

## Dynamic Chamber System to Measure Gaseous Compounds Emissions and Atmospheric-Biospheric Interactions

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Dynamic chamber, Emissions, Ammonia, Nitrogen oxide, Hydrogen sulphide, Hydrogen peroxide

### Abstract

The dynamic flow-through chamber system has been developed in response to a need to measure emissions of nitrogen, sulphur, and carbon compounds for a variety of field applications. The cylindrical chamber system is constructed of chemically inert materials and internally lined with 5mil thick transparent fluorinated ethylene polypropylene (FEP) Teflon to reduce chemical reactions and build up of temperature inside the chamber. The chamber (diameter = 27cm, height = 42 cm, volume = 24.05 L) is designed with an open-ended bottom that can penetrate either soil or liquid to a depth of ~6-8 cm, thus creating a completely enclosed system. Carrier gas (e.g. compressed zero-grade air) is pumped at a constant flow rate (~2 to ~5 lpm), depending on the season. The air inside the chamber is well mixed by a variable-speed, motor-driven Teflon impeller (~40 to ~100 rpm). Many different laboratory and field experiments have been conducted using this dynamic chamber system. Oxides of nitrogen (NO, NO<sub>2</sub>, NO<sub>y</sub>) emissions have been measured from agricultural soils where nitrogen-rich fertilizers have been applied. Ammonia-nitrogen (NH<sub>3</sub>-N) and reduced organic sulphur compounds emissions have been measured using this same technique across a gas-liquid interface at swine waste treatment anaerobic storage lagoons, and agricultural fields. Similar chamber systems have also been deployed to measure uptake of nitrogen, sulphur, ozone, and hydrogen peroxide gases by crops and vegetation to examine atmospheric-biospheric interactions. Emissions measurements have been validated by a coupled gas-liquid transfer with chemical reaction model as well as a U.S. Environmental Protection Agency (EPA) WATER 9 model.

### Introduction

The dynamic flow-through chamber system is a technique that has been developed and modified over the past 25 years in an effort to measure earth-atmosphere and water-atmosphere fluxes of various compounds including biogenic sulphur, oxides of nitrogen, ammonia, and methane. Determination of fluxes for these different gaseous compounds is desirable in order to permit accurate assessment of the relative roles of biogenic and anthropogenic sources in contributing to such phenomena as the atmospheric sulphate and nitrate burdens, acidity in

precipitation due to biogenic emissions, and contribution to aerosol formation through atmospheric photochemical processes in localized areas downwind of suspect sources. Similar systems have also been utilized to measure exposure of plants to various air pollutants and to quantify the uptake of trace gases by plants (e.g., Aneja, 1976; Rogers *et al.*, 1979; Heck *et al.*, 1987; Claiborn and Aneja, 1993).

Hill *et al.* (1978) initially developed this technique to measure biogenic sulphur fluxes from a salt marsh in Long Island, New York. More recently, the dynamic flow-through chamber system has also been used to measure ammonia emissions from agricultural and non-agricultural soils (Roelle and Aneja, 2002), hog waste treatment lagoons (Aneja *et al.*, 2000, 2001a,b), and agricultural crop soils over which liquid hog waste has been applied (Roelle and Aneja, 2002), and biogenic nitric oxide emissions from various types of agricultural soils (Li *et al.*, 1999; Roelle *et al.*, 2001) as well as municipal wastewater treatment plant bio-solids-amended soils (Tabachow *et al.*, 2002). Currently, a study by the North Carolina State University Air Quality research group, in coordination with the U.S. Department of Agriculture National Research Initiative, is underway to measure simultaneous emissions of nitric oxide, ammonia and hydrogen sulphide from swine waste treatment lagoons using this same technique.

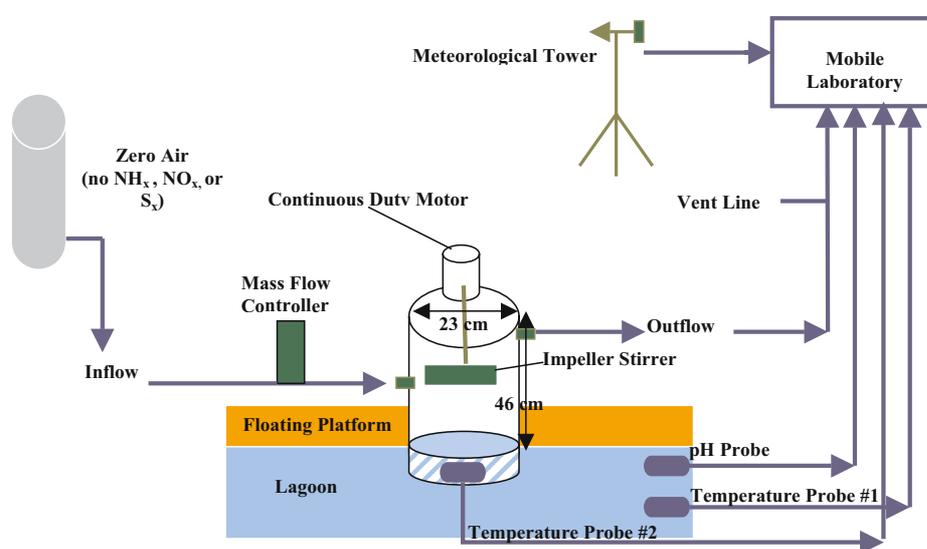
For measuring emissions, the chamber technique has the important advantage of association of a particular emission site and its measurable array of physical, chemical, and microbiological properties with emissions of particular compounds or their reaction products. In addition, gas residence times in the chamber are on the order of minutes so that chemical transformations between emission and analysis may be minimized. The entire chamber system is small, lightweight and easily transportable, thus making a survey of trace gas flux very convenient. Finally, the system is relatively inexpensive and laboratory requirements are low. However, it should be noted that the chamber system cannot completely simulate the ambient environment. The chamber measures over a small area (requires extrapolation) and extrapolation to large scale may be a problem. For measuring fluxes to plants, the dynamic chamber is operated as a well-mixed chamber. Ideally, then, mixing is instantaneous, conditions are uniform throughout the chamber, and exit conditions are representative of internal, well-mixed conditions, thus simplifying calculations of fluxes and mathematical treatment of non-plant surface losses (Aneja, 1976; Claiborne and Aneja, 1993).

#### **Dynamic Flow-Through Chamber for Emissions at the Air-Water/Soil Interface**

In the dynamic emission flux chamber method, a continuously stirred tank reactor (CSTR; Levenspiel, 1962) with an open bottom is placed over an area of interest of soil, mud, or water (Hill *et al.*, 1978). For flux measurements at the air-water interface, a floating platform is used to hold the chamber system above water. A hole is cut in the centre of the platform in which the chamber rests, allowing the bottom of the chamber to penetrate the water surface by 3-4 cm, thus forming a seal between the water surface and the air within the chamber and thereby providing a completely enclosed system in which to measure gaseous fluxes. **Figure 1** depicts a schematic of a typical dynamic flow-through chamber system used to measure gaseous emissions from a swine waste treatment lagoon. For soil measurements, the chamber is placed onto a stainless steel ring

which is then inserted into the soil. Flux measurements are taken ~1 hour after the insertion of the ring into the soil to ensure steady-state conditions have been reached within the chamber.

Over the years construction of the dynamic chamber has been modified. For studies conducted recently, the chamber is generally constructed as follows. The dynamic flow-through chamber system is cylindrical in nature and built from Plexiglas material. Chamber dimensions may vary but are generally about 23 cm inner diameter (i.d.) and 46 cm. in height. The entire closed system is lined on the inside with 2 mil fluorinated ethylene propylene (FEP) Teflon and stainless steel fittings in order to minimize chemical reactions with sample flow.



**Figure 1.** Schematic of dynamic flow-through chamber system configured to measure emissions from a swine waste treatment lagoon.

A sweep gas such as compressed zero-grade air is passed through a Teflon FEP sample line into the chamber. The in-flowing air is monitored by a mass flow controller and subsequently delivered into the chamber. The air inside the chamber is ideally well-mixed by a variable-speed motor-driven Teflon impeller stirrer (speeds generally range from ~40-100 rpm). The dynamic chamber system, with the continuous stirring provided by the impeller, meets the necessary criteria for performance as a continuously stirred tank reactor (CSTR). For performance as a CSTR, the chamber needs to be “ideally” mixed (Aneja, 1976). In ideal mixing, the composition of any elemental volume within the chamber is assumed to be the same as that of any other volume within the chamber. Tracer experiments (residence time distribution) have been used to test the flow and mixing characteristics of the system. The results of these mixing studies

indicated that the dynamic chamber behaved as a “perfect” mixer with negligible stagnancy or channelling (Aneja *et al.*, 2000).

Johansson and Granat (1984) conducted research on pressure differences between the outside atmosphere and air within a chamber using a tilted water manometer, which indicated that pressure differences were below detectable limits (0.2 mm H<sub>2</sub>O). Arkinson (2003) conducted research on temperature difference between the outside atmosphere and air within the chamber. The results indicate that temperature differences are  $\leq 0.4^{\circ}\text{C}$ . The out-flowing gas also flows through a Teflon FEP sample line and is directed into a temperature controlled mobile laboratory, which houses the analytical instruments and data acquisition system. Here, the sample is analyzed continuously for content of the gas of interest. A vent line is fitted to the exiting sample line to prevent pressurization and was periodically bubble tested to check for under pressurization and/or leaks in the enclosed system. Sample lines do not exceed 10 meters.

### Flux Calculations

The following mass balance equation may be used for the dynamic flow-through chamber system and applied to any target gaseous substance of known concentration:

$$\frac{dC}{dt} = \left( \frac{q[C_{air}]}{V} + \frac{JA}{V} \right) - \left( C \left( \frac{LA_w}{V} + \frac{q}{V} \right) \right) - R \quad (1)$$

|       |           |                                                                                                                                 |
|-------|-----------|---------------------------------------------------------------------------------------------------------------------------------|
| where | C         | concentration of gas inside the chamber (ppbV)                                                                                  |
|       | $C_{air}$ | concentration of gas in carrier air (ppbV)                                                                                      |
|       | q         | flow rate of compressed air through the chamber (lpm)                                                                           |
|       | V         | volume of the chamber (L)                                                                                                       |
|       | A         | emission surface area covered by chamber (m <sup>2</sup> )                                                                      |
|       | $A_w$     | inner surface area of the chamber of inner and upper wall surfaces (m <sup>2</sup> )                                            |
|       | L         | total loss of gas in the chamber per unit area (m min <sup>-1</sup> ) due to reaction with inner and upper walls of the chamber |
|       | h         | internal height of the chamber (cm)                                                                                             |
|       | J         | emission flux per unit area ( $\mu\text{g} [\text{gas}] \text{m}^{-2} \text{s}^{-1}$ )                                          |
|       | R         | gas phase reactions inside the chamber                                                                                          |

Since zero-grade air is used as the carrier gas,  $C_{air}$  is equal to zero and gas phase reactions, R, are also assumed to be zero. Since the air inside the chamber is assumed to be well mixed by

the impeller stirrer,  $C$  is assumed to be constant within the chamber. At steady-state conditions, the change of concentration with respect to time  $\left(\frac{dC}{dt}\right)$  is expected to be zero. Therefore equation (1) can be simplified as:

$$\frac{J}{h} = C_{eq} \left( \frac{LA_w}{V} + \frac{q}{V} \right) \quad (2)$$

The loss term,  $L$ , is determined experimentally while equilibrium-state gas concentration ( $C_{eq}$ ), flow rate ( $q$ ) and chamber dimensions ( $V$  and  $h$ ) are all measured. Kaplan *et al.* (1988) has devised a method for calculating loss term by calculating the slope of the plot of  $-\ln\left[\frac{C_{eq}-C(t)}{C_{eq}-C_o}\right]$  versus time ( $t$ ). For this experiment,  $C_o$  is the initial equilibrium state gaseous concentration measured by the chamber system at a constant flow rate (lpm).  $C_{eq}$  is the measured gaseous concentration at a second equilibrium state at an increased or reduced flow rate (lpm) into the chamber system.  $C(t)$  depicts the gaseous concentration at any time,  $t$ , during the transition between the first and second equilibrium states.  $L$  is determined by:

$$L = \left( slope - \frac{q}{V} \right) \left( \frac{V}{A_w} \right) \quad (3)$$

### Dynamic Flow-Through Chamber for Measuring Trace Gas Uptake by Plants

For measuring uptake of gaseous species by plants, and for conducting exposure experiments, it is important to characterize the conditions very near the plant surface under study; thus, assuring well-mixed conditions for such experiments becomes very important. Claiborn and Aneja (1993) constructed a chamber with a 1:1 diameter to height ratio, which is ideal for well-mixed conditions (Uhl and Gray, 1966). The chamber is constructed of a Teflon-coated strap iron frame lined internally with a 5 mil thick Teflon film to allow for maximum light, and even light and temperature distribution. Mixing is provided by a Teflon-coated impeller mounted at the top of the frame, and aided by 3 Teflon-coated baffles. The entire system operates under slight negative pressure, and it is important to assure that there are no leaks into the system, to allow for proper determination of the air flow rate through the system and the initial concentration of the trace gas of interest. The air flow rate through the chamber provides one to two chamber exchange rates per minute. Sample ports are located on the inlet and outlet Teflon pipes. Separate sample manifolds are provided for  $CO_2$ /water vapour and the trace gas of interest. Air samples from the chamber inlet and outlet are alternated automatically to the analyzers so that concentration differences across the chamber are determined using the same analyzer.

In order to determine trace gas uptake, wall losses to the empty chamber surfaces must first be determined. The fraction of the trace gas introduced into the chamber that is lost to the chamber walls during the chamber loss experiment (CL) is determined:

$$CL = \frac{C_{A_o,empty} - C_{A,empty}}{C_{A_o,empty}} \quad (4)$$

where  $C_A$  and  $C_{A_o}$  are the outlet and inlet concentrations, respectively, of trace gas species A, and the subscript *empty* indicates the concentrations measured for the empty chamber experiment.

Total losses (i.e., to both plant surfaces and chamber surfaces) are then measured, and the fractional loss (TL) of the trace gas entering the chamber is similarly determined:

$$TL = \frac{C_{A_o,exp} - C_{A,exp}}{C_{A_o,exp}} \quad (5)$$

where  $C_A$  and  $C_{A_o}$  are, again, the outlet and inlet concentrations, respectively, of trace gas species A, and the subscript *exp* indicates the concentrations measured for the exposure chamber experiment.

### Treatment of Wall Losses

For trace gases that are not very reactive, it is sufficient to subtract the wall losses from the empty chamber experiment from the total trace gas losses from the plant uptake experiments in order to determine the losses to plant surfaces, alone. In other words,

$$BL = TL - CL \quad (6)$$

where BL is the fractional loss of the trace gas to plant biomass surfaces, alone. For very reactive and/or water-soluble species like hydrogen peroxide or nitric acid, however, a more rigorous method of correcting for wall losses must be employed (Claiborn and Aneja, 1993). By treating both wall losses and losses to plant surfaces as two parallel reactions, the fractional loss to the plant biomass surfaces, BL, is calculated from TL and CL,

$$BL = \frac{TL - CL}{1 - CL} \quad (7)$$

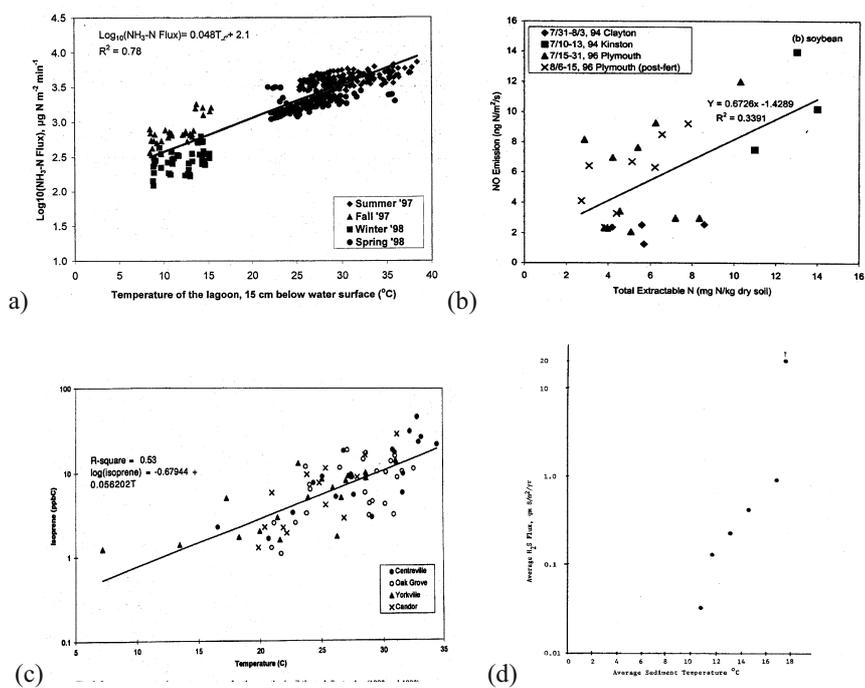
From this equation, it is evident that for species for which the chamber losses are very low, it is acceptable to simply subtract the fractional loss to the walls (CL) from the fractional loss during the exposure chamber (TL).

Finally, fluxes to plant surfaces ( $Q_A$ ) are calculated from the fractional loss to the plant surfaces (BL), the chamber air flow rate (F), the inlet trace gas concentration, and the plant surface area ( $A_L$ ):

$$Q_A = \frac{(BL)(F)C_{A_o,exp}}{A_L} \quad (8)$$

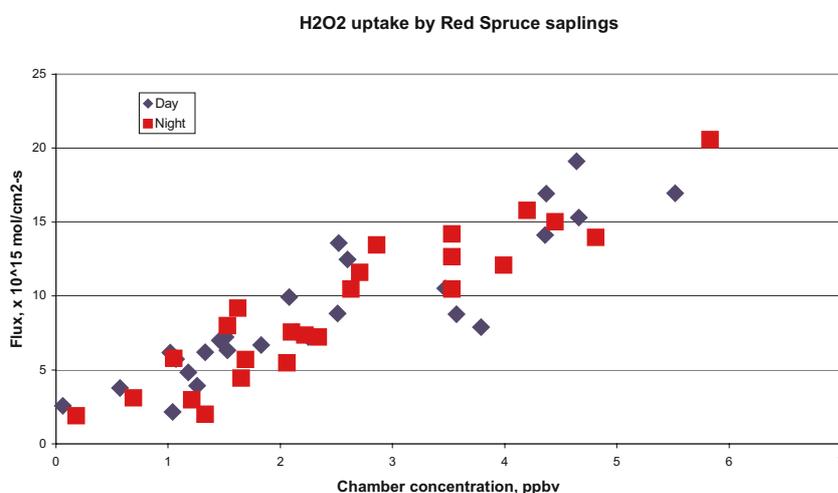
Results

The graphs in **Figure 2** (a,b,c,d) provide results from some field studies undertaken to measure fluxes of selected S, N, and C compounds. **Figure 2a** (Aneja *et al.*, 2001c) reports the log of hourly averaged ammonia-nitrogen flux from a swine waste treatment lagoon plotted against lagoon aqueous phase surface temperature during four different seasonal measurements. The graph shows an observed exponential ( $r^2 = 0.78$ ) relationship between  $\text{NH}_3$  and lagoon water temperature measured over the year. **Figure 2b** demonstrates the effect of soil temperature on NO from an agricultural (soybean) crop soil at four different sites. **Figure 2c** illustrates the temperature dependence of average  $\text{H}_2\text{S}$  emission fluxes from a salt marsh. The emission rate appears to increase semi-logarithmically with increasing temperature within a temperature range of  $\sim 0^\circ\text{C}$  to  $\sim 40^\circ\text{C}$ . Finally, **Figure 2d** represents isoprene (hydrocarbon) concentration plotted against temperature during warm months (April through September). Please note that concentrations (ppbV), which are treated as a surrogate for emission (since the concentration measurements are in close proximity to the source), are reported rather than flux calculations. The graph depicts the linear relationship between the logarithm of isoprene concentration and temperature using data from four sites.



**Figure 2** (a,b,c,d). Emissions of  $\text{NH}_3$  (Aneja *et al.*, 2000), NO (Aneja *et al.*, 2001c), Isoprene (Hagerman *et al.*, 1997), and  $\text{H}_2\text{S}$  (Hill *et al.*, 1978), respectively, versus Temperature at various locations.

The well-mixed chamber was used to measure uptake of gaseous hydrogen peroxide by spruce saplings (coniferous species). Hydrogen peroxide is a highly reactive and water-soluble atmospheric oxidant, for which wall losses are very significant (10-35% for 1-2 air exchanges per minute) and highly variable (standard deviation of 50% for daytime experiments) (Claiborn, 1991). A linear relationship between hydrogen peroxide flux and chamber concentration was apparent for the red spruce saplings (**Figure 3**). Note that there is no significant difference between daytime and night time fluxes. Average deposition velocities were calculated for these experiments, and ranged from 0.08 to 0.12 cm/s, and 0.08 – 0.12 cm/s for daytime and night time values, respectively. In contrast, similar uptake experiments conducted on bean plants (broad leaf plants) resulted in deposition velocities ranging from 0.8 to 1.4 and 0.5 to 0.6 for days and nights, respectively (Claiborn, 1991).



**Figure 3.** Fluxes of gaseous H<sub>2</sub>O<sub>2</sub> to needles of red spruce saplings as measured in well-mixed chamber experiments. Diamonds denote daytime fluxes and squares denote night time fluxes (Claiborn, 1991).

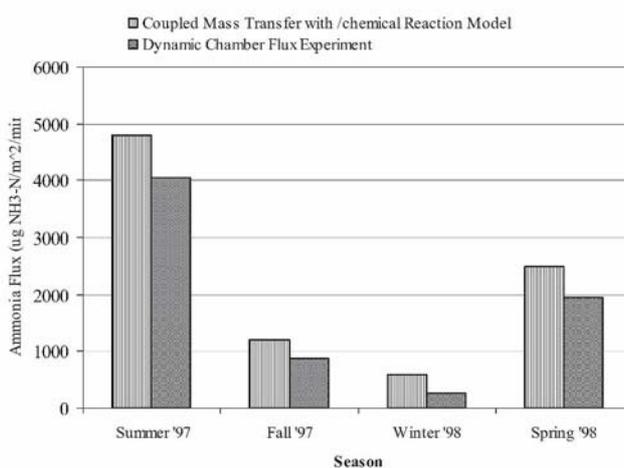
### Data Comparisons

As with any type of experimental procedure, it is desirable to compare data acquired in field studies with controlled laboratory studies and/or related models. Various comparisons with models, as well as other measurement techniques, have been made with data collected via the dynamic flow-through chamber system. Some results are presented in the following discussion.

For model comparisons with the dynamic flow-through chamber system, Aneja *et al.*, (2001d) developed a mass transport model based on the quiescent thin film concept (Danckwerts,

1970), which takes into account molecular diffusion and chemical reactions. **Figure 4** shows seasonal variation comparison of ammonia emissions between modelling results and dynamic chamber system experiments for ammonia emissions from a swine waste treatment lagoon from a field study conducted by Aneja *et al.* (2000). The coupled mass transfer model simulations corroborated experimental results utilizing the dynamic chamber technique and validated the application to the flux equation. Also, **Figure 5** shows how closely the recently developed WATER9 model, based on a set of air emission models that are documented in Air Emissions Models for Waste and Wastewater, U.S. Environmental Protection Agency, (U.S. EPA, 1994), compare with the same set of ammonia emissions data as discussed with the mass transport model previously.

Tabachow *et al.* (2002) conducted and compared the results of nitric oxide (NO) emissions measurements for both *in situ* field and laboratory experiments from unamended and municipal wastewater treatment plant biosolids-amended soil. Based on matching soil temperatures (within 5°C) and water filled pore space (WFPS) ( $\pm 5\%$ ), the ratio of volumetric soil water to total porosity of the soil, five of six scenarios showed no statistically significant difference in the NO flux measurements from the laboratory versus the field studies.



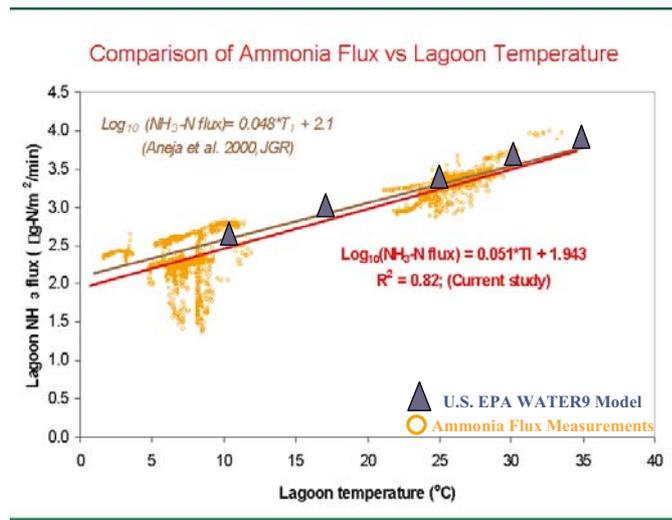
**Figure 4.** Seasonal variation comparison of ammonia emissions between modelling results and dynamic chamber system experiments.

Nitric oxide emissions from soils on a soybean field, measured by the dynamic chamber system (Li *et al.*, 1999), were compared in **Figure 6** with NO fluxes calculated at a 5 meter height utilizing the eddy-correlation method (Gao *et al.*, 1996). In spite of differences in flux magnitudes (note the different scales used), the two show qualitatively similar variations and structure with time. The values of NO soil emissions are greater than the NO fluxes at 5 m, which implies that

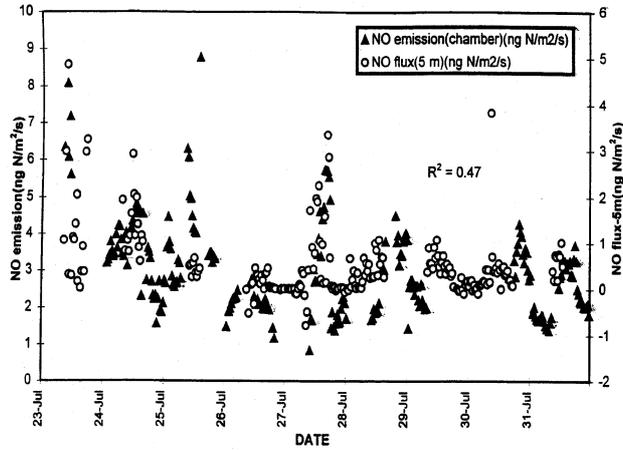
some of the NO might have been converted to nitrogen dioxide (NO<sub>2</sub>) through reactions with ozone and peroxy radicals by the time it reaches the 5-m height level from the source.

In a coordinated research effort (Project NOVA), NO emissions were measured from fine sandy loam soil in a corn field using two different (dynamic and static) chamber techniques. One group from North Carolina State University used the dynamic chamber method while a group from NASA Langley Research Center used a closed box flux technique (static chamber), in which NO fluxes were calculated using the mixing ratio of NO (ppbv) versus time. (Anderson and Levine, 1987). **Figure 7** depicts a difference plot of the composite averaged fluxes calculated by the dynamic chamber technique and the static chamber technique. Upon, statistical analysis, it was shown that there was no statistically significant difference between NO flux as measured using the two different chamber methods.

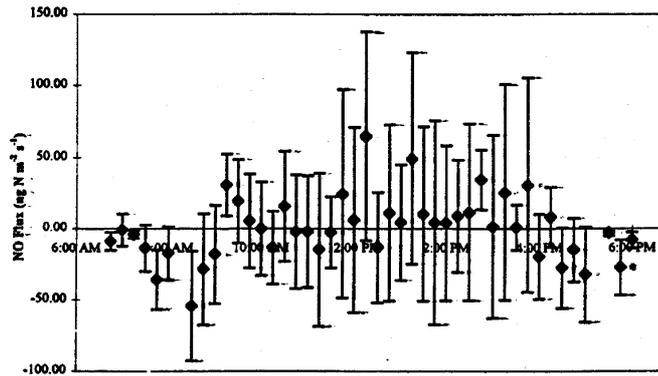
Chamber experiments on uptake by plants provide useful information for the determination of deposition velocities, however, the deposition velocities over forest canopies will be different to those calculated in the chamber experiments. Deposition velocities take into account not only the resistance to mass transfer due to the plant itself, but also the resistance due to the forest canopy structure, and the turbulence over the canopy.



**Figure 5.** Ammonia flux versus lagoon temperature comparison between WATER9 modelling results and dynamic chamber experimental calculated results.



**Figure 6.** Inter-comparison of NO fluxes at 5 meter height using eddy-correlation technique with NO soil emissions using dynamic chamber technique.



**Figure 7.** Difference of NO flux between two chamber techniques (dynamic chamber flux – static chamber flux) versus time of day. Vertical lines indicate one standard deviation of the NO flux measurements made from both chamber techniques.

**Conclusions**

The dynamic flow-through chamber system has been successfully developed in response to a need to measure emissions of nitrogen, sulphur, and carbon compounds for a variety of field applications. Moreover, similar chamber systems have also been deployed to measure uptake of nitrogen, sulphur, ozone, and hydrogen peroxide gases by crops and vegetation to examine

atmospheric-biospheric interactions. Experimental results have been effectively validated by independent flux models.

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