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Estimating the uptake of traffic-derived NO_2 from ^{15}N abundance in Norway spruce needles

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Abstract The ^{15}N ratio of nitrogen oxides (NO_x) emitted from vehicles, measured in the air adjacent to a highway in the Swiss Middle Land, was very high [$\delta^{15}N(NO_2) = +5.7‰$]. This high ^{15}N abundance was used to estimate long-term NO_2 dry deposition into a forest ecosystem by measuring $\delta^{15}N$ in the needles and the soil of potted and autochthonous spruce trees [*Picea abies* (L.) Karst] exposed to NO_2 in a transect orthogonal to the highway. $\delta^{15}N$ in the current-year needles of potted trees was 2.0‰ higher than that of the control after 4 months of exposure close to the highway, suggesting a 25% contribution to the N-nutrition of these needles. Needle fall into the pots was prevented by grids placed above the soil, while the continuous decomposition of needle litter below the autochthonous trees over previous years has increased $\delta^{15}N$ values in the soil, resulting in parallel gradients of $\delta^{15}N$ in soil and needles with distance from the highway. Estimates of NO_2 uptake into needles obtained from the $\delta^{15}N$ data were significantly correlated with the inputs calculated with a shoot gas exchange model based on a parameterisation widely used in deposition modelling. Therefore, we provide an indication of estimated N inputs to forest ecosystems via dry deposition of NO_2 at the receptor level under field conditions.

Key words ^{15}N · Forests · Spruce · *Picea abies* · NO_2 deposition

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Introduction

Dry deposition of reduced or oxidised nitrogen compounds to nitrogen-limited ecosystems such as moors, heathlands, forests and lakes may represent a significant contribution to the nitrogen nutrition of plants in these systems. The main consequences of the increased nitrogen input are acidification of soils (Wilson and Skeffington 1994), eutrophication of terrestrial and wetland ecosystems (Bobbink 1991), nutrient imbalances in the plants (Wellburn 1990), and, on the level of plant communities, the loss of biodiversity in sensitive ecosystems (Bobbink et al. 1992). Nitrogen input may also be a cause of forest decline in Europe (Nihlgård 1985; Schulze 1989; Seith et al. 1994; Manderscheid and Jäger 1993).

In parts of Europe, ecosystem nitrogen loads are dominated by ammonium deposition, whereas the oxidised nitrogen compounds (NO_2, HNO_3) contribute substantially in others (Lövblad and Erisman 1992; Duyzer and Fowler 1994). The precursor of the latter compounds is NO which is mainly emitted by combustion processes in, for instance, vehicles, power plants, garbage and oil burners, although recently much effort has been undertaken to reduce these emissions by catalytic reduction to N_2. NO itself contributes a minor proportion of the deposition, but may be regarded as source of NO_2 in the photochemical equilibrium with ozone. Gas phase removal of NO_2 by the OH radical, producing nitric acid (HNO_3), is rather slow and determines the NO_2 life-time, typically a few days in the troposphere (van Aaalst and Diederen 1985).

HNO_3 and particulate nitrogen (Lovett and Lindberg 1993) are deposited readily (limited only by turbulent transport) on any surface, e.g. cloud droplets or plant cuticles (Cadle et al. 1991; Hanson and Garten 1992), and therefore contribute to nitrate input into the soils mainly by stemflow and throughfall (Eilers et al. 1992). In contrast, the pathway of NO_2 deposition in plants is mainly stomatal, i.e. by gas exchange (Hanson and Lindberg 1991; Duyzer and Fowler 1994). Most plants

are able to assimilate NO_2 acquired by the leaves, by enzymatic reduction to ammonium (Yoneyama et al. 1980; Rowland et al. 1987; Wellburn 1990; Nussbaum et al. 1993).

In Norway spruce, as well as in most conifers and some other trees, nitrate and ammonium assimilation occurs primarily in the roots (Seith et al. 1994), and nitrogen is transported to the shoots in the form of amino acids (Manderscheid and Jäger 1993). NO_2 taken up by the needles is transformed into amino acids (von Ballmoos et al. 1993; Nussbaum et al. 1993). The total uptake rates are linearly related to stomatal conductance, although there is still some discussion about possible internal resistance to NO_2 uptake at very low concentrations (Thoene et al. 1991; Ramge et al. 1993; Rondon and Granat 1994).

Several studies on nitrogen deposition and cycling in forests have recently made use of natural isotopic composition (Virginia and Delwiche 1982; Gebauer and Schulze 1991; Högberg et al. 1992; Gebauer and Dietrich 1993; Durka et al. 1994; Högberg and Johannisson 1994; Buchmann et al. 1995). The variations in the concentration of the less abundant isotope ^{15}N are usually expressed in terms of the isotope ratio ($\delta^{15}N$) defined as follows:

$$\delta^{15}N = (R^{15/14}\text{sample}/R^{15/14}\text{standard}^{-1}) \times 1000(‰) \ ,$$

where atmospheric N_2 is used as the standard, and $R^{15/14}$ denotes the atomic ratio of ^{15}N to ^{14}N. Due to the mass-dependent behaviour of the isotopes, the isotope ratio in a particular chemical compound is influenced by physical isotope effects and biochemical transformations between the various system pools. The extent of enrichment or depletion of ^{15}N associated with assimilation, translocation, mineralisation and nitrogen loss processes in a forest has been partially assessed (Nadelhoffer and Fry 1988; Gebauer et al. 1994; Buchmann et al. 1995; Högberg et al. 1995). For nitrogen oxides, source-specific isotope ratios have been reported (Moore 1977; Heaton 1986; Heaton 1990; Freyer 1991). A quantitative analysis of the source-receptor relationship is possible when the ^{15}N abundance in NO_2 is markedly different from that in the soil. Attempts to relate air pollution to the nitrogen metabolism of conifers and their ^{15}N isotope ratios have been reported by Schlee et al. (1994).

The local and short-term responses of enzyme activities to NO_2 uptake have been investigated at the field sites used in this study, and published elsewhere (Ammann et al. 1995; von Ballmoos et al. 1998). In this study, the effect of the uptake of NO_2 with a particularly high ^{15}N abundance on $\delta^{15}N$ of potted and autochthonous spruce trees is investigated and related to the total NO_2 uptake at these sites.

Materials and methods

Layout of the field sites

Twelve sites with six 10- to 20-year-old spruce [*Picea abies* (L.) Karst.] trees each were selected in a mixed forest (*Galio odorati–Fagetum typicum* on pseudo-gley) in the Swiss Middle Land near Solothurn (47°8′N, 7°35′E, 480 m above sea level, a.s.l.). This forest area is crossed by a busy north-south highway giving rise to an NO_2 gradient. On a transect orthogonal to the highway the annual mean NO_2 mixing ratio was about 20 ppb (parts per billion by volume, 10^{-9}) close to the traffic lane and 5 ppb at a distance of about 900 m, corresponding to the ambient concentration in this densely populated area. The chosen sites were east and west of the highway and included a range of positions, namely forest edge, lower crown, and understorey. At three of the sites, 5 m, 130 m and 980 m (control) west of the traffic lane, 6-year-old potted trees were positioned at 1.5 m above soil from June 1994 until November 1995. These trees had been grown from the same batch of seeds, and were potted in polyethylene pots (20 l, diameter 340 mm, height 260 mm) containing the same soil for all sites (40% bark-compost, 40% peat and 20% sand). They were kept in a forest at the same site until 1994 (von Ballmoos et al. 1998). Grids were placed on top of the pots to prevent needles falling into the pots. Local NO_2 concentrations were obtained at every site as 2-weekly means using passive samplers that selectively retained NO_2 (FUB, Switzerland). A set of three samplers was mounted at each site at a height of about 1.2 m above the ground, or about 15 m for two crown sites. Six of the sites were equipped with sensors for temperature, relative humidity (Rotronic, Switzerland) and photosynthetically active radiation (given as quantum flux density, QFD) (SKL 2610, Skye Instruments, UK) controlled by two data logger stations (Campbell Scientific, UK). Data were recorded as 30-min means. Further information about QFD intensity directly at the shoots used for needle sampling was regularly obtained with an additional, hand-held, but otherwise identical, QFD sensor.

A relevée of the understorey according to the Braun-Blanquet method (Westhoff and Van der Maavel 1973) was conducted in May 1994 at each site over an area of 100 m^2 including all sampled tree individuals. No gradient in the plant community was found among the sites. A qualitative analysis of the soil profiles at all sites showed homogeneously the characteristics of pseudo-gley except at one site (980 m west of the highway) where a transition to para-brown soil was observed. Below the needle or leaf litter, almost no fermentation horizon was visible, and the transition from organic to mineral soil was continuous. In general, only a little litter from the previous year remained, indicating relatively high microbial activity.

Sampling procedures

The current-year needles of the potted trees were sampled in November 1994 and 1995, and needles that had grown in 1993 and 1994 and roots were additionally sampled in November 1995. Soil samples from the pots were taken in July and November 1995.

The current-year needles of all selected field-grown trees were sampled in November 1993 and 1994. Samples of needles that had grown in 1993, 1994 and 1995 were taken in November 1995 at the three sites which also contained the potted trees. At these sites, soil samples were taken at the surface (litter) and at 5 cm and 20 cm depth in November 1995.

For each needle sample, 2–3 g needles (fresh weight) were cut from the twig at about 1.5 m above ground and 15 m above ground, respectively, and stored at 190 K until further use. The projected surface area of the needles was measured with a LI-3000 area meter (Li-Cor, USA) and converted to total surface area by multiplying by 2.65 (Oren et al. 1986). This surface area was used to convert the nitrogen uptake via stomata based on area to a dry weight basis. The remainder of the needles and all the root samples were dried for 24 h at 80°C, immersed in liquid nitrogen and homogenised using a dismembrator for 2 min at maximum speed.

Soil was sampled from the pots and the other sites by taking about 100 g of the topmost 5-cm (below the needle litter) soil layer with a high density of roots (transient organic/mineral horizon). From 15 to 20 cm depth about the same weight of material was sampled. The roots were removed immediately. The soil samples were dried at 105°C for 24 h, ground with mortar and pestal, and sieved through a 0.5 mm mesh. Needle litter was divided into (1) still green, and (2) brown, partly decomposed needle fractions. These samples were dried and homogenised in the same way as the fresh needle samples.

Sampling of NO_x-N

The principle of selective sampling of NO_x compounds by a denuder system follows the rationale presented by Braman et al. (1986), but is based on water-soluble and nitrogen-free coatings, which were partly used by Ferm and Sjödin (1985) and Williams and Grosjean (1987). The denuder system consisted of four tubular denuders (sand-blasted Pyrex tubes, 7 mm × 10 mm × 710 mm) in series for absorption of HNO_3, HONO, NO_2 and NO, with coatings of NaF, Na_2CO_3/glycerine, and KOH/guaiacol (two tubes), respectively. Before the fourth denuder, a solid oxidiser (CrO_3/H_3PO_4) on a firebrick support (Levaggi et al. 1972) was used to convert the remaining NO to NO_2 for absorption of NO-N in the last tube. The gas flow of 25 $cm^3 s^{-1}$ was provided by a pump. The coatings were prepared by wetting the tubes with a methanol (HPLC grade) solution of the respective coating material and drying in N_2 (99.9999%, Carba Gas, Switzerland). Capacity and selectivity tests were performed using pure sources of each gas alone (Braman et al. 1986). Only results of NO and NO_2 are presented here.

After the denuder system had been exposed for 3 days close to the highway (5 m from the traffic lane, near the field sites where needles were sampled), the tubes were eluted twice with 2 ml H_2O; 5 µl of the eluate were used to estimate the total amount of collected nitrite-N, the preferential product of NO_2 and guaiacol, which was about 20 µg N per sample. The remainder of the eluate was concentrated on a Speedvac (Savant, USA) to a suspension of about 20 µl and frozen until further analysis.

δ^{15}N-analysis

Part of the dry needle and soil samples and the concentrated suspensions containing the NO_x-N samples were combusted by an elemental analyser (Carlo Erba, EA 1108) coupled to an isotope ratio mass spectrometer (Finnegan MAT 251). With this system (Pichlmayer and Blochberger 1988), including a dead volume free gas splitting device and GC separation of undesired combustion by-products, a high sample throughput at a low sample consumption of 20–50 µg N with an analytical precision of δ^{15}N of $\pm 0.2‰$ is achieved. The rest of the samples were analysed with a continuous flow system consisting of an elemental analyser (Carlo Erba EA1108) coupled with the CONFLO II interface to the mass spectrometer (Delta S, Finnigan MAT) (Saurer et al. 1997; R. Siegwolf, M. Saurer, J. Bucher, D. Tarjan and U. Hartwig, unpublished work).

Data analysis

The time-resolved data for temperature, relative humidity and QFD were used as driving variables for the shoot gas exchange model described in Table 1 which is based on a calculation of stomatal conductances according to Baldocchi et al. (1987) and Jarvis (1976). These parameterisations are widely used for incorporation into larger-scale canopy stomatal resistance models (Duyzer and Fowler 1994) for NO_2. The parameters and functions specific to spruce used in this study are listed in Table 1. The stomatal conductance, g_s, was obtained as product of three functions, g_p(QFD), $a_v(V_d)$, and $a_t(T)$ for radiation, vapor pressure deficit and temperature, respectively. To estimate the total stomatal uptake of NO_2, the product of conductance and concentration of NO_2, u_N, was integrated from April (after bud break) to October.

For the sites not equipped with sensors, daytime means of temperature, humidity and radiation were estimated by interpolating between the sensor sites. This treatment included extended measurements with a hand-held QFD sensor at all sampled twigs throughout the year. At the positions of the fixed sensors, the correlation coefficient between the estimated quantities and those calculated from the time resolved data was always $r > 0.8$. All statistical results were obtained with the Systat (SPSS, USA) software package.

Results

Airborne δ^{15}N of NO_x

From nine NO_x samples collected every second week between April and August 1994, a mean value of δ^{15}N of NO_2 of $+5.7‰ \pm 2.8‰$ was obtained (Fig. 1) with a

Table 1 Needle stomatal conductance and estimate of uptake of NO_2-N

Function	Formula	Units	Constants	Reference
Model of stomatal conductance	$g_s = g_p(\mathrm{QFD}) \cdot a_t(T) \cdot a_v(V_d)$	ms^{-1}		Grace et al. 1975 Jarvis 1976
Uptake of NO_2-N	$u_N = g_s \cdot \frac{D_{NO_2}}{D_{H_2O}} \cdot \frac{C_{NO_2}}{M_{NO_2}} \cdot 10^{-1}$	nmol cm^{-2} s^{-1}	D_X: diffusion coefficient $D_{NO_2}/D_{H_2O} = 0.63$ C_{NO_2}: concentration (µg m^{-3}) $M_{NO_2} = 46$ g mol^{-1}	
Conductance	$g_p = \frac{1}{r_{min} \cdot (1 + b_s/\mathrm{QFD})}$	m s^{-1}	$r_{min} = 232$ s m^{-1} $b_s = 57$ µmol m^{-2} s^{-1} QFD Quantum flux density (µmol m^{-2} s^{-1})	Jarvis 1976
Temperature correction[a]	$a_t = \frac{(T - T_{min}) \cdot (T_{max} - T)}{400}$	$0 < a_t < 1$	T: temperature (°C) $T_{min} = -5$°C, $T_{max} = 35$°C	Wesely 1987 Baldocchi et al. 1987
Vapor pressure correction[a]	$a_v = \frac{1}{1 + b_v \cdot V_d}$	$0 < a_v < 1$	$b_v = 0.00027$ Pa^{-1} V_d: vapor pressure deficit (Pa)	Wesely 1987

[a] The constants used to calculate the temperature and vapor pressure deficit corrections to the conductance were used by Wesely (1987) and Baldocchi et al. (1987). The parameters used are based on the relationships suggested by Jarvis (1976), which were tested in Sitka spruce in a temperate forest

tendency (not significant) to decrease in the summer. The overall mean $\delta^{15}N$ of NO in the air was lower ($+3.1‰ \pm 5.4‰$) and showed much stronger variation between the early- and late-summer samples. Both the traffic density on this highway and the fraction of heavy-duty vehicles was homogeneous throughout the year. In summer 1994, the speed limit on one traffic lane was partly reduced due to roadworks nearby.

$\delta^{15}N$ of needles, soil and roots of potted trees

The two sets of potted trees exposed 5 and 130 m west of the highway differed strongly in $\delta^{15}N$ of current-year needles after only 4 months' exposure in autumn 1994 compared to the control placed at 980 m west of the traffic lane (Fig. 2). The increments in $\delta^{15}N$ were 2.0‰ and 1.6‰, respectively. One year later, the differences in the current needles persisted (3.2‰ and 1.6‰, respectively), and $\delta^{15}N$ decreased slightly with needle age, as shown by the needles that had grown in 1994 (Fig. 2). In needles that had grown in 1993 (i.e. before exposure to the highway) and were sampled in 1995, $\delta^{15}N$ increased by 1.95‰ and 0.79‰, respectively. In 1995, the soils without needle litter showed the same ^{15}N abundance at the three sites and were 5.0‰ above the $\delta^{15}N$ values observed in the needles of the control. In contrast, $\delta^{15}N$ values of the roots increased from –0.44‰ at the control site by 2.5‰ and 1.0‰ for the sites at 5 m and 130 m distance from the highway, respectively (data not shown in Fig. 2).

$\delta^{15}N$ of needles and soil of field grown trees

Current-year needles of autochthonous trees sampled at all sites in November 1993 and 1994 showed a strong gradient, with $\delta^{15}N$ up to 2‰ 5 m from the highway and around −3‰ 980 m away (Fig. 3). ^{15}N abundance tended to be lower in 1993 than in 1994 (not significant). The understorey site at 75 m had experienced particularly low QFD throughout the year. At the three sites with the potted trees, needles and soil of the field-grown trees were studied in more detail (Fig. 4). Again, $\delta^{15}N$ values of current-year needles were comparable in all three years. In needles that had grown in 1993 and 1994, $\delta^{15}N$ decreased with age by about 1‰ at most, with no significant difference between 1- and 2-year-old needles compared to the corresponding current-year needles. As with needles, both soil samples (5 and 20 cm depths) showed a roughly parallel decrease in $\delta^{15}N$ (Fig. 4). In the topmost soil layer with the greatest density of roots, $\delta^{15}N$ was higher than in the needles by 4.2‰. The difference between 5 and 20 cm depth clearly decreased closer to the highway. The green needle litter collected in 1995 had $\delta^{15}N$ values 0.4‰ below that of the current-year needles, and the values in the brown, partly decomposed needles were 0.3‰ higher than in the green needle litter, with no significant differences among the three sites.

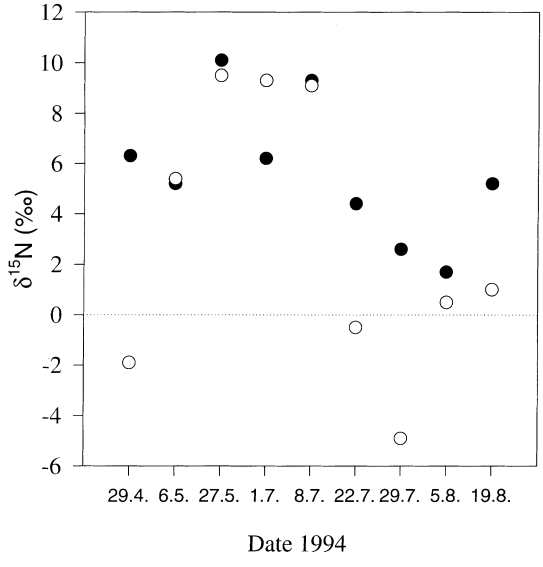

Fig. 1 $\delta^{15}N$ of NO_x in the ambient air along the highway sampled with the denuder tubes, about 10 m from the traffic lane. NO_2 (*solid circles*) and NO (*open circles*) were collected in denuders after removing nitric and nitrous acid from the gas

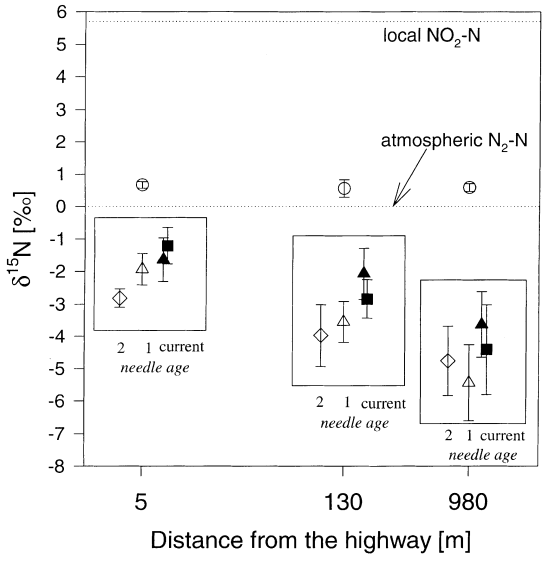

Fig. 2 $\delta^{15}N \pm SD$ in needles and soil (*circles*) of potted trees exposed 5 m, 130 m and 980 m (control) from the highway from June 1994 until November 1995. Needles were sampled as current-year needles (*solid symbols*) in November 1994 and 1995, and as older needles (*open symbols*) in November 1995. Needles that had grown in 1993, 1994 and 1995 are shown as *diamonds*, *triangles*, and *squares*, respectively. For clarity, the different needle age classes (current, 1, 2) are displaced horizontally within the boxes in the plot

Model estimate of uptake of NO_2-N

As suggested in the Introduction, $\delta^{15}N$ in the needles is related to the high $\delta^{15}N$ of NO_2 taken up through the stomata. By means of the model in Table 1, the uptake rate u_N was integrated over the full growing season of

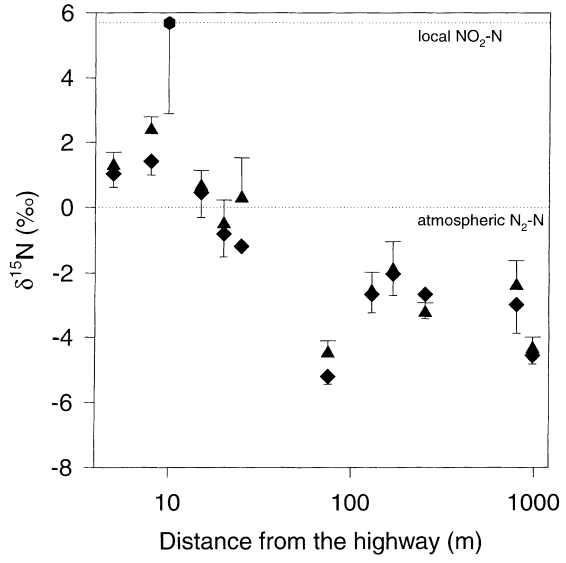

Fig. 3 $\delta^{15}N \pm SD$ of current-year needles of autochthonous spruce trees growing in a transect perpendicular to the highway. Needles were sampled in November 1993 (*solid diamonds*) and November 1994 (*solid triangles*). For comparison, $\delta^{15}N$ of NO_2 collected in 1994 and of atmospheric N_2-N are given (*dotted lines*)

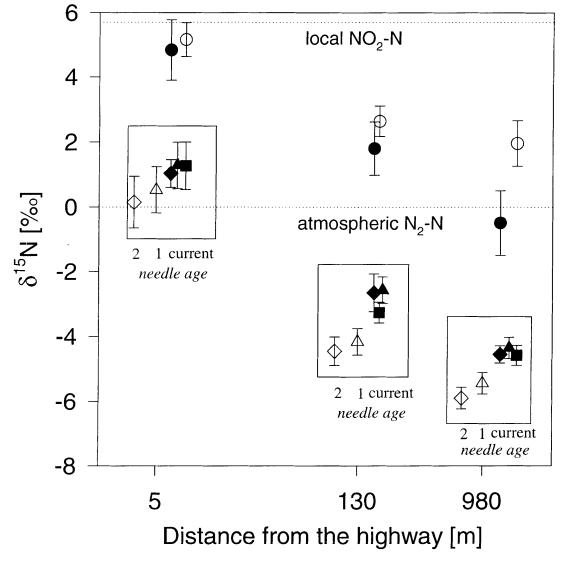

Fig. 4 $\delta^{15}N \pm SD$ in needles and soil of autochthonous trees growing 5 m, 130 m and 980 m (control) from the highway. Needles were sampled as current-year needles (*solid symbols*) in November 1994 and 1995, and as older needles (*open symbols*) in November 1995. Needles that had grown in 1993, 1994 and 1995 are shown as *diamonds*, *triangles*, and *squares*, respectively. For clarity, the different needle age classes (current, 1, 2) are displaced horizontally within the boxes in the plot. The soil samples were taken at depths of 5 cm (circles) and 20 cm (*dots*)

1994 and correlated with the $\delta^{15}N$ of current-year needles in November 1994 (Fig. 5). The correlation coefficient was $r = 0.79$. The linear relation was significant at $P < 0.001$. Most of the needles growing less than 20 m from the traffic lane received more than 10% of the mean N concentration from airborne NO_2-N. The $\delta^{15}N$

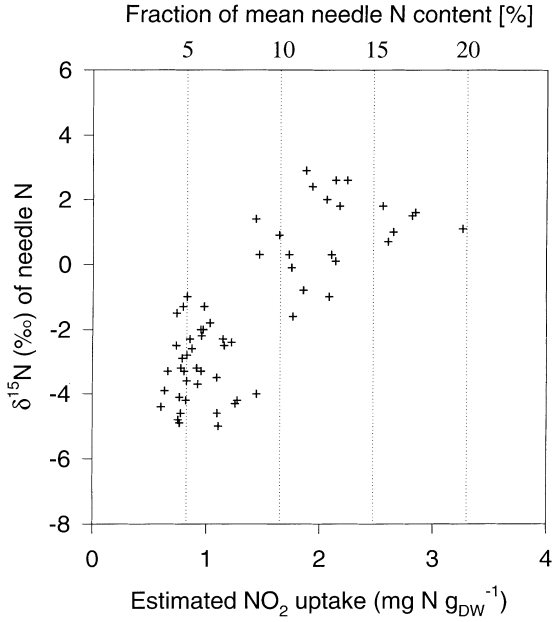

Fig. 5 Relationship between $\delta^{15}N$ of current-year needles and calculated stomatal uptake of NO_2 ($n = 60$, linear relation: $r = 0.79$, $P < 0.001$). The uptake rates based on the locally observed microclimatic variables and the NO_2 concentration were integrated from April (bud break) until October. The estimated NO_2 uptake is given as mass N per mass of needle dry weight (lower x-axis) and as fraction of the mean needle N concentration (upper x-axis)

of the needles was not dependent on their total N concentration ($r = 0.2$), nor was the N concentration dependent on stomatal uptake of NO_2 ($r = 0.15$) (data not shown).

Discussion

$\delta^{15}N$ values of anthropogenic NO_x ($NO + NO_2$) vary widely depending on the source. Whereas $\delta^{15}N$ in fossil fuel is typically close to 0, corresponding to the $\delta^{15}N$ of atmospheric N_2, widely different values have been found for NO_x in combustion gases. Heaton (1990) found $\delta^{15}N$ values between −13‰ and −2‰ in vehicle exhausts directly at the exhaust pipe, which seemed to be affected by varying kinetic isotope fractionation during formation in the different load regimes of the engines. As NO_x rapidly reaches equilibrium with ozone (O_3) in free air, ^{15}N may be further enriched over time in the more oxidised form, NO_2 (Freyer et al. 1993). Therefore, the $\delta^{15}N$ of NO_2 and NO may be expected to vary over the year. Over the source–receptor distances relevant in the present study the NO_x to O_3 ratio was constant, thereby justifying the assumption that $\delta^{15}N$ of NO_2 remained constant with the distance from the source (Freyer et al. 1993). We interpret the surprisingly positive $\delta^{15}N$ values (+5.7‰) of NO_2 as a consequence of local conditions such as traffic density, mean distribution of heavy- and light-duty engines, and average combustion regimes in the engines. In the study by Freyer et al. (1993), positive $\delta^{15}N$ values of NO_x were reported for part of the year,

but a variety of sources with different seasonal emission patterns had to be taken into consideration in the heavily industrialised region studied. An intended monitoring study should concentrate on the sampling of NO_x and analysis of $\delta^{15}N$ from different sources and regions. The purpose of the present study was to make use of the difference of $\delta^{15}N$ in NO_2, spruce needles and soil to provide quantitative evidence for NO_2 uptake into spruce needles in the field, rather than to investigate the details of $\delta^{15}N$ in atmospheric NO_x.

$\delta^{15}N$ values of organic N encountered in temperate forests are usually more negative between $-5‰$ and $-2‰$, compared to the rather positive values in non-forested ecosystems (Nadelhoffer and Fry 1988; Sutherland et al. 1993; Gebauer and Dietrich 1993; Buchmann et al. 1995). The difference is probably caused by the lower N_2-fixing capacity and low nitrogen loss rates in forest soils (Högberg et al. 1995). Because mineralisation discriminates against the heavier ^{15}N, the $\delta^{15}N$ of the remaining organic nitrogen increases as litter decomposes, so that higher $\delta^{15}N$-values are found with increasing depth in the soil (Nadelhoffer and Fry 1994; Gebauer et al. 1994). Since the isotope effect associated with root uptake and assimilation is comparatively small, $\delta^{15}N$ in needles at undisturbed sites mainly reflects the ^{15}N abundance of available nitrogen in the soil layer with the greatest density of roots (Gebauer et al. 1994).

If potted trees are exposed to considerable amounts of NO_2 as in our study, the following mechanisms contribute to the nitrogen pool of the current-year needles and modify $\delta^{15}N$: (1) uptake and assimilation of ammonium and nitrate by the roots, (2) redistribution of amino acids from the older needles or the stem, and (3) uptake of atmospheric NO_2, NH_3 and HNO_3 via gas exchange by all needles. The $\delta^{15}N$ of the needles from the potted trees rose from $-3.7‰$ to $-1.5‰$ within one growing season. When soil-derived N ($\delta^{15}N = -3.7‰$) was mixed with airborne NO_2-N ($\delta^{15}N = +5.7‰$), the contribution of NO_2-N to the N concentration of the needles was then about 25% at the site 5 m from the highway, which is consistent with the maximum NO_2 uptakes estimated from the uptake model (Fig. 5). Since the uptake of NO_2 is limited by diffusion through the stomata and all incorporated NO_2-N is assimilated, there is only a small depletion in the heavier isotope, ^{15}N, due to the lower diffusion constant, associated with these processes. Similarly, assimilation and translocation processes of nitrogen within the plant tend to decrease the $\delta^{15}N$ values. The $\delta^{15}N$ values found in the roots show that considerable transport of assimilated NO_2-N to the roots occurs. Nussbaum et al. (1993) reported export of incorporated NO_2-N to stem and roots of less than 10%, though on a much shorter time scale.

On the other hand, soil $\delta^{15}N$ is defined by the processes stated above (mineralisation, immobilisation and losses) but is additionally coupled to the shoots as the needles provide the main supply of organic N to the trees. In the experiment with the potted trees, this pathway was interrupted by continuous removal of needle litter. The contribution of dry deposition of NO_2 directly on the forest soil is small compared to the pathway via the stomata (Duyzer and Fowler 1994). This was also confirmed in this study, where no measurable effect was found of dry deposition of NO_2 on $\delta^{15}N$ in the soils of the potted trees. The differences in $\delta^{15}N$ found in the different needle age classes basically confirm the results of Gebauer et al. (1993). In the present experiment, the $\delta^{15}N$ of the needles that had grown in 1993 was almost $2‰$ greater than the control value, solely because of translocation of nutrients from the current-year needles and direct uptake of NO_2 during 1994 and 1995, which shows that the nitrogen pool in spruce needles has a high turnover rate.

At the sites of the autochthonous trees, however, these processes have been working for years, and needle litter has provided continuous N input, with a high ^{15}N abundance, into the soil. Therefore, the expected patterns of shifts in $\delta^{15}N$ among the pools (needles of different age, litter, top soil layer, deeper soil) had been established at each site, in spite of the strong gradient of $\delta^{15}N$ with distance from the highway. In the present study, no gradient of N compounds in the air other than traffic-derived NO_x has to be taken into account. Therefore, incorporation of NO_2-N with a high $\delta^{15}N$ was the only factor causing the strong $\delta^{15}N$-gradient found in the needles and, parallel to it, in the soil due to needle litter fall. The fact that soil $\delta^{15}N$ is related to the local behaviour of the needles with respect to NO_2 uptake is also illustrated at the site 75 m from the highway, where NO_2 uptake was rather low in spite of the relatively high NO_2 concentrations.

Since the older needles had been accumulating NO_2-N with a high $\delta^{15}N$ for several years, the only process leading to high $\delta^{15}N$ in the needles, apart from the direct contribution of NO_2-N via the stomata, was recycling of nitrogen from these needles by translocation or via mineralisation of needle litter in the soil. The current needle $\delta^{15}N$ was therefore the result of increased deposition of NO_2 with high $\delta^{15}N$ in the long term. As no significant increase between 1993 and 1995 was observed, these processes seem to have reached a steady state with respect to ^{15}N distribution.

The N input via the stomata calculated with models which are also included in large-scale deposition models showed a significant correlation with $\delta^{15}N$ as a local marker of NO_2 uptake at the level of the needles (Fig. 5). Furthermore, the absolute amount of NO_2-N taken up according to these estimates (10–25% of the needle N-concentration at the more polluted sites) agreed reasonably well with the estimates obtained by the $\delta^{15}N$ measurements at the same sites for the potted trees.

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