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I.E. Galbally¹, C.R. Roy², C.M. Elsworth¹ and H.A.H. Rabich¹

ABSTRACT

A chamber technique for evaluating fluxes of NO and NO_x (NO + NO₂) over soil/plant surfaces is described. A mathematical model involving a constant exhalation rate of NO from the soil/plant surface coupled with a competing concentration dependent uptake process is formulated. This model provides a good fit to the data obtained from chamber measurements and allows the quantitative determination of both net and gross NO and NO_x fluxes over the plant/soil surfaces examined. Measurements of these fluxes and supporting data from a grazed pasture at the Agricultural Research Center, Rutherglen, Victoria during 2 weeks in April 1978 are presented on a microfiche.

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1. INTRODUCTION

The loss of fixed nitrogen from the soil by gaseous exchange with the atmosphere affects the productivity of agricultural and natural ecosystems (Hauck, 1981). Nitrogen oxides released from the soil make a significant contribution to the global concentrations of these gases in the atmosphere. Nitric oxide (NO) and nitrogen dioxide (NO₂) play an important role in the chemistry of the lower atmosphere by modulating the oxidation of many trace gases (Ehhalt, 1981). Nitrous oxide (N₂O) is a precursor for ozone destruction in the stratosphere.

There is a published set of measurements of NO from soil (Galbally and Roy, 1978). These measurements were made using a chamber technique that has been specifically developed for measuring gas exchange at the earth's surface (Galbally and Roy, 1978, 1980).

In this technical report we describe the technique in detail and present data from a new field study of NO and NO_x (\equiv NO + NO₂) exchange over a grazed pasture.

2. SITE DESCRIPTION

The measurements presented in this report were conducted at the Victorian Department of Agriculture Research Station, 6 km east of the Rutherglen township (36°S, 146°E).

Measurements were made at 13 sites located within an area of 200 m², a sub-section of "Paddock 8", a 9 ha field. The field was maintained as long-term annual pasture consisting of subterranean clover (*Trifolium subterraneum* L.), Wimmera rye grass (*Lolium rigidum* Gaud.), and barley grass (*Hordeum leporinum* Link.) and was grazed with approximately 7 sheep ha⁻¹ at the time of the experiment. The field had received superphosphate fertilizer approximately one year prior to these measurements. The soil is an acidic greyish brown loam underlain by yellow clay. Analyses of the soil composition from the 13 sites using standard techniques (Frenay and Wetselaar, 1967) are presented in Table 1.

Table 1: Soil analyses for the various measurement sites. The composition data are in mass mixing ratios relative to dry soil.

Site	Depth Sampled cm	Moisture %	pH	NH ₄ ⁺ ppm	NO ₃ ⁻ ppm	NO ₂ ⁻ ppm	Total N % N
1	0-5	11.3	5.9	6.9	6.6	0.0	0.22
2	"	12.9	4.8	26.4	60.1	2.8	0.19
3	"	16.7	5.6	6.9	8.8	0.0	0.19
4	"	12.5	5.4	2.6	1.5	0.0	0.16
5	"	12.0	6.1	6.7	13.5	1.3	0.17
6	"	10.0	6.0	6.6	5.6	0.0	0.19
7	"	14.8	6.1	7.4	10.4	0.3	0.18
8	"	14.2	6.9	8.4	6.1	0.4	0.16
9	"	13.3	6.6	27.0	19.1	0.6	0.93
10	"	16.2	6.4	5.8	10.5	1.0	0.19
11	"	9.5	6.0	6.0	5.3	0.8	0.18
12	"	9.1	6.3	4.2	5.3	1.0	0.17
13	0-10	-	-	7.6	43.1	-	-
13	10-20	-	-	14.7	22.0	-	-
13	20-30	-	-	2.0	11.4	-	-
13	30-40	-	-	0.7	6.1	-	-
13	40-50	-	-	0.0	3.9	-	-

3. INSTRUMENTATION AND CALIBRATION

Three chambers were used for field measurements of NO and NO_x exchange. These chambers are five-sided with the open face directed towards the soil/grass surface.

One chamber, "L", illustrated in Figure 1, was made of clear perspex, with internal dimensions 0.8 m x 0.8 m x 0.75 m (width x depth x height). The chamber was internally lined with Mylar polyester film (Du Pont) chosen to prevent gas uptake on the walls (see below). The chamber was stirred by a 0.2 m diameter stainless steel fan driven by an 80W external electric motor. Turbulent mixing in the box has been demonstrated to approximate that in the atmosphere under light to moderate wind speeds (Galbally & Roy, 1980). Horizontal wind speeds measured in the box 0.1 m above the base were in the range 0.5 to 1.2 m s⁻¹. Wind direction indicators for both horizontal and vertical flow suggested a toroidal pattern of airflow above the base.

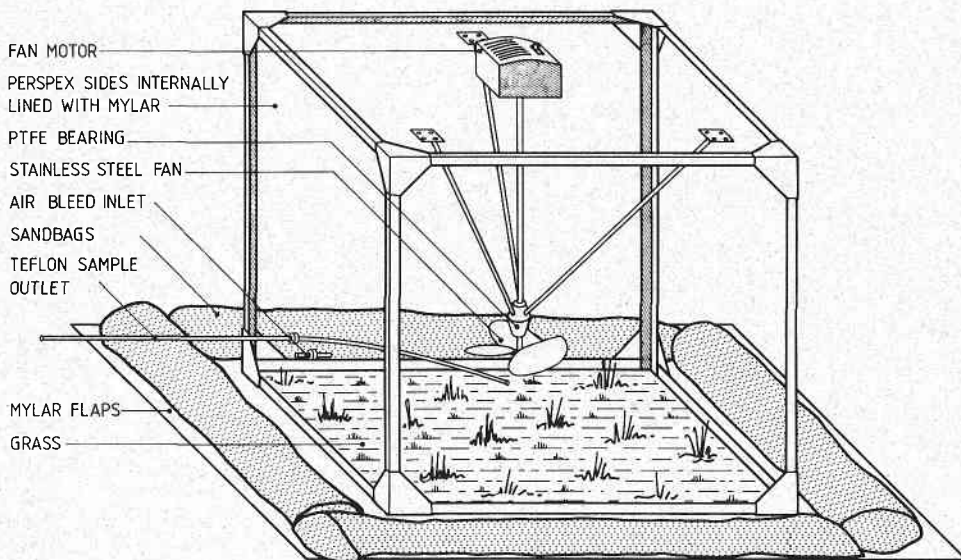


Figure 1. The chamber "L".

Two chambers, "M" and "S", were made of plywood with internal dimensions of 0.76 m x 0.61 m x 0.33 m, and 0.60 m x 0.46 m x 0.23 m (width x depth x height), respectively. These chambers also were lined internally with Mylar polyester film and were stirred by tube axial fans (0.12 m diameter) that had flow capacities of $0.05 \text{ m}^3 \text{ s}^{-1}$. The turbulent mixing in these boxes is assumed to be similar to that for chamber "L".

These chambers were fitted with external Mylar flaps 0.3 m wide attached at the bottom of the vertical walls and surrounding the box (see Figure 1). The flaps were weighed down with sandbags preventing the direct flow of air between the atmosphere and the chamber (via the base of the box) thus sealing the box to the soil/plant surface. A small vent hole 2 mm diameter (in each box) allowed ambient air to enter the box thus equalizing the air pressure between the box and the atmosphere and replacing air withdrawn in the sample line. A pressure deficit in the box can cause an artificially large gaseous release rate (Denmead, 1979). We established experimentally that such an effect did not occur with our measurement technique (Galbally and Roy, 1978). Differential pressure measurements made between the box and the atmosphere gave pressure deficits of $4 \pm 5 \text{ Pa}$ in the 0.75 m height box and $1 \pm 3 \text{ Pa}$ in the 0.33 m height box, in each case the sample being based on approximately 40 measurements made at 30 second intervals.

The chamber in use was connected to the gas analysis instrumentation by PTFE tubing 30 m length and 4.8 mm internal diameter. The gas sample flow rate varied from 1 to $2.7 \times 10^{-5} \text{ m}^3 \text{ s}^{-1}$ depending on the instruments used. Ambient measurements were made before and after the chamber measurements with the inlet at a height of approximately 0.8 m. During the periods when chamber measurements were not being made the sample inlet tube was shortened to 3.0 m length with the inlet at a height of 2.5 m above the soil surface.

Special measurements were conducted with mylar covered baseboards placed under the chambers. These measurements, conducted to detect any "artifact" NO or NO_x uptake or release by the chamber walls, are presented in part 5 of the accompanying tables and identified as "site MB". No substantial uptake or release was detected.

The nitrogen oxides measurements were made with a nitric oxide-ozone chemiluminescent nitric oxide monitor designed and built at

the CSIRO Division of Atmospheric Physics (now named the Division of Atmospheric Research). This instrument has a resolution of 0.05 ppbv of nitric oxide. An earlier version of the instrument was described by Galbally (1977). The instrument was calibrated over the range 1 to 150 ppbv by diluting a 10 ppmv NO in N₂ working standard with NO free air. The working standard had been previously calibrated against a 45 ppmv NO in N₂ Standard Reference Material from the National Bureau of Standards (Washington, USA). The instrument zero was obtained by sampling air that had been irradiated to produce ~700 ppbv O₃ within it. This air was passed through a stirred 9 x 10⁻³ m³ glass chamber at a flow rate of 1.0 x 10⁻⁵ m³ s⁻¹, thereby converting all NO to NO₂ because of the excess O₃ present.

NO_x measurements were made by passing the sample air through a molybdenum catalyst heated to 350°C prior to entering the NO monitor. This catalyst converts NO₂, alkyl nitrites and nitrates, peroxyacetylnitrate and HNO₃ to NO hence the NO_x measurements is the sum of the concentrations of these species within the sampled air.

The sensitivity of the NO monitor varied significantly during the course of these measurements. These variations were due, in part, to fluctuations in the mains voltage and the ambient temperature affecting the ozonizer output within the chemiluminescent detector. The fluctuations in instrument sensitivity occurred on a time scale of 6 to 12 hours. Fourteen daily calibrations gave an instrument sensitivity of 1.54 ± 0.24 ppb volt⁻¹, mean and standard deviation respectively. The chamber data were analysed using the particular calibration made during a set of measurements. The ambient data were analysed using the average calibration as there were several extended periods of ambient data, 1 to 2 days length, when no instrument calibration was performed.

Ozone measurements were made with a McMillan Electronic Corporation model 1100 ozone-ethylene chemiluminescent ozone monitor. This instrument was calibrated against a Dasibi model 1003-AH ultraviolet absorption ozone monitor. The calibration was made over the range 0-500 ppbv using a McMillan Electronic Corporation Model 1000 ozone generator as the ozone source.

Analysis for nitrous oxide, N₂O, was carried out using a Perkin Elmer F17 gas chromatograph fitted with a pulsed electron capture detector

maintained at 350°C. Air was continuously drawn from the sample inlet line at a flow rate of approximately $8.3 \times 10^{-7} \text{ m}^3 \text{ s}^{-1}$. This was passed through a small column containing ascarite and magnesium perchlorate for removal of carbon dioxide and water respectively. The air then passed through a sample loop of a gas switching valve connected to the gas chromatograph injector port. The 5 cm^3 loop of the gas sample valve was flushed with at least 75 cm^3 of sample prior to injection. Gas separation was achieved with $2.4 \text{ m} \times 3 \text{ mm}$ OD columns of Porapak Q and Porapak R with 95% argon/5% methane carrier gas at a flow rate of $4.2 \times 10^{-7} \text{ m}^3 \text{ s}^{-1}$ and an oven temperature of 60°C. The N_2O had a retention time of 4.8 min. Normally 5 or 6 measurements were made during the 30 to 50 minutes that the chamber was in place over the soil surface. A calibration was performed before and after each run. Gas standards were intercalibrated with standards prepared by R.A. Rasmussen of the Oregon Graduate Centre, Oregon, USA.

Chamber S with dimensions $0.60 \text{ m} \times 0.46 \text{ m} \times 0.23 \text{ m}$ was used exclusively for N_2O measurements.

4. METHOD AND THEORY

The following symbols (with dimensions as indicated) are used in this work.

- A area of chamber base, (L^2).
- A_1, A_2, A_3 constants determined in the numerical fit see equation (6).
- C concentration of NO , NO_2 or NO_x , (M L^{-3}).
- \bar{C} volume average concentration within the chamber, (M L^{-3}).
- C_a concentration outside the chamber, (M L^{-3}).
- C_e equilibrium concentration above the plant/soil surface, (M L^{-3}).
- C_s concentration in contact with the plant/soil surface within the chamber, (M L^{-3}).
- E gross exhalation rate through the soil surface for NO , NO_2 , or NO_x , ($\text{M L}^{-2} \text{T}^{-1}$).
- F net exchange at the soil/plant surface of NO , NO_2 , or NO_x , ($\text{M L}^{-2} \text{T}^{-1}$). ($F = E - U$).
- h height of chamber, (L).
- M_i molecular weight of a species, i. (M).
- r_c gas phase resistance for mass transfer between the well-mixed

- zone of the chamber and the underlying surface, ($L^{-1}T$).
- r_s soil and plant surface resistance to uptake of NO , NO_2 or NO_x , ($L^{-1}T$).
- t time from chamber being placed over surface, (T).
- U gross uptake rate at the soil/plant surface of NO , NO_2 or NO_x , ($M L^{-2}T^{-1}$).
- v volume rate of sampling of air from chamber, (L^3T^{-1}).
- ρ_a air density ($M L^{-3}$).
- ψ volumetric mixing ratio of NO , NO_2 or NO_x , dimensionless ($L^3 L^{-3}$).

Measurements of NO , NO_2 and NO_x are reported here in mixing ratio units (ppbv $\equiv 10^{-9}$ vol/vol). Where necessary they have been converted to concentration units using the following formula where M_a is the molecular weight of air

$$C = \rho_a \psi M_i / M_a .$$

The exchange of NO , NO_2 or NO_x between the atmosphere and the soil/plant surface is measured over a particular site by the following technique. The stirred five-sided chamber is placed with its open face to the surface on the site to be measured. The concentration of NO or NO_x within the chamber is monitored. The rate of change of NO (or NO_x) is used to determine the exchange of this species at the underlying surface. The monitoring continues for 10 to 20 minutes and then the chamber is removed from the site.

Our earlier study (Galbally and Roy, 1978) indicated that the same equilibrium concentration of NO was reached within the stirred chamber covering the site irrespective of whether the initial NO concentration was larger or smaller than the final (equilibrium) concentration and this is borne out by data shown in Figures 2a and 2b.

From this we infer that both release (exhalation from the soil) and uptake of NO occurred over the area of surface covered by the chamber. As a model of these processes we assume that the gross NO exhalation rate, E , does not change in the course of a measurement (10 to 20 minutes) and that the gross uptake rate is proportional to the concentration of NO in

contact with the surface. This NO uptake is regulated by a surface resistance to uptake, r_s , (Galbally, 1974) where the uptake equation is

$$U = r_s^{-1} C_s \quad (1)$$

(An alternative model based on the definition of an equilibrium concentration of NO for a particular site can be formulated. This will be discussed in Section 7).

The sample inlet via which air is withdrawn from the chamber, is located in the mixed zone in the vicinity of the fan. We assume in the chambers used here that this well mixed zone is sufficiently large so that to a good approximation the concentration in this zone is equal to the volume average concentration for the chamber. The net exchange at the surface and the concentration in contact with the surface are related to the volume average concentration and the gas phase resistance between the surface and the well mixed zone by the following equation

$$F = \{C_s(t) - \bar{C}(t)\} r_c^{-1} \quad (2)$$

(r_c has been measured for chamber "L", Galbally and Roy, 1980). Also the net flux from the surface is the difference between gross exhalation and uptake

$$F = E - r_s^{-1} C_s(t) \quad (3)$$

(It should be noted that at steady state when $F = 0$, the equilibrium concentration present C_e is, according to equation 3, equal to $r_s E$).

The mass balance of species within the chamber is

$$Ah \frac{d\bar{C}(t)}{dt} = AE + v(C_a - \bar{C}(t)) - A r_s^{-1} C_s(t) \quad (4)$$

i.e. rate of increase in species equals exhalation, plus change due to replacement of sample air, minus uptake at surface.

Combining (2), (3) and (4) to eliminate $C_s(t)$, which cannot be directly measured, gives

$$\frac{d\bar{C}(t)}{dt} = \frac{E}{hX} + \frac{vC_a}{Ah} - \frac{(vX + Ar_s^{-1})}{AhX} \bar{C}(t) \quad (5)$$

where $X = \{1 + r_c r_s^{-1}\}$.

This can be represented by the equation

$$\frac{d\bar{C}(t)}{dt} = Z_1 - Z_2 \bar{C}(t), \quad (5a)$$

where Z_1 and Z_2 represent the appropriate terms from equation (5). This equation has the solution

$$\bar{C}(t) = A_1 + A_2 e^{-A_3 t} \quad (6)$$

where

$$A_1 = \frac{AE + vC_a X}{vX + A r_s^{-1}} \quad (7)$$

A_1 approximately represents the equilibrium concentration C_e at which uptake and exhalation cancel and there is zero net soil/atmosphere flux of NO at the site being considered (provided v is very small).

$$A_3 = \frac{vX + A r_s^{-1}}{AhX} \quad (8)$$

A_3 is closely related to the reciprocal of the surface resistance, r_s^{-1} .

A_1 and A_3 are evaluated by fitting equation 6 to the experimental data. Rearranging (7) and (8) yields

$$r_s^{-1} = \frac{A_3 Ah - v}{\{A + r_c v - A_3 Ah r_c\}}. \quad (9)$$

Also

$$A_1 = \frac{AE + v C_a (1 + r_c r_s^{-1})}{v(1 + r_c r_s^{-1}) + A r_s^{-1}} \quad (10)$$

so

$$E = A_1 r_s^{-1} + \frac{V}{A} (1 + r_c r_s^{-1}) (A_1 - C_a) \quad (11)$$

Two chambers, L and M, were used for the NO/NO_x measurements.

The characteristics of the system were

$$v = 1 \text{ to } 2.7 \times 10^{-5} \text{ m}^3 \text{ s}^{-1}$$

$$r_c = 27 \pm 17 \text{ s m}^{-1} \text{ (Galbally and Roy, 1980)}$$

$$\text{Chamber L } A = 0.64 \text{ m}^2$$

$$h = 0.75 \text{ m}$$

$$\text{Chamber M } A = 0.46 \text{ m}^2$$

$$h = 0.33 \text{ m}$$

Hence

$$r_s^{-1} = \frac{0.48 A_3 - 2.7 \times 10^{-5}}{0.64 - 13.0 A_3} \quad \text{Chamber L,}$$

$$r_s^{-1} = \frac{0.15 A_3 - 2.7 \times 10^{-5}}{0.46 - 4.1 A_3} \quad \text{Chamber M,}$$

$$E = A_1 r_s^{-1} + 4.2 \times 10^{-5} (1 + 27 r_s^{-1}) (A_1 - C_a)$$

Chamber L,

and

$$E = A_1 r_s^{-1} + 5.9 \times 10^{-5} (1 + 27 r_s^{-1}) (A_1 - C_a)$$

Chamber M.

Thus the exhalation rate E and the surface resistance r_s can be derived from experimental data via A_1 and A_3 .

This model of gaseous exchange at a plant/soil surface described in equations (4) to (11) is for a single gas, i.e. NO or NO₂. In the situation where NO_x is measured this model is applicable provided that the NO_x concentration is made up primarily of either NO or NO₂ and the other gas is present in near zero concentration.

It is probable that NO and NO₂ have different exhalation and uptake rates. Therefore if NO_x is measured and both gases are present then the appropriate form of (6) would include two different exponential decay terms. The numerical analysis scheme presented here is not designed for this possibility therefore we limit our analysis to data from three appropriate categories. These are:

1. Measurements of NO exhalation and of NO uptake when NO is injected into the chamber;
2. Measurements of NO_x exhalation for comparison with similar NO exhalation measurements made in set 1; and
3. Measurements of NO_x uptake after NO and excess O₃ have been introduced into the chamber. The excess O₃ present ensures that all NO_x is present as NO₂ because of the fast reaction

$$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2.$$

In category 1 only one gas, NO, is considered. As NO is measured directly and NO₂ → NO conversion is slow, the single gas analysis is valid. In category 2, the measurements are made to test if NO_x exhalation is equivalent to NO exhalation and so our hypothesis (in a statistical sense) is either that NO_x = NO or the contrary for this set. In category 3 the NO_x is (or is thought to be) entirely NO₂. Therefore in all three categories an equation of the form of (6) is appropriate.

For the data evaluation from category 3 measurements, we note that the O₃ concentration in the chamber decreases with time due to O₃ uptake at the underlying surface. Meanwhile NO exhalation into the chamber continues. Initially this NO is converted to NO₂ by O₃ but later with the disappearance of O₃, NO appears in the chamber. For this reason the values of C_e and E derived from fitting the data are inappropriate to either NO₂ or NO but the value of r_s⁻¹ (which is primarily determined by the initial value of hC̄(t)⁻¹dC̄(t)/dt when all the NO_x is NO₂) is reliably

determined. Consequently values of C_e and E are not included in the following tables for data from category 3.

A fourth, supplementary category of data are presented in the following tables. These consist of occasional measurements of the other constituent (either NO_x or NO) made during the period of a set of main measurements of NO or NO_x respectively. These data are included because of their potential value for comparative studies but are not analysed in this paper.

5. ANALYSIS OF DATA

Each set of measurements consists of N data points $t(i)$, $C(i)$, $i=1, \dots, N$ where N lies between 5 and 25. The time t was measured in minutes and the concentration C in ppbv NO or NO_x content.

According to the starting conditions we have two types of curves: exhalation dominant (E) and uptake dominant (U) curves. The C -values of the E -curves increase with t , those of the U -curves decrease.

To evaluate a data set equation (6) was used in a modified form as a set of N equations

$$C_f(i) = A_1 + A_2 e^{-A_3 t(i)} \quad i=1, \dots, N \quad (12)$$

where A_1 , A_2 , A_3 are the unknown constants, the $C_f(i)$ are 'fitted' values which should come as close as possible to the measured values $C(i)$. The physical meaning of A_1 and A_3 are given in equations (7) and (8), A_2 is an integration constant (equivalent to the difference of the initial minus final concentrations).

An appropriate least squares fit which minimized the function S

$$S = \sum_{i=1}^N (C(i) - C_f(i))^2 \quad (13)$$

was calculated yielding a set of coefficients A_1 , A_2 , A_3 . We cut the iterations short when the coefficients were within 0.5% of the ideal minimum of (13)

The final triplet called (A_1, A_2, A_3) was taken as the 'best' solution of the set of equations

$$C(i) = A_1 + A_2 e^{-A_3 t(i)} + H(i) \quad i=1, \dots, N \quad (14)$$

with positive A_2 for U-curves and negative A_2 for E-curves. The $H(i)$ constituted the errors of the fit.

The errors $H(i)$ were real in the sense that even by reducing the inaccuracies of A_j to .01% (a 50 times more stringent value) each of the errors $H(i)$ $i=1, \dots, N$, varied by less than 6% and S improved slightly. This result is important as the following discussion indicates.

The theory of the curve fitting assumes that the $H(i)$ are randomly distributed. This does not hold in all of our calculations. There appears to be significant autocorrelation between the successive values of the error $H(i)$. It can be seen from the data that the differences $H(i)$ in all sets change between positive and negative periods.

We defined 'periods' as being when $H(i)$ was either positive or negative exclusively throughout the time interval in more than two thirds of the sets of measurements.

Using these criterion we find:

(a) for U-curves

NO, positive for $t = 4$ to 10 min negative for $t = 13$ to 17 min
 NO_x, positive for $t = 3, 5, 8$ to 10 min negative for $t = 17, 18$ min; and

(b) for E-curves,

NO, negative for $t = 2, 3, 4$ min positive for $t = 11, 12$ min
 NO_x, negative for $t = 2$ to 5 min positive for $t = 8$ to 14 min

The values of the error term H in these 'periods' did vary: in some sets it was 20% of the value C and in others it is within the accuracy of the measurements (a few percent). The effect was more pronounced in the E curves. We have found no explanation for this.

No formula can be given which expresses the uncertainties of the A_j (and the propagated uncertainties in the values of the physical variables C_e , E and r_s) as functions of the errors of the measured values $C(t)$. However the following statement about the inverse function can be made.

If we consider equation (6) and allow A_1 , A_2 , and A_3 to vary by small increments, in general denoted by δA_j , then

$$\delta \bar{C}(t) = a_1 \delta A_1 + a_2 \delta A_2 + a_3 \delta A_3 \quad (15)$$

By definition, and equation (6) we have

$$a_1 = \frac{\partial \bar{C}(t)}{\partial A_1} = 1$$

$$a_2 = \frac{\partial \bar{C}(t)}{\partial A_2} = e^{-A_3 t}$$

$$a_3 = \frac{\partial \bar{C}(t)}{\partial A_3} = -A_2 t e^{-A_3 t}$$

Typical values of a_1 , a_2 and a_3 are presented in Table 2. From this table it can be seen that variations in $\bar{C}(t)$ where t is very large influence only A_1 . Similarly variations in $\bar{C}(t=0)$ affect only A_1 and A_2 . Variations in $\bar{C}(t)$ for the middle range ($t = 2$ to 8 min) predominately affect A_3 .

Consequently data sets which do not extend to large values of t ($t \sim 20$ min) have limited value in determining A_1 .

The wave pattern that affects $\bar{C}(t)$ during $t = 4$ to 10 min will affect the prediction of A_3 . A systematic 3% bias in measured minus fitted $\bar{C}(t)$ in this range would lead to a more than 20% bias in the value of r_s and subsequently of E .

The RMS residuals of the final fits for each set grouped according to site are compared with the range of NO_x concentrations observed in Table 3. In the worst fit the RMS residual is 14% of the range of NO fitted and typically this RMS residual is 5% of the range analysed. This implies a high degree of correlation between the measured and fitted data as is shown in Figures 2a and 2b.

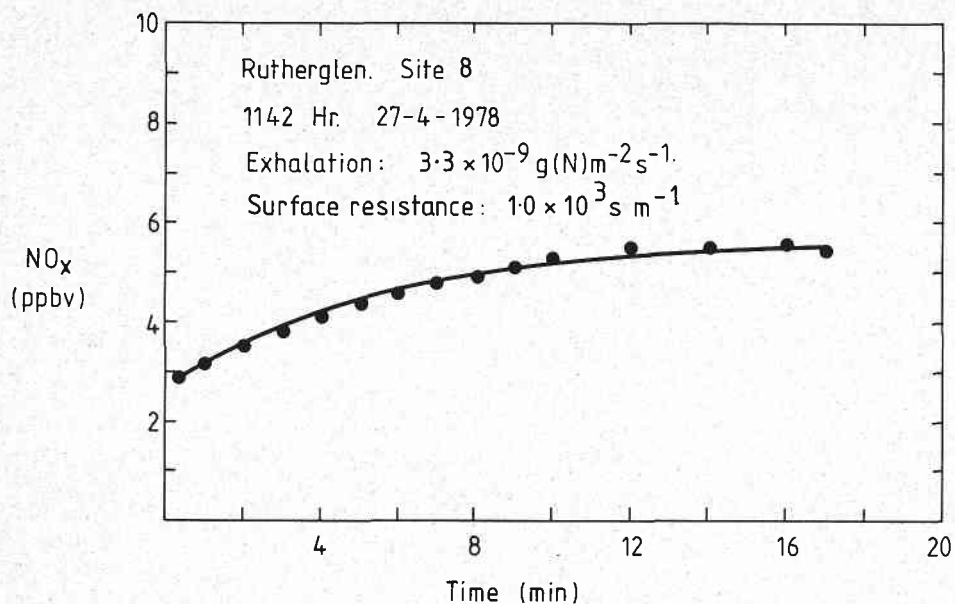


Figure 2(a). Measurement of NO_x within the chamber (solid circles) and the fitted curve for net release from the surface using the theory presented.

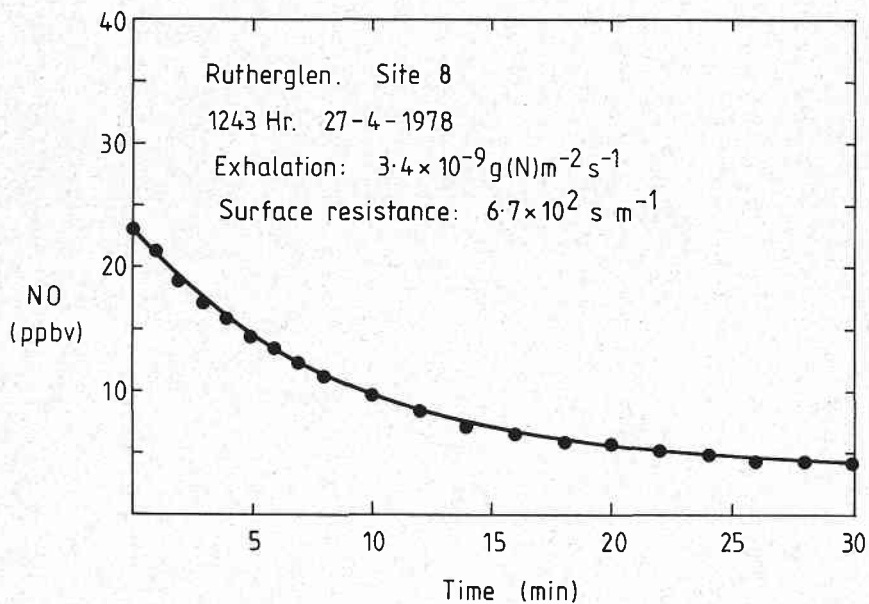


Figure 2(b). Measurement of NO within the chamber (solid circles) and the fitted curve for net uptake by the surface using the theory presented.

TABLE 3: Comparison of the range of NO or NO_x in data sets with the residual RMS of the measured minus fitted data points for those data sets (as stated earlier a set consists of N data points C(i), t(i) from which a value of each of the variables E, C_e and r_s is evaluated).

Site	No. of Data Sets	Maximum Range of NO or NO _x (highest-lowest) in any set ppbv	Residual RMS of measured-fitted data for individual sets		
			smallest	median ppbv	largest
1	10	5	0.2	0.5	0.8
2	9	180	2	2	2
3	7	35	0.5	0.7	0.8
4	5	13	0.2	0.5	0.5
5	9	19	0.2	0.5	0.7
6	7	10	0.2	0.5	0.7
7	7	4	0.2	0.3	0.5
8	6	7	0.2	0.3	0.5
9	10	11	0.3	0.5	0.7
10	7	7	0.3	0.5	0.5
11	9	6	0.3	0.5	0.5
12	5	9	0.5	0.5	0.7
13	5	12	0.5	0.5	0.7

The error analysis shows that an individual value of C_e will be determined to approximately $\pm 5\%$. The values of r_s and E will have greater errors depending on the uncertainty in determining A_3 . As discussed earlier A_3 is highly dependent on the values of the difference, measured minus fitted $\bar{C}(t)$, during the period 2 to 8 min. If this difference fluctuates randomly by $\pm 3\%$ (standard deviation) then a $\pm 20\%$ random uncertainty in values of r_s and E , would follow.

The coefficients of physical interest:

Equilibrium concentration C_e (ppbv)

Exhalation rate E ($\text{g(N)} \text{ m}^{-2} \text{ s}^{-1}$)

Surface resistance r_s (s m^{-1})

are calculated from equations (9) and (11) using the values of A_1 and A_3 obtained. The only unknown quantity in equation (11) is C_a . As a first approximation C_a is replaced by $C(1)$ for E-curves and zero for U-curves.

Despite the accuracy of the fit of A_1, A_2, A_3 to the measured values of a set, the resulting r_s, C_e , and E vary considerably from set to set.

6. DATA TABLES

The following data and graphical representations are presented on the microfiche enclosed with this report.

1. Tables, analyses and graphs of chamber measurements of NO and NO_x .
2. A summary of the evaluations of the data in part 1.
3. A table of the N_2O fluxes measured simultaneously with NO and NO_x fluxes (but not as frequently) and analysed according to the method described in Roy (1979).
4. Ambient atmospheric concentrations of NO, NO_x and O_3 for the period of the field measurements.
5. Artifacts from the chamber measurements found using mylar covering the soil surface.

The following note is applicable to certain of the analyses and tables on the microfiche. Where appropriate the note is mentioned on the microfiche.

Note 1. No analyses of C_e and E are presented as both NO and NO_x are present in the later part of the data.

7. DISCUSSION

The key question at this point is: Does the model fit the data? A typical pair of plots of the measurements and the fitted curves are shown in Figure 2(a and b). The RMS residuals of measured-fitted data are 5% and 11% respectively of the magnitude of the range of concentrations analysed. These and the earlier analyses (Table 3) indicates a good fit to the data.

In previous work (Galbally & Roy, 1978) the flux ($\cong E$) was evaluated using data from the first few minutes after the chamber was placed over the site. In this case the flux, $h\Delta\bar{C}/\Delta t$ is a readily understood physical quantity. The value of r_s can be determined in the same way from data immediately following the injection of NO. (This technique is used to determine r_s for ozone, see Galbally & Roy, 1980).

To illustrate the validity of our full analysis we have compared $h\Delta\bar{C}/\Delta t$ evaluated over the first four minutes of each run with the values of E and r_s from the full analysis using equation (16).

$$h\Delta\bar{C}/\Delta t = E - r_s^{-1}\bar{C} \quad (16)$$

We find (as would be expected) that the equation fits the first four minutes data to within the previously discussed error limits.

It appears that the model presented here is a satisfactory description of this data.

The other outstanding question is whether another model could be used to achieve a similar interpretation of the data. An alternate hypothesis is that there is an equilibrium concentration of NO, C_e , always present at the soil/plant interface with the atmosphere. In this case the flux into the chamber would be

$$F = (C_e - \bar{C}(t)) r_c^{-1} \quad (17)$$

where r_c can be measured and the only unknown is C_e .

The variation of concentration in the chamber would follow the equation

$$C(t) = A_1 + A_2 e^{-A_3 t}$$

where (neglecting some minor corrections)

$$A_1 = C_e \quad (18)$$

and
$$A_3 = \{r_c h\}^{-1} . \quad (19)$$

The difference between this model and that used in the earlier analysis, section 4, is that the previous model places no constraint on the concentration of the gas at the surface. Only the fluxes are constrained in the earlier model and, as shown previously, it accurately represents the data.

We can test the equilibrium concentration model by evaluating the gas phase resistance term from the fitted data using the fitting technique of section 5 and equation (19). The value of r_c obtained can then be compared with the same gas phase resistance term measured independently for the same chamber and a grass surface of similar roughness (Galbally and Roy, 1980). We would expect these two evaluations of r_c to be identical within the limits of experimental error if the equilibrium concentration model is correct.

In fact for chamber L, Galbally and Roy (1980) obtained

$$r_c = 10 \text{ to } 45 \text{ m}^{-1} \text{ s}$$

(5 measurements, O_3 gas, assumption of perfect destruction at surface);

whereas the equilibrium concentration model gives

$$r_c = 900 \text{ to } 2000 \text{ m}^{-1} \text{ s}$$

(17 measurements, NO gas, assumption of equilibrium at surface).

It is inconceivable that the gas phase resistance of the box should be 50 to 100 times larger in one case than the other. Moreover the values of r_c obtained by Galbally and Roy (1980) are consistent with measurements of airflow in the chambers and these values of r_c lead to ozone flux measurements that have been verified by other techniques.

It appears that the value of r_c derived via the equilibrium concentration model is wrong, by a factor of 50 to 100, and hence the model is grossly inconsistent with the available data. Essentially the earth's surface does not behave like a freely evaporating surface of NO.

The essential difference between the equilibrium model and the exhalation/uptake model preferred here is that the latter includes prescription of physical limits to the rate of exhalation and uptake of NO at the underlying surface, but makes no assumption about the

concentrations involved. Irrespective of the behaviour of the atmosphere the net exhalation rate cannot exceed E and the uptake is always limited by r_s^{-1} which is attributed to the soil/plant surface.

We believe that we have developed a reliable method for measuring NO and NO_2 exchange at the earth's surface. A conceptual framework for interpreting these measurements has been presented and validated. An extensive set of measurements from Rutherglen, Victoria, have been presented.

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