An attempt to evaluate sulphur (S) and nitrogen (N) inputs into a forest ecosystem retrospectively by means of stable N and S isotope analysis in tree rings

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Abstract

Sulphur (S) and nitrogen (N) are essential nutrients for plants and can be taken up from both the soil and the atmosphere. Trees grow producing tree rings which contain nutrients according to their availability during each growing period. They hence can provide information on the chronology of S and N impacts on ecosystems and their changes retrospectively and a method allowing to analyse S and N content in tree rings as well as their S- and N-isotopic composition has been developed. Tree rings of oak were analysed for tree ring width, elemental concentration of S, N, Mn, Ba, Al, Ca, K, P and 15 other elements. In order to distinguish between different S and N sources, stable S and N isotope analysis was carried out. It was possible to analyse the isotopic composition of S and N in the tree rings. The results gave insight into the participation of different S and N sources during different growth periods. Together with the concentration of the respective element, the isotopic composition provided useful information on long-term changes in the S and N impacts on forest ecosystems. The results revealed obvious trends of either S and N incorporation for nutritional purposes only as well as their accumulation due to pollution stress. Tree ring width and the elemental composition of the tree rings (especially the Mn/Ba-ratio) provided useful and to some extend necessary data for a valid interpretation of the trends observed. The results demonstrate the feasibility of using the S and N isotope analysis of tree rings as a source of information about changes in S and N impacts on ecosystems.

Keywords: natural isotope variations; tree rings; dendrochronology; S and N pollution; fingerprinting

Zusammenfassung

Retrospektive Analyse von Schwefel (S)- und Stickstoff (N)-Einträgen in ein Waldökosystem anhand der stabilen S- und N-Isotopenanalyse in Jahrringen – Schwefel (S) und Stickstoff (N) sind essentielle Pflanzennährstoffe, die sowohl aus dem Boden als auch aus der Atmosphäre aufgenommen werden können. Bäume bilden beim Wachstum Jahrringe, in die auch die Nährstoffe eingelagert werden. Im Hinblick auf eine Chronologie der Nährstoffversorgung von S und N im Waldökosystem sowie deren Veränderungen

wurde eine Methode zur Analyse von S- und N-Gehalten und deren Isotopenverhältnissen in den Jahrringen ausgearbeitet. Um zwischen verschiedenen S- und N-Quellen unterscheiden zu können, bietet sich die Analyse der stabilen Isotope an, da S und N unterschiedlicher Herkunft sich in ihrer Isotopenzusammensetzung unterscheiden. Jahrringe einer Eiche wurden hinsichtlich des Jahrringzuwachses, der elementaren Zusammensetzung (insbesondere S, N, Mn, Ba, Al, Ca, K und P sowie 15 anderer Elemente) sowie des S- und N-Isotopenverhältnisses untersucht. Die Ergebnisse gaben Einblick in die Beteiligung von S und N aus unterschiedlichen Quellen während verschiedener Wachstumsperioden. So konnte aufgezeigt werden, dass einerseits S und N als Nährstoffe genutzt werden, darüber hinaus aber auch eine Akkumulierung dieser Elemente erfolgt, wenn erhöhte Einträge durch Luftverschmutzung respektive Düngung den Eintrag von S und N in das Waldökosystem verändert haben. Die Jahrringzuwachsänderungen sowie die elementare Zusammensetzung (hier insbesondere das Mn/Ba-Verhältnis) steuern wertvolle, zum Teil für eine Interpretation unabdingbar notwendige Informationen bei. Die Ergebnisse zeigen, dass die stabile S- und N-Isotopenanalyse an Jahrringen einsetzbar ist, um retrospektiv Informationen über Veränderungen im Stoffhaushalt von Waldökosystemen zu erlangen.

1. Introduction

Research into the influence of anthropogenic sulphur and nitrogen pollution on ecosystems has been conducted for many years and stable isotope analysis is an obvious tool for assessing the development of S and N pollution over the years in specific areas. The primary condition for such studies is a distinct difference between the isotopic composition of S and N in the sources and sinks. If this prerequisite is met, changes in S and N pollution patterns can be traced.

Stable isotope analysis has been successfully used to trace pollutant S in the environment and to identify sources of S pollution (WINNER et al. 1978, KROUSE & GRINENKO 1991). Fossil fuels tend to be enriched in ^{34}S (NIELSEN 1974) and therefore, atmospheric S compounds, which mainly stem from the combustion of fossil fuels, are expected to be enriched in ^{34}S. The S present in natural ecosystems has a lower $^{34}S/^{32}S$ ratio.

S is a plant nutrient, but in areas where environmental pollution is present and leads to a surplus S supply, gaseous S species like SO_2 or H_2S entering the plants can lead to severe damage if S is not readily incorporated into the plant's metabolism or detoxified (JÄGER & KLEIN 1980, KELLER 1984, RENNENBERG 1984). Vegetation acquires S by at least two mechanisms: uptake of sulphate from the soil via the root system, and uptake of S from the atmosphere through the stomata on the leaves. S within the plants therefore consists of a mixture from both S sources. Because of their different S isotopic »signatures«, it is possible to distinguish S of atmospheric origin from soil-derived S (e.g. GEBAUER et al. 1994).

For N, the major pollution sources all differ in their characteristic isotopic compositions, and this can be used to reveal the specific origin of N pollution. An increase in the use of ^{15}N stable isotope techniques in ecological research in the past decade (LATJHA & MICHENER 1994) is due to the need for a N tracer. In ecology and ecotoxicology these stable isotopes can easily be used as tracers of change with time (JUNG & JUNGHANS 1981, FAUST 1993, JUNG et al. 1994, 1999, MÖCKER et al. 1996). In environmental monitoring, the determination of $^{15}N/^{14}N$ variations allows to trace origins and quantities, as in diagnosing the impact of

natural and anthropogenic compounds on plants and ecosystems (GEBAUER & SCHULZE 1991, HÖGBERG & JOHANISSON 1993, GEBAUER et al. 1994, HOFMANN et al. 1997, JUNG et al. 1997).

Interaction of ammonia (NH_3) and sulphur dioxide (SO_2) is known to be important in air pollution chemistry and effects soil acidification, nutrient cycling and plant health. The northwest of Lower Saxony in Germany, for example, was classified for a long time as an »area of low level of air pollution«, thus the mean annual SO_2-concentrations measured were below $10\mu g$ SO_2/m^3. Nevertheless the soils were strongly acidified and major damage to the forest ecosystems was noted. A combined analysis of N and S air pollution and the low buffer capacities of the soils finally led to an understanding of the real impacts onto the forest ecosystems. (BÜTTNER 1992, NAGEL et al. 1994). If both substances are released into the air during the same period, they react rapidly and form ammonium sulphate, with the consequence that the concentrations of SO_2 and NH_3 in the air are diminished. Nevertheless, the potential for acidification is maintained and after deposition into the soil system this is realised by microbial activity to its full extent. Therefore the concentrations in the air alone lead to an underestimation of pollution from the air.

In temperate climate zones like Europe, trees produce annual growth rings in which environmental conditions might be archived as metals, nutrients and isotopes in tree rings can be used for the reconstruction of environmental impact chronologies (LEPP 1975, HAGEMEYER 1993). HOFMANN & BORN (1987), who developed special coring and preparation techniques, could show for lead in tree rings of ring-porous tree species (like oak and ash), that the tree-ring chronologies fitted exactly to the history of environmental effects caused by a major local industrial pollution source, when the effects on the soil system and the health status of the tree is regarded. Using the characteristic patterns of elements, isotopes and substances in tree rings and bark together, the specific environmental impacts of various industrial pollution sources onto local ecosystems could be distinguished successfully by this method in further studies (HOFMANN et al. 1998, 2001).

Furthermore, tree rings have been widely used to reconstruct past environmental conditions (SCHWEINGRUBER 1983, DEAN et al. 1996) and several projects aim at, e.g., generating a retrospective analysis of the past climate and the influence of changing levels of atmospheric CO_2 over the last 10 000 years. The changing patterns of tree ring width and of the stable isotope composition of H, C, and O in the tree rings were analysed to provide information thereon (SAURER et al. 1995, 1998). Nevertheless, there is only little literature on analysing S and N and their isotopes in tree rings for long-term chronologies (POULSON et al. 1995, YANG et al. 1996, PEÑUELAS & ESTARTE 1997, HOFMANN et al. 1998).

In the study presented here, we were aiming at a retrospective evaluation of anthropogenic S and N effects on the ecosystem and therefore we analysed N and S and their isotopic composition in tree rings as well as the annual growth changes.

Tree species behave differently concerning uptake, transport and allocation of elements. One major aspect is how the water transport system from the root to the leaves functions as physiological active or soluble substances are translocated with the water. In some genera like *Salix* and *Betula* the water conduction takes place over the whole stem area. Hence these trees cannot give chronologies except for the analysis of tree ring cell compartments that have been stable since ring formation. Ring-porous species like oak

(*Quercus* spp.) and ash (*Fraxinus* spp.) however, transport water only in the vessels of the latest formed ring. Therefore these species are favourable for dendroanalysis. Nevertheless, LEPP & DOLLARD (1974) showed the principal importance of lateral transport over ring boundaries, which has to be assumed for many elements. Further, the type and location for the bounding of the substances in the tree ring tissues is relevant. RADEMACHER (1986) showed that there are three levels of binding elements: a reversible adsorption at the surface of the axial vessel walls, which function as a buffer and ion exchange system in the water transport system from the root to the leaves and therefore highly mobile; secondly, bound at the cell walls of the lateral ray cells and adjacent cells, which is only mobile under certain conditions; and a third within cell compartments, which is usually immobile. HOFMANN & BORN (1986) found that the acidification of the soil, the availability of the elements and the health status of the tree were important factors. They showed that tree ring analysis cannot be expected to replace air pollution measurements directly, but that the analysis of the growth and the chemical composition of the tree rings together reveal an environmental chronology on a biological effect level, which cannot be obtained by physical-chemical measurements alone. The key question is the relative importance of the mentioned processes, how they affect the results and how the results can be interpreted. This has to be investigated for any substance, tree species and local conditions specifically. Results reported here were achieved using oak trees.

2. Materials and Methods

Based on the results of a previous atmospheric pollution monitoring programme (HOFMANN et al. 1998), a rural forest site in Northern Germany was chosen for this study. The level of the atmospheric SO_2 at the site is known to be low (less than 10 $\mu g/m^3$ since 1993), but the area is highly impacted by N from pig and poultry farming and slurry applications (FEDERAL AGENCY FOR ENVIRONMENT 1997). The site and the individual tree was chosen out of a greater population studied in the monitoring programme, thus some interesting environmental changes were known from that site. A recently undertaken change in the soil drainage system is reported by the owner, that finally led to destruction of the root system of the trees and ended in fungal decay and death of some trees. The site, which is about 1 hectare in size, was investigated by CIR-aerial photography in course of the monitoring programme, that covered an area of about 2000 km². Further data were available: pollution data from bark biomonitoring of air pollution loads (S, N, $\delta^{34}S$, 50 elements; 125 sites), biomonitoring with lichens for SO_2 and N impacts (102 sites), data from soil and needle analysis (32 sites), tree ring growth records from 320 trees and dendrochemistry (3 sites).

Tree ring samples were taken for growth analysis by 5 mm increment borer (Suunto) from12 oak trees (*Quercus robur*) at the particular stand. Tree ring width was measured and analysed using the LINTAB/TSAP devices (Rinntech GmbH, Heidelberg, Vers. 3.2). After synchronisation and dating, growth changes were calculated by expressing the yearly growth rates of the individual specimen in percentage to the yearly mean growth rates of the healthy sub-population in the area.

Using these data on life records, a 120-year-old dying oak tree was taken exemplarily for dendrochemical analysis. Sequences covering periods of five years were cut out from a freeze-dried stem disc section, homogenised and divided into four sub-samples according to the different analytical methods:

The S concentration was analysed using an automatic S analyser (LECO SC132). For determining the S-isotope composition of S in the tree rings, all S was extracted from the wood and converted to SO_4^{2-} using a Parr Bomb oxidation procedure (SIEGFRIEDT et al. 1951). The S isotopic composition was measured on the resulting $BaSO_4$ using an elemental analyser (Carlo Erba NA 1500) coupled to a stable isotope ratio mass spectrometer (Finnigan MAT Delta S) according to the method described in GIESEMANN et al. (1994). The S-isotopic composition of the samples is expressed as a $\delta^{34}S$ value, defined as

$$\delta^{34}S\,(‰) = \left(\frac{^{34}S/^{32}S_{sample}}{^{34}S/^{32}S_{standard}} - 1 \right) \times 1000$$

with CDT (meteoritic troilite (FeS) from Canon Diabolo Troilite) being the international standard. Each sample was measured at least twice. The reproducibility was better than 0.5 ‰.

For N isotope analysis, the wood material of the tree rings was washed, dried at 70 °C until weight constancy, and pulverised. N analysis was carried out using the micro-Kjeldahl technique. An aliquot of the resulting ammonium sulphate was used to determine the $^{15}N/^{14}N$ isotope ratios ($\delta^{15}N$ values) using an on-line system (Con Flo-IRMS) consisting of an elemental analyser (Carlo Erba 1108) and a gas isotope mass spectrometer (Finnigan MAT 252). Each sample was converted twice and measured six times. The reproducibility of the $\delta^{15}N$ values of the samples was better than 0.2 ‰ in 90 % of cases (GEHRE et al. 1994). The isotope ratios were expressed as δ values:

$$\delta^{15}N\,(‰) = \left(\frac{^{15}N/^{14}N_{sample}}{^{15}N/^{14}N_{standard}} - 1 \right) \times 1000$$

Ca, Al, Mn and Ba were determined together with 24 other elements in the tree rings using multi-element analysis performed by ICP-MS (inductive coupled plasma mass spectrometer; Perkin Elmer Elan 500). At least one double assay was made per sample. The ICP-MS was calibrated using multi-element standards (simple linear), whereby measurements were made in a series of three dilutions (1:1; 1:10; 1:100) in order to comply with an optimal calibration range for the different orders of magnitude in which element concentrations were present. Potential perturbations are determined by means of a corrective solution and handled in accordance with DIN 38406-29 Section 5.2.2. The data are listed in ppm dwt [µg/g dwt], from which the ratios of Ca/Al and Mn/Ba were calculated.

3.   Results and Discussion

3.1. Sulphur studies

The S concentration in the tree rings (Fig. 1) was more or less constant between 1880 and 1940, reflecting the level of S taken up from the soil and/or atmosphere for nutritional purposes (baseline). Between 1950 and 1980, the S concentration in the tree rings increased, giving evidence of higher S input and a surplus in the amount of S available to the tree. These results tally well with the findings of GUYETTE et al. (1989), who reported an increase in the S content in *Juniperus* sp. tree rings to be closely related to an expansion of industrial activity in the growth area. This mechanism seemed to work until major changes occured in the tree after 1985, when it got infected by fungi.
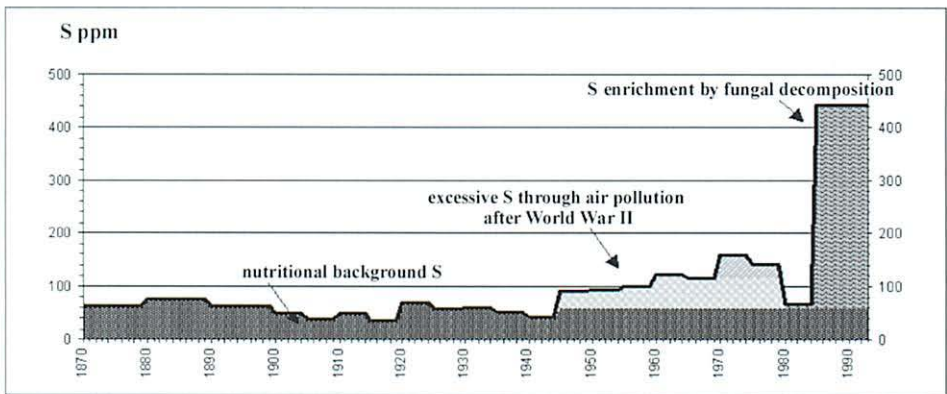

Fig. 1   Sulphur concentration in the tree rings

The Ca/Al-ratio in the soil matrix is known to be an important indicator of soil acidification, that marks a change of soil buffer status. This is reflected by the same ratio in the matrix of the tree rings. GUYETTE et al. (1992) and GUYETTE & CUTTER (1994) reported the special role of the Mn/Ba-ratio in the process of soil acidification by SO_2. While the Ca/Al-ratio describes the status of acidification in general, the Mn/Ba-ratio gives a proxy for the S impact. It is a specific indicator of that portion of the acidification which is caused by the air-pollution deposition of sulphur compounds.

At the location under evaluation, the soil acidity dropped in the period 1935 – 1945, indicated by a drop of the Ca/Al-ratio in the tree rings (Fig. 2). This was followed by a change of the Mn/Ba ratio in these tree rings (Fig. 2) to a level over 1. According to GUYETTE et al. (1992) and GUYETTE & CUTTER (1994), these changes in Mn/Ba as well as Ca/Al specifically indicate that atmospheric sulphur compounds are one major cause in the process of soil acidification in that area. The tree has to manage the surplus supply. One possible sink for S on its way up from the roots to the leaves is the trunk. Here, the cells and vessels may function as a regulative and ion exchange system with a high storage capacity. The nutrient conditions reaching the leaves may hence be kept constant (RADEMACHER 1986). The course of tree ring width (Fig. 3) shows, that growth is still kept on a normal level during this time.
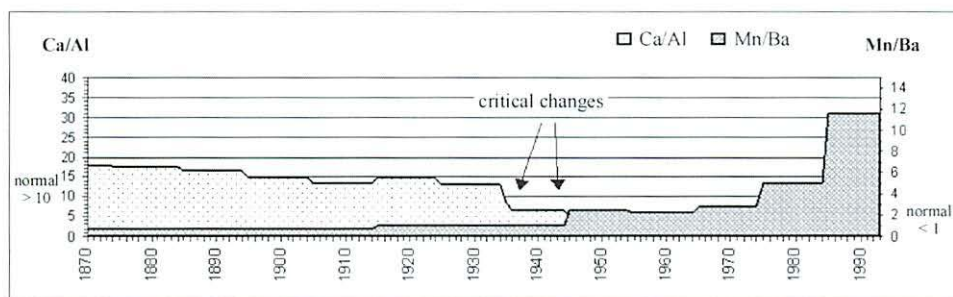
Fig. 2   Ratios of Ca/Al and Mn/Ba in the tree rings indicating ecosystem changes in soil pH due to
acidification and S impacts. Normal soils belong to the exchange buffer status and their soil pH
has values < 4.2, the corresponding Ca/Al ratios in the tree rings are < 10. Ca/Al ratios < 10
indicate a drop of soil pH below 4.2 as critical value for the change to an inferior buffer system
due to acidification. A corresponding increase of the Mn/Ba ratio to values greater 1 indicate
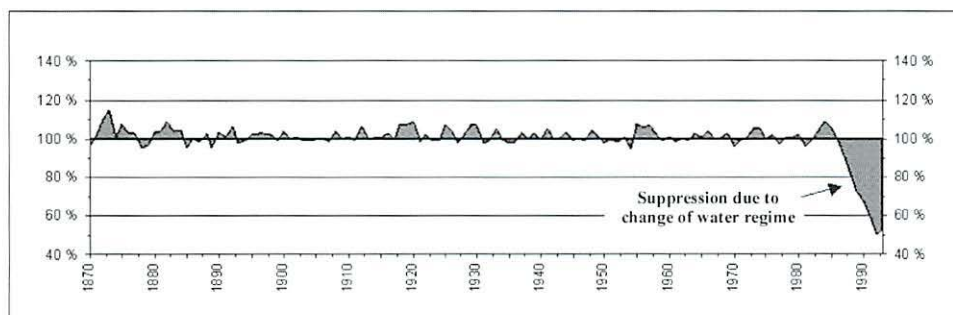that S plays a major role in acidification.

Fig. 3   Growth changes in the tree rings. Percentage growth of the damaged individual compared to
the mean curve of the healthy subpopulation in the area.

Around 1980 the S concentration dropped, then sharply increased in 1985 to an extremely
high level (Fig. 1). The latter goes along with an obvious growth suppression in the tree
rings (Fig. 3). The decline is linked to a major change in the site condition: A change in the
drainage system drowned the plot and the trees showed severe damage, rot, and some
even died. The specimen under evaluation was chosen especially being part of the latter
group. The tree rings from this final period of the life of the tree showed fungal decay.

Highly mobile nutrients such as K are reported to accumulate in the most currently
formed tree rings (LÖVESTAM et al. 1990). For S this seems not to be the case, as trees at
other sites do not show such a sharp increase in the S content in the youngest ring period
(HOFMANN et al. 1998). This observed pattern cannot be attributed only to lateral transport
of S towards the cambium. The sudden high S concentration is much more linked to that
known change in the site conditions and health status of the tree and fungal infestation.
Therefore, the observed high increase of S concentration in the youngest tree rings in
Fig. 1 does not reflect the actual air pollution levels nor the accumulated S burden in the
soil any more, thus the S-air-pollution levels in the area have been decreasing at that time
(NLÖ 1998).

The S-isotopic composition in the tree rings (Fig. 4) changed over the years and clearly shows distinct trends. The $\delta^{34}S$ values first decreased steadily from values over +5 ‰ around 1880 to a value of +0.5 ‰ in 1950. In the area where our research was conducted, peat ($\delta^{34}S$ value: +14 ‰) was the major material used for heating purposes in former times. It was steadily replaced first by coal (with $\delta^{34}S$ values ranging down to −20 ‰) and after the second world war by oil and finally gas ($\delta^{34}S$ values around +10 ‰). The S-isotopic composition of the tree rings seem to reflect these changes in the origin of atmospheric SO_2. After 1950, the trend towards less positive $\delta^{34}S$ values stops characteristically and turns into a slightly rising trend, the $\delta^{34}S$ values became more positive. This change in S-isotopic composition is paralleled by an increase in S concentration in the tree rings (Fig. 1) and is closely related to the general increase in S pollution due to the expanding industrialisation throughout Germany after World War II, which goes along with an expanding use of fossil fuel resources.
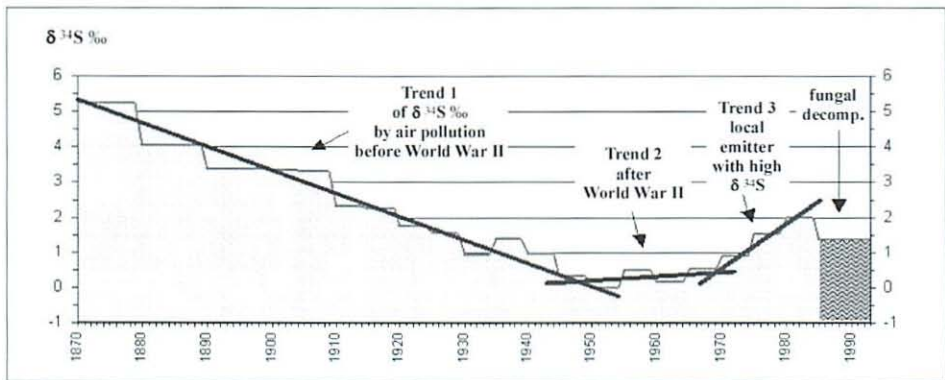

Fig. 4   Sulphur isotope ratios in the tree rings

A third trend can be observed starting around 1970 with a steep increase in the $\delta^{34}S$ values of the tree rings. At this time, a regional S emitter went into operation. Hence, this change in S-isotopic composition probably is closely related to the involvement of S from this emitter and does not reflect the general trend of atmospheric S pollution originating from the long-distance transport. S from the local emission source had high $\delta^{34}S$ values of around +10 ‰, while the average $\delta^{34}S$ values of the SO_2 air pollution in the area under observation in the 1990s was measured in the range of +3 ‰ (HOFMANN et al. 1998). Up to here these trends could be found again in another study at 2 further sites in North Germany (HOFMANN et al. 1998).The impact of this regional emitter was reduced since the mid 1980s, where a drop in the $\delta^{34}S$ values of the tree rings seem to start. However, from the mid 80s on no major change in the S-isotopic composition was observed, although a high increase in S concentration in the tree rings became apparent. This goes along with growth reduction of tree rings and manifest fungal decay. During this period, the S pollution in the area did not increase at all, it even decreased slightly. Thus the fungal infection originates from the root system and leads to a change of the S incorporation, due to a changed health status of the tree. Furthermore, differences in the physiology and metabolism of the fungi compared

to the tree might have an influence on the S-isotopic composition. GIESEMANN et al. (2003) showed that mycelium of the obligate biotrophic pathogen powdery mildew (*Blumeria graminis* f. sp. *tritici*) and the underlying leaf material differed in their S-isotopic composition. They varied depending on the developmental stage of the fungus, implying that differences in the metabolism and/ or translocation of S compounds from the plant into the pathogen occur.

It has to be kept in mind as well that under certain conditions the tree root system might grow into areas more conducive to their development and hence obtain access to S sources of different S-isotopic composition. YANG et al. (1996), for instance, reported a striking link between $\delta^{34}S$ value and the age of tree rings in *Tamarix aphylla*. This tree grows in a desert environment and is adapted to local conditions. The authors stated that their observations are not related to anthropogenic S input into the system, but instead reflect root growth and S uptake from different S sources in the soil of Death Valley where the trees grow, e.g. sulphate from groundwater rather than from surface water. However this seems not to be the case for the trees we have been working on. The soil conditions in the research area became in 1986 much wetter, with partly anaerobic conditions and a changing S availability in the soil-fungi-root system.

3.2. Nitrogen studies

The main sources of N available to plants are ammonium and nitrate in the soil solution either as products of microbial mineralisation, or from artificial fertilisation. In addition, anthropogenic atmospheric N compounds are plant-available. The $^{15}N/^{14}N$ isotope ratio measured in the plant results from the $^{15}N/^{14}N$ ratios of each individual nutritional N source and is proportional to the amount in which either of them is taken up by the plant.

Furthermore, metabolic processes in plants in general discriminate against the heavier ^{15}N isotope. Nevertheless, the N-isotopic composition of different compartments in an ecosystem provides information on the participation of different N sources. The area where the study reported here has been conducted, formerly consisted of peat-land and sandy hills. Between 1910 and 1917, agricultural land use started in this area. It is reported that during this period high amounts of mineral fertilisers were applied for the first time in this area. This led to a period of increased N concentrations in the tree rings about 1910 (Fig. 5) with increased $^{15}N/^{14}N$ ratio (Fig. 6), clearly indicating an input of mineral fertiliser bearing a high $\delta^{15}N$ value. About 5 years later, the N concentration went down again to a level observed prior to the fertilisation period. At the same time, a declining trend in the $\delta^{15}N$ values of the tree rings became obvious and continued through to the beginning of the seventies, shortly interrupted by a slight increase of the $\delta^{15}N$ values in the first half of the fifties. Although the N concentration did not increase in parallel, this change in N-isotopic composition again seems to be due to the use of mineral fertiliser. The N concentrations in the tree rings showed a more or less a steady state until 1950. Thereafter the N concentration in the physiologically inactive heartwood rings increases exponentially up to 1980. From 1981 up to the latest built ring in 1992 we have physiologically active sapwood rings, where translocation processes are possible. Here N increases towards the cambial zone in an over-exponential way.
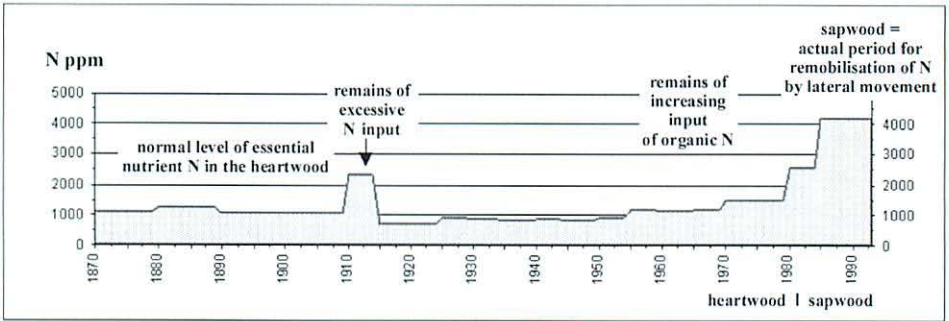
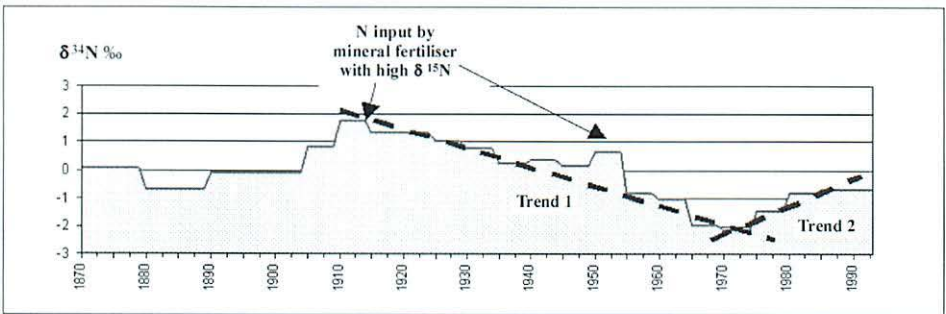Fig. 5   Time course of the nitrogen concentration in the tree rings

Fig. 6   Changes of the $^{15}N/^{14}N$ ratios ($\delta^{15}N$ values) in the tree rings with time

The $\delta^{15}N$ values decreased steadily (except for the interruption mentioned above) until the beginning of the seventies. Then the trend turns into raising $\delta^{15}N$ values up to a plateau in the mid of the eighties, which is kept during the latest periods.

These findings fit well to the land-use data reported: After the second world war, wood was taken out of the forest land, mainly for heating and building purposes. After 1950, agricultural land use was intensified with general application of fertilisers in the research area, but not directly at the forest site. This can clearly be seen in the shift of $\delta^{15}N$ towards more positive values in the mid fifties. In the seventies larger pig and poultry farming started in the region with slurry application to the fields, release of ammonia and input of N into the environment. This was intensified up to the nineties, reaching the highest density of pig and poultry farming and slurry application in Germany with corresponding extremely high NH_3 concentrations in the air (DÖHLER et al. 2002, MOHR et al. 2002).

The changes in the trend of the $\delta^{15}N$ values reflect these changes in land use, fertiliser application and intensification of pig and poultry farming in the area, with the exception of the latest period, when the tree was infected and died.

The N concentrations in the tree rings seem to be kept at a steady level until the 1950s. This indicates a baseline of N, which reflects the tree's ability to control its N supply as a major nutrient. Similar findings are reported by BUKATA & KYSER (2002). Only in the case of

excessive N supply does the N concentration in the tree rings increase markedly. The sharp increase of the N concentration observed starting from the mid eighties on can be due to a mixture of events: an increase in the N impact onto the environment as well as changing soil conditions resulting in growth reduction of the tree rings and fungal infection of the tree followed by its death. Further more, it has to be taken into account, that a known problem in interpreting N data from tree rings is the lateral transport of substances across the ring boundaries via the ray cells (LEPP & DOLLARD 1974). This process must be more or less important depending upon the tree species, the substances and the environmental conditions, but no systematic study has been published. Especially for physiological active substances like the major nutrients, this process is known to be relevant. In the case of N in tree rings, POULSON et al. (1995) and PEÑUELAS & ESTIARTE (1997) found that N is mobilised again in the sapwood and lateral translocation of N towards the active cambium region is assumed. After heartwood formation, relocation is not possible any more.

Taking all the observations and the tree ring data together leads to a picture of the history of environmental impacts and tree reactions at the site under evaluation. They reveal that in the course of the long-lasting S impacts through air pollution and resulting soil acidification, the major ecosystem change in the buffer system of the soil had already started 50 years ago. In the following years, the concentrations within the tree, first of S, than of N, changed. The xylem tree rings function as a physiological regulative and detoxifying sink (RADEMACHER 1986). When healthy, and if N is not supplied in surplus, N gets remobilised from the older rings as storage system towards the cambial zone, where N as nutrient is demanded for tree ring growth (POULSON et al. 1995). S however seems not to be translocated from tree ring to tree ring. If both the S- and N-inputs increase excessively, the xylem may function as a regulative sink, where substances which are not needed or even would be of toxic potential are stored. If these regulative functions are not sufficient, the substances will flow on towards the leaves in the crown, leading to observable effects on photosynthesis, growth and health status. The intermediate phase, where effects are not yet obvious, can last for many years or even decades. In the case of the tree we report on here, some 40 years after the ecosystem first changed, a secondary local change in the water drainage system led to the final breakdown of the tree's basic functions resulting in growth reductions, fungal infections and death of the tree.

4. Conclusion

These initial results prove that the S concentration and the stable S-isotope ratio as well as the N concentration and N-isotope ratios can be analysed successfully in tree rings. They all clearly showed trends over time which reflect the reaction of the tree to the recorded history of environmental impacts on the ecosystem with respect to local conditions and the changing inputs of S and N.

The results furthermore show that the interpretation of one parameter on its own is difficult. Only by considering elemental, isotopic and growth data together a better understanding of what happened in the ecosystem can be obtained.

The results emphasise that the incorporation of substances into the tree rings is not a passive mirror of pollution levels in the environment. Furthermore, they suggest that

substance concentration data as well as growth data of tree rings are bioindicators in the sense that they give a record of the complex reactions of the tree to changing environmental conditions. The physiology and health of the tree play an important part in how the uptake, metabolism, transport, and incorporation takes place. Naturally, a tree has to control its internal conditions like any other organism. These biological effects are recorded in the tree rings.

Consequently, the value of dendrochemistry should be more seen in a supplementary way instead of replacement of technical measurements of environmental conditions. They provide us with information on the history of biological effects, giving us a clue when major changes in the system and health status occurred and limits were exceeded. This information is most valuable as it cannot be evaluated by any other technical means.

5. References

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