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First detection of nitrogen from NO_x in tree rings: a $^{15}N/^{14}N$ study near a motorway

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Abstract

Nitrogen isotope analysis (δ^{15}N) of tree rings is potentially useful for evaluating the temporal development of the nitrogen (N) deposition to forests and for studying the long-term effects of N accumulation in ecosystems. To test this hypothesis, we investigated three sites across a pollution gradient in differing distances (20,150,1000 m) from a motorway in Switzerland, which was built in 1965. We sampled four *Picea abies* trees per site, whereby we extracted the tree ring cores with hot water and solvents before the isotope analysis to remove mobile N storage compounds, and determined the isotope variations in the stem wood for the period 1928–2000. While tree ring growth was not affected by the construction of the motorway, the δ^{15}N values were increasing by up to 7.9‰ after 1965 at the most polluted site, indicating the uptake of NO_x from car exhausts, although the signal was highly variable. Isotopically heavy NO_x emissions were observed in an earlier study at the same location resulting in a δ^{15}N-gradient of recent needles from +1.3‰ to −4.4‰ with increasing distance from the motorway. This gradient was also reflected in the tree rings, but dampened by a factor of about 2 compared to the needles. For the trees near the motorway, the total nitrogen concentration in the tree rings varied in parallel with the δ^{15}N values ($r^2 = 0.52$). This enabled us to apply a mass balance equation for reconstructing the isotope signal of N originating from the car exhausts for the period 1965–2000, with the δ^{15}N of NO_2 in the range +1.3‰–+6.4‰. The more distant sites were much less affected by the traffic and their isotope ratio reflected the influence of varying proportions of isotopically heavy (NO_2) and light (NH_x) deposition. We conclude that the analysis of tree ring ^{15}N variations is a promising tool for the detection of the role played by nitrogen deposition to the forests.

Keywords: *Picea abies*; Air pollution; Dendroecology; Nitrogen deposition; Stable isotopes; Nitrogen dioxide

1. Introduction

Nitrogen deposition to nitrogen-limited forest ecosystems is receiving considerable attention because it affects ecosystem functions and processes, and may have either positive or negative effects on plant growth (Aber et al., 1989). Increased atmospheric levels of nitrogen oxides ($NO_x = NO + NO_2$) and ammonia gases ($NH_x = NH_3 + NH_4$) are related to human activities like agriculture and the combustion of fossil fuels. Particularly, in industrialized areas these compounds contribute a significant N input via dry and wet deposition to plants and soil, and to the gaseous uptake by the plant leaf stomata. Positive effects might include fertilization of N-limited ecosystems fostering increased carbon-sequestration (Norby, 1998). Negative effects relate to nutrient imbalances, resulting, e.g., in changes in the C/N ratio (Tietema et al., 1998) and in reduced root/shoot

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ratios of trees (Brunner and Brodbeck, 2001) possibly affecting tree stability. Biodiversity losses and landscape changes may be induced (Köchy and Wilson, 2001), and pollution problems caused by increased nitrate leaching to ground waters and soil acidification (Schleppi et al., 1999; Schulze, 1989; Wellburn, 1990). One crucial problem with the analysis of these effects in natural ecosystems is their intrinsic long-term nature, consisting of relatively low, but steady N-inputs for decades. Nitrogen is slowly accumulating in the ecosystems and detrimental effects might suddenly and unexpectedly occur when a threshold level is reached. Furthermore, nitrogen effects are not isolated, but confounded with other long-term changes like increasing atmospheric CO_2 and climate change. For example, an increasing trend in forest growth has been observed in the second half of the past century in many regions of Europe, but it is not clear if such an increase has been induced by an increase in nitrogen deposition, atmospheric CO_2 concentrations, or temperature (Spiecker et al., 1996).

A unique possibility to study long-term effects of N deposition to forests could be the analysis of $^{15}N/^{14}N$ in tree rings. The nitrogen isotope ratio in compounds produced from anthropogenic activities may be significantly different from the natural, background N in the soil (Freyer, 1991). For instance, the ^{15}N of pollution NO_x was mostly reported in the range from −5‰ to +5‰, whereas ammonia from animal waste, probably the most important source of atmospheric ammonia, is more depleted (Heaton, 1986; Macko and Ostrom, 1994). The relative importance of different sources of N for the plant N budget can thus be derived at the leaf level (Ammann et al., 1999; Siegwolf et al., 2001). This approach might also be useful for retrieving information on the long-term N-deposition to forests, by analysing tree rings. A drawback of this method, however, is the occurrence of lateral transport of N in the stem wood, which may dilute or obscure any time-related information (Cowling and Merrill, 1966; Levy et al., 1996). It is known since long that trees recover N from dying cells, usually during the process of conversion from sapwood to heartwood cells (Meerts, 2002; Merrill and Cowling, 1966). This can be understood from the perspective of the nutrient-use efficiency of the plant, and probably prevents the nitrogen-content in tree rings from being a useful monitoring tool for N deposition. Nevertheless, the $^{15}N/^{14}N$ ratio might be less affected by these processes provided that fractionation during the above-mentioned N-recovery is minor. This may hold in particular when tree cores are extracted with solvents before the analysis, thus reducing the amount of mobile N in the wood (Sheppard and Thompson, 2000). Studies with ^{15}N-tracer application also showed that a distinct ^{15}N-peak remained in the corresponding tree rings many years after the tracer was applied, although the tree rings before and after the tracer application may also be enriched (Elhani et al., 2003; Hart and Classen, 2003).

To date only very few studies have attempted to analyse the natural abundance of $^{15}N/^{14}N$ in tree rings, and the interpretation was partly hampered by the absence of any information on the ^{15}N input signal (Poulson et al., 1995). It is unclear whether the observed ^{15}N trends in the tree rings were related to changing N deposition or reflected isotope fractionations associated with the N-recovery processes. Further, the variability of the tree-ring ^{15}N signal between different trees from a particular site has not been studied in detail to determine the reliability of the trees as environmental records. In this study, we analysed tree rings from *Picea abies* trees growing at differing distances from a motorway in Switzerland, thus being exposed to differing amounts of NO_x from car and truck exhausts. It is known from a previous study at this location that the $^{15}N/^{14}N$ ratio of NO and NO_2 from the exhausts is higher than the background inorganic soil N (Ammann et al., 1999). Accordingly, a ^{15}N gradient was found in needles of potted trees as well as in needles and soil of autochthonous trees growing in differing distance to the pollution source, consistent with the uptake of N from NO_2. NO_2 may thus be regarded as an alternative fertilizer. In contrast, NO is not readily taken up by the leaves due to its low solubility in water, but would rather be toxic. Here, we investigated to what degree the well-defined input-signal from $^{15}NO_2$ could be recovered in the tree rings. Furthermore, the time course of the signal should be investigated to monitor potential changes of car emissions during recent decades, and also to observe the tree-ring signal prior to the motorway construction in 1965. We thus consider the experimental design ideal as a test case for assessing the use of $^{15}N/^{14}N$ in tree rings as an environmental monitoring tool.

2. Materials and methods

2.1. Study sites

The experiment was carried out in a mixed forest (*Galio odorati-Fagetum typicum*) in Switzerland near Solothurn (47°8′N, 7°35′E, 480 m a.s.l.). Annual mean temperature is about 8.8°C and precipitation amount 1020 mm. Three sites were selected along a transect perpendicular to a motorway that crosses the forest in North–South direction. The sites were 20 m (S1), 150 m (S2) and 1000 m (S3) distant from the road to the West, which is the main wind direction. Four Norway spruce [*Picea abies* (L.) Karst.] trees were chosen at each site and three cores per tree taken with a 0.5 cm diameter increment borer. Soils are pseudo-gley (pH 4–4.5), with a nitrogen content of 0.3% ± 0.05% in the top soil layer. For a detailed site description see Ammann et al. (1999).

In 1993–1995 extensive sampling of needle and soil material as well as NO_x concentration and isotope measurements were carried out. The annual mean NO_2 concentration was about 20 ppb close to the motorway and decreased to about 5 ppb at 1000 m distance, close to normal background concentration in this area. The isotope analysis on NO_2 sampled with denuder technique showed an average value of $\delta^{15}N = +5.7‰ \pm 2.8‰$, with no clear seasonal variations. The $\delta^{15}N$ of NO was $+3.1‰ \pm 5.4‰$, thus somewhat lower, but more variable (Ammann et al., 1999). The total nitrogen deposition to the forest at 365 m distance to the motorway amounted to 31 kg $ha^{-1} a^{-1}$, determined as the sum of the contributions of N from NH_3 (11 kg $ha^{-1} a^{-1}$), from NH_4^+ (7 kg $ha^{-1} a^{-1}$), and from NO_y (13 kg $ha^{-1} a^{-1}$).

2.2. Time course of traffic and NO_x emissions

The traffic on the highway at this location is among the highest in Switzerland connecting the cities and agglomerations of Basel and Zürich to Bern. The automated vehicle-counting station close to the experimental site indicated an average number of 57,500 vehicles per day in the year 2000 (data provided by the Bundesamt für Strassenverkehr), with no strong seasonal variations. The number of heavy vehicles ($>3.5\,t$ total weight) was 6570 during working days in the year 2000, thus amounting to ca. 11% of the total number of vehicles. The changes during the recent decades are shown in Fig. 1a, indicating the steady increase of traffic from 1967 onward at this location. For comparison, the model-estimated NO_x emissions from traffic for whole Switzerland are shown (BUWAL, 1995), whereby the temporal evolution with an increase until the 1980s and a decrease later can be assumed to be similar at the study site (Fig. 1b). The reduction in emissions after about 1985 is commonly assigned to the widespread use of catalysts.

2.3. Analysis

The tree cores were extracted in a Soxhlett-apparatus to remove extractable N-compounds, first for 18 h in a 50:50 mixture of toluene and ethanol, then for 18 h in ethanol, and then for 18 h in distilled water. This method had been tested before (unpublished results) and is similar to the extraction technique used in Sheppard and Thompson (2000). Ring width measurements were made to the nearest 0.01 mm using Time Series Analysis and Presentation (TSAP) measurement equipment and software package (Frank Rinn, Heidelberg, Germany). The rings were clearly visible and crossdating was possible. For the isotope analysis, sections consisting of three tree rings each were cut from the core with a razor blade. We did not analyse individual rings because the ^{15}N signal is assumed to be diluted over a few years due to lateral transport. Therefore, it is probably not possible to retrieve environmental information with an annual resolution, but rather longer-term variations may be apparent. Only samples after 1928 were considered where tree rings from all four trees from all sites were available. The samples were milled, and typically 15–17 mg of it enclosed in tin capsules. The analysis was done by combustion in an elemental-analyser connected in continuous-flow mode to an isotope-ratio mass-spectrometer (Delta-S, Finnigan, Bremen, Germany). Due to the low N-concentration of the wood samples (relative to the C-content) the usual measurement procedure for organics was modified by measuring a blank (empty tin capsule) after every sample. The $\delta^{15}N$-reproducibility for the repeated analysis of a wood sample was about 0.3‰. The N-concentrations were determined from peak area determination with the mass-spectrometer (relative precision $+-3\%$). The isotope values are given as relative deviations from the international standard (atmospheric N_2) in the δ-notation: $\delta^{15}N = [(^{15}N/^{14}N_{sample})/(^{15}N/^{14}N_{air}) - 1]^{*}1000$, whereby the calibration relied on the analysis of the standards IAEA-N1 and IAEA-N2.

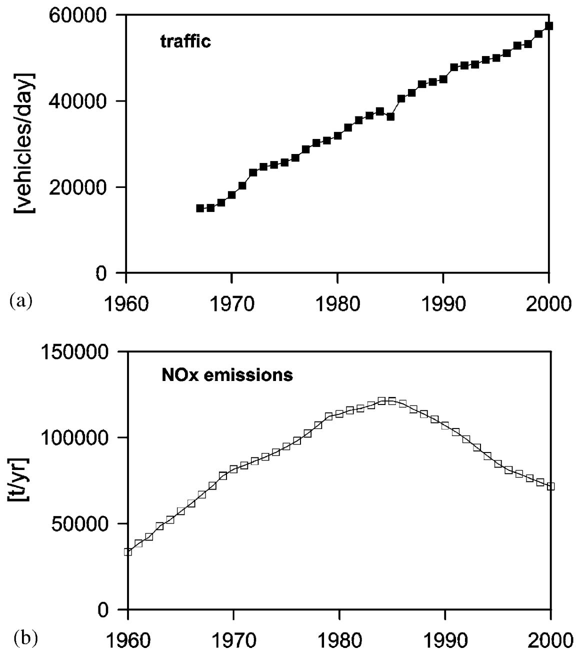

Fig. 1. Time course of estimated traffic on the motorway near the study site (total traffic of 24 h in both directions) (a) and the total estimated NO_x emissions of traffic in Switzerland (b).

3. Results

The average ring-width curves for the three sites located at differing distances to the motorway are shown in Fig. 2. The variability among the sites was relatively high until 1930, which could have been caused by the low number of trees at the beginning of the investigated period. The oldest trees germinated 1890 at S1, 1902 at S2, and 1900 at S3. Stand age is thus roughly 100 years, but younger trees were also present in this managed forest. Relatively low growth rates were observed in the 1940s, and they may be related to the frequent warm and dry summers during this period in Switzerland. After the construction of the motorway in 1965, the site S1 nearest to the motorway, tended to have reduced growth. The lowest ring-width values for S1 during the whole series were recorded in 1966 and 1967. This short period of reduced growth could be related to adverse effects from the motorway construction. Generally, the three sites showed a high degree of common variance in the period 1940–2000, indicating that climate was the major factor determining the tree ring width variations. The traffic emissions do therefore not appear to have negatively affected tree growth.

The nitrogen concentration signal in the tree rings was clearly disturbed after the construction of the motorway in 1965 for the site S1 (Fig. 3a). While the N-concentration was about 0.05% prior to 1965, up to five times higher concentrations (0.27%) were reached afterwards. The four trees at this site, however, did not react in a similar manner, but showed strongly differing signals. Three out of the four trees analysed had a N-concentration higher than background during some time, but the increased values were varying strongly, with tree No. 2, for instance, having higher levels only in the seventies. In comparison, the time course of the N-concentration for the sites S2 and S3 was much more complacent (Fig. 3b,c). The values during most of the time were around 0.05%, similar to the pre-1965 period for S1, and slightly increased to about 0.1% in the last two decades of the record. This increase resembles patterns found in the literature (Meerts, 2002) and may reflect rather a natural, physiological effect (not caused by increased N-deposition), related to higher levels of N in the living cells of the sapwood.

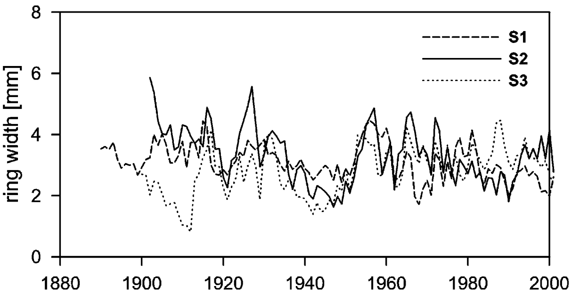

Fig. 2. Average ring width chronologies for *Picea abies* at the three investigated sites in differing distance to the motorway. The distance is 20 m for S1, 150 m for S2 and 1000 m for S3.

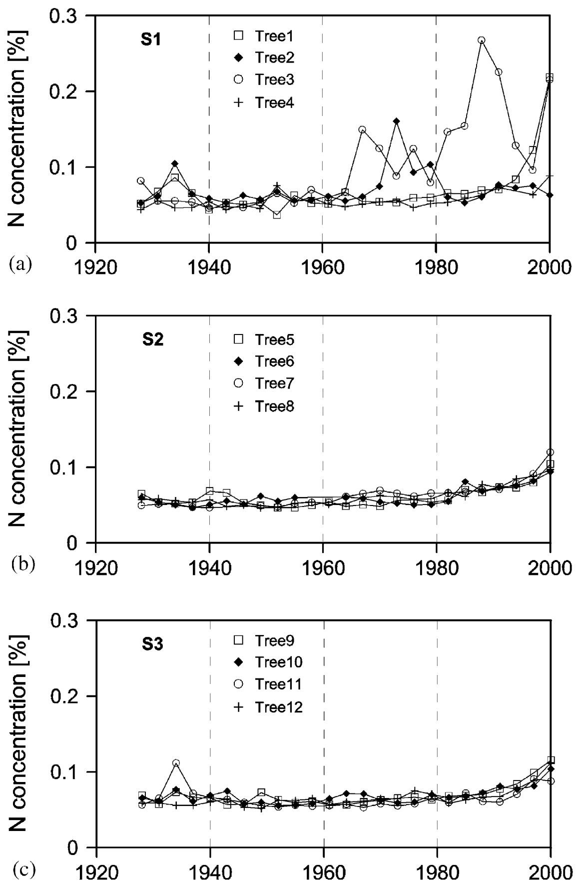

Fig. 3. The N concentration in the tree rings (3-year-intervals) for individual trees for the sites (a) S1; (b) S2; (c) S3.

The $\delta^{15}N$ values of the tree rings for site S1 were in the range from about −4‰ to +1‰ in the pre-1965 period (Fig. 4a). Afterwards, higher values were observed, with the pattern of variation strikingly similar to the N-concentration (Fig. 3a). Trees no. 1, 2 and 3 from S1 had increased ^{15}N after 1965 when comparing to the values found for S2 and S3 (Fig. 4b and c). The highest $\delta^{15}N$-value was found for tree no. 3 in 1988, which is also the sample with the highest N-concentration. We compared the $\delta^{15}N$-values of this tree with the non-responding tree no. 4, which has values in the range of S2 and S3. A difference of 7.9‰ was observed in 1988 reflecting the maximal enrichment by heavy $^{15}NO_x$ during the investigated period. On the other hand, the $\delta^{15}N$-results for the sites S2 and S3 indicated no major disturbances, but also little common variance among individual trees. Overall, there was a slightly decreasing trend at these sites. The average values for the period 1993–1995 at the three sites may be compared to *Picea abies* needle values that were obtained during an earlier study (Ammann et al., 1999). Current-year needles sampled in 1993, 94,

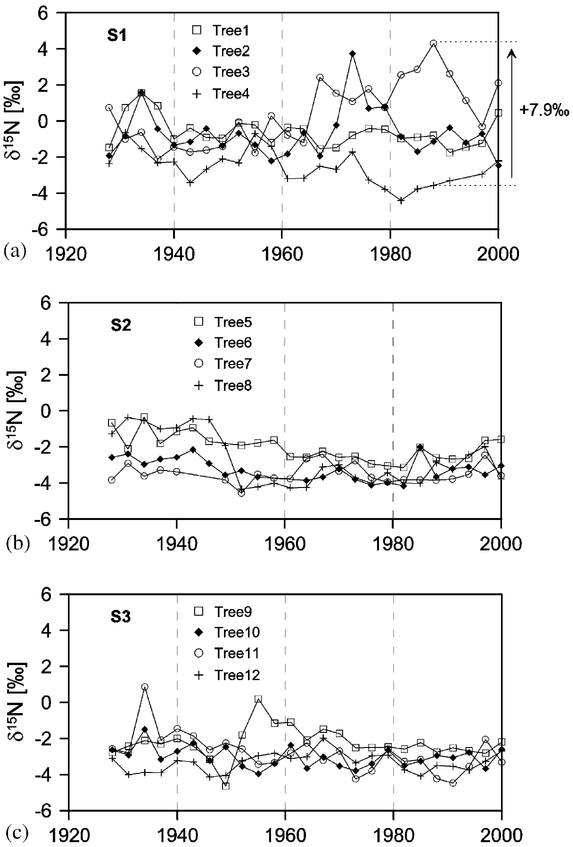

Fig. 4. The δ^{15}N-values of the tree rings (3-year-intervals) for individual trees for the sites (a) S1; (b) S2; (c) S3.

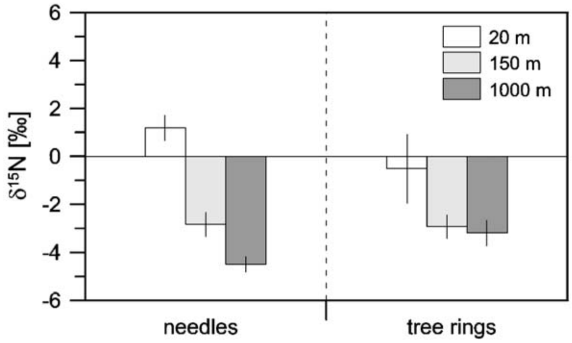

Fig. 5. The average δ^{15}N-values ($\pm$SD) of the tree rings and current-year needles for the period 1993–1995 at the three sites in differing distance to the motorway.

and 95 had an average value of $+1.3‰\pm0.4‰$ close to the motorway, decreasing to $-2.6‰\pm0.6‰$ at the intermediate site and to $-4.4‰\pm0.4‰$ in 1000 m distance (Fig. 5). The tree-ring values corresponding to the same time period showed a similar, but less clear trend, as the difference between S1 and S3 was only about half the value compared to the needles (Fig. 5). This reflects a dilution of the $^{15}NO_x$-signal as recovered in the tree rings, for instance caused by lateral transport and partial mixing of N of previous periods in the stem. The gradient with distance from the motorway was also observed in the soil but shifted to more positive values by about 5‰, reflecting the long-term input signal from the needle litter fall and subsequent fractionations during mineralization (Ammann et al., 1999).

The similar pattern of δ^{15}N and N-concentration for S1 clearly indicate that the increased levels of N are the result of N-deposition with a high δ^{15}N-value. This can be further evaluated by a correlation analysis. As shown in Fig. 6a, there is a relationship between the N-concentration and δ^{15}N. This relation is not linear, which can be understood on the basis of a two-member mixing model (see e.g. (Keeling, 1958). We assume that the N input to the tree rings originates from two sources, $N_{background}$ (from soil) and $N_{emission}$ (from car exhausts) with differing isotope ratios, $\delta^{15}N_{background}$ and $\delta^{15}N_{emission}$, respectively. Thus, the following equation applies:

$$\delta^{15}N_{tree\ ring} = \frac{(\delta^{15}N_{background}N_{background} + \delta^{15}N_{emission}N_{emission})}{N_{background} + N_{emission}}. \quad (1)$$

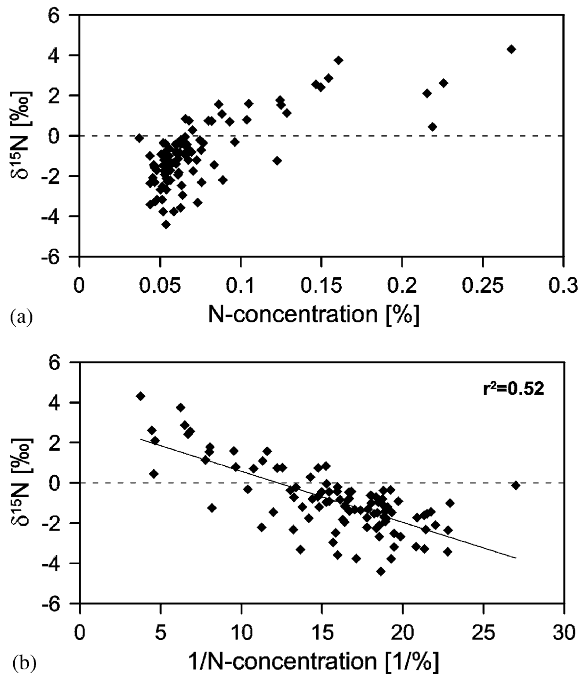

Fig. 6. The relationship between the N-concentration in the tree rings and δ^{15}N (a) and between the inverse of the N-concentration and δ^{15}N (b) for the site S1 close to the motorway.

Furthermore, the total input into the tree ring is $N_{tree\ ring} = N_{background} + N_{emission}$, the integral of which is measured as N-concentration in the tree ring. Rearranging the equation yields:

$$\delta^{15}N_{tree\ ring} = \frac{(\delta^{15}N_{background} - \delta^{15}N_{emission})}{N_{tree\ ring}} \times N_{background} + \delta^{15}N_{emission}, \quad (2)$$

which is a linear equation of the form $\delta^{15}N_{tree\text{-}ring} = \text{constant}/N_{tree\text{-}ring} + \delta^{15}N_{emission}$, i.e. linear in $1/N_{tree\ ring}$ with the y-intercept $\delta^{15}N_{emission}$. This two-member mixing model reasonably well explains part of the variability of the data as shown in Fig. 6b. The same $\delta^{15}N$ data as in Fig. 6a shown versus 1/N-concentration of the tree rings clearly results in a linear relationship with a squared correlation coefficient of $r^2 = 0.52$. This significant correlation holds only for the site S1, while $r^2 = 0.00$ was found for S2 and $r^2 = 0.06$ for S3 applying the same procedure. The y-intercept of the regression line then indicates the average $\delta^{15}N$ value of the emissions, which can be attributed to NO_x. This is 3.1‰ for the calculation involving all tree rings from S1. The direct uptake of NO may be neglected as NO is not incorporated in significant amounts by the leaves, so that the reconstructed signal should reflect NO_2. Much of the NO_2, however, is rapidly produced in the atmosphere from NO by the reaction with ozone (Kukkonen et al., 2001), so that we cannot clearly differentiate between N originating from NO or NO_2.

The same analysis may now be applied to individual time periods instead, considering that $\delta^{15}N_{emission}$ may not have been constant over time as implicitly assumed in Eq. (2), where all tree rings have been pooled. The regression analysis shown in Fig. 6b is thus done based on the values of the four trees for each individual tree ring period, and the $\delta^{15}N_{emission}$ values taken from the y-intercept from the individual regression lines. Accordingly, the $\delta^{15}N_{emission}$ values can be calculated for the period 1965–2000 (Fig. 7). The regression calculation does only provide a useful estimate for the post-1965 period, where significant increases in N-concentration and $\delta^{15}N$ occurred (see Figs. 3a, 4a). Accordingly, the uncertainty in $\delta^{15}N_{emission}$ calculation (SE of y-intercept) is much larger for earlier tree rings (see as an example the value for 1962 in Fig. 7). This makes sense, however, as the motorway was constructed in 1965, and therefore car emissions should obviously not show up in the tree rings at any earlier time point. The reconstructed $\delta^{15}N_{emission}$ showed rather constant values of +5‰ from 1965 to about 1987, while the values decreased slightly in recent years.

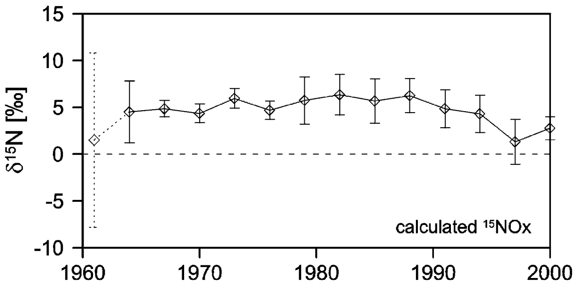

Fig. 7. Time course of the reconstructed isotope signal of NO_x (±SE). These values are calculated from the tree-ring data with a two-member mixing-model.

4. Discussion

A forest was exposed to large amounts of traffic exhaust for 35 years, but the increased N-deposition did not induce any changes in ring width of *Picea abies* trees at the site closest to the motorway compared to less exposed sites. Also no changes were observed in the understory plant community at these sites (Ammann et al., 1999). This does not necessarily mean that there was no fertilizing effect of the N-deposition from NO_2, but this might only have compensated the detrimental effects of other compounds such as dust and sulfur dioxide also emitted by the traffic. That NO_2 from car emissions was indeed taken up by the trees was clearly shown by the isotope signal of the needles and gas exchange modelling, as well as by stimulated activity of the enzyme nitrate-reductase in needles (Ammann et al., 1999). The contribution of NO_2 uptake to the N-content of needles was estimated to 10–25%. This could have a positive effect on growth in this relatively nitrogen-poor ecosystem. Results from growth-chamber fumigation with NO_2 showed similar responses, where the needle uptake of NO_2-N resulted in increased growth, but also in reduced root/shoot ratios in poplar trees, thus acting differently than nitrogen-fertilizer added to the soil (Siegwolf et al., 2001). Our results being from a field study, where NO_2 is affecting tree growth not in isolation but rather in combination with other environmental factors, can be understood either in terms of the forest as a highly resistant ecosystem not affected by the car emissions at all, or as the net result of both positive and negative effects levelling out. While this may seem to alleviate concerns regarding the pollution of forests and tree health, the balancing of positive and negative effects found in our study may be fortuitous, and may also not hold forever because the N deposition and N accumulation in the soil will continue in the future.

After the NO_2-N is metabolised in the needles, N is transported as nitrate or amino acids to the stem where it is used in living cells, either in the form of proteins, as storage compounds, or partly bound to structural forms such as lignin polymers (Elhani et al., 2003). Accordingly, the NO_2-incorporation close to the motorway was reflected in the tree rings as increased N-concentration and $\delta^{15}N$ values after 1965. The simultaneous occurrence of high N-concentrations and high $\delta^{15}N$ values gives us a good means to reliably detect the car emissions. The increased N-concentrations alone could have multiple causes and may not as easily be used as an indication of the pollution effect. The high variation among the trees found in our study, however, probably makes it impossible to infer the past evolution of the N-deposition in a quantitative manner. The time course of the estimated emissions of NO_x for Switzerland (Fig. 1b) is apparently not visible in the tree rings (i.e. the increase until 1985 and the subsequent decrease due to emission regulations). It could be that the decrease of emissions near the motorway was not as pronounced as for whole Switzerland because of the particularly strong increase in motorway traffic (Fig. 1a). An important finding is that no increased values in the tree rings were observed before 1965, which would have indicated major movements of N-compounds between the tree rings. Nevertheless, it is difficult to find an explanation for the differing behaviour of four trees growing within an area of approximately 20×20 m in an apparently homogenous stand. While it is clear that the NO_2 and its ^{15}N-signal are taken up by the needles, this additional nitrogen apparently does not continuously show up in the stem wood, but only in certain periods. This could be reflecting internal N-cycling in trees and the varying need of the trees to rely on reserves or refill them depending on N-availability and climatic conditions.

The strong variations in the N-concentration and $\delta^{15}N$-values do not prevent, however, these data to be useful for assessing the isotope signal of the incorporated NO_2. As the increased N-values are only found at the site closest to the motorway, this signal can be unambiguously related to the NO_2 emitted by the traffic. A mixing-model allows calculating the isotope signal of the "pure" N-deposition from the tree-ring signal which is a mixture of both background- and NO_2-N. The $\delta^{15}N$ of NO_2 reconstructed over the period 1965–2000 indicated a rather constant positive value with a slight decrease in the recent decade. This decrease might be related to the widespread use of catalysts, which may differently fractionate NO_x produced from atmospheric N_2 during combustion in the engine. An alternative explanation could be the reduced speed limit in recent years due to the maintenance and repair of the road. Direct sampling and analysis of NO_2 in 1994 at this location indicated $\delta^{15}N$ of $+5.7‰ \pm 2.8‰$ (Ammann et al., 1999), thus consistent with the value of $4.3‰ \pm 2.0‰$ calculated from the tree rings with the mixing model for the period 1993–1995.

The "background"-signal of ^{15}N at the more distant sites was slightly decreasing over time, in particular from 1930 to 1950, which might be caused by the combined influence of different pollution sources. These relatively small natural variations are more difficult to understand, as they do not reflect the isotope signal of a single pollution source, as is the case for the site near the motorway. Results from the literature suggest that the two major sources for N pollution, NO_x and NH_x, can be distinguished isotopically, as higher values were reported for NO_x compared to NH_x. For instance, mosses growing near roadsides in London had an average $\delta^{15}N$-value of $+3.7‰$, but a value of $-7.8‰$ was reported for mosses near agricultural sources, e.g. cattle farms (Pearson et al., 2000). In northern Germany, positive $\delta^{15}N$ of needles of Scots pine was observed near cities, becoming more negative with distance from the industrial areas (Jung et al., 1997). Therefore, the declining trend in the tree rings in our study until about 1950 (Fig. 8) suggests the NH_x deposition to the forest to have grown faster than the NO_x deposition, which reflects the intensification in agricultural production. A relatively constant ratio of NH_x/NO_x deposition was observed after 1950 (Fig. 8). Decreasing trends during the 20th century were observed in most previous tree ring studies concerning $\delta^{15}N$. For two eastern hemlock trees (New Hampshire, USA, Poulson et al., 1995), for tree rings of oak (*Quercus pubescens*) as well as leaves of various herbarium specimen from the western Mediterranean (Peñuelas and Estiarte, 1997), and for one of two ponderosa pine trees growing in the Sierra Nevada Mountains of California (Hart and Classen, 2003). While no clear causes for the observed ^{15}N-decrease were provided in these studies, potential explanations include changes in the isotopic composition of available N, similar to the hypothesis outlined above for our site, or long-term changes in the fractionation due to lower nitrogen losses or use of increasingly mineralized N. Such changes could reflect the increasing demand for N in rising atmospheric CO_2 (Peñuelas and Estiarte, 1997).

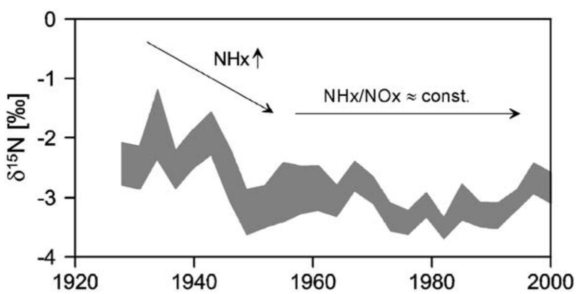

Fig. 8. Background $^{15}N/^{14}N$-variation in tree rings representing the average of the sites S2 and S3, while the width of the band indicates the uncertainty of the mean ($\pm$SE). The arrows indicate the approximate direction of the long-term changes and possible causes.

5. Conclusions

Although our conclusions may not necessarily hold for other tree species, since ^{15}N uptake depends on species (Evans, 2001; Koopmans et al., 1996) and other site conditions (Högberg, 1997), our study shows some obvious limitations and some chances for the use of ^{15}N in tree rings as environmental monitoring tool. Although not the amount, but only the isotope signal of NO_2 could be reconstructed, this may constitute important information for using ^{15}N in atmospheric deposition studies, which are particularly rare in forest ecosystems due to the difficulties in throughfall collection and sound sampling of the forest water flux (Thimonier, 1998). Our data suggest that there were no major changes in the isotope ratio of traffic NO_2 over the past 35 years despite major developments in engine design. This data may be useful for other retrospective ^{15}N-investigations at sites where a mixture of pollutants was deposited as our data confine the range of $\delta^{15}N$ of NO_2 to the range of about $+1.3‰$ to $+6.4‰$ (derived from Fig. 7). Similar studies might be successfully conducted at other sites close to pollution sources to gain more insight into the past evolution of the N-deposition. The pollutant signal was, however, only evident in direct proximity to the motorway but already disappeared in 150 m distance. This is consistent with the strong dilution of pollution plumes (Vogel et al., 2000), because apparently air transport was strongly hindered by the forest canopy. For the more distant sites, we cannot preclude from our data that biological processes and related isotope fractionations in the stem wood might influence these relatively subtle changes, but a possible explanation is that the ^{15}N-variations over the past are related to the changing proportion of NH_x and NO_x deposition.

An increase in forest growth trends has been documented (Spiecker et al., 1996) and increased atmospheric nitrogen deposition is retained as one of the possible causes of such increase. The brevity of the historical records of deposition measurements renders empirical analysis of recent changes inconclusive. Experimental nitrogen fertilization studies have been undertaken, but they may have limited application to the study of the effects of chronic nitrogen deposition as they produce longer lasting effects in forest ecosystems. Our results suggest that the analyses of tree ring ^{15}N variations are promising tools for investigating the nitrogen deposition to forests. Moreover, regional analyses of tree-ring ^{15}N-variations could enable the mapping of the impact of nitrogen deposition on forest ecosystems, assessing the input of pollutant nitrogen into plant communities. Such information is worldwide strongly needed (Stewart et al., 2002). Policy makers need to know as much as possible about the extent and natural baseline variation of nitrogen deposition. This information is necessary to evaluate international political measures to control air quality, and to identify the needed measures to be undertaken at the national level especially in forestry and agriculture, and for establishing the trade off of emission control for the industry.

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References

Aber, J.D., Nadelhoffer, K.J., Steudler, P., Melillo, J.M., 1989. Nitrogen saturation in northern forest ecosystems. Bioscience 39 (6), 378–386.

Ammann, M., Siegwolf, R., Pichlmayer, F., Suter, M., Saurer, M., Brunold, C., 1999. Estimating the uptake of traffic-derived NO_2 from ^{15}N abundance in Norway spruce needles. Oecologia 118 (2), 124–131.

Brunner, I., Brodbeck, S., 2001. Response of mycorrhizal Norway spruce seedlings to various nitrogen loads and sources. Environmental Pollution 114 (2), 223–233.

BUWAL, 1995. Vom Menschen verursachte Luftschadstoff-Emissionen in der Schweiz von 1900 bis 2010. Schriftenreihe Umwelt Nr. 256, Bern, 420pp.

Cowling, E.B., Merrill, W., 1966. Nitrogen in wood and its role in wood deterioration. Canadian Journal of Botany 44 (11), 1539–1554.

Elhani, S., Lema, B.F., Zeller, B., Brechet, C., Guehl, J.M., Dupouey, J.L., 2003. Inter-annual mobility of nitrogen between beech rings: a labelling experiment. Annals of Forest Science 60 (6), 503–508.

Evans, R.D., 2001. Physiological mechanisms influencing plant nitrogen isotope composition. Trends in Plant Science 6 (3), 121–126.

Freyer, H.D., 1991. Seasonal variation of $^{15}N/^{14}N$ ratios in atmospheric nitrate species. Tellus 43 (1), 30–44.

Hart, S.C., Classen, A.T., 2003. Potential for assessing long-term dynamics in soil nitrogen availability from variations in $\delta^{15}N$ of tree rings. Isotopes in Environmental and Health Studies 39 (1), 15–28.

Heaton, T.H.E., 1986. Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere—a review. Chemical Geology 59 (1), 87–102.

Högberg, P., 1997. ^{15}N natural abundance in soil-plant systems. New Phytologist 137, 179–203.

Jung, K., Gebauer, G., Gehre, M., Hofmann, D., Weissflog, L., Schuurmann, G., 1997. Anthropogenic impacts on natural nitrogen isotope variations in *Pinus sylvestris* stands in an industrially polluted area. Environmental Pollution 97 (1–2), 175–181.

Keeling, C.D., 1958. The concentration and isotopic abundance of atmospheric carbon dioxide in rural areas. Geochimica Et Cosmochimica Acta 24, 322–334.

Köchy, M., Wilson, S.D., 2001. Nitrogen deposition and forest expansion in the northern great plains. Journal of Ecology 89 (5), 807–817.

Koopmans, C.J., Tietema, A., Boxman, A.W., 1996. The fate of ^{15}N enriched throughfall in two coniferous forest stands at different nitrogen deposition levels. Biogeochemistry 34 (1), 19–44.

Kukkonen, J., Harkonen, J., Walden, J., Karppinen, A., Lusa, K., 2001. Evaluation of the CAR-FMI model against measurements near a major road. Atmospheric Environment 35 (5), 949–960.

Levy, G., Brechet, C., Becker, M., 1996. Element analysis of tree rings in pedunculate oak heartwood: An indicator of historical trends in the soil chemistry, related to atmospheric deposition. Annales Des Sciences Forestieres 53 (2–3), 685–696.

Macko, S.A., Ostrom, N.E., 1994. Pollution studies using stable isotopes. In: Lajtha, R., Michener, K. (Eds.), Stable Isotopes in Ecology and Environmental Science. Blackwell Scientific Publications, Oxford, UK, pp. 45–62.

Meerts, P., 2002. Mineral nutrient concentrations in sapwood and heartwood: a literature review. Annals of Forest Science 59 (7), 713–722.

Merrill, W., Cowling, E.B., 1966. Role of nitrogen in wood detoriation: amounts and distribution of nitrogen in tree stems. Canadian Journal of Botany 44, 1555–1580.

Norby, R.J., 1998. Nitrogen deposition: a component of global change analyses. New Phytologist 139 (1), 189–200.

Pearson, J., Wells, D.M., Seller, K.J., Bennett, A., Soares, A., Woodall, J., Ingrouille, M.J., 2000. Traffic exposure increases natural ^{15}N and heavy metal concentrations in mosses. New Phytologist 147 (2), 317–326.

Peñuelas, J., Estiarte, M., 1997. Trends in plant carbon concentration and plant demand for N througout this century. Oecologia 109, 69–73.

Poulson, S.R., Chamberlain, C.P., Friedland, A.J., 1995. Nitrogen isotope variation of tree rings as a potential indicator of environmental change. Chemical Geology 125, 307–315.

Schleppi, P., Bucher-Wallin, I., Siegwolf, R., Saurer, M., Muller, N., Bucher, J.B., 1999. Simulation of increased nitrogen deposition to a montane forest ecosystem: partitioning of the added ^{15}N. Water Air and Soil Pollution 116 (1–2), 129–134.

Schulze, E.D., 1989. Air pollution and forest decline in a spruce (*Picea abies*) forest. Science 244, 776–783.

Sheppard, P.R., Thompson, T.L., 2000. Effect of extraction pretreatment on radial variation of nitrogen concentration in tree rings. Journal of Environmental Quality 29 (6), 2037–2042.

Siegwolf, R.T.W., Matyssek, R., Saurer, M., Maurer, S., Günthardt-Goerg, M.S., Schmutz, P., Bucher, J.B., 2001. Stable isotope analysis reveals differential effects of soil nitrogen and nitrogen dioxide on the water use efficiency in hybrid poplar leaves. New Phytologist 149 (2), 233–246.

Spiecker, H., Mielikäinen, K., Köhl, M., Skovsgaard, J.P., 1996. Growth trends in European forests. European Forest Institute, Springer, Berlin Heidelberg, 372pp.

Stewart, G.R., Aidar, M.P.M., Joly, C.A., Schmidt, S., 2002. Impact of point source pollution on nitrogen isotope signatures ($\delta^{15}N$) of vegetation in SE Brazil. Oecologia 131 (3), 468–472.

Thimonier, A., 1998. Measurement of atmospheric deposition under forest canopies: Some recommendations for equipment and sampling design. Environmental Monitoring and Assessment 52 (3), 353–387.

Tietema, A., Boxman, A.W., Bredemeier, M., Emmett, B.A., Moldan, F., Gundersen, P., Schleppi, P., Wright, R.F., 1998. Nitrogen saturation experiments (NITREX) in coniferous forest ecosystems in Europe: a summary of results. Environmental Pollution 102, 433–437.

Vogel, B., Corsmeier, U., Vogel, H., Fiedler, F., Kuhlwein, J., Friedrich, R., Obermeier, A., Weppner, J., Kalthoff, N., Baumer, D., Bitzer, A., Jay, K., 2000. Comparison of measured and calculated motorway emission data. Atmospheric Environment 34 (15), 2437–2450.

Wellburn, A.R., 1990. Why are atmospheric oxides of nitrogen usually phytotoxic and not alternative fertilizers? New Phytologist 115, 395–429.