Dissertationes Forestales 71

UV-induced NO_y emissions in gas-exchange chambers enclosing Scots pine shoots: an analysis on their origin and significance

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Academic Dissertation

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ABSTRACT

It is essential to have a thorough understanding of the sources and sinks of oxidized nitrogen (NO_y) in the atmosphere, since it has a strong influence on the tropospheric chemistry and the eutrophication of ecosystems. One unknown component in the balance of gaseous oxidized nitrogen is vegetation. Plants absorb nitrogenous species from the air via the stomata, but it is not clear whether plants can also emit them at low ambient concentrations. The possible emissions are small and difficult to measure.

The aim of this thesis was to analyse an observation made in southern Finland at the SMEAR II station: solar ultraviolet radiation (UV) induced NO_y emissions in chambers measuring the gas exchange of Scots pine (*Pinus sylvestris* L.) shoots. Both measuring and modelling approaches were used in the study. The measurements were performed under noncontrolled field conditions at low ambient NO_y concentrations.

The chamber blank i.e. artefact NO_y emissions from the chamber walls, was dependent on the UV irradiance and increased with time after renewing the Teflon film on chamber surfaces. The contribution of each pine shoot to the total NO_y emissions in the chambers was determined by testing whether the emissions decrease when the shoots are removed from their chambers. Emissions did decrease, but only when the chamber interior was exposed to UV radiation. It was concluded that also the pine shoots emit NO_y. The possible effects of transpiration on the chamber blank are discussed in the summary part of the thesis, based on previously unpublished data.

The possible processes underlying the UV-induced NO_y emissions were reviewed. Surface reactions were more likely than metabolic processes. Photolysis of nitrate deposited on the needles may have generated the NO_y emissions; the measurements supported this hypothesis. In that case, the emissions apparently would consist mainly of nitrogen dioxide (NO_2), nitric oxide (NO) and nitrous acid (HONO). Within studies on NO_y exchange of plants, the gases most frequently studied are NO_2 and NO (=NO_x). In the present work, the implications of the emissions for the NO_x exchange of pine were analysed with a model including both NO_y emissions and NO_y absorption. The model suggested that if the emissions exist, pines can act as an NO_x source rather than a sink, even under relatively high ambient concentrations.

Keywords: NO_x deposition, compensation point, nitrate photolysis, chamber blank

ACKNOWLEDGEMENTS

My first step towards this thesis were taken in spring 1999 when I discussed possible themes for my master's-thesis-to-be with Prof. Pepe Hari. Having said my interests were more with solar radiation than soil, Pepe proposed that I'd start to look at UV-induced NO_x emissions from trees that had lately been observed at the SMEAR II station. At that time I had no idea what it meant, but I said yes and gradually got to understand what is going on in the chambers — occasionally not. But in any case, here we now are, and my doctoral thesis is completed, which is very good!

I give my warmest thanks to Pepe for taking me into his group, supervising this work, being always ready to discuss, and for teaching me to think scientifically. I also thank my other supervisor, Prof. Markku Kulmala, for the interest he has shown in my work and for supporting it from the physics side of the research group in many ways.

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LIST OF ORIGINAL ARTICLES

The thesis is based on the following research articles which are referred to in the text by their Roman numerals:

I	Pertti Hari, **Maarit Raivonen**, Timo Vesala, J. William Munger, Kim Pilegaard, Markku Kulmala. 2003. Ultraviolet light and leaf emission of NO_x. *Nature*, 422: 134.
II	**Maarit Raivonen**, Petri Keronen, Timo Vesala, Markku Kulmala, Pertti Hari. 2003. Measuring shoot-level NO_x flux in field conditions: the role of blank chambers. *Boreal Environment Research* 8: 445 – 455.
III	**Maarit Raivonen**, Boris Bonn, María José Sanz, Timo Vesala, Markku Kulmala, Pertti Hari. 2006. UV-induced NO_y emissions from Scots pine: Could they originate from photolysis of deposited HNO_3? *Atmospheric Environment* 40: 6201-6213.
IV	**Maarit Raivonen**, Timo Vesala, Liisa Pirjola, Nuria Altimir, Petri Keronen, Markku Kulmala, Pertti Hari. Compensation point of NO_x exchange: net result of NO_x consumption and production. Submitted manuscript.

Author's contribution:

I	M. Raivonen participated in writing the paper and she was responsible for the experimental work and data analysis.
II	M. Raivonen was the principal author of the article and she was responsible for the experimental work and data analysis, except the transmittance measurements of quartz and Plexiglas.
III	M. Raivonen initiated the study and she was the principal author. She was responsible for the experimental work and data analysis, except implementing the rinsing experiment and calculating the CO_2 fluxes.
IV	M. Raivonen was the principal author of the study. She was responsible for the experimental work and data analysis, except estimating the stomatal conductances.

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1. INTRODUCTION

1.1 Background

Nitrogen is a very common component in the atmosphere: about 78% of the air consists of dinitrogen (N_2) molecules. This N_2 is chemically inert, meaning that it does not react with anything under common atmospheric conditions. However, in certain circumstances, such as in the metabolism of nitrogen-fixing micro organisms or in some industrial processes, N_2 can be fixed. These fixed, reduced and oxidized nitrogen species are now ready to participate in atmospheric chemistry. The main reduced form of nitrogen is ammonia (NH_3), which contributes to the fertilizing nitrogen input into ecosystems and the formation of atmospheric aerosol particles. However, a much more central role in atmospheric chemistry is played by oxidized nitrogen. The main primary product of oxidation is nitric oxide (NO), with small portion of nitrogen dioxide (NO_2). Once in the air, NO oxidizes further to NO_2 so easily that NO_2 is more abundant in the normal atmosphere. These species, together referred to as nitrogen oxides (NO_x), are among the key components of tropospheric chemistry.

Lightning is a major natural source of tropospheric NO_x. In the extreme heat of the lightning channel, N_2 and oxygen (O_2) molecules dissociate and form NO (Goldenbaum and Dickerson 1993). The functioning of some soil microbes generates NO as a by-product, the principal processes being nitrification (oxidation of ammonium ions (NH_4^+) to nitrate (NO_3^-)) and denitrification (reduction of NO_3^- or nitrite (NO_2^-) to N_2 or N_2O). The NO emission rate and magnitude are dependent on soil nitrogen availability, soil moisture and soil temperature, and the emissions are highest from cultivated fertilized soils, but low from forests and other natural systems (Ludwig et al. 2001). Anthropogenic NO sources include fuel combustion and biomass burning. Within these, the temperatures can be high enough to dissociate N_2 and O_2, and NO is also released when the burning materials contain fixed nitrogen (Logan 1983). In addition to these, the troposphere receives a small input of NO_x from the stratosphere.

Table 1 shows the estimated global NO_x emissions for the years 1860, 1993 and 2050, according to Galloway et al. (2004). Before industrialization and until the 19th century, lightning was the most important NO_x source. However, during the 20th century anthropogenic emissions, especially from fossil fuel burning, increased remarkably, while soil as a source has also grown in importance, because soil fertilization (human-made and natural, i.e. originating from increased deposition) increases emissions.

Table 1. Past, present and future global NO_x emissions (Tg N yr^{-1}) in (Galloway et al. 2004).

	1860	**1993**	**2050**
Lightning	5.4	5.4	5.4
Soils	2.9	5.5	8
Energy prod. (incl. fossil fuel burning)	0.6	27.2	57
Biomass burning	3.6	7.2	10.5
Stratospheric injection	0.6	0.6	0.6
TOTAL	**13.1**	**45.9**	**81.5**

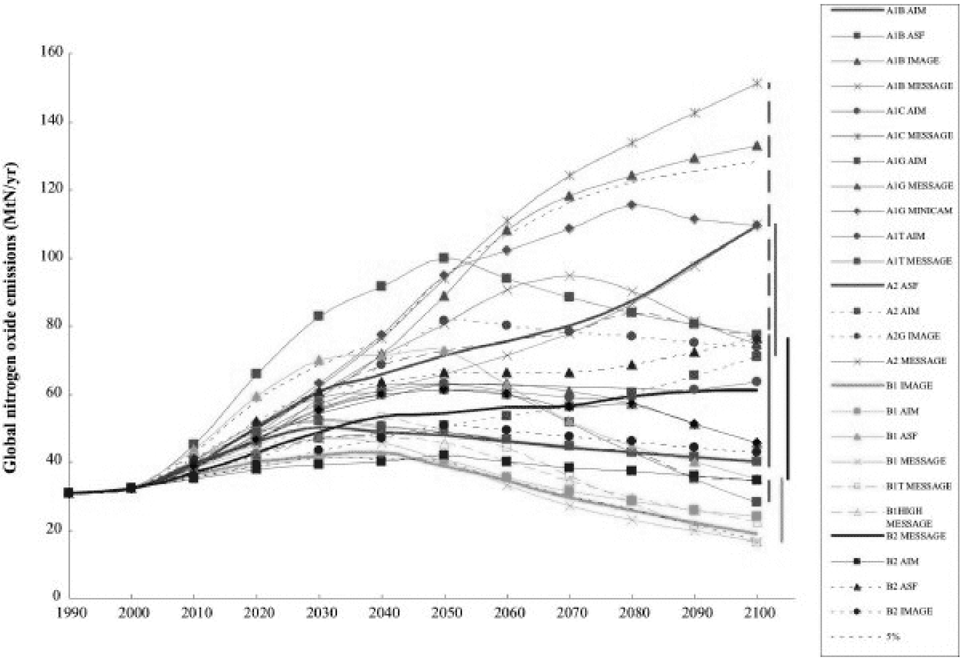

Figure 1. Divergence of NO_x emission predictions based on different scenarios by the IPCC (Fig. 5–9 of Special report on emission scenarios, IPCC, 2000). Reprinted in black and white, using a different caption with permission from the IPCC Secretariat.

Galloway et al. (2004) predicted that emissions will continue to increase, but contrasting estimates exist. The Intergovernmental Panel on Climate Change IPCC (2000) compared several different emission scenarios (Fig. 1). All of them projected increasing emissions until the year 2020, after which they diverge, mainly depending on how the future of fossil fuel use is seen in each scenario. None of the scenarios included emissions from soils. The industrialized regions of the world, such as the USA and Europe, have already reduced their NO_x emissions; e.g., Europe reduced its emissions almost 35% from 1990 to 2005 (European Environmental Agency (EEA) 2007). However, emissions are continuing to increase strongly in the developing countries (IPCC 2007).

In the atmosphere, NO_x species become oxidized further to nitric acid (HNO_3), which is the main oxidation product, nitrous acid (HONO), the nitrate radical (NO_3), dinitrogen pentoxide (N_2O_5) and various organic nitrogen species, such as peroxyacyl nitrates (PANs, $RC(O)OONO_2$), among others (Fig. 2). The group of reactive nitrogen is often referred to as NO_y. NO_x as well as NO_y species are trace gases: they make up less than 1% of the earth's atmosphere, and the concentrations are not high in relative values. The usual NO_x concentrations at rural sites are only a few parts per billion (ppb), being well below 1 ppb in the most remote areas, while in urban regions the concentrations are generally at tens of ppb and the peak values in large cities have approached 1000 ppb (International Programme on Chemical Safety (IPCS) 1997, Seinfeld and Pandis 1998). Of all the NO_y species, NO and NO_2 are the ones present in the highest concentrations close to major anthropogenic NO_x sources, i.e. in urban areas. However, in remote and rural locations and in aged air masses, the relative importance of the more oxidized NO_y species increases.

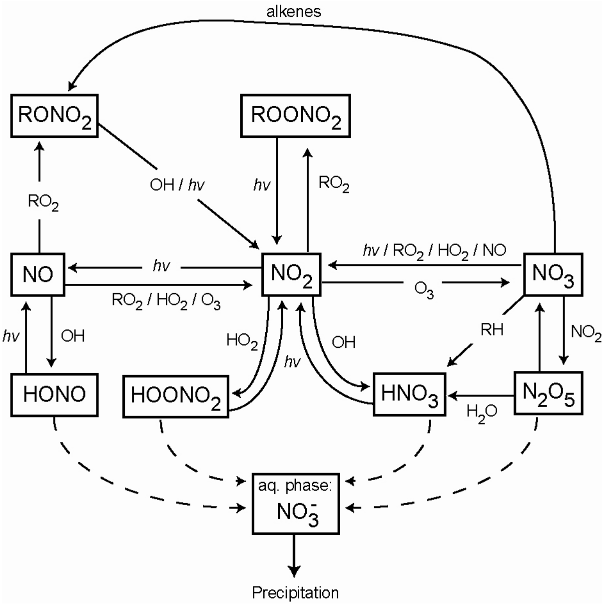

Figure 2. NO_y chemistry according to Seinfeld and Pandis (1998).

PAN especially is relatively abundant in rural areas. It dissociates by heat, but under cool conditions it is in general very stable and can thus transport NO_x in the upper troposphere over long distances. After downward mixing, it can also release active NO_x in rural areas (Moxim et al. 1996).

One reason for the interest in tropospheric NO_x concentrations is that abundant NO_x directly harms living organisms. NO_x exposure can cause visible injury, inhibition of photosynthesis and reduction of growth in plants, and lung structural alterations and problems with lung functioning in animals and humans, especially asthmatics (IPCS 1997, Wellburn 1990). However, these effects have mostly been found in concentrations of several hundred ppb, which do not usually occur in the atmosphere. When the concentrations of NO_x are at their usual atmospheric levels, their importance lies in participation in essential atmospheric chemical reactions.

Nitrogen oxides directly affect the concentrations of tropospheric ozone (O_3) and the hydroxyl radical (OH), which are two important oxidants in the atmosphere (Fig. 3). The net production rate of O_3 is dependent nonlinearly on the NO_x concentration present: whether the increase in NO_x produces or destroys O_3 is dependent on the relative concentrations of pollutant gases in the air. In rural areas, NO_x increase typically enhances O_3 production, while in urban areas it may lead to decrease in O_3 (Seinfeld and Pandis 1998). OH radicals are produced via three routes that are all associated with NO_x: reaction of water vapour with electronically excited oxygen atoms that originate from O_3 photolysis, HONO photolysis and reaction of hydroperoxy (HO_2) radicals with NO. NO_x also contributes to the formation of nitrate-aerosols. The atmospheric balance of NO_x is thus relevant to climate change, since O_3 is a greenhouse gas, OH radicals reduce methane (CH_4) which is an even stronger greenhouse gas and the nitrate aerosols have a cooling effect on the earth (Kulmala et al. 1995). The net effect of NO_x emissions on warming has

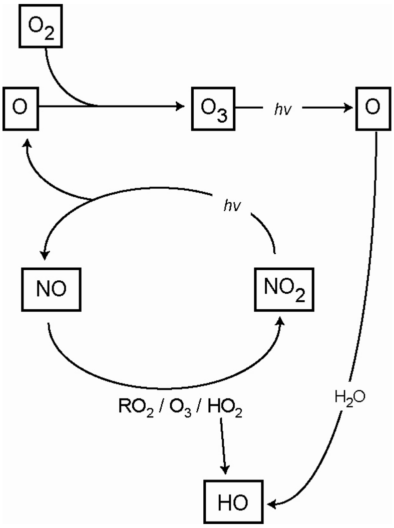

Figure 3. Schematic of the association between NO_x, O_3 and OH cycles.

not yet been determined, due to the complexity of these three different processes (IPCC 2007).

NO_x disappear from the air mainly in wet and dry deposition of HNO_3 and particulate nitrate onto terrestrial surfaces. HNO_3 is one of the most water-soluble atmospheric gases, and after the dissolution to water that is present on all atmospheric surfaces (Sumner et al. 2004) it dissociates to NO_3^-. NO_3^- deposition has a major effect on Earth, since nitrogen is the most important plant nutrient. In most terrestrial and also many oceanic ecosystems, net primary production is limited by nitrogen availability, and increased growth due to increasing nitrogen deposition (NO_3^- together with NH_3) was observed (Holland et al. 1997, Magnani et al. 2007). Hence, nitrogen deposition is crucial to climate change, because it also affects the carbon (C) cycle (Gruber and Galloway 2008). This eutrophication also has negative effects; e.g. it can alter the species composition, favouring those with high nitrogen-demand, and in aquatic ecosystems the excess growth can lead to lack of O_2 (Vitousek et al. 1997). Nitrate deposition is harmful because it is also acidic; acid rain can injure, for instance, conifer needles (Bäck and Huttunen 1992). When negative NO_3^- ions move through soils, they take nutrient cations along, which again increases the leaching of toxic aluminium (Al).

It has been suggested that, in fact, deposition of HNO_3 and NO_3^- on Earth's surfaces may not be an irreversible sink for NO_x. For instance, Honrath et al. (1999) and Dibb et al. (2002) observed NO_x and HONO emission from snow in sunlight irradiation, and this was attributed to photolysis of nitrate. The emissions were considered an important source of reactive nitrogen in areas with otherwise low pollutant levels, such as the snow-covered and remote polar areas. Grannas et al. (2007) showed that the atmospheric effects of these emissions occurring at a time when the global warming is changing Earth's cryosphere, can be significant. Zhou et al. (2003) also demonstrated production of NO_x and HONO from HNO_3 photolysis on glass surfaces and suggested that these reactions may also occur on other terrestrial surfaces, such as on vegetation.

The biosphere is one of the uncertain components in the atmospheric balance of gaseous NO_x. It is known that soils can emit NO, and the factors affecting the emissions are understood to some degree. However, it is not known how vegetation covering the soil contributes to the role that an ecosystem as a whole plays in the total NO_x balance (Lerdau et al. 2000). Plants can absorb NO_x via their stomata, at least at ambient NO_x concentrations above the background levels (e.g. Sparks et al. 2001), but it is not clear what they do when the concentration approaches zero. Some studies have shown that plants can then emit NO_x (e.g. Wildt et al. 1997). How frequent this really is remains unknown, partly because measuring the NO_x exchange of plants at very low concentrations means small fluxes that are near the detection limits of instrumentations. However, the possible NO_x emission from plants is definitely an interesting phenomenon. Over large vegetated areas in the world the atmospheric NO_x concentrations are usually very low. Thus, the vegetation may act as an NO_x source, and not remove NO_x emitted by the soil.

1.2 NO_y fluxes on plant leaves

Basic nitrogen metabolism in plants

Nitrogen is the most important plant nutrient, since plants need it quantitatively much more than other nutrients. Nitrogen is used, for instance, in proteins and nucleic acids. Plants take up nitrogen via their roots, mainly as NH_4^+ and NO_3^- (Tischner 2000). NH_4^+ can be assimilated as such into different organic compounds, but NO_3^- must first be reduced to NH_4^+. The enzymes taking care of the reduction are nitrate reductase (NaR), which reduces NO_3^- into nitrite (NO_2^-), and nitrite reductase (NiR) that transforms NO_2^- to NH_3:

$$NO_3^- \xrightarrow{NaR} NO_2^- \xrightarrow{NiR} NH_3$$

NO_3^- reduction occurs either in the roots or in the shoots, and NO_3^- can be stored before use in several parts of the plant. However, when the supply of NO_3^- is low, which is usually the case in forests, the reduction and assimilation already occur in the roots.

NO_y deposition

Hill (1971) showed that plants remove nitrogenous pollutant gases, especially NO_x, from the air via their stomata. Nitrogen of the gaseous NO_x can be assimilated and utilized in plant metabolism (e.g. Yoneyama and Sasakawa 1979), and the same seems to apply to HONO (Schimang et al. 2006).

Gas molecules move from the air into the plant by diffusion. The flow of a gas through plant stomata is controlled by the degree of stomatal opening and the concentration difference between the ambient air and substomatal cavities (e.g. Nobel 1991). The solubility of the gas into the cell wall liquid and rates of other reactions consuming the dissolution products determine how rapidly the gas disappears. In other words, these factors determine how close the external concentration is to the concentration inside the stomata. They are often referred to as the internal or mesophyllic resistance of the flux.

Of all the NO_y species, NO_2 is the one most widely studied in the context of stomatal uptake. Its uptake rate is dependent on the degree of stomatal opening (e.g. Rondón and Granat 1994, Geßler et al. 2002), but observations on the relationship between external and internal NO_2 concentrations are diverse. In some cases, there have been no signs of limitation other than the stomatal control: with a constant degree of stomatal opening the NO_2 uptake flux was dependent linearly on the external NO_2 concentration (Rondón et al.

1993, Rondón and Granat 1994, Geßler et al. 2002). In other studies, the fluxes were smaller than had been predicted only on the basis of external concentration, indicating the internal reactions to be so slow that the NO_2 concentration inside the stomata could not be considered zero (Johansson 1987, Thoene et al. 1991, Rondón et al. 1993, Thoene et al. 1996, Teklemariam and Sparks 2006).

There are strong candidates for these internal reactions. Ramge et al. (1993), using a mathematical model, determined whether apoplastic antioxidants, especially ascorbic acid, could contribute to the reduction of NO_2 after it entered the stomata. The experimental observations on NO_2 uptake rates, found in the literature, fitted with their model when it included the antioxidants. This theory was supported by Teklemariam and Sparks (2006), who found that higher leaf ascorbate concentrations were associated with higher leaf NO_2 uptake rates in several plant species. Furthermore, Eller and Sparks (2006) found that the degree of stomatal opening, apoplastic ascorbate concentrations and NaR activity explained the NO_2 deposition fluxes fairly well. NaR apparently controlled the flux by determining how rapidly the nitrate, formed within the dissolution, disappeared from the cell wall. The authors suggested that the observed variation in the NO_2 uptake rates, or in the relationship between external and internal NO_2 concentrations, could have originated from differences in NaR concentrations in different plant species.

The leaf surfaces can also be a small NO_2 sink (Hanson et al. 1989, Geßler et al. 2002). Mechanisms suggested to be responsible for this nonstomatal absorption include irreversible adsorption and/or cuticle penetration (Lendzian and Kerstiens 1988), bacterial activity (Papen et al. 2002) and absorption by thin water films on leaf surfaces (Thoene et al. 1996, Weber and Rennenberg 1996). However, observations on the effect of relative humidity (RH), in which the thickness of water films is dependent, on non-stomatal absorption, are not consistent: sometimes the RH had an effect (Thoene et al. 1996, Weber and Rennenberg 1996), sometimes not (Grennfelt et al. 1983, Johansson 1987, Rondón et al. 1993).

There are also studies on fluxes of NO_y species other than NO_2. Uptake of NO into the stomata has generally been negligible or clearly lower than that of NO_2, apparently because the solubility of NO in water is lower (Johansson 1987, Hereid and Monson 2001, Teklemariam and Sparks 2006). Although the fluxes are small, they are apparently controlled by the degree of stomatal opening and ambient concentration (Teklemariam and Sparks 2006). PANs are also taken up by plants and the degree of stomatal opening controls the flux (Hill 1971, Sparks et al. 2003, Teklemariam and Sparks 2004). The absorption is not as large as for NO_2; Teklemariam and Sparks (2004) showed its magnitude is closer to the values measured for NO. PAN is mainly taken up by the stomata, not adsorbed by the surface (Doskey et al. 2004). In the only study on HONO uptake (Schimang et al. 2006), HONO uptake was significant, proportional to the ambient HONO concentration and linearly related to stomatal conductance. HNO_3 apparently forms deposits mainly on the leaf surfaces, since it is a very reactive species, and deposits effectively on every surface it contacts (Seinfeld and Pandis 1998, Sievering et al. 2001).

NO_y emission

Of the NO_y species, only NO_x also appears to be emitted from plants. However, it remains a controversial issue: emission of NO_x has been suggested and also observed, but not always. It is generally believed that at ambient concentrations below a certain threshold, i.e. the compensation point, plants can emit NO and NO_2. However, not all canopy-level measurements support this idea: vegetation also appeared as an NO_x sink at low concentrations (Jacob and Wofsy 1990, Kirkman et al. 2002).

At the leaf or branch level, observations have been variable. Thoene et al. (1991) measured NO_2 exchange of Norway spruce (*Picea abies* (L.) *H. Karst.)* and detected neither deposition nor emission at concentrations below 2.6 ppb. Rondón and Granat (1994) found, with both Norway spruce and Scots pine (*Pinus sylvestris* L.), that the NO_2 fluxes at concentrations lower than 1 ppb were usually below the detection limit of their instrumentation and no NO_2 emission was observed. Geßler et al. (2000) observed no significant emission of NO_2 from beech (*Fagus sylvatica* L.) leaves in clean air. By contrast, Rondón et al. (1993) discovered NO_2 emission from Scots pine at concentrations below 0.7 ppb, Weber and Rennenberg (1996) from wheat (*Triticum aestivum* L.) at concentrations lower than 1.15 ppb, Hereid and Monson (2001) from corn (*Zea mays* L.) leaves below 0.9 ppb, Sparks et al. (2001) from tropical wet forest species below 0.52–1.60 ppb, and Geßler et al. (2002) from spruce below 1.7 ppb.

Theories concerning the mechanisms that underlie the emissions have been suggested mainly for NO. All started apparently from Klepper (1979), who observed NO and NO_2 emission from soybean (*Glycine max* (L.) Merr.) plant tissue that had been treated with an herbicide that blocked nitrite reduction. He proposed that the emissions originated from reactions between the accumulated NO_2^- and plant metabolites. Later, Wildt et al. (1997) conducted an extensive study showing that several higher plants emit NO. Emission was found only when the plants received NO_3^- as nutrient, not when the nutrient solution contained NH_4^+ only. Thus, also here the emission was apparently dependent on the existence of NO_3^- or NO_2^- in leaves. These NO emissions were positively related to carbon dioxide (CO_2) uptake rate but not to stomatal aperture. Sparks et al. (2001) found that the NO_2 compensation points were higher in plants with high leaf nitrogen content, which indicates that the emissions were associated with the nitrogen metabolism. Interestingly, the emission rate was not related to the degree of stomatal opening or to the photosynthesis rate.

The NO molecule has raised interest in biology because it acts as a gaseous signaller both in animals and plants. The journal Science even chose NO as the "molecule of the year" in 1992 (Koshland 1992). In plants, it is involved in the regulation of stomatal closure, germination and defence responses (Lamattina et al. 2003). Synthesis of NO has been studied, and the two most important mechanisms appear to be that NaR produces NO from nitrite, and that a nitric oxide synthase (NOS) produces NO from arginine (Crawford 2006). The excess NO, which can be emitted via the stomata, may come from the reaction between NaR and nitrite. Meyer et al. (2005) suggested that essential plant functions such as stomatal control would probably not be regulated by a reaction this uncertain: NaR strongly prefers NO_3^- over NO_2^- and moreover, not all plant leaves contain NO_2^-, since in some species and under some conditions NO_3^- is already assimilated in the roots. Hence, Meyer et al. speculated that the NO produced by NaR is only an unnecessary side product.

1.3 Measuring leaf-level NO_y fluxes

Gas exchange in plants is measured with chambers. A plant, or part of a plant, is enclosed in a chamber that usually has an inlet for air to enter and an outlet for air samples that go to gas analysers. Changes in the concentration of the gas of interest are monitored, and by knowing how the measurement system works, one can estimate which part of the concentration change was due to plant functioning. The two main methods used in chamber measurement are steady-state and nonsteady-state (Livingston and Hutchinson 1995). The former means that the chamber is closed for so long a time that the gas concentration inside no longer changes, i.e. it reaches the steady state. In this case, the flux magnitude is derived from the concentration difference between the inlet and outlet of the chamber. Nonsteady-state chambers are not closed long enough to reach the steady state, but the flux is determined based on the rate of concentration change during the short measurement time. NO_x fluxes have been studied using mainly the steady-state system (e.g. Hereid and Monson 2001, Geßler et al. 2002).

NO_x is a problematic gas in chamber measurements, because it is adsorbed and desorbed on the chamber walls, depending on the conditions. This must be taken into account in analysing the measurement data. The term chamber blank means the portion of the total flux that originates from the reactions of NO_x with the chamber walls and should always be determined in measuring NO_x fluxes. Usually, there is another similar but empty chamber monitored alongside the plant chamber to provide an estimate on the chamber blank. For instance, Gut et al. (2002) and Teklemariam and Sparks (2006) calculated the NO_x flux from the difference in concentration between the outlet of the plant-containing chamber and the empty chamber. A different procedure was used by Hereid and Monson (2001): they conducted empty-chamber measurements before and after each leaf measurement, with the same chamber. In addition to estimating the chamber blank, researchers have attempted to diminish it by preconditioning the chamber walls with O_3- (e.g. Weber and Rennenberg 1996) or NO_2- enriched air (Hereid and Monson 2001).

The behaviour of the chamber blank has not usually been described in articles on NO_y exchange of plants, but there are exceptions. Rondón and Granat (1994) reported that their empty chamber turned from an NO_2 sink to a source when the NO_2 concentration in the air entering the chamber fell below 3–6 ppb. The chamber blanks did not correlate with RH, light intensity or temperature. Teklemariam and Sparks (2004) observed that in their PAN flux measurements, there were no significant absorption or memory effects, and that the PAN concentration was not affected by irradiance, temperature or RH. Schimang et al. (2006) measured the HONO exchange of plants and also analysed the behaviour of the chamber blank. The authors observed HONO losses on chamber walls that were a first-order process in relation to HONO concentration, and they also suggested that at low concentrations, light-induced production of HONO on the chamber walls begins to be comparable to the losses.

Chemical reactions on chamber walls have been studied in further detail in experimental gas-phase chemistry, where the background reactivity of the environmental chambers is a common problem. Suggested wall reactions directly related to NO_y include: dark hydrolysis of NO_2 that produces HONO, photo-induced HONO production from NO_2, photo-induced off-gassing of NO_x and N_2O_5 hydrolysis on the walls (Carter and Lurmann 1991). Zador et al. (2006) concluded for their smog chamber that from the many wall reactions possible, wall production of HONO and HCHO (formaldehyde) apparently accounted for most of the production of reactive species. The magnitude of HONO production is dependent on RH, irradiance level, temperature, and the amount of NO_3^- previously adsorbed on the walls (Killus and Whitten 1990).

In NO_x flux measurements, one complication is the gas analyser. Most often the NO_x concentrations are measured with a chemiluminescence method, in which NO reacts with O_3 producing characteristic luminescence whose intensity is linearly proportional to the NO concentration. The chemiluminescence signal is quenched by humidity. Gerboles et al.

(2003) observed a signal quenching of 8% when the water content was increased from dry air to 80% RH. Otherwise the analyser works well when it is used for NO only. Additional problems arise when the total NO_x or NO_2 is measured; NO_2 must be converted to NO before detection, and this conversion is often not specific for NO_2, since other nitrogenous species can also be converted. The most common method, conversion on a heated molybdenum (Mo) surface, reduces at least HNO_3 (100%), HONO (100%), PAN and other organic nitrates (nearly 100%), and HCN (hydrogen cyanide; 68%) to NO (Gerboles et al. 2003). Fehsenfeld et al. (1987) used hydrated crystalline ferrous sulphate ($FeSO_4$) instead of Mo for the surface conversion and reported significant interferences of n-propyl nitrate and PAN. Another method of conversion is photolysis: these photolytic converters are considered more specific for NO_2. Steinbacher et al. (2007) compared Mo and photolytic converters at two rural sites in Switzerland and concluded that only 70–83% of the 'NO_2' detected with the Mo converter was really NO_2. However, Ryerson et al. (2000) estimated that their photolytic converter also detected HONO with an efficiency of 37%. These findings suggest that the measurement results must be interpreted with care.

1.4 Ultraviolet radiation

The sun emits radiation over the entire electromagnetic spectrum. However, most of it does not reach the earth's surface, since gases in the atmosphere absorb the photons (Fig. 4). O_2 and O_3 molecules remove nearly all radiation below 290–300 nm, while wavelengths above 800 nm are largely absorbed by water and CO_2 molecules. Between these limits, there is the near-ultraviolet (near-UV) region (300–400 nm) and the visible light region (400–700 nm), where most of the solar energy is concentrated originally; radiation in these regions can also penetrate through the atmosphere most easily (Seinfeld and Pandis 1998).

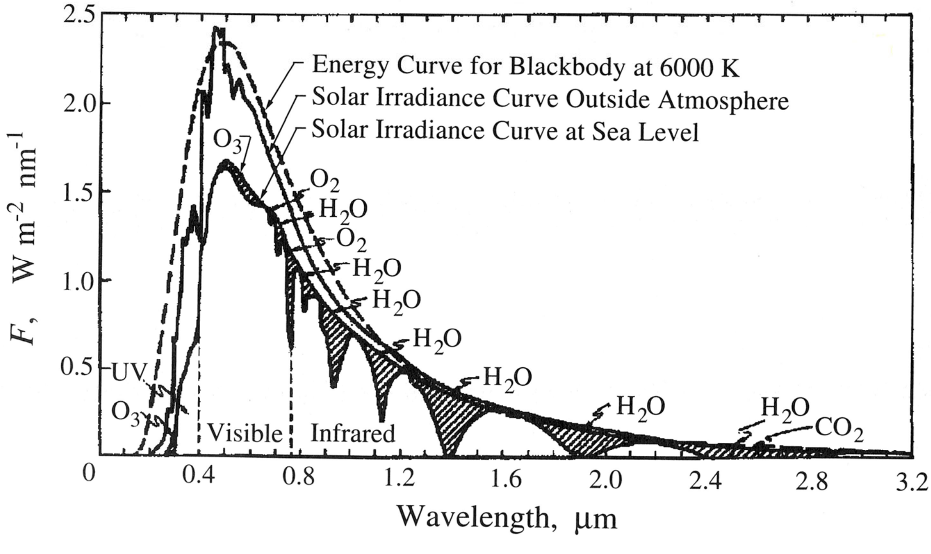

Figure 4. Solar spectral irradiance at the top of the atmosphere and at sea level. Shaded regions indicate the molecules responsible for absorption (Seinfeld and Pandis 1998; reprinted with permission of John Wiley and Sons, Inc).

The UV regions have been defined as follows: wavelengths 100–280 nm are called UV-C, 280–315 nm are UV-B, and 315–400 nm are UV-A (ISO standard 21348). Of these, all UV-C and most of the UV-B are absorbed in the atmosphere, and therefore, approximately 98% of the total UV radiation at sea level is UV-A. This is good for life on the earth, since shortwave radiation can harm living organisms, e.g. by altering their DNA. The shorter the wavelength of electromagnetic radiation, the more energy it carries within (Eq. 1):

$$E = \frac{hc}{\lambda} \qquad (1)$$

where E is energy (J), h is Planck's constant (6.626×10^{-34} J s^{-1}), c is the speed of light (approx. 3×10^{8} m s^{-1}) and λ is the wavelength (m). UV radiation is not energetic enough to remove protons or electrons from atoms and molecules, i.e. to ionize them, but it can dissociate atmospheric compounds more easily than visible light. Thus, UV radiation plays a significant role in driving atmospheric chemistry.

A possible connection between solar UV radiation and NO_y exchange in plants was observed when the gas exchange of Scots pine was monitored with the chamber method at the Station for Measuring the Forest Ecosystem - Atmosphere Relations (SMEAR) II station: when UV radiation entered the chambers, the NO_y emissions increased clearly (Raivonen 2000). The same phenomenon also occurred in an empty chamber, but there was also some indication of emissions from the pine needles. The observation was entirely novel and its implications for plant physiology and air chemistry are very interesting.

2. AIMS OF THE PRESENT STUDY

The overall aim of the study was to analyse the effect of solar UV radiation on NO_y emissions in gas-exchange chambers. The specific aims were:

1) to evaluate the NO_y flux measurement system used at the SMEAR II station and the reliability of the produced data

2) to review the potential processes underlying the UV-induced NO_y emissions and

3) to quantify the NO_y emissions and assess their implications for plants and the atmosphere.

3. MATERIAL AND METHODS

3.1 Measurements

This work is largely based on analyses of NO_y flux chamber measurements performed at the SMEAR II station (Hari and Kulmala 2005) in Hyytiälä, southern Finland during the years 2001 –2004. The site is relatively remote and the mixing ratios of pollutant gases thus low. The nearest settlement, Korkeakoski, is located 8 km away. The NO_x concentrations in

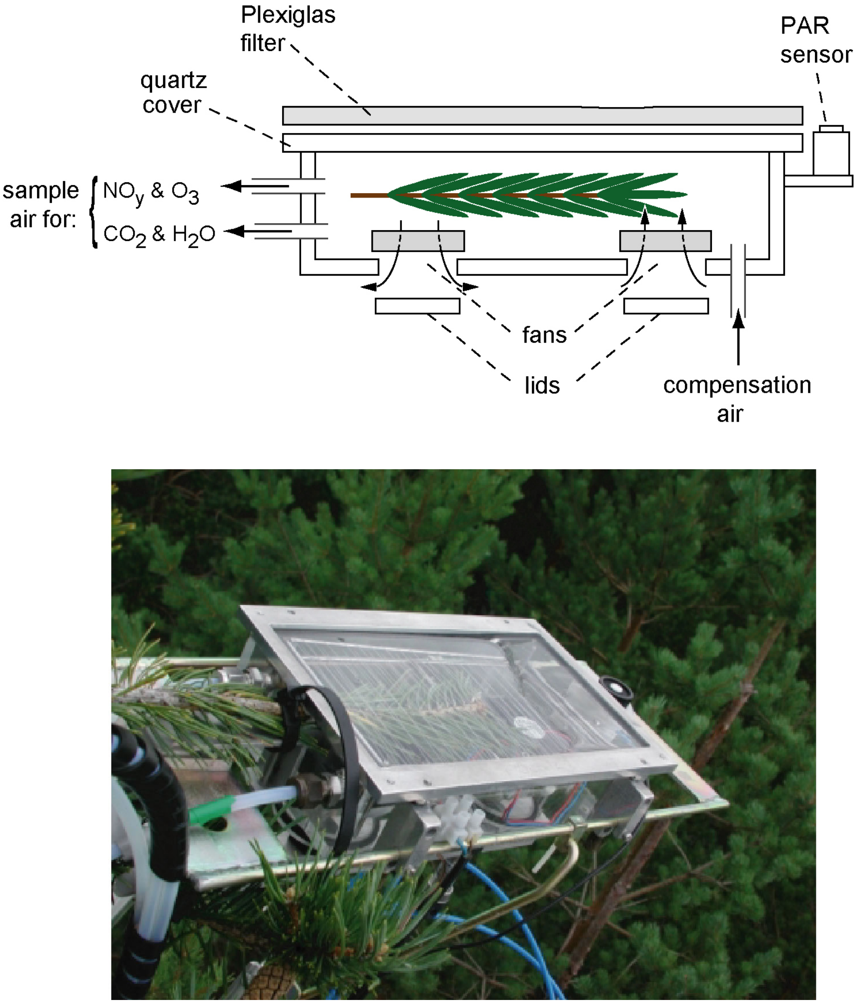

Figure 5. Schematic illustration and a photograph of the chamber used in this study. In the illustration, the arrows show the direction of airflows. The two lids are closed when the measurement begins. There were two tubes for sample air: one channelled the air to the NO_y and O_3 analysers, the other to the H_2O and CO_2 analysers. Photo taken by Pertti Hari.

Hyytiälä were generally around 1 ppb, with a maximum in spring and winter and minimum in summer (Kulmala et al. 2000).

The soil on the site consists of coarse, silty glacial till. The NO_3^- concentration in the soil is low: in June 2003 it was 0.4 mg kg^{-1} in humus and mineral soil, compared with 4 mg kg^{-1} of NH_4^+ (M. Pihlatie, pers. comm.). The soil NO emissions were also very low (Kesik et al. 2005). The forest is a homogeneous Scots pine stand sown in 1962. During the years 2001–2004, the trees were 14 – 16 m tall.

Chamber system

The nonsteady-state chamber system was described in detail in Hari et al. (1999) and Kulmala et al. (1999). Several chambers monitored the gas fluxes of Scots pine trees; each chamber enclosed one shoot of a full-grown tree, and there were often more than one chamber per tree. The same shoots were monitored over the summers in 2001 and 2002 but were renewed for the summer of 2003 and again for 2004, due to ageing needles. The chambers were installed at the tops of the trees to minimize shading. One empty chamber served as a reference.

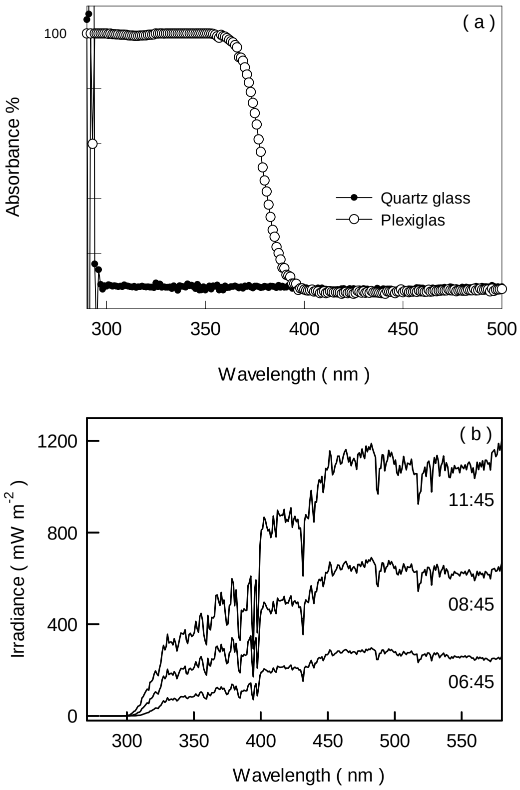

Figure 6.
(a) Absorbances of the quartz and Plexiglas covers at 290–500 nm. Adopted from Study II. (b) Solar irradiance at wavelengths 290–580 nm in Hyytiälä on 5th August 2004 at 06:45, 08:45 and 11:45. Measured with a radio-spectrometer (Bentham, UK).

The chambers used for monitoring the NO_y fluxes were box-shaped with a volume of one dm^3 (Fig. 5). The boxes were made of Plexiglas and the inner surfaces were coated with FEP (fluorinated ethylene propylene) Teflon film. The Teflon films on the chamber surfaces were renewed every spring and also several times later in the summer (after the year 2001). The upper walls, i.e. the covers, of the boxes were made of quartz glass, which transmits UV radiation. When the UV wavelengths needed to be filtered away, a Plexiglas plate was installed on top of the quartz cover (Fig. 6). The boxes had two round holes in the bottom for letting ambient air enter the chamber when no measurement was being performed. Inside the chamber, fans ventilated the interior and kept the air well mixed. A copper-constantane thermocouple monitored the temperature inside the chamber.

A computer controlled the measurement of the gas concentrations and relevant environmental factors for the chambers; each chamber was measured two to four times per hour. When the measurement was initiated, a pump pulled sample air into the gas analysers and after a short while, the lids in the chamber bottom closed. The sample was fed into the gas analysers through two heated and light-shielded tubes. The sample air was replaced by ambient air flowing from outside of the chamber at an equal rate.

Figure 7 shows an example of the data measured during a single measurement period. The values were recorded at 5-s intervals. Solar irradiance remained constant, since cloudiness did not change during the measurement. The lids closed 5 s after measurement was initiated and opened again after 65 s, during which chamber temperature increased several degrees. The ambient temperature was approximately 3 degrees lower than the chamber temperature with open lids. In the chamber, CO_2 and O_3 were deposited, while water (H_2O) and NO_y were emitted. This was seen as a decrease or increase in the gas concentrations during the closing.

Instrumentation for measuring the NO_y concentrations

From summer 2002 onwards, the fluxes of NO and NO_y were monitored at the SMEAR II station. Both were measured using chemiluminescence NO_x analysers, model TEI 42S (Thermo Environmental Instruments, Franklin, MA, USA) equipped with an Mo converter. Thus, the system was specific for the NO fluxes, but in the 'NO_x' mode other nitrogen-containing compounds were also detected. These apparently included HONO and organic nitrates and nitrites, e.g. the analyser misinterprets all PAN as NO_2. In our case, HNO_3 was not believed to pass through the sample lines and in-line particle filters; hence, the flux measurement system was expected to detect all NO_y species except HNO_3. In the first two sub studies, the measured fluxes are referred to as NO_x and in the latter two as NO_y. However, they all are NO_y.

Radiation measurements

A sensor for photosynthetically active radiation (PAR) (LiCor 190 SB) was attached to the chambers outside (see Fig. 5). UV irradiance, 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).

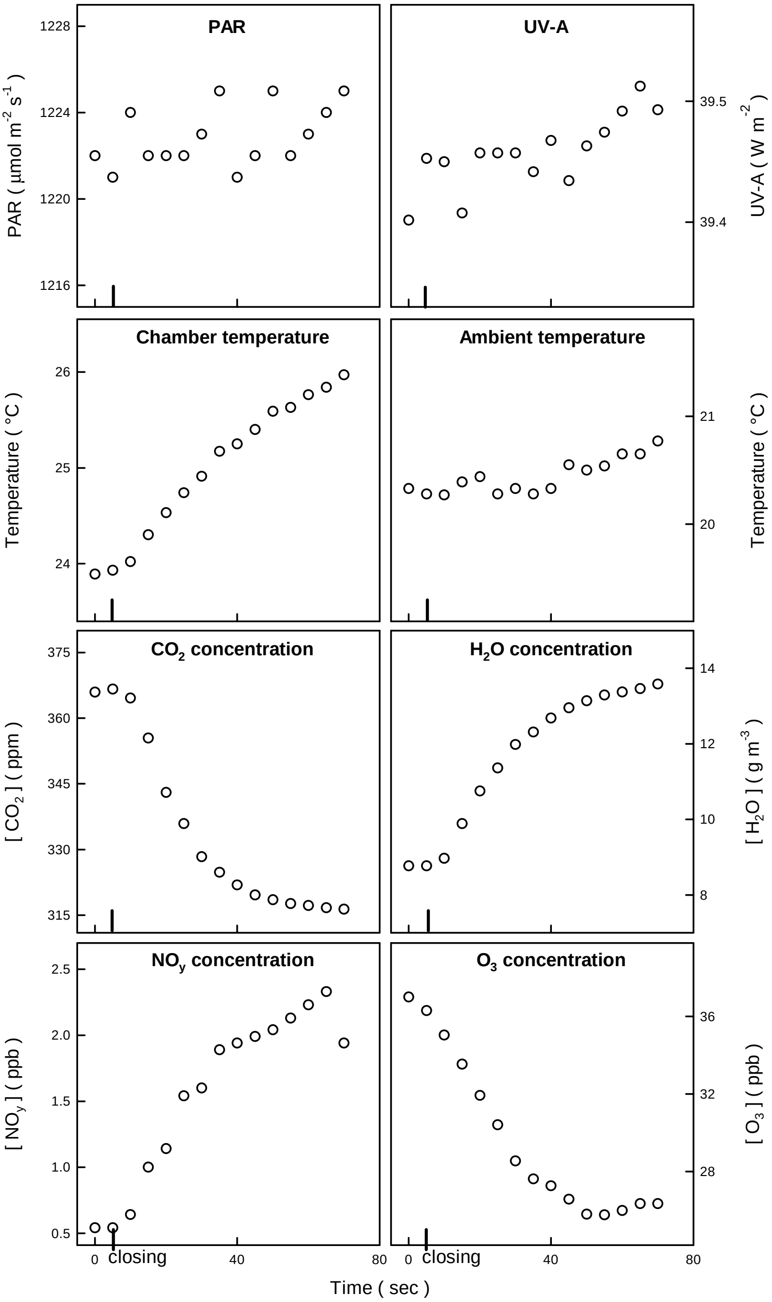

Figure 7. An example of data recorded during a single measurement period in a chamber that enclosed a pine shoot. The thick tick marks show when the chamber lids were closed.

Generating a known water vapour flux in the chamber

These results on simulated transpiration have not been published elsewhere, other than in this thesis. The system for creating a known water vapour flux in a chamber was originally developed for calibrating transpiration measurements at the SMEAR station (Kolari et al. 2004). The chamber was monitored, following the normal measurement routine. However, the compensation air was not ambient, but compressed air that had been humidified in a thermally insulated pressure vessel with water on the bottom. The air was fed into the chamber via a tube at a flow rate equal to the sample flow. The humidity was adjusted by controlling the temperature of the pressure vessel. The gas concentrations in this compensation air were measured in between the chamber measurements by feeding the air directly to the gas analysers. The NO_y concentration did not change on the way through the compression but it was nearly ambient. Measurements with RH exceeding 75% were excluded because the water flux is unreliable at high RH (P. Kolari, personal communication).

3.2 Methods of data analysis

Determining the total flux in a chamber

The gas concentrations in the sample air were recorded every 5 s during the 1 min the chamber was closed. The NO_y flux was determined from the concentration change during the chamber closing, and the NO_y concentration of the compensating air was taken from data recorded while the chamber was still open (Fig. 8). The fluxes in the chambers were so small that they often were barely above the detection limit of the system, and the measuring noise was considerable. The flux determination method described below allowed us to use all existing information from a single measurement period (II). The method was a modification of those presented in Aalto (1998) for CO_2 and in Altimir et al. (2002) for O_3.

The processes that changed the NO_y concentration inside the chamber included sample flow into the gas analyser q_a ($m^3\ s^{-1}$), compensating airflow of ambient air q_c ($m^3\ s^{-1}$) and flux J ($\mu mol\ s^{-1}$) due to the sinks or sources of NO_y inside the chamber (chamber walls, the shoot). The volume of the chamber was denoted by V (m^3), NO_y concentration at moment t by $C(t)$ µ (mol m^{-3}) and concentration in the compensating air by C_c ($\mu mol\ m^{-3}$). Now the measured concentration change could be associated with the processes in a mass balance equation (Eq. 2).

$$\frac{V\,dC(t)}{dt} = q_C\,C_C - q_a\,C(t) + J \tag{2}$$

Since q_a and q_c are equal, the solution of the differential equation for $C(t)$, the quantity that is measured, is Equation 3:

$$C(t) = (C(0) - C_c - \frac{J}{q})e^{-\frac{qt}{V}} + \frac{J + qC_c}{q} \tag{3}$$

Here the only unknown factor is the flux *J*, which was assumed to be constant during the measuring period. *J* was found by fitting Equation 3 to the measured NO_y concentrations. The fitting was performed by Mathematica software (Version 4; Wolfram Research, Inc., Champaign, IL, USA), which uses the Levenberg-Marquardt method for minimizing the sum of squares. Figure 8 demonstrates the fit.

Analysing the relationship between solar radiation and NO_y fluxes

The irradiances of UV-A and UV-B radiation, as well as the PAR intensity, were monitored simultaneously with the NO_y fluxes. The relationship between these was analysed by fitting a linear regression model with the least squares method.

Blank correction procedure

The chamber blank was estimated by monitoring NO_y (and other) fluxes in a constantly empty chamber. The setup was such that the empty chamber was included in the normal measurement routine; it was measured 2–3 times per hour, similar to the shoot chambers. All the chambers were similar and were treated similarly.

The observations made on the behaviour of NO_y fluxes in the empty chamber (II) are reviewed more closely in the Results section, but the blank correction procedure is explained here. The correction methods were based on three observations. Firstly, at low ambient NO_y concentration, the NO_y emissions in the empty chamber were linearly dependent on UV-A irradiance. Secondly, the NO_y fluxes (or the regression coefficient of the UV-A dependency) measured in several similar empty chambers simultaneously were not equal, but differed significantly. Thirdly, UV-A irradiance alone did not explain the NO_y flux, but there were other unknown factors that affected, one of them probably the ambient NO_y concentration.

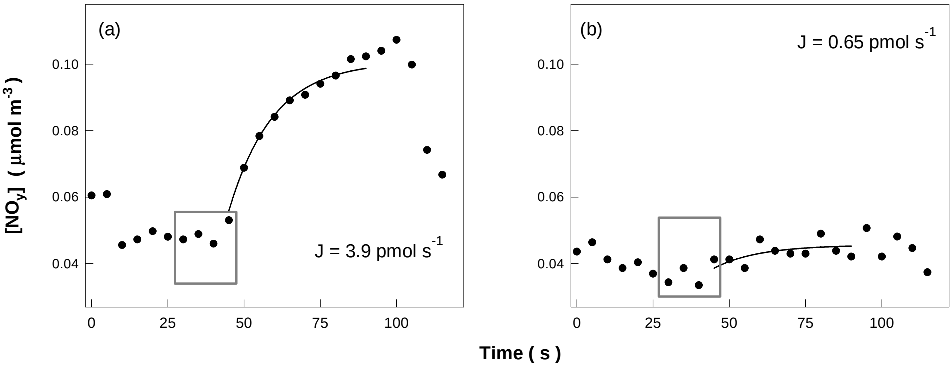

Figure 8. Illustration of how the NO_y flux was determined. The average of the points marked with the box was used as the ambient concentration, and the mass-balance equation was fitted to the data points, starting from the chamber closing. *J* (µmol s^{-1}) denotes the flux. (a) is an example of a measurement period with a large flux and little noise, while (b) shows the contrasting situation. Redrawn from Study II.

The best option for blank correcting on low-NO_y days seemed to be to use the UV-A regression estimated in the same chamber where the pine shoot was monitored. In the present study, this method was used for several days when the pine shoots had been removed from their chambers for a couple of hours around noon. Thus, it was possible to determine the linear UV-A regression of the NO_y fluxes during these hours. The total flux, chamber + shoot, was corrected with this number for the rest of the day.

Since the branch removals described above were not a common practice at the site, this study also used data in which the blank was taken directly from the reference chamber. The NO_y fluxes of the reference chamber were taken as such, and subtracted from the shoot chamber flux. The NO_y flux in the empty chamber was always measured just before or just after a shoot chamber. Due to the UV dependency of the fluxes, all measurement pairs in which the difference in solar UV-A irradiance between the blank measurement and the shoot-flux measurement was greater than 5 W m^{-2} were excluded. This latter method was applied in IV for blank correcting the NO_y consumption data, as well as in all data in III that were shown as corrected (flux of the shoot).

Analyzing the NO_y exchange of a pine shoot

The NO_y exchange of pine shoots was assumed to consist of three processes: consumption on the needle surface, consumption in the stomata and production of NO_y on the needle surface. All these were formulated in a model for which the parameters were derived from the blank-corrected NO_y flux data of two pine shoots (IV). The behaviour of the net flux under different environmental conditions was evaluated based on the modelling results.

NO_y consumption was defined as the negative flux direction. Consumption on the needle surfaces was dependent linearly on the external NO_y concentration as a first-order process. Consumption in the stomata was set to depend linearly on the concentration gradient between the air and substomatal cavities and on the degree of stomatal opening as represented by stomatal conductance for NO_2, g_{NO2} (mm s^{-1}). An internal concentration was introduced in the model by assuming a balance between diffusion and the consuming reaction at the mesophyll surface.

The value for g_{NO2} was determined from the conductance for CO_2, g_{CO2}, by scaling with the ratio of the diffusion coefficients of NO_2 and CO_2 in the air, i.e. 0.9855 (Massman 1998). The value for g_{CO2} was obtained from simultaneous measurements of CO_2 exchange, using the optimal stomatal control model of photosynthesis (described in Hari and Mäkelä 2003). The low measuring accuracy and precision at low *vpd* (water vapour pressure deficit) made the conductance calculation unreliable at low light and at low *vpd*. In addition, the model structure does not allow determination of the conductance at low *vpd*. On this basis, approximately 70% of the available data were selected. The parameters for the NO_y consumption model were taken by fitting the model to data recorded during an episode of high NO_y concentration, because only then was the deposition of NO_y evident.

Since the NO_y production correlated slightly better with UV-A radiation than with UV-B radiation, only UV-A was included in the production model. A nitrite-dependent physiological NO/NO_2 production did not seem probable in the trees growing at SMEAR II, thus, no effect of stomatal control and no production without UV-A were assumed. This was formulated as a linear model, in which the production flux was dependent only on UV-A irradiance. The parameter was estimated by fitting the model to data collected over several days when the NO_y emission had been especially evident. Only measurements obtained at ambient NO_y concentrations below 0.8 ppb were included in the analysis.

The compensation point of the NO_y exchange of a plant is defined as the ambient concentration at which the net flux is zero, i.e. at which the consumption and production rates are equal. Hence, the compensation point was estimated by setting the net flux to zero and solving the ambient concentration for different combinations of the degree of stomatal opening and UV-A irradiance.

4. RESULTS

The ambient NO_y concentrations at SMEAR II were generally low, around 1 ppb. Under these conditions, the NO_y fluxes in the gas-exchange chambers were emission rather than deposition. However, when a rare high-NO_y episode occurred, the fluxes turned into deposition (Fig. 9). This was evident in chambers that enclosed pine shoots, but the emissions of the empty chamber also ceased. The results in chapters 4.1–4.3 include only low concentration condition; 4.4 also treats higher concentrations.

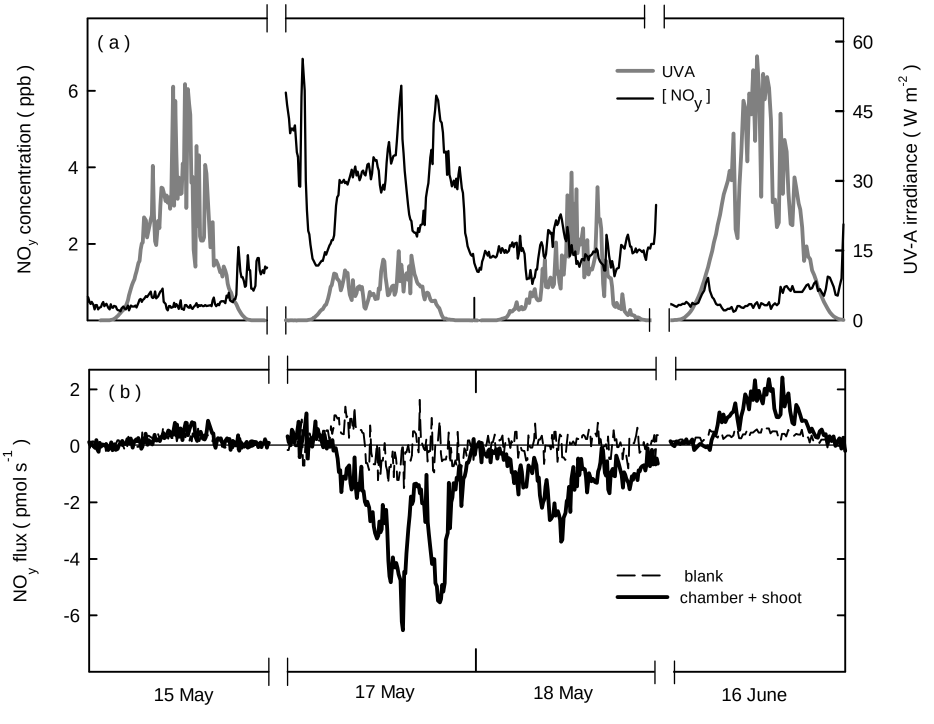

Figure 9. (a) Ambient NO_y concentration, UV-A irradiance and (b) measured NO_y fluxes on four days in summer 2001. On the 15 May and the 16 June the conditions were normal for the Hyytiälä site, with low NO_y concentration. On 17–18 May the concentration became exceptionally high.

4.1 The phenomenon

The first preliminary observations on the effect of UV radiation on NO_y emissions were made when UV-transparent quartz covers were installed on the chambers instead of UV-opaque Plexiglas covers (Fig. 10) (II). The phenomenon was investigated further simply by interchanging the covers in chambers that enclosed pine shoots (in later phases of the study, UV was filtered by installing the Plexiglas plates on top of the quartz covers). The emissions were lower with Plexiglas and increased immediately when solar UV radiation was allowed to enter the chamber. A similar effect was seen in the empty chamber. Moreover, the magnitude of the emissions in the empty chamber was similar or sometimes even higher than that obtained simultaneously in a shoot chamber. Emissions in all chambers, including the empty one, closely followed the solar irradiance (Fig. 11). Since the emissions already revived in the mornings before the UV-B irradiance, UV-A appeared to drive the emissions. The proportion of NO in the total NO_y flux was negligible (III).

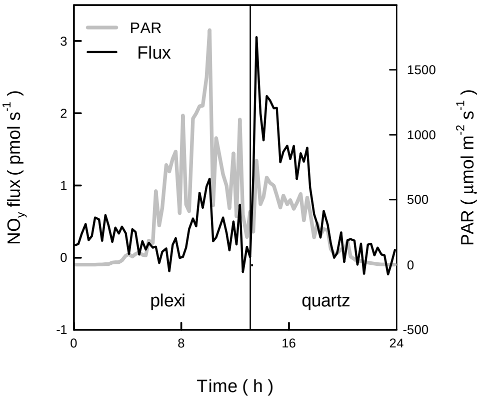

Figure 10. Change in the NO_y fluxes in the empty chamber when the UV-opaque Plexiglas cover was replaced with a UV-transparent quartz cover. The replacement is marked with the vertical line.

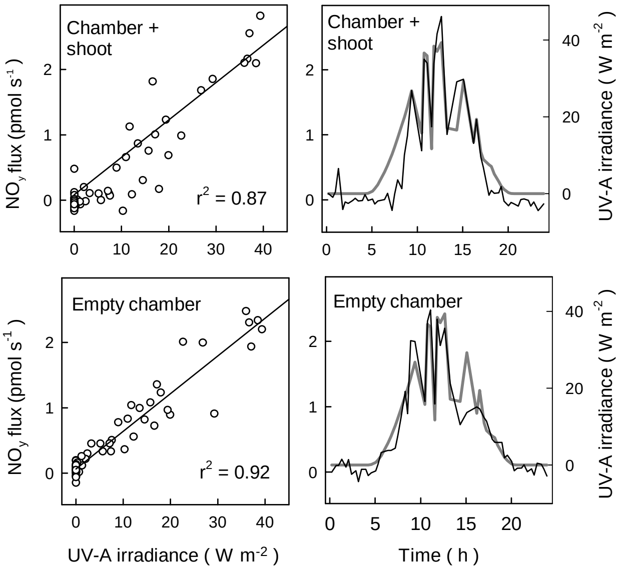

Figure 11. NO_y emissions in both a shoot chamber (upper panel) and an empty chamber (lower panel), and solar irradiance on a sunny day with some clouds. The left panel shows the linear regression of the emissions with the UV-A irradiance, and the right panel shows how these two, emissions (black line) and irradiance (grey line), show similar variation.

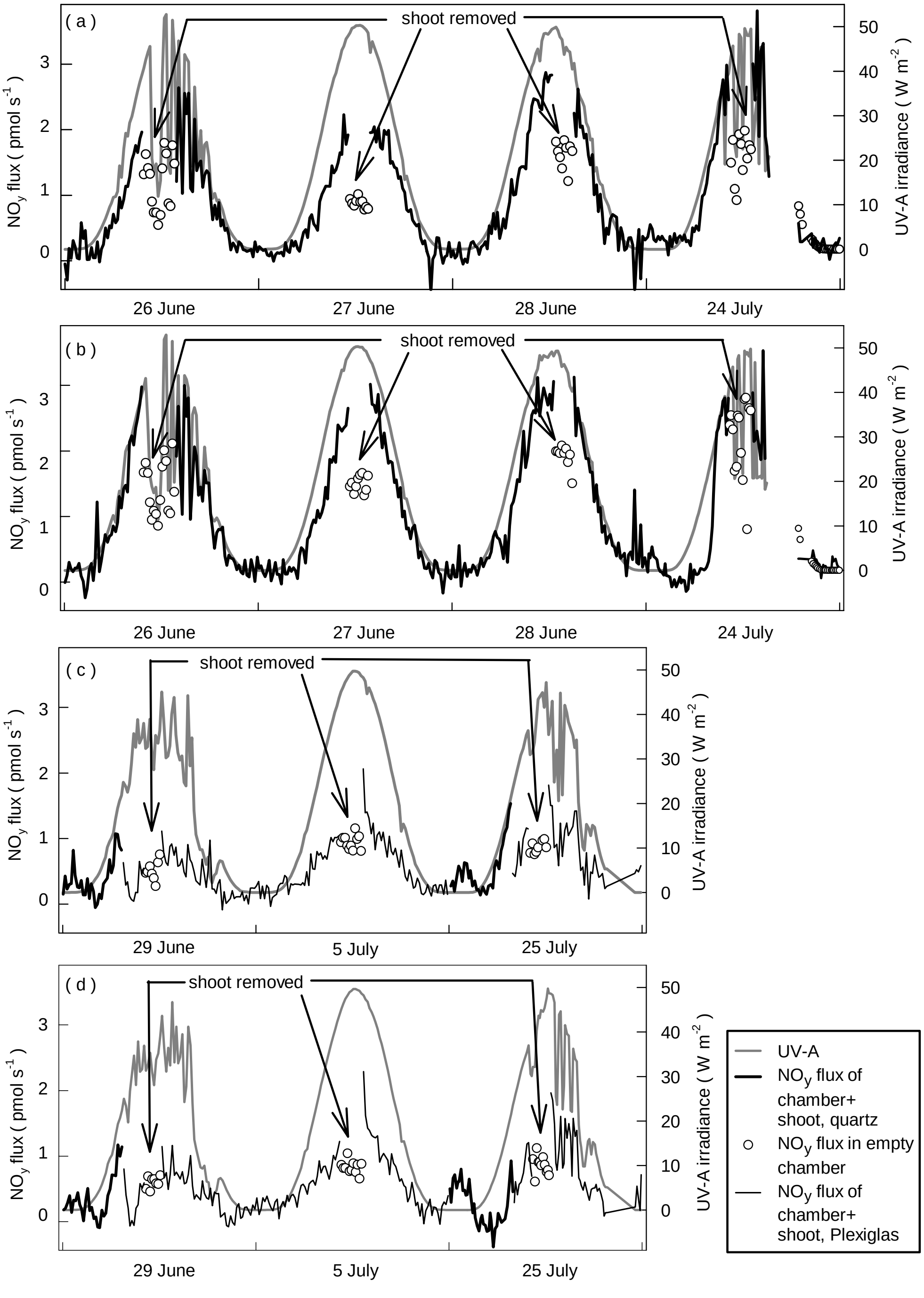

Figure 12. Measured NO$_y$ fluxes of the days when the pine shoots were removed from their chambers for a couple of hours at midday. (a), (b) Data of two chambers having a UV-transparent quartz cover (redrawn from Study IV). (c), (d) Data of two chambers with Plexiglas covers.

It was not certain whether there were any NO_y emissions from the pine shoots or only from the chamber walls. This was checked by removing the shoots from their chambers for several hours at midday, to determine whether the NO_y flux was altered by the removals (I). Change did occur: the emissions decreased when the branch was removed. However, this occurred only when UV radiation was entering the chamber. There was also small visible drop in the flux when the branch removal was performed with the Plexiglas cover, but minor compared with the drop with UV radiation (Fig. 12).

The maximum total (chamber + shoot) emissions at the strongest irradiance levels were app. 6 pmol s^{-1} or 0.28 ng s^{-1}, assuming it to be NO_2. The estimated maximum emissions from the pine shoots were app. 0.06 nmol s^{-1} m^{-2} of total needle area or 0.2 nmol s^{-1} m^{-2} of projected needle area, which corresponds to 2.8 ng s^{-1} m^{-2} or 9 ng s^{-1} m^{-2} of NO_2.

4.2 Technical issues

NO_y fluxes in the empty chamber

When the interior of the empty chamber was covered with FEP Teflon film, the UV-associated emissions decreased remarkably. However, the positive effect of teflonizing was not permanent. Emissions from the teflonized chamber, when related to prevailing solar irradiance, also increased with time, despite frequent cleaning of the chamber (II). In summer 2002 the Teflon films were renewed several times, and the NO_y emissions dropped with each new Teflon coating (Fig. 13). This also occurred during the following summers: the emissions increased steadily until the Teflon coating was renewed. As seen in the figure, the dependence of the chamber blank on solar irradiation was slightly different on cloudy and rainy days; the regression coefficients could be higher than on surrounding sunny days.

We also observed that although separate chambers were treated similarly, their emission levels without pine shoots differed, sometimes by as much as 2-fold.

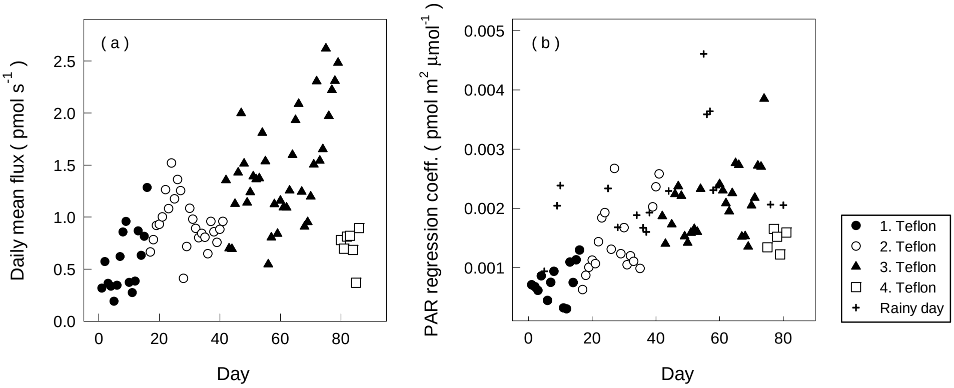

Figure 13. Daily values of the chamber blank in summer 2002 presented (a) as daily mean NO_y fluxes and (b) as daily regression coefficients between PAR irradiance and NO_y flux. The consecutive Teflon coatings are separated by different symbols. Redrawn from Study II.

Effect of water flux on the NO_y flux

When a living pine shoot is enclosed in a chamber, the water flux inside the chamber changes. Pine shoots transpire, which means a positive water flux and rising humidity in a closed chamber, especially in absolute humidity. Increase in RH is not as significant, since the temperature also rises (maximum 3 degrees in sunshine) while the chamber is closed. For instance, during the measurement in Figure 7, the RH increased from 48% to 66%. In an empty chamber there is no source of water, hence the humidity remains quite constant. The effect of the changing humidity on the NO_y flux in a chamber was studied by generating artificial transpiration in an empty chamber. The idea was to simulate realistic transpiration levels and a drop to zero, which occurs when a living shoot is removed from the chamber.

The simulation was performed on a single day in summer 2006. Unfortunately, it became increasingly cloudy as the water flux was decreased to zero; thus, the visual impression is that the NO_y emission decreased with irradiance, as usual (Fig. 14). However,

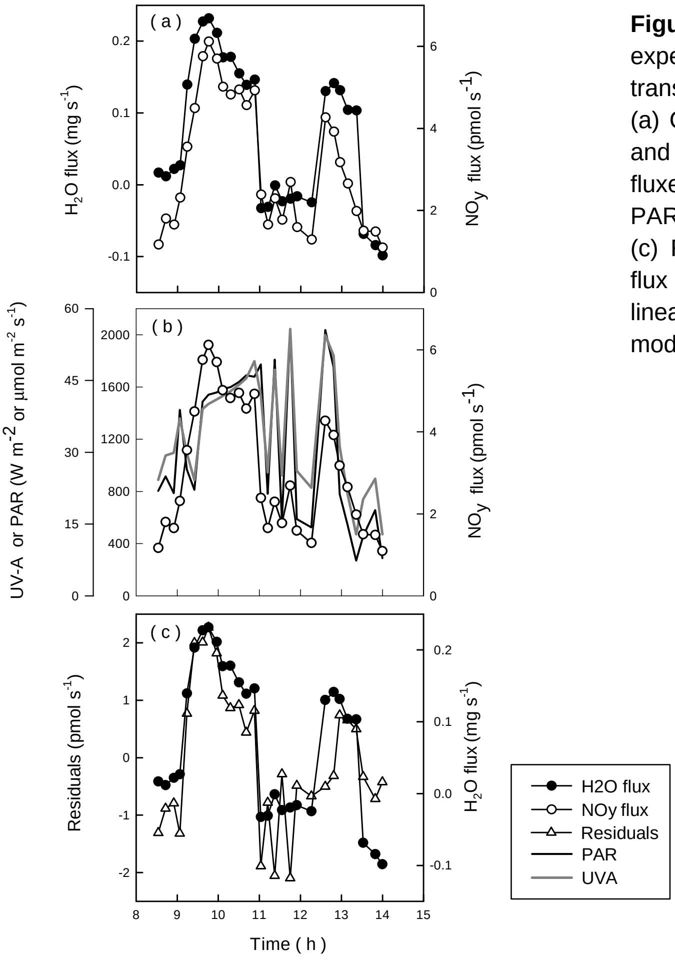

Figure 14. Results of the experiment with artificial transpiration.

(a) Generated H_2O fluxes and simultaneous NO_y fluxes. (b) NO_y fluxes, PAR and UV-A irradiance. (c) Residuals of the NO_y flux calculated from the linear PAR regression model, and the H_2O flux.

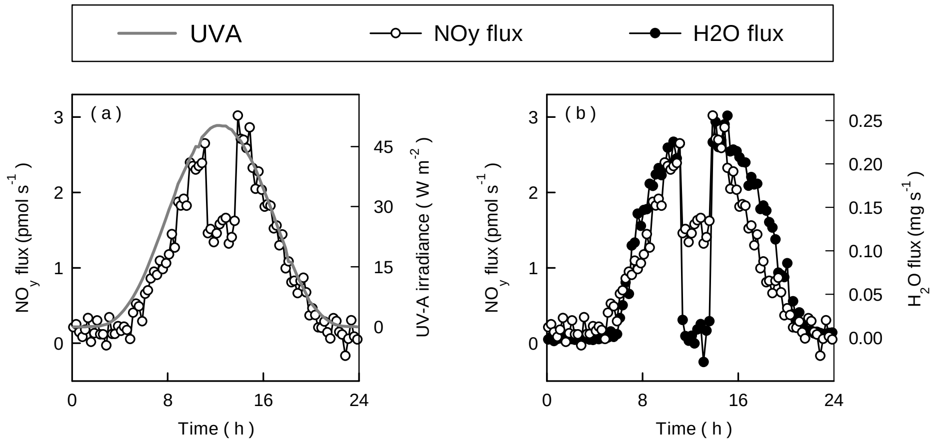

Figure 15. Change in NO$_y$ flux and transpiration on the 27 June 2001, when a pine shoot was removed from its chamber. (a) compares the UV-A irradiance and NO$_y$ flux, and (b) shows transpiration and the NO$_y$ flux.

when the linear regression between PAR intensity and the NO$_y$ emissions was determined, its residuals (measured flux minus the modelled flux) followed the changes in water flux. ‘Transpiration’ explained 52% (r^2) of the variation that irradiance did not explain.

The change in total NO$_y$ flux was similar to that which occurred when the living pine shoot was removed from the chamber. During actual branch removals, the transpiration dropped by app. 0.25 mg s^{-1}, while the NO$_y$ emissions dropped by app. 1 pmol s^{-1} although the irradiance level remained constant (Fig. 15). During the simulation, H_2O dropped 0.2 mg s^{-1}, and the additional drop in NO$_y$ emissions, not explained by changes in light, was app. 2 pmol s^{-1}.

4.3. Origin of the emissions

Association with plant metabolism

In the present study we analysed whether the NO$_y$ emissions could be of metabolic origin by comparing them with the CO_2 deposition, i.e. photosynthesis (III). Both these fluxes are dependent primarily on solar irradiance, and thus the chamber measurements showed roughly a similar daily course for these fluxes. However, especially on sunny and warm days, the effects of other factors also were apparent in the CO_2 exchange rate.

The linear increase in the photosynthesis rate in relation to solar irradiance in the morning began to saturate around noon, due to both closing of the stomata and limitations in the dark reactions of photosynthesis (Hari and Mäkelä, 2003). In addition, on warm days the regression plot between solar irradiance and stomatal conductance sometimes formed a clockwise loop, because the *vpd* (vapour pressure deficit) increased during the day and the plant began to control excessive transpiration by closing the stomata.

The characteristics of the CO_2 exchange were not reflected in the NO$_y$ fluxes. Figure 16

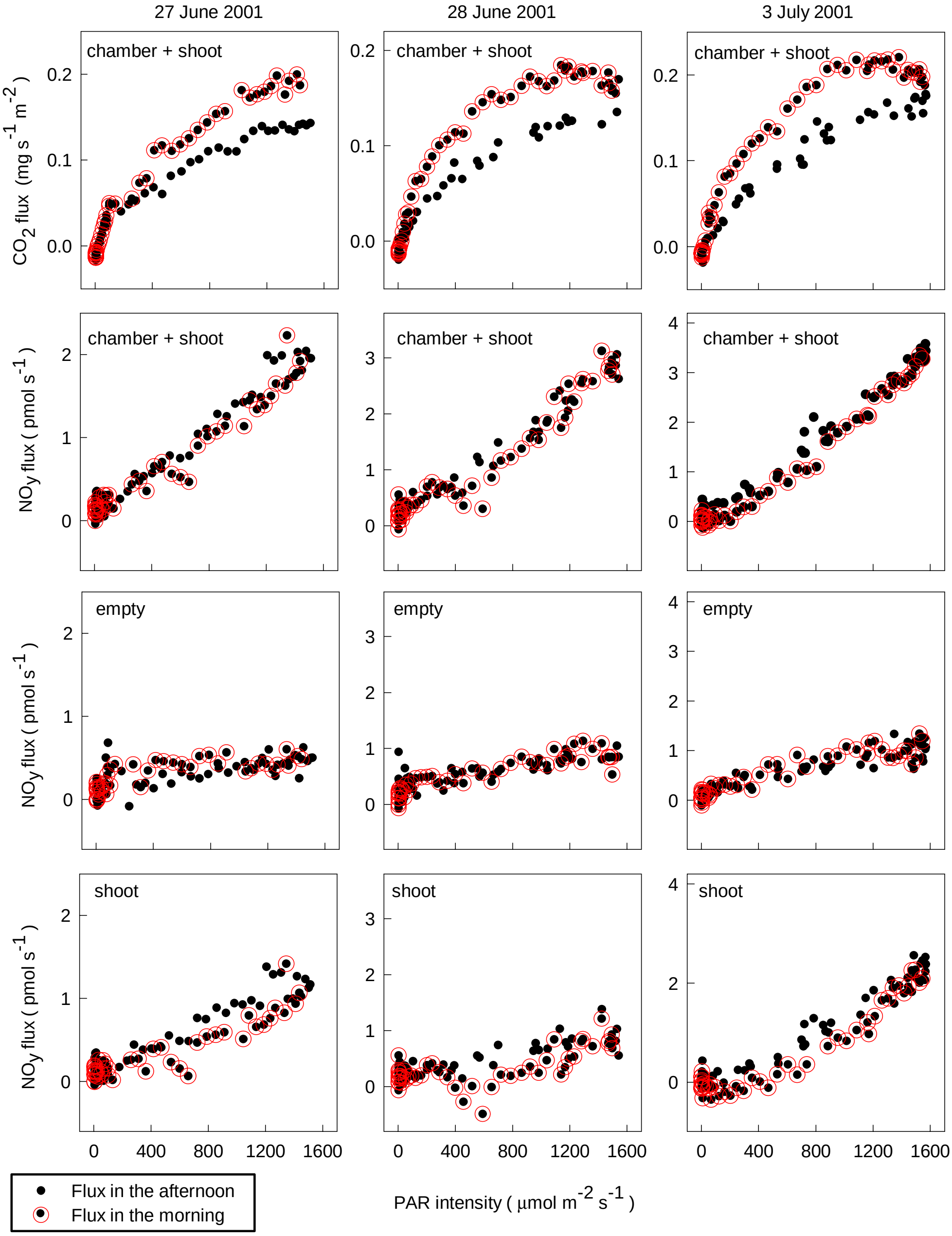

Figure 16. Comparing the dependencies of NO_y fluxes and simultaneous CO_2 fluxes on the PAR intensity. Results are from three sample days. A positive CO_2 flux means CO_2 uptake while positive NO_y flux shows NO_y emission. In all plots, the red circles highlight the morning fluxes from midnight till noon. The first row shows the CO_2 fluxes; the second row shows the NO_y fluxes in a chamber with a pine shoot inside; the third row shows the NO_y fluxes in the blank chamber; the lowest row shows the NO_y fluxes addressed to the pine shoot only. Partly redrawn from Study III.

shows three example days on which the CO_2 was clearly saturating and formed the loop. The regression between solar irradiance and NO_y flux was not saturating, but the linear increase also continued to the highest irradiances. Looping of the NO_y flux was variable. Generally, there was no clear difference between morning and afternoon NO_y emission levels, although the CO_2 fluxes looped. Sometimes the NO_y flux formed a slight clockwise loop similar to that of CO_2, and sometimes the loop was even very slightly reversed compared with that for CO_2. This was the case with both the total flux of shoot + chamber and the estimated flux from the shoot. Plotting the NO_y fluxes against the CO_2 fluxes showed that the NO_y emissions were not directly proportional to photosynthesis.

Effect of cleaning the pine shoot

To determine whether the UV-induced NO_y emissions could have originated from needle surfaces from a photodissociation reaction of accumulated nitrate or some other compound, the effect of cleanliness of the needle surface on the emissions was studied (III).

In summers 2001–2003, two similar chambers monitored two similar pine shoots simultaneously. Since the openings of the chambers were at the bottom, the chamber interior was never exposed to rain. The shoots were inside the chambers throughout the summers, and the NO_y emissions in the two shoot chambers were very similar, of the same magnitude and developing similarly. This is illustrated in Figure 17, showing the NO_y fluxes in two shoot chambers in the late summers of 2001–2004.

In summer 2004 the effect of cleaning was tested by keeping one pine shoot (and chamber) untouched, while the other was regularly cleaned. In June, all the chambers (including the blank) were cleaned, the Teflon film covering them was renewed and one of the pine shoots was rinsed with tap water. During the following 10 weeks, this shoot was rinsed approximately weekly, while the other shoot remained untouched. The chamber surfaces were not washed intentionally, but the bottom and partly the vertical walls were in contact with water, hence, the surfaces of the chamber were always cleaned somewhat when the shoot was rinsed. No new Teflon films were installed during summer. As a result, the NO_y emissions were lower in the chamber in which the shoot was kept clean (Fig. 17), and the difference increased towards late summer. Unfortunately, the reference chamber was not rinsed with the shoot chamber. The total emissions of the cleaned shoot plus the chamber enclosing it were eventually even lower than those of the separate blank.

The rinsing affected the amount of NO_3^- on the needle surfaces. In November 2004, the amount of NO_3^- was determined on the two shoots inside the chambers, as well as on two free shoots that were alongside the chambers. The nonwashed shoot had app. 6.4 mg N m^{-2} of NO_3^- on, while the one washed (not washed in September–November) had only 2.8 mg N m^{-2}. The two reference branches outside were even cleaner, with 0.5 and 0.8 mg N m^{-2}.

We also tested whether the presence of NO_3^- on the surfaces of dead pine needles is sufficient preconditioning for observing UV-induced NO_y emissions (III). The NO_y concentrations and their responses to changes in UV conditions were monitored inside a chamber that had either a cleaned dead Scots pine branch inside, or a branch that had been dipped into a strong ammonium nitrate (NH_4NO_3) solution after cleaning. This heavy NO_3^- exposure resulted in nearly 60 mg N m^{-2} of total needle area. Natural, ambient UV radiation was filtered, using a Plexiglas plate on top of the quartz glass cover of the chamber. The experiment was performed in Valencia, Spain, on 6th June 2004. The NO_y concentration in the chamber showed a clear response to UV exclusion, but only when the branch with NO_3^- treatment was inside the chamber (Fig. 18).

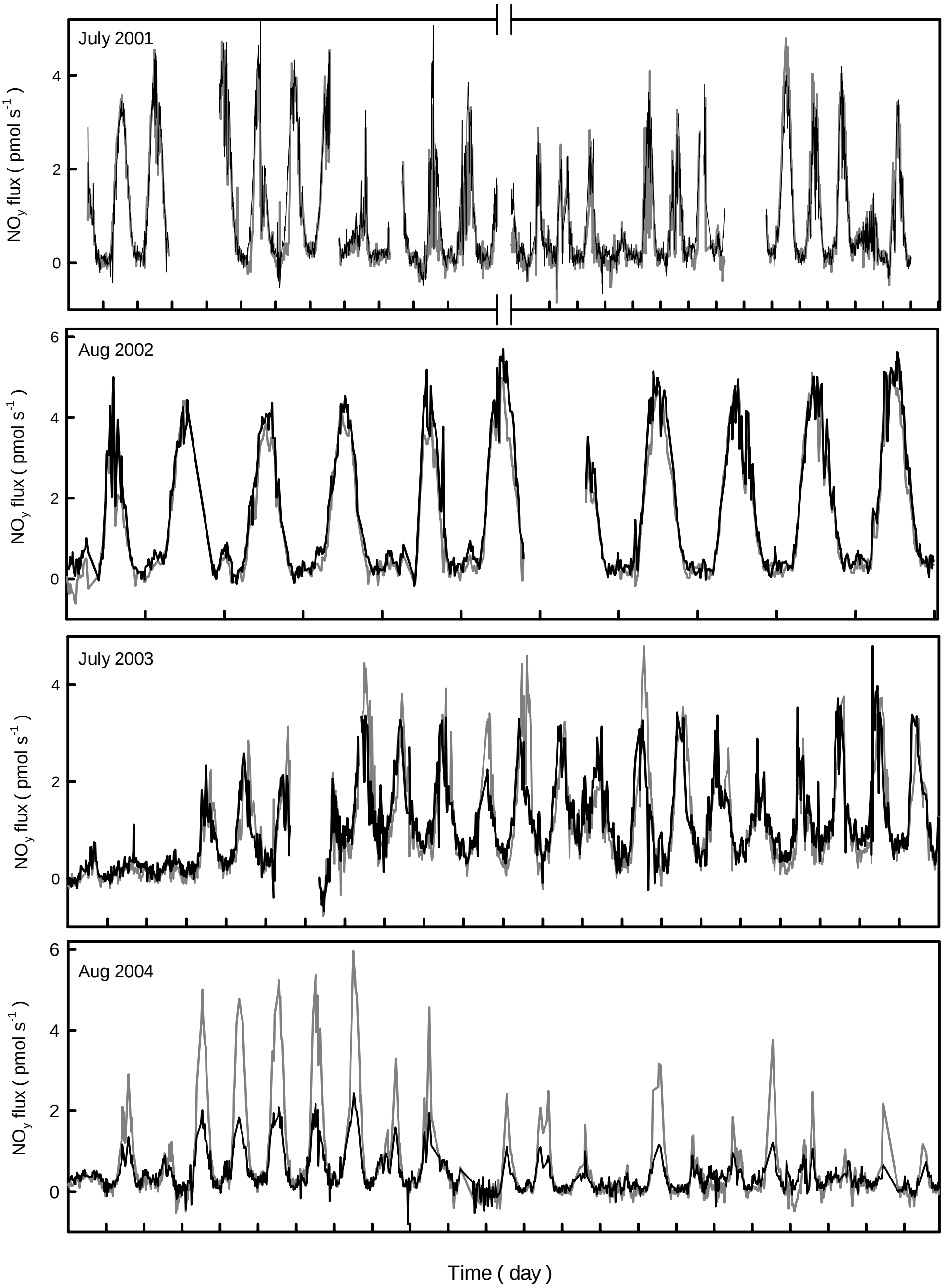

Figure 17. Total NO$_y$ fluxes in two similar shoot chambers (grey and black line) on 2–31 July 2001, 15–25 August 2002, 10–31 July 2003 and 1–23 August 2004. In the first three summers, the chambers were treated identically: the same cleaning and reteflonizing procedures were performed for both chambers. In 2004, in one chamber (black line) the pine shoot was regularly rinsed, while in the other (grey line) the shoot was kept untouched.

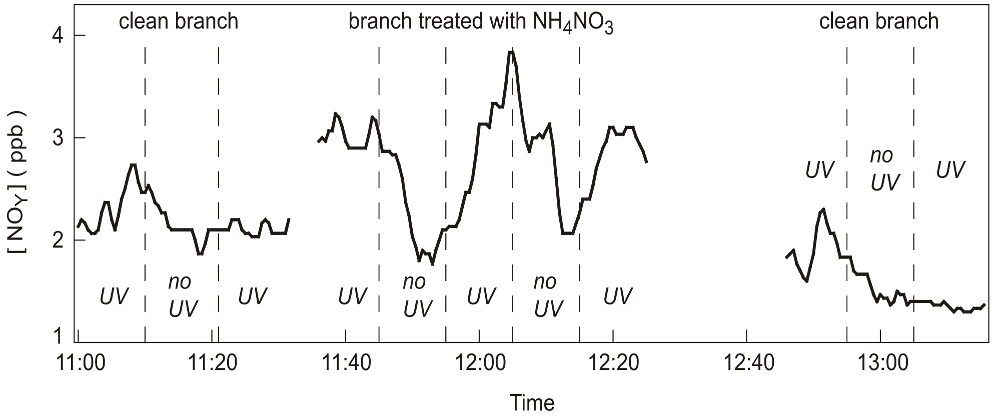

Figure 18. Effect of UV radiation on the NO_y concentration in a chamber that enclosed either a clean pine branch or a branch that had been treated with NH_4NO_3 solution. The branches were dead and dry, cut from the tree. The UV wavelengths were filtered away, using a Plexiglas plate. Adopted from Study III.

4.4 Net exchange of NO_y (IV)

Models used in the analysis

Consumption by the stomata was dependent linearly on the concentration gradient between the air and substomatal cavities, and on the degree of stomatal opening that was represented by g_{NO2} (mm s^{-1}). The internal concentration was derived by assuming balance between diffusion and the consuming reactions at the mesophyll surface (Eq. 4).

$$g_{NO2}(C_E - C_I) = a_1 C_I \tag{4}$$

where, C_E is external NO_y concentration (µmol m^{-3}), C_I stands for internal concentration (µmol m^{-3}) and a_1 is the reaction rate at the surface (mm s^{-1}). Solving for C_I results in:

$$C_I = \frac{g_{NO2}}{a_1 + g_{NO2}} C_E \tag{5}$$

When the nonstomatal consumption on the needle surfaces was assumed to be dependent linearly on the ambient NO_y concentration, the total consumption flux J_C (nmol m^{-2} s^{-1}) became:

$$J_C = -g_{NO2}\left(C_E - \frac{g_{NO2}}{a_1 + g_{NO2}} C_E \right) - a_2 C_E \tag{6}$$

where a_2 is the constant rate of nonstomatal consumption (mm s^{-1}). The NO_y production J_P (nmol m^{-2} s^{-1}) was presented by a simple linear model:

$$J_P = a_3 I_{UVA} \tag{7}$$

where a_3 is a parameter (with the dimension nmol W^{-1} s^{-1}) and I_{UVA} is UV-A irradiance (W m^{-2}). A positive flux hence denotes production, while negative shows consumption. The net NO_y flux, J_{net}, is the sum of the two processes of consumption and production:

$$J_{net} = -g_{NO2}\left(C_E - \frac{g_{NO2}}{a_1 + g_{NO2}} C_E\right) - a_2\, C_E + a_3\, I_{UVA} \tag{8}$$

Results of the analysis

Results of the parameter estimation are presented in Table 2. The values of parameter a_1 can be related to the range of stomatal conductances that were used for the estimation: the maximum for shoot 1 was app. 1.2 mm s^{-1}, and for shoot 2 app. 0.8 mm s^{1}. This suggests that in shoot 1 the rate of reactions on the mesophyll surfaces was 68% of the maximum g_{NO2}, while in shoot 2 it was 43%. NO_y consumption on the needle surfaces (parameter a_2) appears minor relative to the absorption by the stomata: it cannot exceed the stomatal consumption even at the minimum g_{NO2} of 0.05 mm s^{-1}.

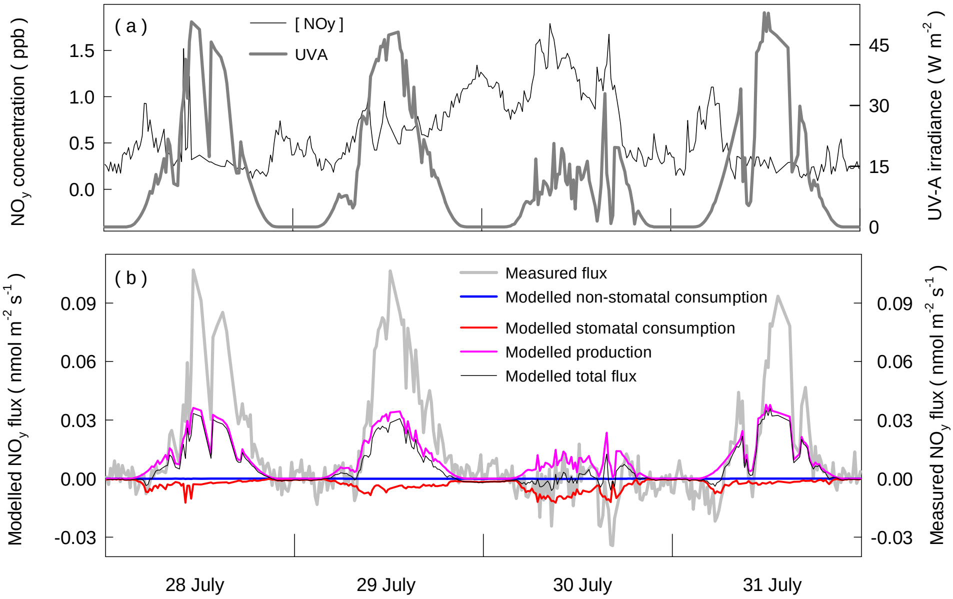

Figure 19. Comparing the measured and modelled NO_y flux for shoot 2 on 28–31 July 2001. (a) The ambient NO_y concentration and UV-A irradiance of these days. (b) The components and the total of modelled NO_y fluxes and the measured NO_y fluxes.

Table 2. Values of the model parameters (see Eq. 4–7) estimated for two pine shoots.

Parameter	Shoot 1	Shoot 2
a_1 (mm s^{-1})	0.812	0.343
a_2 (mm s^{-1})	0.0108	0.0037
a_3 (W^{-1} s^{-1})	0.000826	0.000715

Figure 19 shows how the model performed for the last 4 days of July 2001. The days were chosen since they formed one of the longest time periods during that summer with no gap or other interruption in the measurements. The most evident result here was that the emissions were much higher than the model predicted. The ambient NO_y concentration remained quite low during these days, thus, the consumption was also small. However, the effect of consumption can be seen, e.g. on 30th July. The modelled value for J_{net} was lower than the modelled NO_y production, and it followed the measured flux more closely than did production only. In the early morning of 31st July, the ambient NO_y concentration was slightly elevated, making the estimated consumption increase, which decreased the value for J_{net} below that of the modelled emissions and which was closer to the observed flux. In fact, the measurement showed stronger deposition than the model predicted.

Whether production or consumption dominates J_{net} is dependent on the combination of g_{NO2}, I_{UVA}, and C_E. Generally, the predictions of the model can be examined with the concept of the compensation point, i.e. the value of C_E at which the J_{net} equals zero. Figure 20 shows the compensation points for different values of g_{NO2} (of the range observed within these measurements) as a function of I_{UVA} using the parameters of shoot 1. The compensation point was strongly dependent on I_{UVA} and g_{NO2}, decreasing with an increasing degree of stomatal opening, and increasing with increasing I_{UVA}. At an I_{UVA} of 40 W m^{-2}, the compensation point remained above 2 ppb and rose to 4 ppb when the g_{NO2} decreased to 0.5 mm s^{-1}. Compensation points of several ppb were also obtained with lower I_{UVA}, app. 20 W m^{-2}, combined with a g_{NO2} of 0.1–0.5 mm s^{-1}. Our measurements suggested that this is a realistic combination occurring at the SMEAR II station.

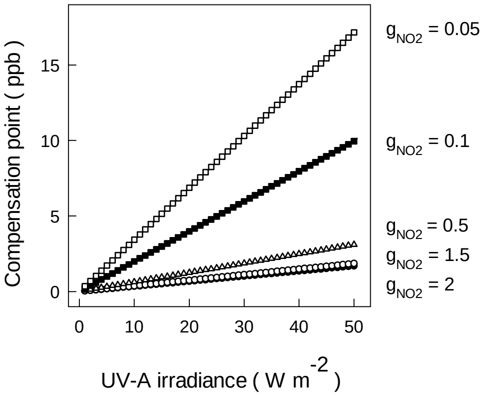

Figure 20. Dependence of the NO_y compensation point on UV-A irradiance, at different stomatal conductances for NO_2 (mm s^{-1}, values for each set of points are shown on the right), estimated from data obtained with a single pine shoot. The compensation points are shown for conditions of 20 °C and normal ambient pressure. Adopted from Study IV.

5. DISCUSSION AND CONCLUSIONS

Measuring NO_y fluxes with chambers

The NO_x fluxes of plants have often been measured in the laboratory or greenhouse (Thoene et al. 1996, Weber and Rennenberg 1996, Wildt et al. 1997, Geßler et al. 2000, Gut et al. 2002). The gas concentrations in the air entering the chambers have also been controlled under field conditions (Johansson 1987, Rondón et al. 1993, Geßler et al. 2000, Hereid and Monson 2001, Sparks et al. 2001, Geßler et al. 2002). No other studies, in addition to ours, have monitored NO_x fluxes under completely noncontrolled ambient conditions, probably because using the chamber method with chemically reactive NO_x is demanding, even with controlled quantities of other chemical compounds in the system. For example, O_3 oxidizes NO to NO_2; thus, the effects of O_3 must be prevented or determined. In several studies, O_3 was removed from the inlet air (Rondón et al. 1993, Geßler et al. 2000).

An evident requirement for proper NO_x flux measurements is, of course, an NO_2-specific gas analyser. Even if the gases entering the measuring system are controlled and only NO_2 used as the NO_y, the possible emissions of other NO_y species disturb the measurement. Based on the present study and the literature, flux measurements are relatively straightforward when the concentration of NO_x is so high that the flux is one of deposition. Our empty chamber at least differed clearly from those enclosing shoots at high ambient concentrations; although there was some deposition in the empty chamber, it was nowhere near the deposition fluxes observed in those with shoots. Even if the chamber blank caused some uncertainty in the magnitude of the deposition flux, it apparently cannot obscure any clear NO_x uptake by the plant. At low concentrations, however, the situation is complicated. In our case, the chamber caused significant systematic error in the measurements, and distinguishing the fluxes that were related to the plant from those that came from the chamber surfaces was difficult. Other researchers have often neglected these measurements at such low concentrations, since they have been below the detection limits of the systems used.

One important observation that should be given more detailed future study is the effect of simulated transpiration on the NO_y emissions from the chamber walls. In case this association actually exists, a separate always-empty blank chamber may not be useful, due to lack of transpiration. Our observations in the chambers suggest that only the chamber surface may enable a photochemical NO_y-producing reaction, but that the reaction rate may be dependent on water. In general, the background reactivity in environmental chambers is dependent on RH (Killus and Whitten 1990). The data presented in Zhou et al. (2003) indicate that the photochemical HONO production on the glass surface also peaked immediately after the RH was elevated. However, it is difficult to evaluate whether these findings are relevant for explaining the observations made in the present study. Transpiration in a shoot does not maintain the water concentration in a chamber above the ambient level when the chamber is open and not measuring, due to effective ventilation. Therefore, the humidity rises only when the chamber is closed, which is quite a short time for any changes in the state of the chamber walls to occur. Moreover, the chemical and physical conditions in our field measurements are not controlled, and there is a myriad of chemical species present, but at relatively low concentrations compared with the purely gas-phase chemistry experiments.

The sub studies in this thesis also report other results, contradicting the notion that the NO_y emissions from the shoot are simply an artefact caused by transpiration. First of all, the emission level was higher in the blank chamber than in some of the shoot chambers, e.g. in late summer 2004, after the pine shoot in one of the chambers had been frequently cleaned with water. This indicates that even if the transpiration affected the NO_y-producing reaction on the chamber walls, the general level is determined by something else, the strongest candidate being the level and composition of the accumulated deposition on the chamber walls. In addition, we found that the daily NO_y emissions related to solar irradiance do not form a loop. This, however, would be expected if the transpiration affected the emissions, since the daily transpiration also forms a loop. In any case, this aspect requires further study, and the effects of water flux should be analysed in detail.

Generally, to effectively measure small NO_y fluxes, all the reactions on the chamber walls should be eliminated. Frequent renewing of the Teflon coatings and cleaning of the chamber surfaces with water, or another suitable solvent, reduced the chamber blank. However, preventing the surface reactions completely seems impossible, especially under field conditions, where unknown amounts of compounds can freely flow into the chambers. It may not be reasonable to perform these as pure field measurements at all, but it would be worthwhile to control the gases and chemical species entering the chamber. The price one pays for controlled conditions is that some naturally existing environmental factor relevant for the study may be missed, and the measurements would thus diverge from those obtained under natural conditions. At the SMEAR II station, nitrate accumulated on those pine shoots that were enclosed in chambers, shielded from rain. Although they differed from the free shoots in this sense — this has even promoted the SMEAR group to develop a new type of chamber, that allows the pine shoots to be exposed to rain and fog most of the time — a complete lack of nitrate would have been perhaps a bigger loss. Another type of improvement in these measurements would be to try to increase the signal by increasing the plant surface in the chamber and minimizing the ratio of chamber surface area to volume. A spherical chamber would be better than a box in this respect.

Solar UV irradiance certainly affects the chamber blank, and this should be taken into account when measuring the NO_y fluxes with chambers. UV radiation also appears to affect the NO_y fluxes of a plant, and thus, excluding the UV from the measurement, e.g. by using a UV-opaque chamber material or a lamp that emits only visible light, may bias the results.

What is the origin of the UV-induced NO_y emissions?

If the pine branches emit NO_y under UV exposure, the first question to consider is whether the emission comes from plant metabolism or from a surface reaction similar to the one generating NO_y on the chamber walls. The two main (nonexclusionary) theories of metabolic mechanisms generating NO_x are that the nitrate reductase (NaR) produces NO from nitrite, and that an nitric oxide synthase (NOS) produces NO from arginine (Crawford 2006). Significant NO escape from plants appears to be a consequence of the NaR reaction occurring in leaves in which NO_2^- has accumulated. Needles of the Scots pine trees at SMEAR II most likely do not contain accumulated NO_2^-, since pines prefer to metabolize NO_3^- already in the roots, especially when the NO_3^- supply in the soil is low as at the Hyytiälä site. There apparently is some NO_3^- and NO_2^- in the needles because of atmospheric NO_x dissolving in the apoplastic water, but not significant amounts. Thus, the NaR- NO_2^- reaction is not likely to be relevant in the SMEAR II needles.

Wildt et al. (1997) observed NO emission that apparently originated from plant nitrate metabolism, from free nitrite inside leaves. They found that the NO emission rate had a more or less linear relationship with the CO_2 uptake rate, and concluded that the NO emissions were related to photosynthetic activity. The present study analysed the association between photosynthesis and NO_y emissions. The analysis was not very powerful, because the main pattern with both CO_2 uptake and NO_y emission is dependent on solar irradiance. However, the conclusion was that the NO_y emissions were not associated with the CO_2 exchange, since their relationships with solar irradiance were slightly different. The NO_y emissions were linearly dependent on irradiance under all conditions, while the CO_2 uptake rate saturated at high levels of irradiance and the NO_y emissions did not form a loop as the CO_2 uptake did sometimes on warm, sunny days. This loop appears partly because the degree of stomatal opening in relation to irradiance is usually higher in the morning than in the afternoon. Even if a metabolic mechanism producing NO_y was not related to photosynthesis itself, the release of NO_y should occur via the stomata and the stomatal control should affect it. The linear dependency on solar irradiance fitted much better with the idea of a photochemical reaction.

A photochemical surface reaction was also supported by the finding that the chamber history is crucial in NO_y fluxes. When the Teflon coating on the chamber walls was new and all the surfaces clean, the emissions were lower than after the chamber had been measuring undisturbed for longer periods of time. The emissions increased both in the empty chamber and shoot chambers. In the empty chamber, the emissions decreased every time the Teflon surfaces were renewed. When two similar shoot chambers were monitored over the summer, the difference being that in one the shoot was untouched while in the other the shoot was rinsed with tap water at regular intervals, the emissions in the rinsed chamber became clearly lower. During the three previous summers, the NO_y fluxes in two similar shoot chambers were very similar. The deficiency in the experiment was that not only the shoot but also the chamber walls became coated with water, making it now impossible to determine how well the walls, in fact, were cleaned. In any case, washing the shoot and possibly the chamber with water influenced the NO_y emissions, indicating that water-soluble compounds are somehow associated with this phenomenon.

The precursor of the emissions from the surfaces was hypothesized to be NO_3^-/HNO_3, which was supported by published research on photo-generated NO_y emissions from snow and glass surfaces. Honrath et al. (2000), Dibb et al. (2002), and Cotter et al. (2003) observed light-induced NO and NO_2 emission from snow only if it contained NO_3^-. The absorption spectrum of NO_3^- in aqueous solutions shows a weak absorption band at approximately 260–330 nm, the maximum being at 302 nm (Mack and Bolton 1999). A stronger band occurs at such short wavelengths (maximum near 200 nm) that they do not exist in the solar spectrum on the earth's surface. Cotter et al. (2003) found that the NO_x production in snow stopped when radiation at wavelengths below 345 nm was filtered away, which was consistent with the idea of nitrate photolysis being the NO_x source. Zhou et al. (2002, 2003) showed that photolysis of HNO_3 also produces NO_x and HONO on glass surfaces. Ramazan et al. (2004) proposed that the mechanism of this is that HNO_3 forms complexes with water on surfaces, and these complexes are photolysed. It thus seems clear that on some surfaces nitrate photolysis generates gaseous NO_y, at least NO_x and HONO.

For the NO_y emissions observed at SMEAR II, the first condition to fulfil is to not exceed the nitrate deposition at the site. This was evaluated by comparing the emissions with HNO_3 + NO_3^- deposition estimated from European Monitoring and Evaluation Programme (EMEP) measurements at the Ähtäri site, app. 100 km away from Hyytiälä, and HNO_3 concentrations measured during the Biogenic Aerosol Formation in the Boreal Forest

(BIOFOR) campaign at SMEAR II (Janson et al. 2001). Based on these, the nitrogen deposition was at least 5–10 times higher than the emissions, hence, there should have been enough nitrate to allow for the emissions. In particular, we observed that the pine shoots that had been inside the chambers, thus not exposed to cleaning rain and fog, accumulated nitrate compared with free shoots outside the chambers. We also showed (in the experiment performed at CEAM; III) that the NO_y concentrations in a Teflon chamber were dependent on the presence of UV radiation, if the pine needle surfaces in the chambers had been treated with nitrate. With clean pine needles, the concentration was not affected by UV filtering (Fig. 18). The concentration changes were not very large, considering that the nitrate treatment had resulted in abundant nitrate on the pine needles, much more than under the natural conditions in Finland. It is difficult to evaluate the significance, since the conditions were so different. For example, in the small chamber the compensating air consisted of purified air from a bottle, with RH near zero, and the pine shoot was dead, thus not transpiring. However, UV radiation clearly affected the NO_y production in the chamber and only when there was nitrate inside.

Why the phenomenon has not been observed in other studies on NO_y exchange in plants could be a consequence of measuring mainly at higher concentrations and under controlled conditions, and not exposing the chamber interior and the plant to UV radiation. For instance, Schimang et al. (2006), who acknowledged the possibility of photo-induced HONO emissions from the plant surfaces but did not observe any, used chamber material that transmitted only radiation of wavelengths above 350 nm. Thus, the absorption band of nitrate was filtered away. A study somewhat supporting the nitrate photolysis theory is that of Geßler et al. (2000), who measured NO_2 exchange on beech trees, both in a field area with high nitrate deposition and in a lab with greenhouse-grown seedlings and apparently a

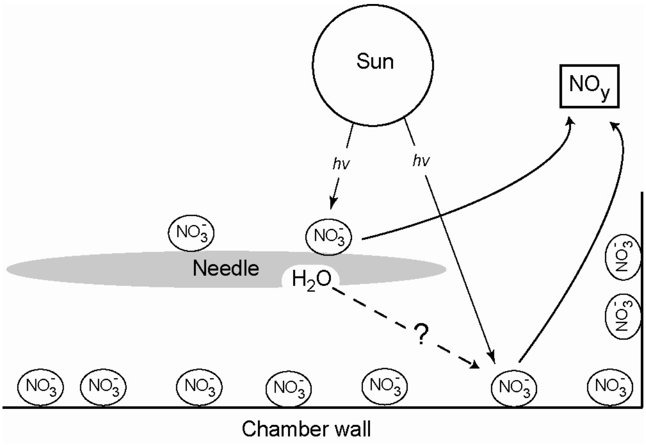

Figure 21. Schematic of the processes assumed to occur in the gas-exchange chamber. Nitrate molecules are attached on the chamber and needle surfaces and UV photons dissociate them, which produces NO_y. Water transpired by the needles may affect this dissociation reaction on the chamber surface.

lamp as the light source. Their chamber was made of borosilicate glass, which transmits UV radiation, although the transmission at 302 nm is only 40%. They observed emission of NO_2 at near-zero concentration in the field, but not in the lab.

In canopy-level studies, observing these emissions may be more difficult. There is in any case the NO emission from the soil, which can explain any upward NO_x flux. Horii et al. (2004) observed that at low concentrations, the net NO_x flux of the forest approached zero, and they suggested that it was because NO_x was emitted from the upper canopy, as our study (I) reported.

It has been quite convincingly shown that under some conditions and on some surfaces, photolysis of nitrate produces gaseous NO_y. The crucial question here is which materials can act as the producing surface. Based on the observations presented here, the FEP Teflon film and/or quartz glass walls of the gas-exchange chambers and, more importantly, Scots pine needles apparently can, while other plants would probably behave similarly. Figure 21 illustrates the processes suggested to occur in the chambers.

Composition of the emitted NO_y

To evaluate the implications of the observed NO_y emissions, the chemical composition of the bulk NO_y should be known. The only NO_y species that was actually measured individually was NO. Generally, the NO flux was negligible. In the measurement system at SMEAR II, O_3, for instance, was always present to oxidize NO molecules to NO_2. The estimations showed that NO losses of about 42% or 58% (depending on the set up) were expected; hence, small NO fluxes could become nondetectable. However, concentrations above approximately 0.26 ppb were not reduced below the detection limit. Based on this, the possibility of a significant NO flux can be excluded and we conclude that the emissions consisted mainly of compounds that the analyser detected as NO_2.

The NO_y analyser used in this study apparently detected all NO_y species, except HNO_3, which is retained by the sample lines and particle filters. The conversion efficiencies for species other than NO_2 are nearly 100% in this type of NO_x analyser (Gerboles et al. 2003, Steinbecher et al. 2007). This basically suggests that any chemical reaction converting one NO_y species (exclusive of HNO_3) to another in the gas phase cannot be detected as net emission in the chamber. The precursor was not measured by the gas analyser, due to adsorption on the surfaces. For instance, the heterogeneous formation of HONO by NO_2 and water should not, in principle, appear as a change in NO_y concentration, since HONO and NO_2 are both measured in the same way by the measurement system.

The HNO_3/nitrate photolysis on snow and glass surfaces produces NO_2, NO and HONO. In the snow studies, the observed HONO production compared with NO_2 production was app. 40% (Beine et al. 2002), 25% (Dibb et al. 2002), or even lower (Honrath et al. 2002). Beine et al. (2006) suggested that the generation of HONO is low when the snow is alkaline. Zhou et al. (2003) found that on glass surfaces, only NO_2 was produced at 0% RH, but HONO production was initiated when RH increased. The authors suggested that NO_2 is the primary product of HNO_3 photolysis, and HONO is generated from the NO_2 produced in a reaction with water. They observed the proportions of HONO and NO_x to be nearly equal at 50% RH. NO production was negligible compared with that of NO_2.

The chamber and needle surfaces at SMEAR II were acidic rather than alkaline and the RH was, naturally, above zero, sometimes approaching 100%. Hence, the best estimate for the composition of the UV-induced NO_y emissions in the chambers is that they consisted of NO_2 and HONO, with NO_2 being slightly more abundant.

Implications for NO_x exchange in plants

The role of vegetation in the atmospheric balance of NO_x is dependent on the atmospheric NO_x concentration. At high concentrations, plants absorb NO_x (or at least NO_2) from the air, but at concentrations low enough they may possibly emit NO_x. The limit concentration at which plants turn from absorbers into emitters is the compensation point. The present study suggested that the limit concentration is not a single constant number but is dependent on the degree of stomatal opening (which, in turn, is dependent on different environmental factors) and UV-A irradiance, which determines the processes that induce the deposition and emission fluxes. The estimations suggested that the compensation point decreases with an increasing degree of stomatal opening and increases with increasing UV-A irradiance. The variation is wide and, what is most distinctive in comparison to previous studies, the compensation point can increase to several ppb under normal environmental conditions.

This thesis was based on measurements of NO_y fluxes, not NO_x or NO_2. Hence, the crucial question is to what extent the results reflect the properties of NO_x exchange. Basically, the justification for comparing them with the results of previous NO_x and NO_2 studies is that the most probable process underlying the UV-induced NO_y emissions is nitrate photolysis, which produces mostly NO_2. In this case, the emissions would also include some HONO, and this portion, perhaps close to 50%, would cause some overestimation of the NO_x flux and the compensation points.

In evaluating the reliability of the compensation point estimation, the effect of the assumed UV-induced emissions comes naturally under the spotlight. The model would have provided different results if it had not included the emissions. In the model, the internal NO_y concentration was defined as proportional to the external concentration and the degree of stomatal opening, which suggests that with no NO_y emission, the compensation point would be zero. At all concentrations above this, the flux would be deposition to the needles. Another way to acquire a zero net flux is to have zero a_1 (the reaction rate at the surface) and a_2 (rate of non-stomatal consumption), meaning no processes removing NO_y would exist, however high the ambient concentration. This is not realistic, according to the current level of understanding of NO_x uptake metabolism. Thus, the nonzero compensation points originated only from the emission assumption.

The compensation point would also rise above zero if the emissions were of metabolic origin. Metabolism was not included in the model used in this study, since it was not considered relevant for the pines at SMEAR II. It could, however, be implemented in the model in a manner similar to that of stomatal consumption (Eq. 6). The parameter would then describe the rate of an NO_y-releasing process on the mesophyll surface. This process would maintain an internal NO_y concentration that would equal the compensation point (if there were no surface reactions releasing NO_y). Most likely, this NO_y production would not be constant either, which suggests that the compensation point would also vary. The NO_2 emissions observed by others were of the same magnitude as the NO_y emissions studied here, 0.01–0.05 nmol m^{-2} s^{-1} (Hereid and Monson 2001, Geßler et al. 2002), indicating that they could govern the compensation point in a manner similar to that of the UV-induced NO_y emissions.

The most extreme of the compensation point values obtained were high, more than 20 ppb. They should be tested under laboratory conditions, since a combination of high UV irradiance with near-zero stomatal aperture and high ambient NO_y concentration does not occur in the field. The UV-induced NO_y production is still a poorly understood phenomenon. It is not known whether the process actually would behave similarly at very high and low concentrations, which was one of the assumptions underlying the model. In case the UV-induced emissions are from a photochemical reaction of NO_3^-/HNO_3, their magnitude could be affected by the amount of accumulated material on the needle surface, which in turn is affected by weather and time. The comparison between measured and modelled NO_y fluxes (Fig. 19) may reflect this: the data were measured approximately one month later than those that were used for estimating the model parameters, thus the pine shoots had had time to accumulate more NO_3^-. NO_y production inside the chambers may thus be higher than on the branches outside, since rain washes the latter. However, there are regions where NO_3^- deposition is high and the climate dry; thus, the amount of NO_3^- accumulated on the leaf surfaces could be much higher than in the chambers at SMEAR II.

In conclusion, it seems an oversimplification to consider single constant compensation points of NO_x exchange in plants, when it so obviously either varies or is zero, depending on whether NO_x production in or on the plant is expected or not. The NO_x exchange could rather be implemented in process models. There is a level of understanding on how the consumption of NO_x inside the plant occurs, since several studies have indicated NaR activity and that the apoplastic ascorbate is significant for removing NO_x that has entered the plant stomata (Eller and Sparks 2006). The NO emissions of metabolic origin should also be studied more at branch or plant level to enable determination of their atmospheric significance. They seem to require accumulated NO_2^- inside the plant leaves, and Wildt et al. (1997) observed that the emissions occurred, depending on the form of nitrogen the roots receive, NO_3^- or NH_4^+, even in same plant species. It would be interesting to know whether plants in general would begin to emit NO if they simply received enough NO_3^-. Thus, the compensation point of vegetation in an area would be dependent on the NO_3^- load in the soil, and it would increase since nitrogen deposition has been predicted to undergo future increase. This would also increase emissions from the leaf surface, since the amount of NO_3^- deposited would be higher.

Atmospheric implications

It is evident that when the airmass carries high concentrations of NO_y in Hyytiälä, vegetation acts as a sink for them. These occasions are rare, but the effect of trees should in any case be considered in air chemistry models.

If there were NO_y production on plant surfaces, it also would contribute to the atmospheric budget of NO_x. The review paper by Grannas et al. (2007) on photochemistry in snow discussed the fate of photo-generated NO_x. Apparently a portion of the emitted NO_x reacts rapidly to reform HNO_3, which deposits rapidly back on the snow, the proportion depending on the conditions. Some studies have indicated that NO_x and HONO can largely escape to the atmosphere. In contrast, others observed that the circle was almost closed: once NO_x was released from photolysis, it was rapidly redeposited as HNO_3.

The contribution of the UV-induced NO_y emissions in the air concentrations at SMEAR II was roughly estimated by adding them in a new air chemistry model SOSA (M. Boy, personal communication). They were introduced as an NO_2 flux that comes from a flat surface 20 m in height, depending linearly on UV-A irradiance as 0.004 nmol W^{-1} s^{-1} × UV-

A (W m^{-2}). This gave a maximum emission at strong UV-A around 0.2 nmol m^{-2} s^{-1}. They were compared with NO_2 concentrations measured at SMEAR II. For July 2003, the result of the comparison was that the NO_2 emitted from the trees would have formed less than 5% of the NO_2 observed at the lowest levels (up to 200 m in height). Thus, using this estimation, we suggest that locally the emissions are not very significant compared with other NO_x sources.

Assuming an average NO_y emission of 0.05 nmol s^{-1} m^{-2} of forested area for 10 h d^{-1}, results in a total emission of about 18 mmol d^{-1} ha^{-1}, or 250 mg of nitrogen. The estimation of daytime HNO_3 deposition at SMEAR II resulted in 1–14 ng N m^{-2} s^{-1}. Assuming an average HNO_3 deposition of 5 ng m^{-2} s^{-1} for those 10 h means 1.8 g of nitrogen deposited as HNO_3. Thus, approximately 15% of the deposition would be released back to the air, but apparently part of it would soon be redeposited back on the surfaces.

On a global scale: if the emissions would occur throughout the year as estimated above, 250 mg d^{-1} ha^{-1} of boreal forest over an area of app. 15 million km^2, they would release 135 kt of nitrogen. Compared with the NO_x emissions shown in Table 1, the emissions from trees would be 3% of those released from soils, 0.5% of those released in energy production and 0.3% of total N emitted as NO_x. If they were extrapolated to all the world's forests (area 48 million km^2), the percentages would increase to 8%, 2% and 1%. This is a large amount. Naturally, in large areas of the world the air concentrations of NO_y are high, hence, the fluxes would be deposition, and the situation would be different when trees are covered by snow etc. In any case, the calculated values are so high that further studies are needed before the global significance of the UV-induced NO_y emissions from trees can be determined.

Conclusions

Emission of NO_x from plants is an inadequately known phenomenon. Plants are able to produce NO in their metabolism, and it has been suggested that part of this NO could escape from the plant, forming the NO_x emissions that have sometimes been observed in flux measurements at near-zero ambient concentrations. These observations have been rare, either because NO_x is not always emitted, or because interpreting the measurements is too complicated. However, it would be important to know the whole story about NO_x or NO_y emissions, since they have implications both for plant and atmospheric science.

The present study indicated that solar UV radiation releases reactive oxidized nitrogen, NO_y, from Scots pine shoots. The emissions most probably came from the needle surfaces, not from metabolism via the stomata. This was a novel observation and interesting for several reasons. In atmospheric chemistry, photochemical surface reactions producing NO_x on plant leaves have not been considered as an NO_x source, nor have they been taken into account in analysing leaf-level gas exchange in plants. Our estimations showed that with these UV-induced emissions from leaf surfaces, a plant would act as an NO_y source rather than a sink at ambient concentrations of several ppb, much higher than is usually believed. Rough calculations showed that the emissions could contribute a small percentage to the local NO_y concentrations, and form an unignorable source of nitrogen on a global scale. It is, however, too early to estimate these, since open questions still remain on the phenomenon.

That in this study the chamber measurements were performed at low ambient concentrations and under natural conditions, thus preparing the way for observing the emissions, was an advantage, but this was also the main complication. The artefact NO_y

fluxes originating from the measurement system disturbed the analysis significantly, and the origin of the artefacts is still not completely known or under control. Solar UV radiation and contamination of the chamber surfaces clearly affected the chamber blank, but the role of transpiration requires further experimental work.

Although the chamber blanks, artefacts and non-specific NO_x analysers are problematic, the theory of nitrate photolysis generating NO_x and HONO on the needle surfaces is plausible. It is in accordance with the observations: the activity of the emissions when filtering away UV wavelengths is very similar to what has been observed on snow and glass surfaces. In general, the phenomenon appears very inorganic, with the emissions increasing when surfaces become dirty, always responding to UV radiation, and depending linearly on the irradiance.

This phenomenon must be taken into account in studying the NO_x or NO_y exchange of plants. Some of the other emission observations reported in the literature may also have been affected by surface reactions. When the metabolic processes are examined in further detail, the UV-induced emissions from surfaces generally bias the measurements. However, when the fluxes of NO_y are studied at the ecosystem level, these surface reactions are an inseparable part of the system and should be taken into account as part of the total flux.

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