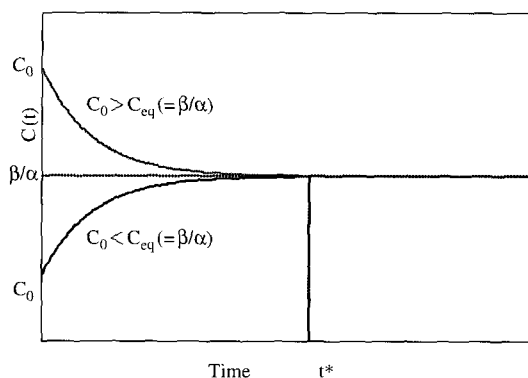


Fig. 2. Change of NO concentration in the chamber with time. C_0 is the initial concentration of NO at the inlet of the chamber and $C_{eq} (= \beta/\alpha)$ is the equilibrium concentration. t^* is the time to reach a steady state.

$$\frac{\beta - \alpha C(t)}{\beta - \alpha [C]_0} = e^{-\alpha t} \quad (5)$$

Solving the equation (5) for the flux of soil NO, J becomes:

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

As time approaches infinity, J becomes as follows:

$$J = h \left\{ \left(\frac{Q}{V} + \frac{L}{h} + \sum_{i=1}^n k_i R S_i \right) C(\infty) - \frac{Q}{V} [C]_0 \right\} \quad (7)$$

In the equation (7), $C(\infty)$ 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

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

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

$$J = h \left\{ \frac{Q}{V} (C_{eq} - [C]_0) \right\} \quad (9)$$

This simple steady state solution 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 (Davidson *et al.*, 1991; Shepherd *et al.*, 1991; Slemr and Seiler, 1991; Williams and Fehsenfeld, 1991; Johansson and Sanhueza, 1988; Johansson *et al.*, 1988; Parrish *et al.*, 1987; Williams *et al.*, 1987; Johansson and Granat, 1984). 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 be possibly underestimate of soil NO flux without considering chemical loss reactions and uptake by wall. This may result significant errors of natural NO emission inventories over large scale areas for the model estimation. For this reason, it is important to correct the soil NO emission data, especially for use in a photochemistry modeling study on a regional basis.

4. SENSITIVITY ANALYSIS OF THE CHEMICAL LOSS EFFECTS ON THE FLUX CALCULATION

For the sensitivity analysis of the NO flux, time changes of the NO concentration inside the chamber have been calculated at given initial and field conditions ($[NO]_0 = 0.2$ ppbv, $[O_3] = 5$ ppbv, $J_{NO} = 3$ ng m⁻²s⁻¹, and $V = 27.6$ L, $h = 0.47$ m) resulted from a rural grassland field NO flux experiments, SOS (Southern Oxidant Study) site SONIA (Southeastern Oxidant of Nitrogen Intensive Analysis) in Candor, North Carolina during summer season. The changes of NO concentration inside the chamber with time were compared and examined under the different conditions. For the radical species concentrations to consider the chemical reactions involved, such as OH, HO₂ and RO₂, were referred from literature reviews (Warneck, 2000; Pitts and Pitts, 1986). A strong diurnal variation of HO₂ at clean air site in Oregon was observed with a maximum during the day of 2×10^8 molecules cm⁻³ and a minimum of 2×10^7 molecules cm⁻³ at night (Hard *et al.*, 1992). The nighttime average concentration was

$\sim 3 \times 10^7$ molecules cm⁻³. In order to calculate chemical loss of NO by reaction with HO₂ near the ground surface, the nighttime average of HO₂ was assumed to be HO₂ number density near ground surface. This estimate could be regarded as a conservative value for HO₂ at the surface. The number density of CH₃O₂, 1.5×10^7 molecules cm⁻³, was used to estimate the loss reaction of NO by RO₂ in the chamber.

The loss effect of NO by Teflon coated-wall reaction in the chamber was estimated, base on the result from Kaplan's total loss term experiment (Kaplan *et al.*, 1988). Wall loss term (L) was taken from the difference between the Kaplan's total loss and the chemical loss we calculated. L of 0.02 cm s⁻¹ was estimated and was one order of magnitude less than deposition velocity of NO on soil or cement surface.

Using the given information, the estimate of total loss ($L_{total} \equiv L/h + \sum k_i RS_i$) by wall and the first order chemical reactions of NO in the chamber was 0.185 min⁻¹. Loss by reaction with O₃ appeared to be the largest contributor to L_{total} (72%). Loss by wall reaction was the second largest contributor (16%); and loss by reaction with HO₂ was the third largest contributor (8%) to total loss of NO. The remaining loss effects are attributed to the reactions of NO with RO₂ and OH.

Fig. 3 shows the time changes of the NO concentration inside the chamber with the given conditions at a constant flow rate ($Q = 5$ L min⁻¹). The NO inside chamber for the different cases with and without loss reactions were calculated and plotted as a function of time in Fig. 3. The plot shows that the concentration of NO reaches a steady state within 15 to 30 minutes and more quickly with the addition of loss effects. The equilibrium concentration, C_{eq} , decreases with the addition of loss effects; i.e. C_{eq} without any loss effects was ~ 1.9 ppb and C_{eq} with all loss effects was 0.9 aerosol@plaza.snu.ac.kr ppb. It implicates that the difference between the C_{eq} estimated with and without loss effects induces the error in the NO flux calculation when the loss terms are neglected in the mass balance equation of the flow-through dynamic chamber system. In case of

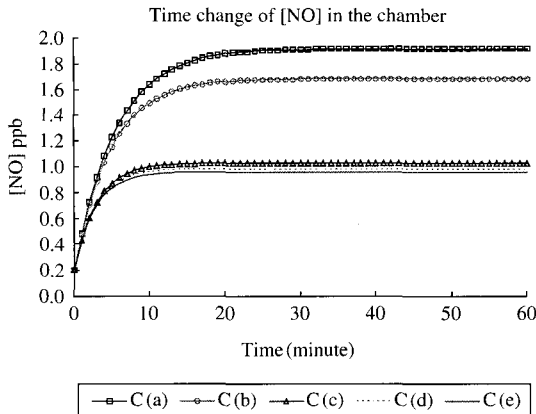


Fig. 3. Plots of time rate of change of NO concentration in the chamber calculated with and without chemical loss reactions at 5 L min^{-1} flow rate; $C_{(a)}$ without any losses, $C_{(b)}$ with wall loss, $C_{(c)}$ with wall loss and O_3 reaction, $C_{(d)}$ with wall loss, O_3 reaction and HO_2 reaction, and $C_{(e)}$ with wall loss, O_3 reaction, HO_2 reaction, CH_3O_2 reaction and OH reaction.

$Q = 5 \text{ L min}^{-1}$ NO flux calculated without consideration of any loss terms (J_{wo}) was $1.3 \text{ ng m}^{-2} \text{ s}^{-1}$, while the flux calculated including primary loss terms (J_{NO}) was $3 \text{ ng m}^{-2} \text{ s}^{-1}$. The results of the two calculations suggest that as much as 55% total NO flux from soil could be underestimated by when the loss terms are neglected.

The equilibrium concentrations of NO (C_{eq}) were plotted as a function of increasing flow rates in Fig. 4(a) with and without wall loss and chemical reaction terms in the chamber. C_{eq} is physically determined by the balance between emission from soils and dilution from the air outside and deposition in the chamber. C_{eq} decreases with increase flow rate because the dilution effect becomes dominant. C_{eq} also decreases with the addition of the loss terms in Fig. 4(a). The time required to reach a steady state, t^* , was also plotted as a function of flow rate in Fig. 4(b). The trend is similar to C_{eq} with flow rate. As flow rate increases, t^* decreases both with and without loss terms. The results shows that the time to reach a steady state takes less than an hour when $Q \geq 4 \text{ L min}^{-1}$. The differences of C_{eq} and t^* between the values of with and without loss

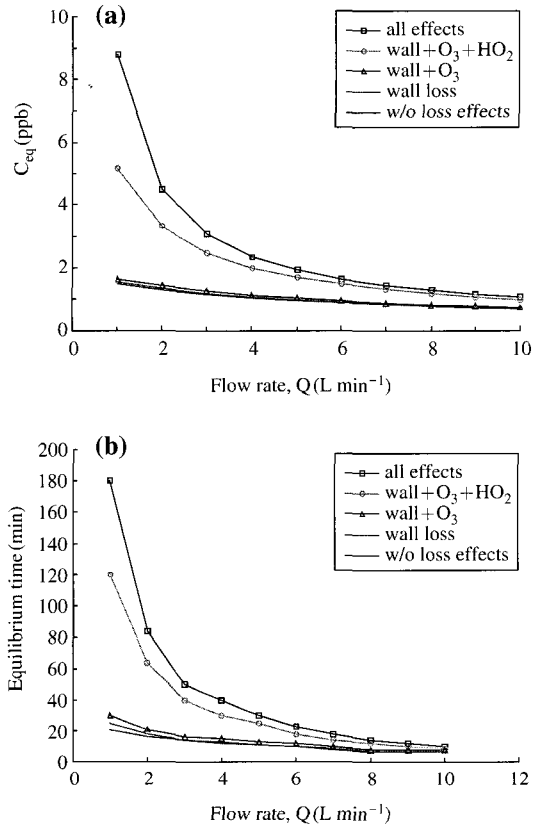


Fig. 4. Plots of (a) equilibrium concentration of NO (C_{eq}) in the chamber and (b) time (t^*) to reach steady state as a function of flow rates (Q) at given conditions of $[\text{NO}]_0 = 0.2 \text{ ppb}$ $[\text{O}_3] = 5 \text{ ppb}$ and flux at steady state $J_{\text{NO}} = 3 \text{ ng m}^{-2} \text{ s}^{-1}$.

terms drastically decrease with increasing flow rate, and the differences are insignificant when $Q \geq 10 \text{ L min}^{-1}$.

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. Total flux of NO (J_{NO}) was defined sum of J_{wo} (the first term in equation (8)–no loss effects) and J_{rxn} (the second term in equation (8)–with only primary chemical loss and wall loss terms). Therefore, J_{wo} and J_{rxn} can be expressed as follows:

$$J_{\text{wo}} = h \left\{ \frac{Q}{V} (C_{\text{eq}} - [\text{C}]_0) \right\} \quad (10)$$

$$J_{rxn} = h \left\{ \left(\frac{L}{h} + \sum_{i=1}^n K_i RS_i \right) C_{eq} \right\} \quad (11)$$

where $i = 1, 2, 3, 4$ and RS_i is the concentration of each reactant species in reaction (a), (b), (c) and (e); i.e. $[HO_2]$, $[CH_3O_2]$, $[OH]$ and $[O_3]$, respectively. Physically and mathematically it is clear that soil NO flux determined by the flow-through chamber method is underestimated when the loss terms are neglected. The ratio of J_{rxn} to total flux of NO (J_{rxn}/J_{NO}) indicates the error in the calculation of total soil NO flux by neglecting loss terms. Fig. 5 shows the flux calculated with and without loss terms as a function of flow rate through the flux chamber system. J_{rxn} decreases with increase flow rate. This is mainly due to the lower equilibrium concentration in the chamber as Q increases. On the other hand, J_{wo} increases with increase 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 flow rate. It is notified that the equilibrium concentration does not significantly change when $Q \geq 10 L \min^{-1}$ in Fig. 4(a). 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

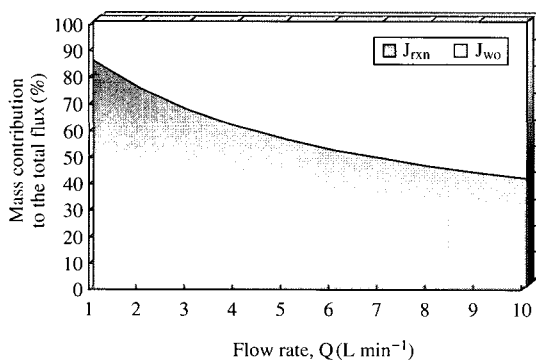


Fig. 5. Effects of chemical loss of NO on the total NO flux from soils. Total is sum of fluxes with (J_{rxn}) and without (J_{wo}) loss effects. Ratio J_{rxn}/J_{total} indicates the error in total NO flux from soils.

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

In most cases, chemical loss of NO in the atmosphere results in the production of NO_2 . NO is usually converted to NO_2 by reaction with O_3 and HO_2 in ambient air. Of course, the reaction of NO_2 with OH radical is an important removal process of NO_2 from the atmosphere. However, since the global average number density of OH is 5×10^5 molecules cm^{-3} (Warneck, 2000) which is much smaller than number density of O_3 , the loss of NO_2 by reaction with OH in the chamber can be ignored. Thus NO_2 flux from soils including NO_2 production by reaction of NO with O_3 , HO_2 , and RO_2 and wall loss reaction may be also calculated as follows;

$$\begin{aligned} J_{NO_2} &= h \left\{ \frac{Q}{V} ([NO_2]_{eq} - [NO_2]_0) \right\} \\ &+ h \left\{ \frac{L}{h} [NO_2]_{eq} - \left(\sum_{i=1}^n k_i RS_i \right) [NO_2]_{eq} \right\} \\ &= J_{wo}^{NO_2} + J_{rxn}^{NO_2} \end{aligned} \quad (12)$$

Resulting from field measurements, soil NO_2 fluxes are approximately an order of magnitude smaller than those of NO and sometimes reported negative flux when chemical reactions are neglected. Calculated flux with chemical reaction, $J_{rxn}^{NO_2}$ can contribute either positively or negatively to total NO_2 flux depending on the relative magnitudes of the loss and production of NO_2 in the chamber.

5. SUMMARY AND CONCLUSIONS

The flow-through flux chamber method has been used in field measurements of NO_x 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. A general flux calculation formula from the mass balance equation was derived by considering the

dominant chemical reactions, i.e. reaction of NO with O_3 , HO_2 and CH_3O_2 in the chamber, and loss to the chamber wall to determine the magnitude of those effects on total soil flux.

The simple flux formula which has been used usually in field measurements only applies to a steady state with no consideration of wall and chemical reactions in the chamber. The equilibrium concentration, C_{eq} , is an important parameter in the determination of the soil flux. C_{eq} is physically determined by the balance between emission from soils and dilution from the air outside and deposition in the chamber. NO deposits on to the soil surface when ambient air concentration near ground (C_0) is greater than C_{eq} ; NO releases from the soil surface when C_0 is lesser than C_{eq} . It suggests that the soil acts as a sink or a source for NO depending on the balance between ambient concentration and the equilibrium concentration.

Chemical loss effects on total NO flux from soils were found to be significant in the sensitivity analysis under a given field condition adapted from at Candor, North Carolina during SOS-SONIA experiment campaign. NO Loss by reaction with ozone was the largest contribution to total loss of NO (72%). Wall reaction loss was the second largest contribution (16%) and loss by HO_2 reaction was the third largest contribution (8%).

The system shows that C_{eq} decreases with increase flow rate because the dilution effect becomes dominant. The time required to reach a steady state, t^* , decreases both with and without loss terms as flow rate increases. The results shows that the time to reach a steady state takes less than an hour when $Q \geq 4 \text{ L min}^{-1}$. The differences of C_{eq} and t^* between the values of with and without loss terms drastically decrease with increasing flow rate, and the differences are insignificant when $Q \geq 10 \text{ L min}^{-1}$.

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 range of the error in total soil NO flux 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 flow rate. The results revealed that the equilibrium

concentration does not significantly change when $Q \geq 10 \text{ L min}^{-1}$. 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 chemical reactions.

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