

Assessment of field monitoring of plant fluxes of oxidized nitrogen with two types of detectors

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Chemiluminescence-based measurements of oxidized nitrogen can be specific to NO_x or can also detect other NO_y compounds, depending on the equipment. We monitored chamber fluxes of oxidized nitrogen in Scots pine shoots under field conditions, and changed from a NO_y measurement to the more NO_x-specific measurement. The aims of this study were to evaluate how the NO_x measurement system performs in comparison with the NO_y measurement system in dynamic field measurements, and whether the new measurements provide information on the composition of the NO_y emissions reported in earlier studies. We found that absolute NO_x concentrations were slightly more inaccurate than the earlier NO_y concentrations but that the new analyzer led to an improvement in the measurement of NO_x fluxes. Simultaneous NO_y and NO_x flux measurements from chambers indicated that the measured NO_y fluxes often include compounds other than NO_x. We found no clear plant-related NO_x emissions.

Introduction

Natural ecosystems are significant factors in the atmospheric budget of gas-phase nitrogen oxides (NO and NO₂, together denoted as NO_x) because soil microbial processes are one of the largest sources of atmospheric NO. The soil source of NO has been estimated to account for up to 21 Tg N yr⁻¹, which is of a similar order of magnitude to that which emanates from the burning of fossil fuels (Davidson and Kinglerlee 1997). Plants can absorb NO_x, especially NO₂ from the air (Hereid and Monson 2001, Teklemariam and Sparks 2006) and thus vegetation can significantly reduce the net soil emissions to the atmosphere (Davidson and Kinglerlee 1997).

The role of vegetation in the atmospheric budget of NO_x is not fully resolved. Some measurements have indicated that plants themselves are a source of NO and NO₂ at low ambient concentrations, with the threshold concentration for NO₂ being around 1 ppb (Rondón *et al.* 1993, Sparks *et al.* 2001, Geßler *et al.* 2002). However, the existence of a compensation point i.e. a certain threshold concentration at which the flux would turn from net deposition into net emission has been questioned by some authors because NO_x emissions have not always been observed (Chaparro-Suarez *et al.* 2011, Stella *et al.* 2013). In areas remote from anthropogenic NO_x emission sources, the ambient concentrations of NO_x are so low that any net fluxes from vegetation

would be expected to occur as emissions, if the compensation point exists. Hence, the role of plants in the atmospheric NO_x budget is unclear for a large proportion of global vegetated areas.

The measurement of NO_x concentration is not a straightforward task. NO can be detected accurately and easily even with relatively simple and inexpensive commercial chemiluminescence NO analyzers, but NO_2 detection techniques are often limited by interference from other compounds. In a chemiluminescence analyzer, NO molecules are oxidized to electronically-excited NO_2 by ozone (O_3) produced by an integrated generator. When returning to the lower ground state energy level, the molecules emit light whose intensity is directly proportional to the original NO concentration. It is possible to use the chemiluminescence method to measure total NO_x , but it requires conversion of the NO_2 component of NO_x to NO before its subsequent re-oxidation. This phase is not specific to NO_2 as other nitrogenous compounds can also be converted to NO . Of the conversion methods, heating with molybdenum, for example, is especially inaccurate: heating has been shown to convert 100% of nitrous acid (HONO) and nitric acid (HNO_3), nearly 100% of peroxyacyl nitrates (PAN) and 68% of hydrogen cyanine (HCN) to NO (Gerboles *et al.* 2003 and references therein). A more reliable and specific conversion method is photolysis by blue light. However, this method may also convert some HONO , although with a lower efficiency than that for NO_2 so it also has its limitations (Ryerson *et al.* 2000). Moreover, photolysis by blue light is subject to negative interference as a consequence of photolysis of volatile organic compounds (VOC) in the converter (Villena *et al.* 2012). Another NO_2 detection technique is luminol-chemiluminescence whereby NO_2 oxidizes a luminol solution in the presence of oxygen (O_2), and this produces chemiluminescence. This method is subject to interference from O_3 and PAN (Kelly *et al.* 1990). Concentrations of NO_2 can be measured specifically by spectroscopic methods such as laser-induced fluorescence (Thornton *et al.* 2000) and cavity ring-down spectroscopy (Fuchs *et al.* 2009). However, these methods have only recently become commercially available, thus there is limited knowledge as to the

stability and maintenance required for long-term measurements. The chemiluminescence method combined with blue-light conversion for NO_2 is currently recommended by the World Meteorological Organization (WMO 2011).

The field measurement station SMEAR II (Station for Measuring Forest Ecosystem–Atmosphere Relation; Hari and Kulmala 2005) in central Finland has been measuring chamber fluxes of oxidized nitrogen of Scots pine (*Pinus sylvestris*) shoots since 1996 [together with carbon dioxide (CO_2), water (H_2O) and O_3 fluxes]. Prior to 2006, we used the chemiluminescence method with a heated molybdenum converter for the concentration measurement, and after that date the chemiluminescence method was used with a photolytic converter. As far as we are aware, SMEAR II is unique in carrying out continuous monitoring of leaf-level fluxes of oxidized nitrogen. The station is located in a remote area, with ambient NO_x concentrations generally around 1 ppb.

The goal of long-term monitoring puts some constraints on the chamber measurement system design and capabilities. The system is designed to keep the enclosed pine shoots in conditions as close to the ambient as possible. This means that the chambers are open to ambient air for most of the time and that the actual period that the chamber is closed to obtain a flux measurement is very short. As such, the concentration measurements must be made quickly. As a consequence, it is not possible to use the NO_x analyzers in their automatic mode, which would involve the automatic checking of the zero level (background luminescence). Each concentration measurement would take so long that it would make the flux measurement too slow. The faster measurement is possible only when running the analyzers in the manual mode whereby the analyzer does not perform the automatic zero correction. Instead, we record the zero values manually once a week, interpolate the correction factor for the days between those measurements, and correct for the zero when processing the data. The underlying assumption is that the zero level does not vary randomly but it changes gradually over time. The absolute concentrations in the chamber measurements are thus not fully accurate but they include some uncertainty about the zero offset level.

However, this does not affect the flux measurement that is based on detecting the concentration change in the chamber; the zero offset level is included in all the concentrations and thus gets cancelled out in the flux calculation.

During the first decade of the measurements, we used the heated molybdenum conversion system and therefore included all reactive nitrogen that passed through the sampling system, that is, we measured NO_y fluxes. During the few high- NO_y -episodes observed at the station, the NO_y fluxes were clearly characterized by deposition (Raivonen *et al.* 2009). Most of the time, the ambient concentrations were low and the net fluxes were emissions rather than depositions. The chamber caused some problems for accurate measurements as the chamber walls clearly emitted NO_y (Raivonen *et al.* 2003). However, total emission levels increased when the pine shoots were inserted into the chambers, indicating that the tree shoots also emitted NO_y (Hari *et al.* 2003). The emissions from this source seem to be associated with solar UV radiation and they gradually grew over time if the shoot (or the chamber) was not cleaned. In a previous study, we also suggested that the emissions from the tree shoots originated from their needle surfaces as a result of photolysis of nitrate or HNO_3 deposited on these needle surfaces (Raivonen *et al.* 2006). This reaction had been reported to produce NO_x and HONO on snow (Dibb *et al.* 2002) and glass surfaces (Zhou *et al.* 2003). Although we could not exhaustively demonstrate that some of the emissions we observed came from the tree, in addition to those that emanated from the chamber surfaces, it seemed probable that this occurred. Our hypothesis is supported by Zhou *et al.* (2011) who observed HONO production in a forest canopy. The HONO levels correlated with the nitrate load on leaf surfaces and also with the rate constant of nitrate photolysis, and thus they suggested that HNO_3 photolysis was the source of HONO.

It was obvious that the NO_y emissions we detected might include nitrogen compounds other than NO_x , the strongest candidate being HONO. In order to obtain a more accurate measure of NO_x , we changed to the blue light photolytic NO_2 conversion method in 2006, and NO_x fluxes have been measured by this method since then.

This study had two aims:

1. to evaluate the performance of the photolytic NO_x concentration measurement system compared with the NO_y concentration measurement system in long-term field measurements where the gas analyzers are used without the automatic zero offset correction, and
2. to find out whether the new measurements could provide more detailed information on the composition and source (i.e. the chamber surfaces or the tree shoot) of the NO_y emissions observed in our earlier studies.

Material and methods

Chamber flux measurements

The gas-exchange chamber system used at SMEAR II has previously been described in several papers (Altimir *et al.* 2002, Raivonen *et al.* 2003). The chambers are installed in Scots pine treetops at a height of around 15 m to minimize shading. Each chamber encloses one pine shoot, and in addition, we periodically monitor the fluxes in one empty (blank) chamber. The chambers used for this study are box-shaped, with a volume of 1 dm³. They are predominantly made of methacrylate plastic, with the exception of the upper wall, which is made of quartz glass. The inside plastic surfaces of the chambers are coated with fluorinated ethylene propylene (FEP) adhesive film. There are two round openings in the chamber bottom that are closed only during the flux measurement. Two fans mix the air and ventilate the chamber.

The system is automatic. There are 12 chamber lines measured in sequence. When a certain chamber is sequentially sampled, magnetic valves open its lines and pumps start to draw air samples to the gas analyzers. The sample flow rate is 4 dm³ min⁻¹. The chamber lids usually close after five seconds have elapsed. An equal volume of ambient air is drawn into the chamber at a rate equal to that lost in the sample. The chamber is closed for about one minute and the gas concentrations of the air samples are recorded at five-second intervals. Temperature inside the chamber and the irradiance of the pho-

tosynthetically active radiation (PAR) on top of the chamber were also measured. Other relevant environmental parameters such as ultraviolet irradiance and air pressure are measured at the station (Hari and Kulmala 2005).

There are two sample tubes for each chamber; their length is 64 m, and the diameters are 4 mm and 6 mm respectively. The tubing is composed of FEP. The tubes are heated to avoid condensation of water, and they are darkened in order to prevent photochemical reactions of their contents. In addition to the NO and NO_x analyzers, O₃, H₂O and CO₂ analyzers are also connected to the chambers. The residence time of the sample air in the tubes in transit to the respective NO, NO_x and O₃ analyzers is approximately 37 seconds. When a particular chamber is not in the measuring phase, there is a constant flushing of the sample tubes with ambient air.

In the present study, we used flux data collected in May–July 2006 which covers the period when the NO_y and NO_x fluxes were measured in parallel. During that time, we measured fluxes using four chambers: one blank and three chambers containing shoots. The blank chamber was of the same box-type as in our previous NO_y studies (Raivonen *et al.* 2003) and it was only used for measurements for a short period of time i.e. from 17 May to 7 June 2006. During this period, only one of the shoot chambers used was of a similar box-type, hence we concentrated on it and the blank chamber in the present analysis. The shoot chamber had been installed in November of the previous year and it had successfully measured fluxes over the winter without disturbance. On 17 May 2006, the chamber around the shoot was replaced by a clean and newly teflonized, identically designed box chamber. The blank chamber was also installed immediately after cleaning and teflonizing its surfaces.

Concentration measurements

In the chamber-flux measurements, we use the TEI 42CTL analyzers (Thermo Environmental Instruments, Franklin, MA, USA) to measure NO and NO_x (and NO₂); the previous NO_y analyzer was model TEI 42 S from the same com-

pany. The NO_x analyzer is equipped with a blue light converter BLC (Droplet Measurement Technologies, Boulder, CO, USA). The BLC was installed into the earlier NO analyzer in April 2006. Therefore, until the beginning of July 2006, we were able to monitor and compare NO_x fluxes measured by the BLC-equipped analyzer and NO_y fluxes measured with the old molybdenum converter. In July, the molybdenum converter was removed and we continued with parallel measurements of NO and NO_x fluxes.

In addition to the measurement in the chambers, NO and NO_x concentrations are measured on a mast that was originally 73 m tall (in 2010 the mast height was increased to 127 m). Atmospheric concentration profiles of NO and NO_x among other parameters are measured at six different heights on the mast. The relevant analyzer at these six NO_x measurement positions is the TEI 42 CTL (changed to a 42i-TL in May 2011) (Thermo Environmental Instruments, Franklin, MA, USA). The sample lines are made of polytetrafluoroethylene (PTFE) and the residence time of the sample air in the tubes is 20 s.

All the analyzers described above can be run in automatic mode whereby the NO and NO_x (or NO_y) measurements are automatically corrected for a dynamic zero reading. The zero level is determined by directing the air sample together with the O₃ flow through a prereactor where the excited NO₂ molecules return to the ground state prior to the luminescence measurements being taken, thus only the background luminescence is measured. Hereafter in this paper this zero reading is called the PRE value. It is also possible to measure the PRE value with the ozonator switched off (ozonator-off PRE). The ozonator-off PRE setting gives the background signal without any luminescence caused by O₃ and thus represents the dark current of the sensor. This value is dependent on temperature. The total PRE values, with the ozonator switched on, are used for the zero correction. It is possible to eliminate the temperature effect by subtracting the ozonator-off PRE value from the total PRE value. The difference leaves us with the residual variability of the PRE level.

At the SMEAR II station, the analyzer of the mast measurements is run in the automatic mode; as opposed to the analyzers of the cham-

ber flux monitoring, which are run in the manual mode whereby the analyzer does not perform the automatic PRE correction.

The NO, NO_x and NO_y analyzers are calibrated using diluted NO in a nitrogen gas mixture from a cylinder of a known concentration. This gives the span correction factor. We estimated that the inaccuracy of our span values causes about ±10% inaccuracy in the flux. In addition, we calibrated the NO_x and NO_y analyzers with known concentrations of NO₂. Until 2011, these were generated using a permeation oven and after that date diluted from NO₂ in a nitrogen gas mixture cylinder or from NO in a nitrogen gas mixture cylinder with the gas-phase titration method. The accuracies of the concentrations of the calibration gases according to the manufacturers (during the years relevant to this study: Air Liquide Deutschland GmbH, Krefeld, Germany), are ±5%.

In the present study, we compared the concentrations of gases that had been measured in the chambers when they were still open (i.e. almost ambient air) with those measured simultaneously on the mast, inside the canopy. We analysed nearly two years of data in two phases: the first phase from June 2005 to April 2006 when the NO₂ converters in both the chamber and the mast measurements still used the heated molybdenum method, and the second phase from April 2007 to March 2008 when we used the photolytic converters. We filtered these data for quality. Periods with technical problems or other obscuring and confounding factors were removed, and three-hour averages were calculated from the remaining data. We also closely investigated the PRE values of the NO and NO_x analyzers that were manually recorded during the years 2006–2012, and we compared them with the values obtained from the old NO and NO_y analyzers in 2004–2006.

Processing the chamber data

Each flux measurement (chamber closure) produces a number of concentrations measured at five-second intervals; this number varies a little between the different setups. Before the flux calculation is performed, the raw data are corrected

according to the calibration values. There are five steps in this correction procedure. Some of them are related to the changes in the calibration of the analyzer and some to the changes in the actual physical conditions that occurred at the time of measurement as compared with those at the time of analyzer calibration.

These five correction steps used are:

1. Correction for the zero offset in the analyzer (PRE correction).
2. Correction for the change in the pressure in the measurement chamber of the analyzer as compared with that at the time of analyzer calibration.
3. Correction for the change in the sample mass flow as compared with that at the time of analyzer calibration.
4. Correction for changes in the span calibration of the analyzer.
5. The NO₂ conversion efficiency (mean ± SD = 0.4 ± 0.06) of the blue-light converter is taken into account (exclusive to the NO_x measurement).

Before the fifth step, we calculated the NO₂ concentration by subtracting the NO concentration from the NO_x concentration. The PRE correction is the most significant factor that affects the level of the final (corrected) NO and NO_x concentrations.

Chamber flux calculation

After the data are corrected as described above, and the ppb values are converted into mol m⁻³, the flux rates are calculated. As reported by Raivonen *et al.* (2003), we achieve this by solving the mass balance equation:

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

where V is the chamber volume (m³), $C(t)$ is the concentration at moment t (μmol m⁻³), q_c is the compensating airflow (m³ s⁻¹), C_c concentration in the compensating air (μmol m⁻³), q_a is the sample flow into the gas analyzer and J is the flux (μmol s⁻¹). Since q_a and q_c are equal, the solution of the differential equation is:

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

The flux J is found by fitting the solution into the concentration data measured during chamber closure. As C_c , we use the mean of concentrations that were measured from the air sampled over a 30 s period when the chamber was still open.

Comparisons

We answered the questions set in the beginning of the study by making the following comparisons:

1. We determined whether there was any difference in the accuracy of the concentrations produced by the two measurement methods when they are used without the automatic PRE correction, by comparing the concentrations of NO, NO₂, NO_x and NO_y measured in the chambers when they were still open (ambient air) with those measured simultaneously on the mast. We assumed that the automatically PRE-corrected concentrations from the mast are accurate. To ensure that the ambient concentrations were as close as possible in both places, the mast and the chambers were separated horizontally by approximately only 50 m.
2. We evaluated the sensitivity of the concentration measurement methods to the properties of the sample air by scrutinizing the time series of recorded PRE values for the NO, NO_x and NO_y analyzers.
3. We assessed the composition and source of the NO_y emissions by comparing the simultaneously measured NO_x and NO_y fluxes measured in both a seasoned and a fresh shoot chamber, and by comparing the NO_x and NO_y fluxes measured in the shoot and blank chambers.

Statistical analyses

We tested whether the differences between the NO, NO₂ and NO_y concentrations measured using the chambers and simultaneously from the mast were statistically significant using a

paired t -test. We used three-hour averages of the concentrations. Our data were not completely normally distributed but the sample sizes ($n = 2063$ for the NO and NO_y concentration pairs in 2005–2006 and $n = 2480$ for the NO and NO₂ concentration pairs in 2007–2008) were so large that slight departures from normality are acceptable. The correlation between ultraviolet-A (UV-A) irradiance and the NO_y and NO_x fluxes was analysed using linear regression through minimization of the sum of squared residuals.

We also used the paired t -test to assess whether the largest NO_y emissions and the simultaneous NO_x emissions in the shoot chamber were higher than the corresponding emissions in the blank chamber. Since the measurement frequency in the blank chamber was lower than in the shoot chamber (around 40 min vs. 20 min), we calculated the shoot chamber fluxes as averages of two measurements. We included the highest 25% of the shoot chamber NO_y emissions (averages) and the parallel NO_x fluxes in the test and compared them with the temporally closest blank chamber NO_y and NO_x measurements. In addition, we filtered out pairs in which the difference in the UV-A irradiance between the shoot chamber and blank chamber measurement had been higher than 10 W m⁻² since solar irradiance and NO_y emission rate are strongly correlated. The final number of pairs was 129.

We performed all the statistical analyses using the built-in functions of the Matlab software (ver. R2010a).

Results

Accuracy of the concentration measurements

Comparisons of gas concentrations between chamber and mast

The ambient NO concentrations recorded using the chamber system were constantly higher than those measured from the mast, independent of the period considered. During the period 2005–2006, the mean difference was 0.2 ppb (paired t -test: $t_{2062} = 76.748$, $p < 0.0001$) and during 2007–2008 it was 0.4 ppb (paired t -test:

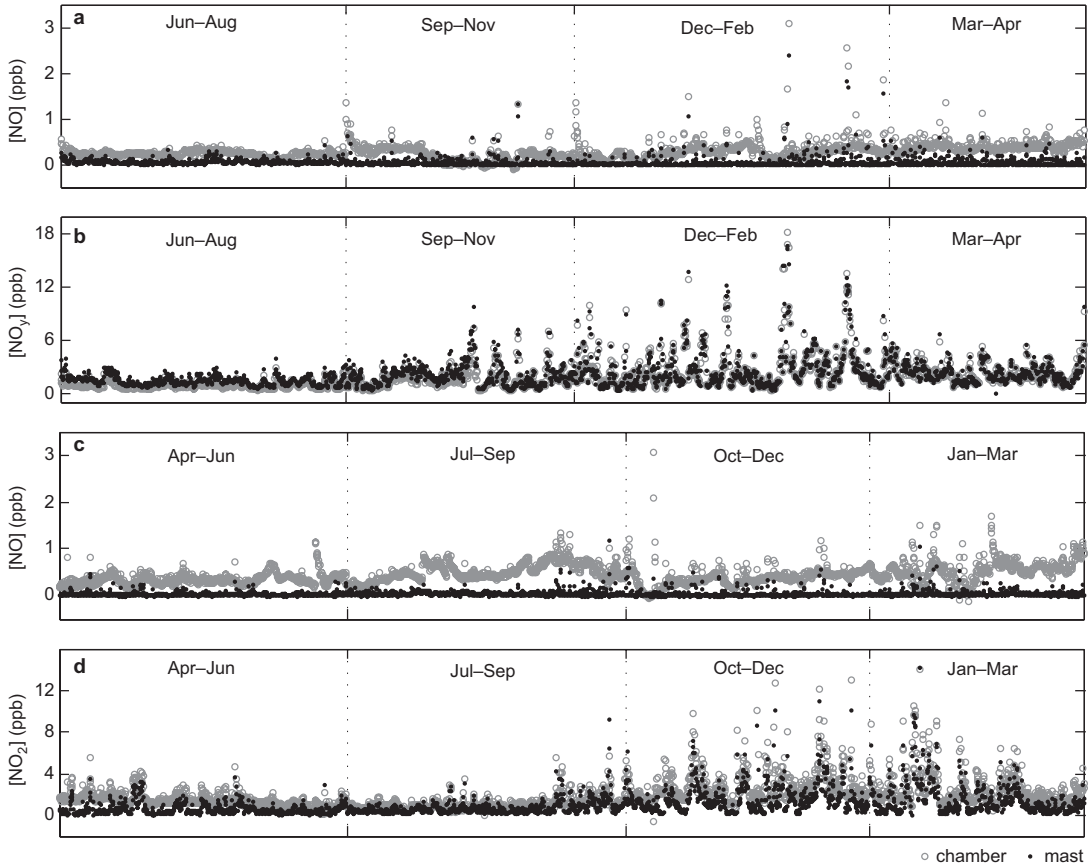


Fig. 1. Time series of NO, NO_y and NO₂ concentrations measured from samples taken from the chambers and from the mast. Each point represents the mean of one three-hour period. (a and b) Measurements obtained during 2005–2006 when we used the molybdenum converter. (c and d) Measurements obtained during 2007–2008 when we used the photolytic converter. Vertical dashed lines are shown for guidance.

$t_{2479} = 103.435$, $p < 0.0001$) (Fig. 1). Almost all of the NO₂ concentration values from the chamber system were higher than those measured from the mast; the differences varied but often exceeded 1 ppb (mean difference 0.45 ppb; paired t -test: $t_{2479} = 40.828$, $p < 0.0001$). In contrast, the NO_y concentrations measured by the chamber system were usually lower than those measured from the mast (mean difference 0.2 ppb; paired t -test: $t_{2062} = 24.694$, $p < 0.0001$).

In general, the overall difference in NO_y concentration values between chamber and mast seemed to be smaller than the difference in the total NO_x concentration values (NO + NO₂) between chamber and mast (Fig. 2). During the period November 2005 to April 2006 when the NO_y concentrations were relatively high, the dif-

ferences between the values obtained from the mast and from the chambers approached zero.

Trends in the PRE values

There were slight seasonal variations both in the PRE values and in the difference between the PRE values and the ozonator-off PRE values (i.e. in the residual variability of the PRE value that is left after eliminating the temperature dependency) (Fig. 3), especially for the NO and NO_x analyzers. The values were at their highest in summer. The only noticeable anomalies in the NO and NO_x PRE values were during the years 2008 and 2010. The year 2012 was also atypical for NO_x concentration measurements

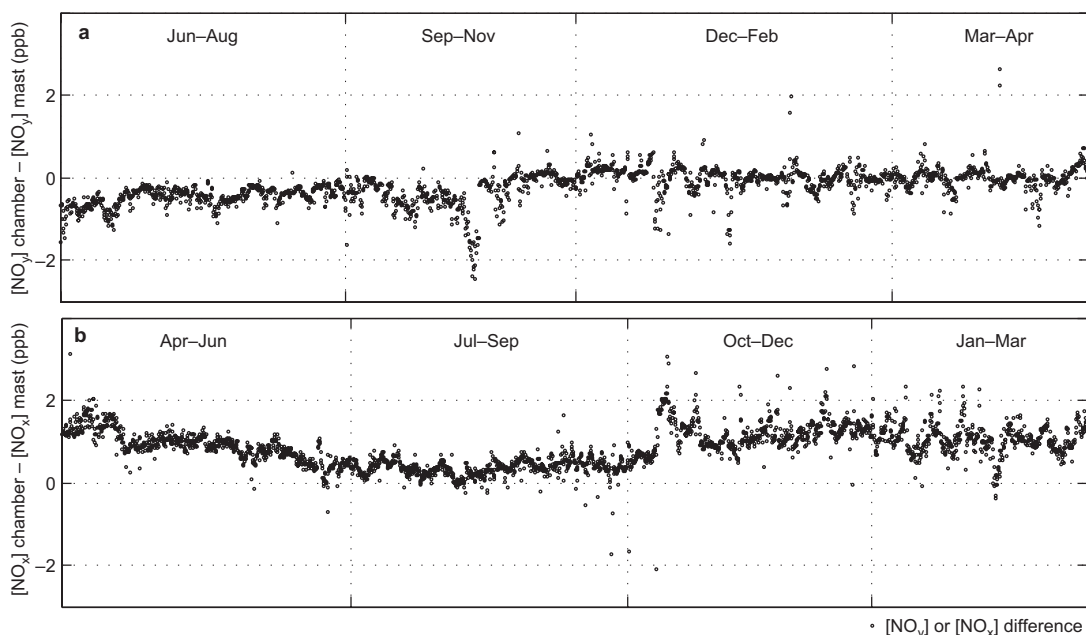


Fig. 2. Differences between the three-hour mean concentration values measured using the chambers and from the mast, (a) NO_y in 2005–2006 and (b) NO_x in 2007–2008. Negative values show that the concentration value from the chamber was lower than the value from the mast.

when the PRE values were higher than normal in spring and/or summer. We observed that the analyzer signal often temporarily increases after a break in the measurements. The reason for this is not clear. It can be due to contamination that originated from the exhaust line and spread by diffusion into the measurement chamber. Such an anomaly occurred in June 2012 when the NO_x signal level noticeably increased as a consequence of a power failure at the station.

The residual variability of the PRE value (Fig. 3) was highest for the NO_x analyzer: mean \pm SD = 0.6 ± 0.3 ppb. The corresponding value for the NO analyzer during 2006–2012 was 0.4 ± 0.2 ppb (SD). The comparable value for the NO_y analyzer, during the period analysed here (2004–2006), was 0.1 ± 0.06 ppb (SD).

Fluxes in the chambers

During the period analysed here, the NO_x emissions in the shoot chamber were lower than the NO_y emissions but they showed a diurnal pattern similar to the NO_y emissions. The emissions in

the shoot chamber before installing the clean chamber on 17 May 2006 (Julian day 137) correlated well with the UV-A irradiance: $r^2 = 0.92$ for NO_y fluxes and $r^2 = 0.81$ for NO_x fluxes (Fig. 4).

When the overwintered, seasoned shoot chamber was replaced by a fresh clean chamber on 17 May 2006, the daytime NO_y emissions dropped dramatically (Fig. 5). During the three days prior to the installation of the clean chamber, the mean NO_y emission rate at noon was about 13-fold higher compared with the mean midday NO_y emission rate during the first three days after the clean chamber was installed. The NO_x emissions also decreased after installing the clean chamber but this was not as large a decrease: the mean NO_x emission rate at noon before the installation was about five-fold higher than that recorded after the installation. In June, the NO_x and NO_y emissions, in particular, gradually increased in the shoot chamber (Fig. 5). A similar increase occurred in the other two shoot chambers, which were of a different type but which were also exchanged for cleaned chambers in May or June (data not shown). At the end of June, the daytime NO_y emission rates were

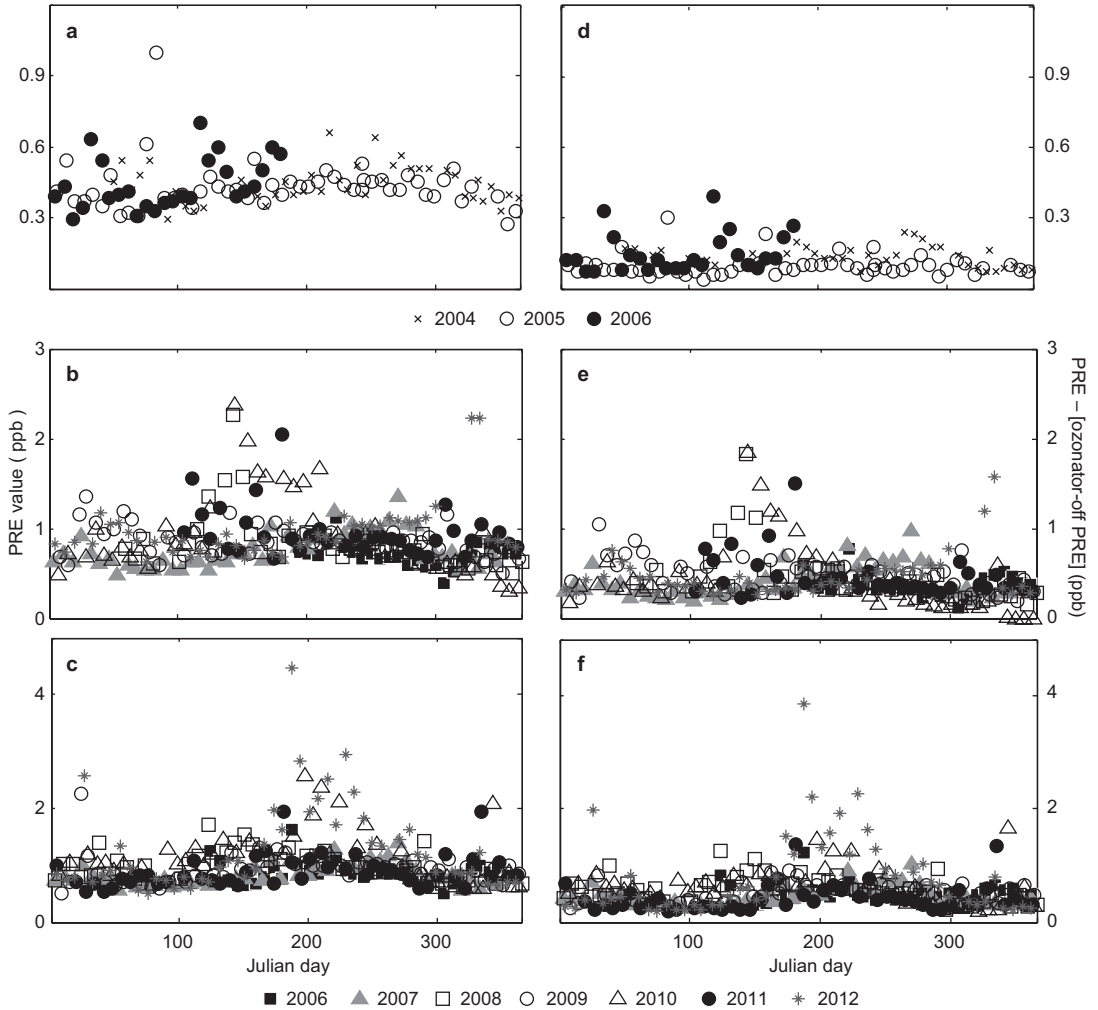


Fig. 3. On the left panel, manually recorded total PRE values over the years (a) for the NO_y analyzer, (b) for the NO analyzer and (c) for the NO_x analyzer. These values were used for correction of the measured concentrations. On the right panel, PRE values without the temperature dependency (residual variability of the PRE value) (d) for the NO_y analyzer, (e) for the NO analyzer and (f) for the NO_x analyzer.

around six to eight-fold those of the NO_x emissions. The NO fluxes in July were very small.

Simultaneous flux measurements from the blank chamber and the (clean) shoot chamber (Fig. 6) showed that the highest NO_y emissions (i.e. the highest 25% of the fluxes) from the shoot chamber were larger than the corresponding NO_y emissions from the blank chamber (mean difference 0.34 pmol s⁻¹; paired *t*-test: $t_{128} = 10.296$, $p < 0.0001$). There was not as clear a difference between the simultaneous NO_x emissions and they were practically of the same magnitude. However, the paired *t*-test indicated that

the NO_x emissions were slightly higher in the blank chamber (mean difference 0.082 pmol s⁻¹; paired *t*-test: $t_{128} = 5.323$, $p < 0.0001$). The NO_x emissions of the blank chamber remained below 1 pmol s⁻¹ for most of the time. In the shoot chamber, the NO_x flux as well as the NO_y flux occasionally turned to deposition, in contrast to the blank chamber. The NO_y emissions in the shoot chamber had a clearer diurnal pattern right from the beginning of this period. The difference between the NO_y flux and the NO_x flux also had a diurnal pattern in the shoot chamber; in the blank chamber the diurnal pattern was not as obvious.

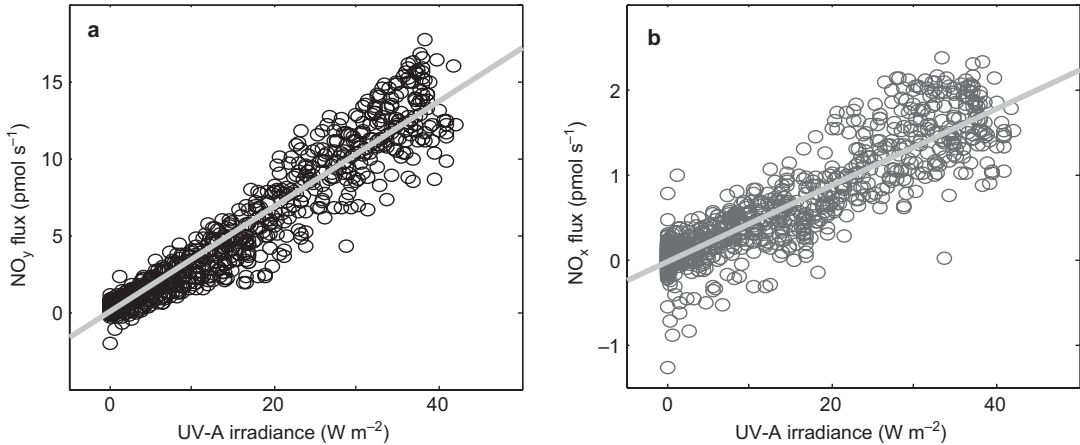


Fig. 4. Regressions between UV-A irradiance and (a) the NO_y flux ($y = 0.343x + 0.023$, $r^2 = 0.92$) and (b) the NO_x flux ($y = 0.0451x - 0.020$, $r^2 = 0.81$) in the shoot chamber before the chamber was replaced by a clean chamber. The period is 4–16 May 2006.

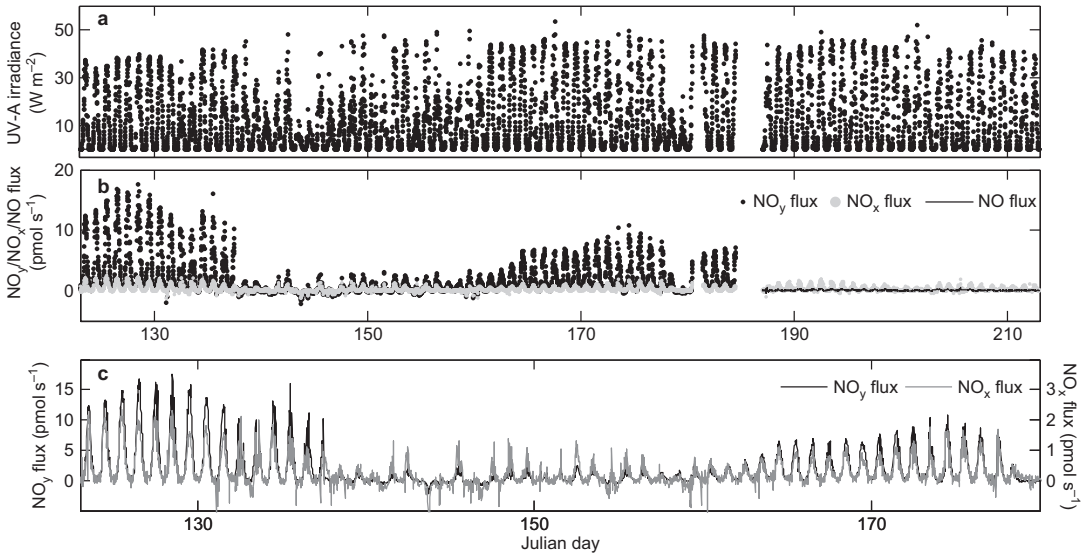


Fig. 5. (a) UV-A irradiance and (b) simultaneous NO_y , NO_x , and NO fluxes in a shoot chamber in May–July 2006. (c) NO_y and NO_x fluxes in the shoot chamber. The clean chamber was installed on 17 May 2006 (Julian day 137).

Discussion and conclusions

Evaluation of the concentration measurement systems

Our results indicated that when using the gas analyzers without the automatic zero offset correction in field conditions, the NO_y measurement system (chemiluminescence with heated molybdenum converter) performs slightly better than the NO_x measurement system (chemilumi-

nescence with photolytic converter) in producing accurate concentrations. The manually zero-corrected NO_y concentrations in the chamber and those of the mast measurements where the automatic zero-correction is used were on average more similar than the NO_x concentrations during the period analysed here, although still not exactly the same. However, the mean absolute differences between the NO_x concentrations measured in samples obtained from the chambers and those measured at the mast were small.

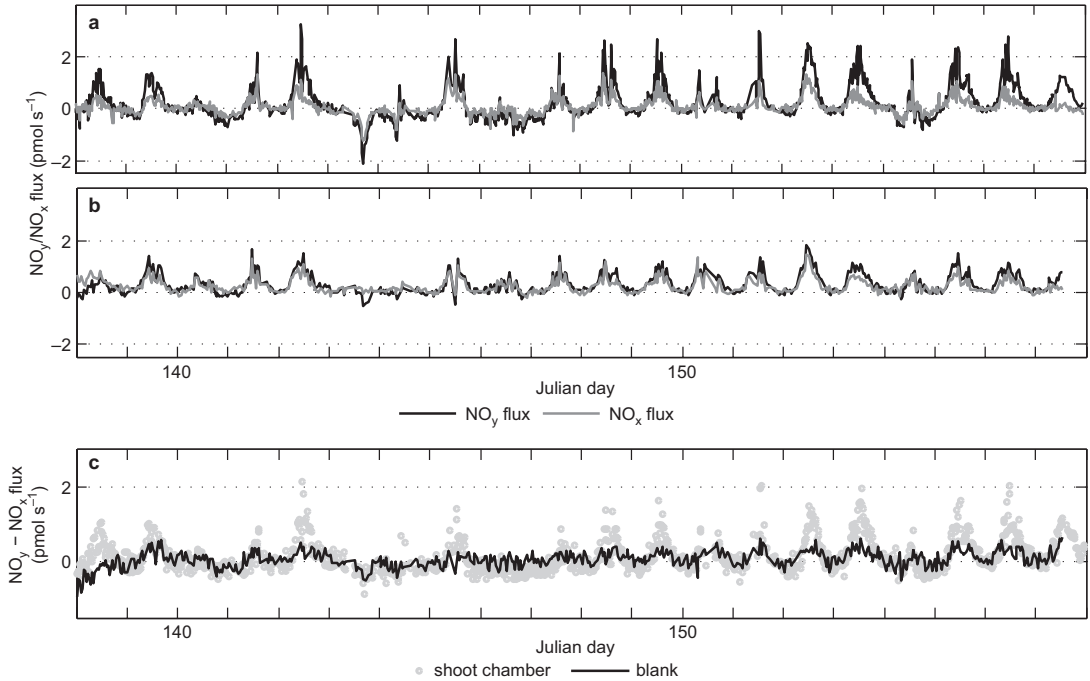


Fig. 6. NO_y and NO_x fluxes in (a) the shoot chamber and (b) the blank chamber. (c) Differences between the NO_y and the NO_x fluxes in the shoot chamber and in the blank chamber. The period is 18 May–6 June 2006.

We emphasize that the flux measurement itself does not require accurate absolute concentrations, as the flux is calculated from the difference in concentrations over time, although accuracy is needed, for instance, when studying the compensation point or the dependency of the flux on the ambient concentration. Therefore, additional concentration measurements with automatic zero-correction are necessary alongside the flux measurement.

One reason for the lower accuracy when using the photolytic converter may be that the NO and NO_x detection systems seem to be more sensitive to the properties of the sample air than the older NO_y measurement system we used. The PRE values and the residual variability of the PRE value obtained from the previous NO_y analyzer during the 2004–2006 period were generally low compared with the PRE values of the NO and NO_x analyzers used since 2006. Moreover, the PRE values of the NO and NO_x analyzers often showed more seasonal variation, being higher in summer than in winter. These variations were probably due to the fact that the background concentrations of many atmospheric gases are higher

in summer than in winter. We tested the sensitivity of the blue light converter to VOCs by introducing a bottled VOC mixture into the analyzer but it did not result in a signal of any significance. Nonetheless, our best guess is that it is the higher VOC concentrations that occur in summer that affect the background levels of the NO_x analyzer, directly or indirectly. VOC compounds have been found to affect the signal of photolytic converters (Villena *et al.* 2012).

It has been reported that the signal levels of chemiluminescence analyzers were affected by changes in atmospheric pressure and sample pressure (Doval-Miñarro *et al.* 2011) but not significantly by temperature (Doval-Miñarro *et al.* 2012). Accordingly, we take the pressure differences between the moment of instrument calibration and measurement into account when processing our data. Gerboles *et al.* (2003) reported that signal decreased by 8% when the relative humidity of the sample air increased from 0% to 80%. Signal quenching caused by humidity did not seem to affect our measurements significantly as the variation in ambient humidity in our study was not so large and according to

Gerboles *et al.* (2003) the quenching effect is relatively small.

A chamber measurement system with a longer measurement time would allow for automatic zero-level correction. Indeed such a system was used by other research groups (e.g. Hereid and Monson 2001, Gefßler *et al.* 2002, Chaparro-Suarez *et al.* 2011, Breuninger *et al.* 2012, 2013) but is incompatible with the dynamic chamber system. However, the dynamic chambers we used in this study have advantages for long-term field monitoring. To date, nearly all studies on NO_x exchange of plants have been short-term field or lab-based studies. The value of continuous field monitoring is that it provides valuable data for model development and validation as well as information on how the processes respond to long-term changes in the environment.

Chamber fluxes

During the period when we simultaneously monitored the NO_y and NO_x fluxes in the chambers, they almost always occurred as emissions and rarely as depositions, and for most of the time the NO_y emissions were higher than the NO_x emissions. In this context, NO_y flux is not a good proxy for NO_x flux in field chamber measurements. There evidently is something in the system that is only detectable by the NO_y analyzer, and whose emission increases over time, which becomes significant in long-term monitoring of the fluxes. Possible contamination of the chambers (Raivonen *et al.* 2003, Raivonen *et al.* 2006) does not seem to be as big a problem with the photolytic converter as was the case with the NO_y measurement. Although both the NO_x and NO_y emissions in the shoot chamber increased over time, the absolute increase was clearly smaller for the NO_x emissions than for the NO_y emissions.

It now seems obvious that the UV-induced NO_y emissions observed in our earlier studies (Hari *et al.* 2003, Raivonen *et al.* 2006) included possible nitrogenous compounds other than NO_x . Other NO_y compounds that can be detected by the molybdenum converter and could possibly be a component of the NO_y fluxes are HNO_3 ,

HONO and PAN (Gerboles *et al.* 2003). We can probably exclude the very reactive compound HNO_3 as it should not be able to pass through the sample lines and in-line particle filters in our measurement system. It should be noted, however, that photolytic NO_x detection systems are probably also limited by interference from some other compounds, for example, HONO (Ryerson *et al.* 2000). Hence, even the photolytically measured NO_x fluxes do not necessarily consist of only NO and NO_2 .

We are not aware of any other published studies that compared the measurements of NO_y and NO_x fluxes at the leaf level. However, molybdenum and photolytic converters have been compared in other types of studies. For instance, Steinbacher *et al.* (2007) measured NO_2 concentrations in rural Switzerland using these two methods and found that only 43%–83% (depending on the site) of the NO_y was actually NO_x . Xu *et al.* (2013) found that the two conversion methods gave relatively similar results when measuring atmospheric NO_x concentrations close to the emission sources, in urban areas, but at a rural site the molybdenum method overestimated the NO_x concentrations by as much as 130%–260%. In remote locations and in aged air masses, there is an increase in the relative importance of the more oxidized NO_y species.

Zhou *et al.* (2011) measured HONO fluxes in a forest using the eddy covariance method and measured emissions of HONO. The source of HONO seemed to be the photolysis of HNO_3 . Their analysis indicated that HONO was the main product of the photolysis, which contradicts the findings of the earlier studies done with other surface materials for which the main product was NO_x (Zhou *et al.* 2003). Zhou *et al.* (2011) suggested that the HONO/ NO_x ratio becomes greater (~1–5) in field conditions where water and organic compounds are present, thus enabling further chemical reactions. This is very interesting in the light of our flux measurements. We certainly had water vapour and VOC present in our system, so the proportion of HONO could be higher than NO_x as a result of HNO_3 photolysis on the surfaces of the pine needles. Photo-induced HONO and NO_x emissions from leaf surfaces were strongly supported by the studies of Zhou *et al.* (2011) and Zhang *et al.* (2012).

However, it was contradicted by Seok *et al.* (2013) who studied the canopy processes of NO_x using the molybdenum converter and by modelling them as canopy exchanges. Those authors included the leaf-surface nitrate photolysis factor in their model as a source of NO_x but found that this did not explain all the measured NO_x patterns they observed. However, the inclusion of the NO_2 compensation point in the model did improve the model fit.

Although HONO emissions from leaf surfaces seem to be possible (Zhou *et al.* 2011, Zhang *et al.* 2012), the present data did not provide a clear indication of NO_y compounds being emitted from the pine needles. Comparisons between the simultaneous fluxes in the blank chamber and in the newly installed clean shoot chamber showed that the NO_x emissions from both were more or less similar. The NO_y emissions rose higher in the shoot-containing chamber and they also had a clearer diurnal variation than the NO_y emissions of the blank chamber; these emissions might have originated from the pine needles. However, installation of the fresh clean chamber around the pine shoot caused a dramatic drop in NO_y emissions to levels similar to the blank chamber, which indicates that the high NO_y emissions observed before the installation had only come from the walls of the seasoned chamber. By the time that the blank chamber had been removed, the NO_y emissions from the shoot chambers had started to increase, so we do not know whether the blank chamber would have given a similar measurement. NO_y emissions from blank chambers have usually had a similar tendency to increase over time (Raivonen *et al.* 2003).

Whether our measurement system is generally able to detect the low plant-related NO_x fluxes can be evaluated by a comparison with literature values. The typical all-sided needle area in our shoot chambers has been around 0.02 m². Using this area as a standard, the published NO_2 deposition rates at an ambient NO_2 concentration of about 4 ppb and with open stomata were approximately 4 pmol s⁻¹ (Rondón and Granat 1994) and 3 pmol s⁻¹ (Chaparro-Suarez *et al.* 2011) for Scots pine, and 1 pmol s⁻¹ (Thoene *et al.* 1991, Breuninger *et al.* 2013) and 0.2 pmol s⁻¹ (Geßler *et al.* 2002) for spruce.

Maximum reported NO_2 emission rates were 1.5 pmol s⁻¹ (Wildt *et al.* 1997) for several different plant species, and 0.5 pmol s⁻¹ (Hereid and Monson 2001) for corn. The maximum NO_x emission rate in our blank chamber during the period analysed here was about 1 pmol s⁻¹. Hence, we are able to detect these low NO_x fluxes despite the emissions from the chamber walls, at least when the chambers are maintained and kept clean.

We assume that one reason for the conflicting reports on the NO_x fluxes in conditions of low ambient concentrations is simply that the chamber measurements are complicated and often the detection limit of the instrumentation is too high to detect the small fluxes that occur in these conditions. In general, innovative experimental studies that directly focus on testing the main hypotheses concerning the processes behind possible NO_x emissions are required to answer the question: Do plants really emit NO_x ? Several studies have indicated that physiological NO_x emissions depend on the nitrogen status of the plant, especially the availability of free nitrate (NO_3^-) or nitrite (NO_2^-) in the plant leaves (Klepper 1979, Wildt *et al.* 1997, Meyer *et al.* 2005). For instance, testing the effect of different nitrogen nutrients (NO_3^- or ammonium) on the NO_x exchange of plants (*see* Wildt *et al.* 1997) would be useful both in the laboratory and in the field. Perhaps experiments with labelled nitrogen could also disclose whether the plants are able to emit NO_x that originated from the soil nitrogen. Another possibility is that NO_x emission from vegetation is generated by photochemistry on the leaf surfaces, which recycles deposited NO_3^- back to the atmosphere. This possible route should also be studied further, both in the laboratory and under field conditions.

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