

Measuring shoot-level NO_x flux in field conditions: the role of blank chambers

Maarit Raivonen¹⁾, Petri Keronen²⁾, Timo Vesala²⁾, Markku Kulmala²⁾
and Pertti Hari¹⁾

¹⁾ *Department of Forest Ecology, P.O. Box 27, FIN-00014 University of Helsinki, Finland*

²⁾ *Department of Physical Sciences, P.O. Box 64, FIN-00014 University of Helsinki, Finland*

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We monitored NO_x fluxes in an empty chamber and in chambers containing Scots pine shoots. Our aims were to observe how the chamber blank behaves in non-controlled field conditions and at low ambient NO_x concentrations, to find ways of reducing deleterious wall effects, and to evolve a method for a blank correction. We found that solar ultraviolet radiation induced NO_x emission from the chamber walls. Comparisons between blanks of several chambers showed that the chambers were not identical. We therefore recommend that a separate blank chamber will be monitored together with the branch chambers in long-term field measurements. At regular time intervals, all of the chambers should be measured simultaneously while empty and the regression between the UV irradiance and NO_x flux determined for each chamber. In case the chambers differ from each other, the blank could be corrected with the UV-regression coefficients obtained.

Introduction

Oxidised nitrogens are important atmospheric compounds, particularly NO_x (= NO + NO₂), which participates in the production and destruction of tropospheric ozone and acidification of rainwater (Seinfeld and Pandis 1998). One factor in the atmospheric NO_x balance is its fluxes into or out of vegetation. Many studies have shown that plants absorb NO_x from the atmosphere (Johansson 1987, Thoene 1991, Rondón *et al.* 1993, Weber and Rennenberg 1996, Sparks *et al.*

2001). However, these observations have been made in conditions in which the mixing ratios are high (several parts per billion, ppb), compared with normal background levels in a rural atmosphere (below one ppb). While some observations of NO_x emission at low concentrations exist (e.g. Wildt *et al.* 1997, Sparks *et al.* 2001), generally the capability of plants to emit NO_x is controversial (Lerdau *et al.* 2000). Measuring NO_x fluxes at low ambient concentrations is essential for understanding what is happening every day in most of the vegetated areas of the world.

NO_x fluxes between the vegetation and atmosphere have been measured at two levels: canopy level and leaf level. In the latter case, a single leaf, branch, or plant is enclosed into a chamber, and changes in gas concentrations in the chamber air are monitored. This typically provides more detailed information about plant functioning than do the canopy-level studies.

Environmental factors should be considered in chamber-based measurements. The temperature rises easily inside the chamber. Excessive temperature changes are usually prevented somehow; chambers can even be thermostated (Geßler *et al.* 2000, Hereid and Monson 2001, Sparks *et al.* 2001). Fans mix the air to diminish boundary-layer resistance and concentration differences within the chamber volume.

Electromagnetic radiation has an important role in NO_x flux measurement. Ultraviolet radiation has been observed to affect NO_x flux of pine shoots (Hari *et al.* 2003). Moreover, oxidised nitrogen is photochemically active. For instance, ultraviolet or visible light dissociates NO₂, HNO₃, NO₃ and HONO (Seinfeld and Pandis 1998). The chamber material determines the wavelengths that enter the chamber. Many plexiglass types absorb the ultraviolet portion of the solar spectrum (Röhm GmbH & Co., Germany). FEP teflon, by contrast, transmits UV radiation (DuPont, Wilmington, DE, USA). Quartz glass provides a natural spectral composition inside the chamber since it is also transparent for short wavelengths, including UV-B radiation (CRC 1990).

In chamber experiments, the main complication with chemically reactive NO_x is its reactions on chamber surfaces. These surfaces are likely to adsorb and release NO_x. Accordingly, the measured signal is always a combination of the fluxes produced by the plant and chamber walls. The wall effects — or chamber blank — can be determined by monitoring the fluxes in an empty chamber, either in the particular chamber used for the plant (Hanson *et al.* 1989, Rondón *et al.* 1993, Rondón and Granat 1994, Wildt *et al.* 1997, Hereid and Monson 2001, Sparks *et al.* 2001) or in another chamber that is similar to the leaf chamber (Thoene *et al.* 1991, Weber and Rennenberg 1996, Geßler *et al.* 2000, Geßler *et al.* 2002).

Plant researchers' reports on the NO_x exchange do not usually deal with the behaviour of the chamber blank. The reason may be that the wall effects cause significant uncertainties only at low ambient NO_x concentrations. Moreover, the environmental conditions of experiments are often controlled. An artificial light source and purified air which is humidified and mixed with known quantities of NO_x and O₃ are typical arrangements (Thoene *et al.* 1991, Rondón *et al.* 1993, Rondón and Granat 1994, Hereid and Monson 2001, Sparks *et al.* 2001). In Hanson *et al.* (1989), Thoene *et al.* (1991) and Wildt *et al.* (1997), the chambers were adsorbers rather than emitters. Rondón and Granat (1994) reported that their empty teflon chamber emitted NO₂ at concentrations below 2 ppb and adsorbed it at concentrations of 10 to 15 ppb, with a compensation point appearing at 3 to 6 ppb. They observed no relationship between the NO₂ flux and light intensity, temperature or relative humidity.

Another kind of chamber research has analysed the emission of oxidised nitrogen from chamber walls more intensively. In environmental chambers where air-chemical reactions have been studied, chamber surfaces are a NO_x source (Carter and Lurmann 1991). This seems to be a problem, particularly when experimenting with low or zero NO_x concentrations. Carter (1999) reported that NO_x offgasing rates were higher in used chambers than in new, clean ones and that the process might be light induced. However, the exact mechanism is unknown.

The knowledge about leaf-level NO_x fluxes at low background concentrations in the rural atmosphere is incomplete, making long-term monitoring in the field necessary. It is under these conditions that the chamber method is most challenging. We monitored leaf-level NO_x flux of Scots pine (*Pinus sylvestris*) at the SMEAR II measuring station (Station for Measuring forest Ecosystem–Atmosphere Relation) in southern Finland (Vesala *et al.* 1998). There the background concentrations are low (less than one ppb). We observed a clear deposition of NO_x onto the pine shoots during the few days when ambient NO_x reached exceptionally high levels, and clear NO_x emissions on some sunny days when the shoots were exposed to solar UV radiation (Hari *et al.* 2003). This paper deals with the

blank chamber. Our objectives were to analyse the behaviour of the blank chamber in a non-controlled environment and at low background concentrations, to find ways of reducing deleterious wall effects, and to propose a method for the blank correction.

Measurements

Chambers

The SMEAR II station (Vesala *et al.* 1998) is located in Hyytiälä, southern Finland (61°N, 24°E). The forest is a homogeneous Scots pine stand sown in 1962. Our automatic chamber system is described in, for example, Hari *et al.* (1999) and Kulmala *et al.* (1999).

Two (in 2001) or three (in 2002) chambers monitored the gas fluxes of the Scots pine; each enclosed one shoot of a full-grown tree. The chambers were installed at the top of the trees in order to minimise a shading effect. One empty chamber served as a reference. A computer controlled the measurement of gas concentrations and relevant environmental factors for each chamber; each chamber was measured two to three times per hour.

The chambers used for monitoring the NO_x fluxes were box-shaped with a volume of one dm^3 (Fig. 1). The boxes were made of plexiglass and the inner surfaces were coated with a FEP teflon film. The upper walls, i.e., the covers of the boxes were removable. We used two different materials in the chamber covers: plexiglass and quartz glass. The boxes had two round holes at the bottom for letting the ambient air enter the chamber when no measurement was taking place. At the holes inside the chamber, fans ventilated the interior and kept the air well mixed.

A copper-constantane thermocouple monitored the temperature inside the chamber. A sensor for photosynthetically active radiation (PAR) was attached outside the chamber (LiCor 190 SB). Ultraviolet radiation, both UV-A (315–400 nm) and UV-B (280–315 nm), were monitored in a tower above the forest canopy (Solar 501A UVA and Solar 501A UVB, Solar Light Co., Philadelphia, PA, USA).

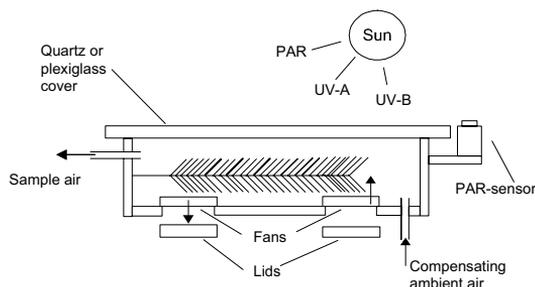


Fig. 1. Schematic illustration of our chamber. The arrows show the direction of airflow for sample air, compensation air, and flow caused by the fans. The lids are closed for the measurement period.

Concentration measurement

For measurement periods, lids closed the holes at the bottom of the chamber and sample air was directed to flow through the gas analysers (NO , NO_x , O_3 , CO_2 , and H_2O). The compensation air was ambient air that came from outside the chamber. The gas concentrations of the sample air were recorded every five seconds during the 60 seconds of closing plus an extra period while the chamber was open again. Since the distance from the chambers to the gas analyser was 35–37 meters, a pipe delay was present in the measurement. The closing of the chamber, i.e., the moment when the NO_x concentration started to rise, appeared in the data 40–45 seconds later than it actually happened (Fig. 2).

The flux calculation method is sensitive to the NO_x concentration of the compensation air. It was thus essential to monitor the concentrations directly from the chamber air while the chamber was open. We used this as the concentration in the compensating air.

The instrument for measuring NO_x concentration was a chemiluminescence analyser (TEI 42S, Thermo Environmental Instruments, Philadelphia, PA, USA). In the NO mode, it detects the concentration of NO by first oxidising it to excited NO_2 and then detecting the intensity of the radiation that the excited NO_2 emits. In the NO_x mode, which we mostly used, NO_2 is first converted to NO in a molybdenum converter. This phase is not specific to NO_2 ; other nitrogen-containing compounds, such as HNO_3 and organic nitrates and nitrites, also convert into

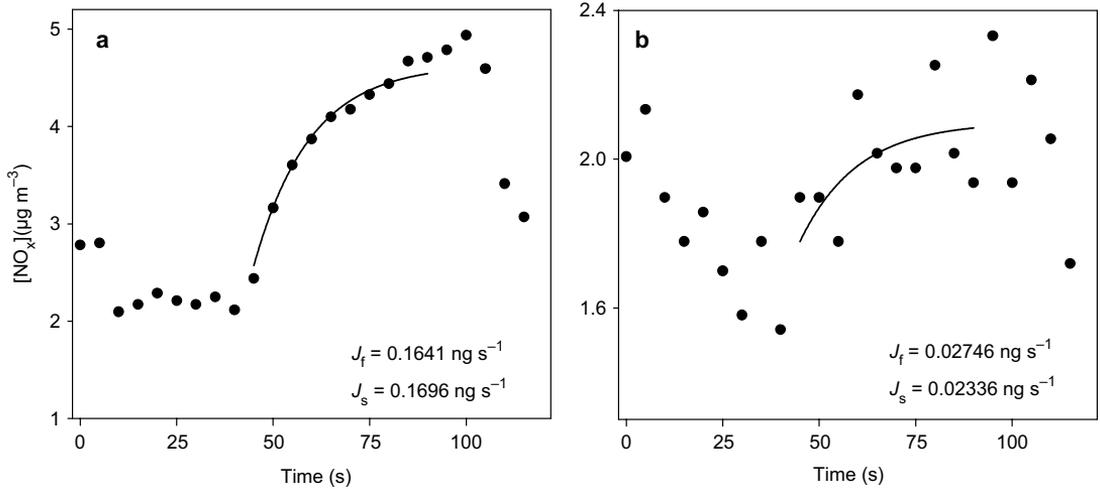


Fig. 2. Two different representative measurement periods, and a demonstration of the fitting method. (a) Concentration data for a measurement period with a relatively large flux. Here the pipe delay is clear. (b) Smaller flux with a small signal-noise ratio. The curves show the fitted mass-balance equation. Flux with the simple difference method was calculated using those same points into which the equation was fitted. J_f stands for the flux that results from fitting, J_s denotes the simple calculation.

NO (Winer *et al.* 1974). In our case, the air that entered the chambers certainly included nitrogen oxides other than NO and NO₂. The analyser misinterprets all PAN as NO₂. HNO₃ is not believed to pass through the sample lines and in-line particle filters.

Determining the flux

Fluxes in our chambers — both in the empty one and in those chambers that contained a pine shoot — were so small that they often barely passed the detection limit (0.1 ppb) of the gas analyser (accuracy was around 0.3 ppb). Measuring noise was evident. We did, however, develop a method for determining the fluxes from this noisy data.

Most of the time, the fluxes in the empty chamber were emission instead of deposition. Figure 2 shows two typical measurement periods. In the first period the concentration change during the closing of the chamber was steady (Fig. 2a), whereas in the second period it contained a considerable measuring noise (Fig. 2b). Basing the calculation of the flux on the apparent concentration change during the closing of the chamber, i.e., on a difference

between two points, is doubtful. This is why we employed the following method that allows us to use all information that we have from one measurement period. This method is a modification of those presented by Aalto (1998) for CO₂ and by Altimir *et al.* (2002) for O₃.

Here we simply determine the total NO_x flux inside the chamber, an empty one or a chamber with a pine shoot inside. We do not separate the shoot from the chamber walls at this phase.

Processes that change the NO_x concentration inside the chamber are sample flow into the gas analyser q_a (m³ s⁻¹), compensating airflow of ambient air q_c (m³ s⁻¹), and flux J (g s⁻¹) due to the sinks or sources of NO_x inside the chamber (chamber walls, the shoot). Let us denote the volume of the chamber by V (m³), the concentration at a moment t by $C(t)$ (g m⁻³), and the concentration in the compensating air by C_c (g m⁻³). Now the measured concentration change can be connected to the processes in a mass balance:

$$\frac{VdC(t)}{dt} = q_c C_c - q_a C(t) + J. \quad (1)$$

Let us then solve the differential equation for $C(t)$, the quantity that is measured. Since q_a and q_c are equal, the solution is:

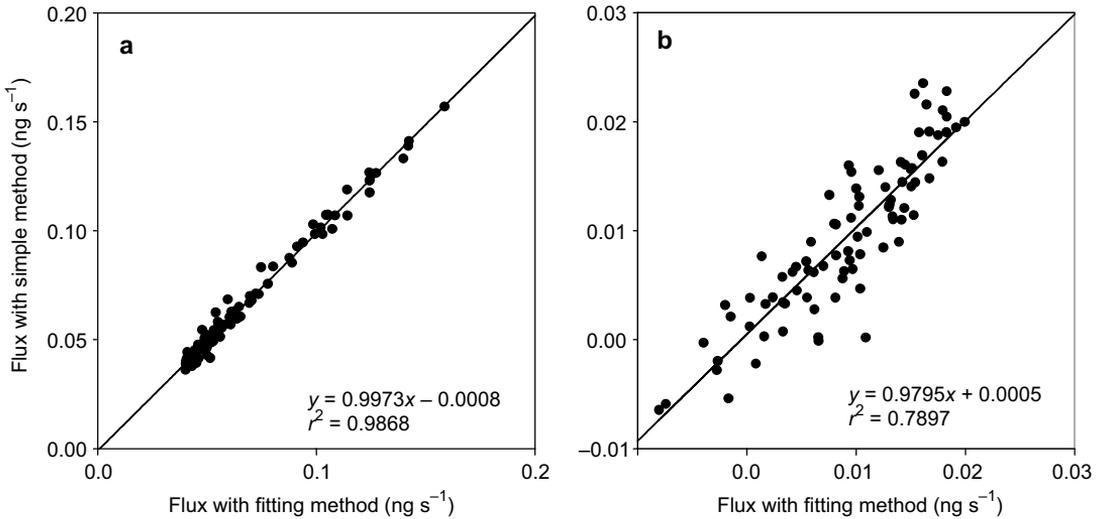


Fig. 3. Comparison of the two methods for calculating NO_x fluxes. Data are from two normal days in summer 2002. (a) shows the fluxes that were greater than 0.04 ng s⁻¹ when calculated with the fitting method, and (b) shows fluxes lower than 0.02 ng s⁻¹. The noise appears more in (b).

$$C(t) = \left[C(0) - C_c - \frac{J}{q} \right] e^{-\frac{qt}{V}} + \frac{J + qC_c}{q} \quad (2)$$

Here the only unknown factor is the flux J that is assumed to be constant during the measuring period. This, in fact, is a slight simplification because the flux probably decreases during the closing when the NO_x concentration rises. J is found by fitting Eq. 2 to the measured NO_x concentrations by minimising the sum of squared residuals. We fitted the equation with Mathematica software (Version 4; Wolfram Research, Inc., USA) that uses the Levenberg-Marquardt method for minimising the sum of squares. Figure 2 demonstrates the fitting. Now this flux can be related, for example, to the needle area or chamber surface area.

We compared the fluxes that the fitting method produced with those determined with a simple difference method. In the latter, one determines the flux for each five-second interval using the following equation:

$$J = V \frac{C(t_2) - C(t_1)}{t_2 - t_1} + q \frac{C(t_1) + C(t_2)}{2} - qC_c \quad (3)$$

Here $q = q_a = q_c$. The concentration change is taken from the difference between the two points $C(t_1)$ and $C(t_2)$, and the average NO_x concentration in the sample air during the time interval $t_1 - t_2$ is the average of $C(t_1)$ and $C(t_2)$. The NO_x flux of the whole measurement period would then be the average of these five-second fluxes. When it came to large fluxes, these two methods did not differ markedly (Fig. 3a). Small fluxes, however, scattered more, reflecting the low signal-noise ratio (Fig. 3b).

Chamber blank

Ultraviolet radiation

We found that the spectral composition of electromagnetic radiation inside a chamber affects the chamber blank. We controlled the entrance of ultraviolet radiation into the chambers by using different types of chamber covers. The quartz glass cover transmitted UV wavelengths, whereas the plexiglass cover absorbed them (Fig. 4). When a UV-opaque cover was replaced by a UV-transparent one, NO_x emissions increased clearly (Fig. 5). UV radiation seems to induce a NO_x flux from the chamber walls.

When examining the relation between solar

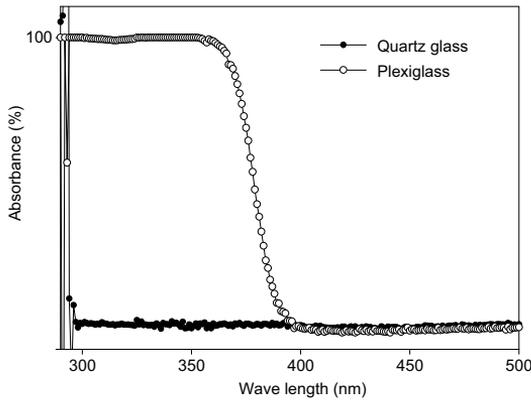


Fig. 4. Absorbances of quartz and plexiglass at 290–500 nm. Measured with a radiospectrometer (Bentham, UK) (for a detailed description of the instrument, see Boy and Kulmala (2002)).

UV irradiance and the flux in the empty chamber, one notes that the emission depends on UV irradiance. Figure 6 presents typical emission data for the day (7 July 2001) that the empty chamber had a quartz glass cover. The flux had a clear diurnal pattern (Fig. 6a) and it followed the changing irradiance. NO_x flux seemed to correlate a bit better with UV-A irradiance (Fig. 6b) than with UV-B irradiance (Fig. 6c). The r^2 values were 0.865 and 0.782, respectively.

The chamber blank was much smaller with the UV-opaque cover, but was still considerable. With the plexiglass cover, our chamber also emitted NO_x , and the daily emission had a slight diurnal pattern (Fig. 7).

Evolution of the chamber blank

We tested the impact of coating the plexiglass walls of our empty chamber with a FEP teflon film on the chamber blank. The effect was clear; teflon reduced NO_x emissions. Figure 8 presents the dramatic drop in the flux that occurred when we put teflon coating on the plexi surface for the first time. Emissions decreased to 2%.

Unfortunately, the positive effect of teflonising was not permanent. Emissions from the teflonised chamber increased with time. In summer 2001, we noticed that emissions from the empty chamber grew rapidly over the summer, in spite of cleaning the chamber with deionised water or

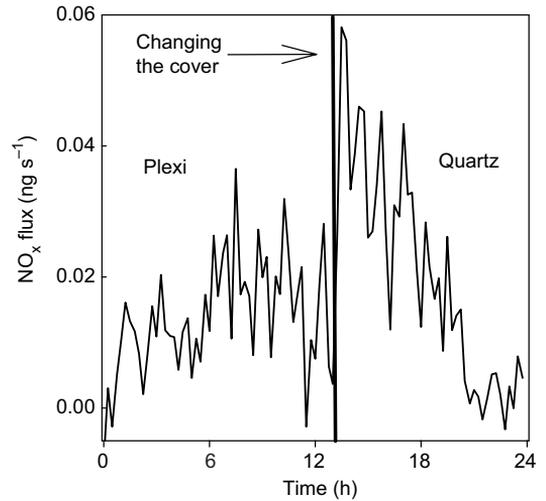


Fig. 5. Change in NO_x emissions of the empty chamber when the UV-opaque plexiglass cover was replaced by a UV-transparent quartz cover.

alcohol at one- or two-week intervals (Fig. 9a). In summer 2002, we renewed the teflon at the end of April and May, at the beginning of July, and at the end of August. NO_x emissions dropped with every new teflon coating (Fig. 9b). However, the effect was not as good as we expected based on the first successful teflon experiment (see Fig. 8). Over the summer, the chamber blank did not once drop as low as it had been in the spring. Moreover, for most of the summer, it remained higher than the maximum for 2001.

Since the daily mean NO_x flux depends strongly on the weather, especially on daily sunshine, it is not a reasonable characteristic for examining the development of the teflon surfaces. On sunny days, the mean NO_x emission is higher than on cloudy days, irrespective of the condition of the teflon film. That is why we calculated regression coefficients between UV-A or PAR irradiance and the flux for 2001 and 2002. PAR was used for 2002 because we did not obtain a complete series of UV irradiance for summer 2002. The regression between UV-A irradiance and PAR irradiance is close to linear. Figure 10 demonstrates that these regression coefficients also increased with time.

The occasional high regression coefficients mostly came from days when the weather was cloudy and rainy (Fig. 10b). Naturally, on these days, the relative humidity was also high and the

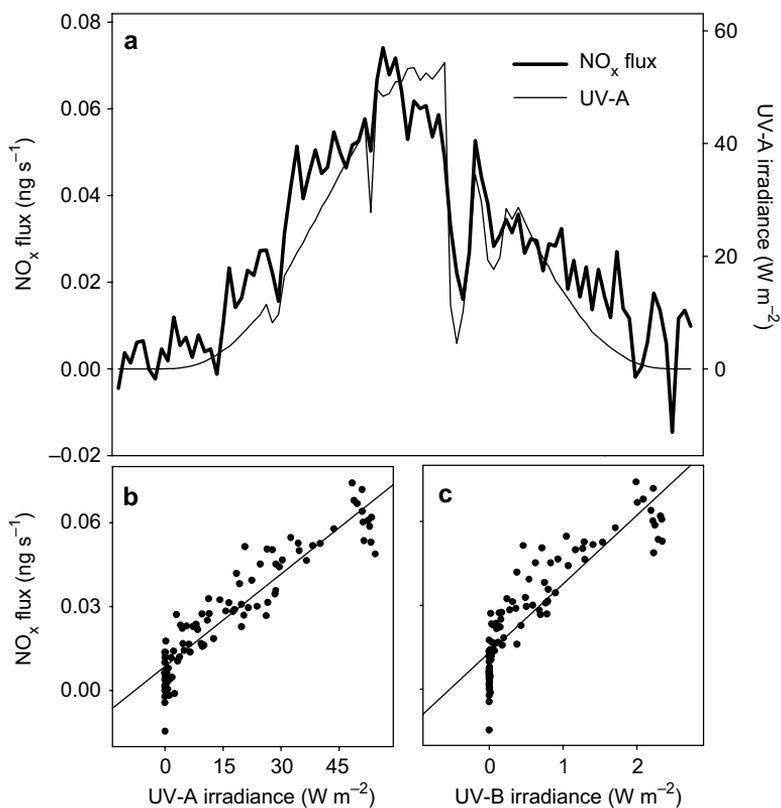


Fig. 6. Relationship between UV irradiance and NO_x flux in the empty chamber on 7 July 2001. — **a:** The thick black line is the NO_x flux; the thinner black line shows UV-A. — **b:** Regression between UV-A and NO_x flux. The regression equation is $y = 0.0011x + 0.0086$; $r^2 = 0.865$. — **c:** Regression between UV-B and NO_x flux. The regression equation is $y = 0.024x + 0.0132$; $r^2 = 0.782$.

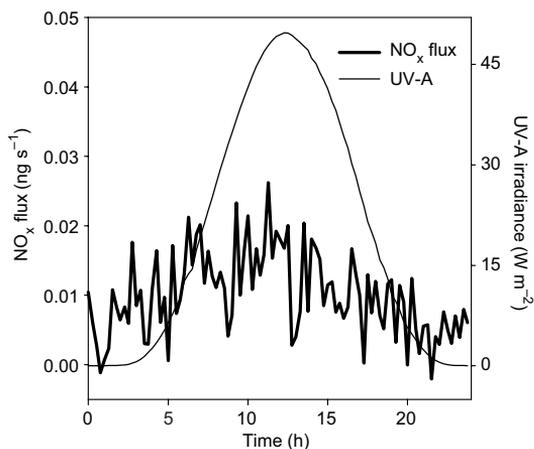


Fig. 7. Pattern of NO_x flux in the empty chamber when it has a UV-opaque cover. Data is from 5 July 2001. The thicker black line is the NO_x flux; the thin black line shows UV-A irradiance.

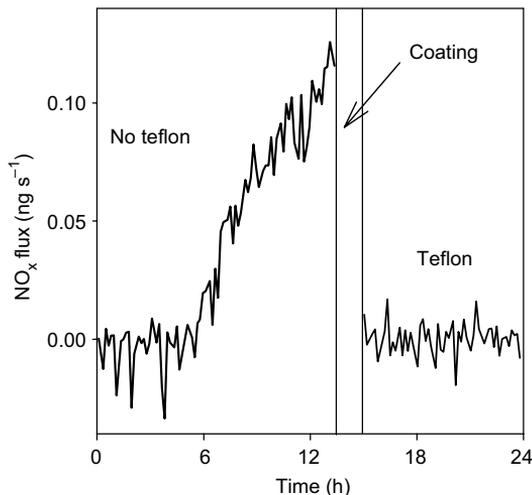


Fig. 8. Change in NO_x flux when the plexiglass chamber was coated with a FEP teflon film. Data is missing from time 13:00–15:00, when the teflonising was performed.

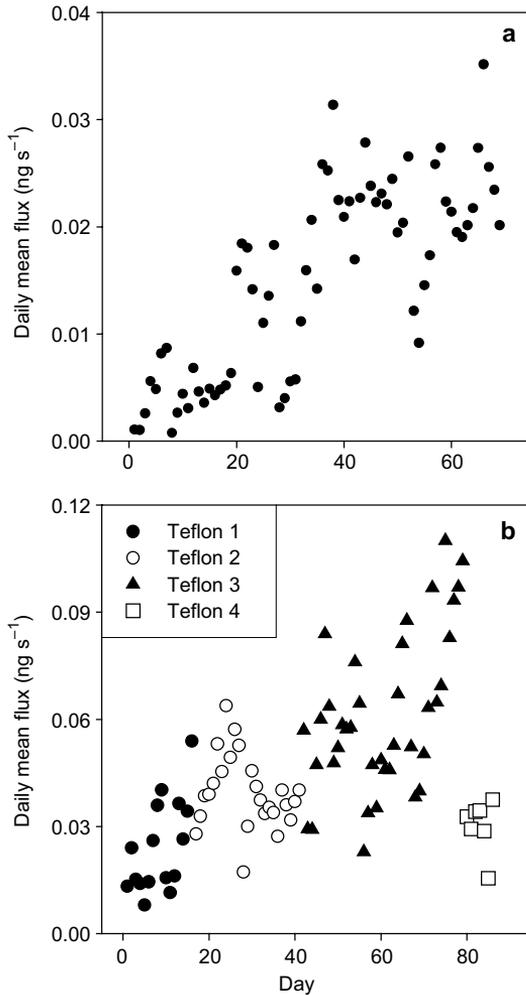


Fig. 9. Development of the chamber blank presented as daily mean NO_x fluxes. — **a:** Summer 2001 from May to August. — **b:** Summer 2002 from May to the beginning of September. In 2002, consecutive teflon coatings are denoted by different symbols. The days when there was something wrong in the measurements have been excluded.

temperature was lower than on sunny days. It is difficult to separate the effects of all of these factors.

Differences between chambers

When the estimation of the chamber blank is based on a separate control chamber, the underlying assumption is that all chambers behave similarly. This assumption is not, however, self-evident given the large variability in the emis-

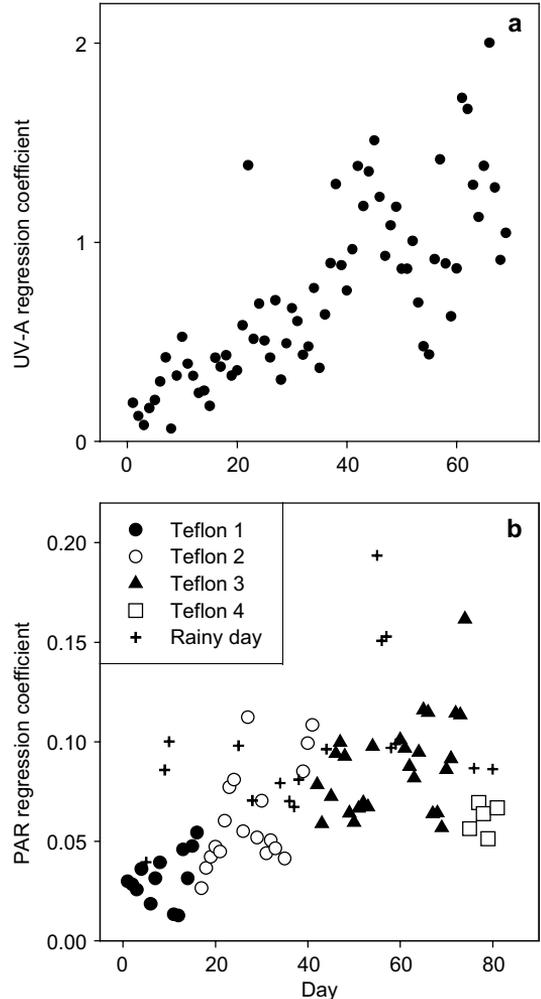


Fig. 10. Change in the regression coefficient between **(a)** UV-A irradiance and NO_x flux in summer 2001, **(b)** PAR irradiance and NO_x flux in summer 2002. In 2002, consecutive teflon coatings are denoted by different symbols. All cloudy and rainy days are denoted by +. The days when there was something wrong in the measurements have been excluded.

sions of an empty chamber.

A few times in 2001 and 2002, we monitored several empty chambers: the blank and the chambers that normally enclosed pine shoots simultaneously. Data — which are now UV-A or PAR normalised fluxes — from these experiments are collected in Fig. 11. Based on these sparse results, emissions in one chamber may be even two-fold compared with those in the other chamber. In 2001, the differences between chambers tended to increase towards the end of the

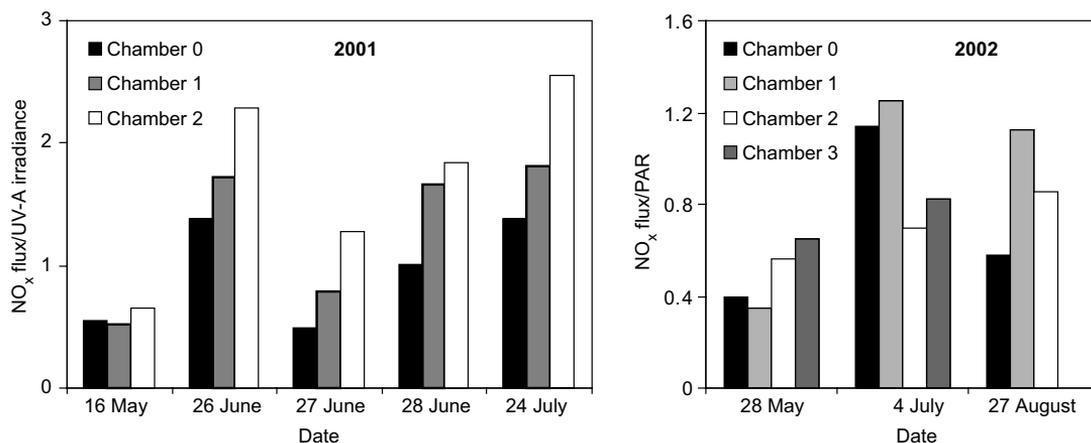


Fig. 11. Comparing the blanks of different chambers. In 2001, we had three similar chambers, in 2002 four. Chamber 0 is the blank that was always empty. Chambers 1–3 usually had a pine shoot enclosed. Data are shown as the ratio between NO_x flux and UV-A or PAR irradiance.

summer. The chambers that normally enclosed a shoot seemed to emit more NO_x than the continuously empty chamber.

Results from 2002 do not show as clear a trend as those from 2001. Fluxes on 28 May and 4 July were measured just before renewing the teflon coating, 27 August was measured with clean surfaces, just after renewing.

Discussion and conclusions

We analysed the behaviour of the empty shoot chamber that we use when blank-correcting our shoot-level NO_x flux measurements. We aimed to find out (1) how reliable an estimate that empty chamber provides, and (2) how to perform the correction.

The smaller the NO_x flux, the smaller the signal-noise ratio, and the more difficult it is to detect the flux in the measured data. We ended up determining the NO_x fluxes in our chambers with our novel method that utilises all possible data and, consequently, reduces the noise effect.

Emission rather than deposition dominated the NO_x fluxes in our empty chamber. Papers about leaf-level NO_x flux of plants do not usually present any chamber-blank data. They merely state that an empty control chamber was used for estimating possible adsorption and desorption of NO_x to or from the chamber walls. Rondón and Granat (1994) observed that their

chamber emitted NO_x at ambient concentrations below 2 ppb. This is in accordance with our results since the concentrations at our station typically are as low.

Values for the chamber blank were at their lowest when the chamber had a new, clean teflon coating. However, NO_x emissions increased with time, and renewing the teflon coating on the chamber surfaces did not invariably result in a near-zero flux for some unknown reason.

Solar ultraviolet radiation was found to induce NO_x emission from the empty chamber. Emissions followed changes in the UV irradiance. To the best of our knowledge, this has been discussed earlier only in Hari *et al.* (2003).

Some substance accumulating on the chamber walls appears to govern the chamber blank. Chamber walls adsorbed it from the air, and ultraviolet radiation released it as NO_x or as some other compound that our analyser detects. One hypothesis is that nitrate or nitric acid deposited on the walls was photolysed by UV radiation. This would produce NO_x , HONO, or another nitrogenous compound (Seinfeld and Pandis 1998). Zhou *et al.* (2002) observed HONO production on a glass manifold when it was exposed to sunlight. They speculated that it was a result of nitrate or HNO_3 photolysis. Honrath *et al.* (2000) presented the same explanation when sunlight released gaseous NO_x from snow particles. Also Knipping and Dabdub (2002) suggested that surface-mediated processes return

nitric acid to the atmosphere. Another explanation for the emissions from the chamber surfaces may be that some micro-organisms produce NO_x in the presence of UV radiation.

We observed that fluxes measured simultaneously in different chambers were not the same. Whether by chance or not, the 2001 emissions were greater in those chambers that usually had a pine shoot inside. These differences were sufficiently large to cause significant uncertainties in the flux determination, because the NO_x fluxes in the empty chamber were usually of the same magnitude as the fluxes measured with the shoots.

In conclusion, when monitoring small NO_x fluxes at low concentrations, the chamber blank has to be followed carefully. Values stay low when the chamber surfaces are clean. One helpful operation is to renew the teflon surface at intervals of a few weeks. Since blanks of different chambers are not identical, the best solution is to take the blank from the same chamber that is used for the plant. However, this is laborious in field measurements where the intention is to obtain a long time series. A more practical method is to use a separate control chamber.

NO_x emissions in an empty chamber are dependent on the radiation intensity. Thus, environmental conditions should be stable when measuring the chamber blank and the NO_x flux of the plant, or the changing irradiance should be taken into account. An option for the blank correction is that at regular time intervals (around once per week), all chambers will be simultaneously monitored while empty. Then the UV-A regression equation should be determined for every chamber. In case the chambers differ from each other the blank can be corrected with the obtained UV coefficients.

Thus far, our group has used a separate control chamber without regular comparison with other chambers. This means that routinely measured data include significant uncertainty. To obtain more reliable measurements, we should implement the procedure described above.

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