Research Square

Preprints are preliminary reports that have not undergone peer review.
They should not be considered conclusive, used to inform clinical practice,
or referenced by the media as validated information.

Re-analyses of archived spruce needles provide insights into the air pollution history and ongoing climate change

Jürgen Franzaring

Juergen.Franzaring@uni-hohenheim.de

University of Hohenheim

Martin Greve

Landesforsten Rheinland-Pfalz

Alexander Schaum

University of Hohenheim

Torben N Lundt

University of Hohenheim

Friederike Bischof

University of Hohenheim

Andreas Schweiger

University of Hohenheim

Research Article

Keywords: permanent plots, forest monitoring, rare earth elements (REE), mercury, NIRS, environmental archives, stable isotopes

Posted Date: November 12th, 2026

DOI: https://doi.org/10.21203/rs.3.rs-11438964/v1

License: This work is licensed under a Creative Commons Attribution 4.0 International License.
Read Full License

Additional Declarations: No competing interests reported.

Re-analyses of archived spruce needles provide insights into the air pollution history and ongoing climate change

Jürgen Franzaring[1], Martin Greve[2], Alexander Schaum[3], Torben N. Lundt[3], Friederike Bischof[4], Andreas Schweiger[1]

[1]Department of Plant Ecology (320b), University of Hohenheim, 70599 Stuttgart, Germany
[2]Research Institute for Forest Ecology and Forestry, Landesforsten Rheinland-Pfalz, 67705 Trippstadt, Germany
[3]Department of Process Analytics (150j), University of Hohenheim, 70599 Stuttgart, Germany
[4]Core Facility Hohenheim (640), 70599 Stuttgart, Germany

Correspondence: Jürgen Franzaring (Juergen.franzaring@uni-hohenheim.de) **ORCID** 0000-0002-9198-2147

Abstract

Archived foliage can reveal environmental changes beyond measurements made during routine monitoring. We evaluated archived Norway spruce (*Picea abies*) needles from two German forest monitoring plots to reconstruct pollution histories and investigate nutrient and physiological responses to environmental change. 167 annual composite samples of living first-year and third-year needles and dead litterfall needles were reanalysed for elements, stable isotopes, and near-infrared (NIR) spectra. Reanalysed lead concentrations agreed with original measurements ($R^2 = 0.90$), supporting retrospective heavy metal analyses. Lead declined markedly, and rare earth element concentrations more than halved. Mercury decreased comparatively little over time. Dead needles generally contained higher pollutant concentrations than living needles. Carbon isotope discrimination increased, particularly in dead needles, while nitrogen isotope signatures became increasingly depleted in ^{15}N over time. These temporal trends reflected overlapping influences of atmospheric deposition, nutrient acquisition, and changing growing conditions (i.e. annual mean temperature and precipitation sums). NIR spectra distinguished needle classes and sampling years more strongly than sites. Compositional predictions were modest ($R^2 = 0.17–0.39$), whereas sampling year was predicted more accurately ($R^2 = 0.70$). Environmental spectral changes could not be separated from storage-related ageing. Our analyses show that archived needle samples provide retrospective pollution records over long periods of time, but organic stability and interacting environmental influences constrain interpretation of long-term trends.

Keywords: permanent plots, forest monitoring, rare earth elements (REE), mercury, NIRS, environmental archives, stable isotopes

Paper submission to European Journal of Forest Research

Acknowledgements

We are grateful to the Federal State of Rheinland-Pfalz for continuously supporting the Forest Monitoring Programme for many decades. We thank Florian Frank, Heidrun Haase und Laura Diener for checking the sample archives and preparing sub-samples for the analyses.

Introduction

Monitoring element levels in conifer needles has a long tradition in Germany as a diagnostic tool for nutrient imbalances and productivity losses in foresty (Hüttl 1992). Serious environmental concerns caused by atmospheric pollution and the novel type of forest dieback (Waldsterben) in the early 1980s prompted the federal states to initiate dense regular monitoring programmes (covering rasters of 8 x 8 km), especially in the highly endangered mountain areas. Examples were the investigations on permanent plots in Southern German forests, e.g. Ökologisches Wirkungskataster (ÖKWI) in Baden-Württemberg (Franzaring et al. 2010) and the Bavarian Spruce Needle monitoring network (LfU 2018). Due to the general decrease in pollution levels and financial restrictions in the early 2000s, most of the Federal programmes have been ceased meanwhile.

However, spruce needles are still being sampled on a lower number of plots and on an irregular basis in Germany. Examples are the Environmental Specimen Banking (UPB www.umweltprobenbank.de) and the German Soil Surveys (BZE Bodenzustandserfassung I to III, BMEL 2021). Latter investigations have been integrated into the transboundary ICP Forests Programme (International Co-operative Programme on the Assessment and Monitoring of Air Pollution Effects). Being a trans-national, northern hemispheric initiative, the programme studies the impact of ongoing environmental changes in forest ecosystems, with a key focus on tree and soil health (UN/ECE, 2023). Analyses of conifer needles provide critical insights into the nutritional status and pollutant loads over time, which show interactions with the Europe-wide acidification, eutrophication and climatic change (Lorenz et al. 2008; Rautio et al. 2020). Weiss (1999) compiled a comprehensive review of essential element and heavy metal concentrations in spruce needles from the older literature and element reference levels in the wood of spruce have been provided by Offentaler & Weiss (2008). Latter may be used as a reference to dendrochronological studies on the history of pollution.

In recent years, the number of ICP forest monitoring plots and selected trees has decreased in many places due to storms, repeated droughts, over-ageing, severe needle loss and calamities (Michel et al., 2024; Ferretti et al., 2025), so that older trees will consecutivley have to be replaced by younger specimens and probably species. Future and retrospective analyses of archived samples must be based on the same tree cohorts and should go back in time for a few decades. Such investigations can give insights into the rising environmental levels of emerging pollutants, e.g. organic flame retardants, persistent PFAS as well as rare earth elements (REE), which will be used in greater quantities in the future. In the case of the heavy metal mercury, which has not much been studied in regular forest monitoring programmes (except Wohlgemuth et al. 2022), analyses of needle material for retrospective analyses will be better suited than e.g. dendrochronological analyses due to the unambiguous dating. Another reason is that leaves/needles are the primary receptor of gaseous air pollutants, whereas the translocation mechanisms for Hg and other metals/chemical compounds to the stems/tree rings via the xylem are not fully understood (McLagan et al. 2022; Monaci & Baroni 2025; Boonen et al. 2025).

In present contribution, we will focus on the concentrations of certain elements (nutrients and heavy metals) and the composition (C:N, ash and reflective properties) of ground samples of alive and dead needles that have been collected on two forest monitoring plots during the years 1983 and 2019. Towards the end of the 40-year period, spruce has seen massive die-back all-over Central Europe due to the long-term effects of air pollution, which was recently and, in the future, will be aggravated by climate change and severe droughts (Anders et al. 2025). Also in Switzerland, Braun et al. (2025) documented a nine-fold increase in mortality for Norway spruce after the drought years following 2018 especially under high N deposition.

While geological backgrounds and forest management of the two plots do not differ much, we hypothesize that i) the increasingly drier and warmer conditions have left an imprint on the chemistry and composition of the samples, which can be observed both in needles that were still alive and already dead at the time when the samples were gathered. While classical pollutants, e.g. lead and other heavy metals show a decrease in concentrations, we hypothesize that ii) rare earth element (REE) concentrations are showing an upward trend due to the increased use of these elements in the energy and digital transition. With the rising global temperatures and the loss in forest cover, the evasion of toxic mercury could become more pronounced, so we hypnotized that iii) despite the overall decreases in recent Hg emissions, the uptake of Hg^0 in leaf organs will not change much over time. Last but not least, the climatic changes during the recent decades, the earlier onset of vegetation growth and worsened growth conditions would leave an imprint in the material so that we hypothesized iv) that isotopic signatures and NIR spectra of the ground needles have changed over time and clearly differ between the alive one-year and three-year old needles and the dead needles that were collected in the litter.

The overall objective of our study was to test, whether archived material can be used as a retrospective tool for pollutants and elements that had not been addressed in the original studies. We presumed that the storage of the samples under dark, dry and cool conditions would not affect the chemical composition of the material and that leaf organs may better reflect the environmental contamination than tree rings.

Materials and methods

Spruce (*Picea abi*es (L.) H. Karst.) is an important forest and timber tree species that for centuries has been cultivated outside its native range in Central Europe (Seim et al. 2022) but nowadays faces severe challenges from dieback. In Rhineland-Palatinate, the Federal Land with the highest share of forest area in Germany (48%), it covers more than 15% of the land area (3rd forest inventory, https://bwi.info).

The original data and samples used in present study were provided by the Research Institute for Forest Ecology and Forestry (Forschungsanstalt für Waldökologie und Forstwirtschaft, FAWF) and were derived from two representative permanent plots, namely Idar-Oberstein (Hunsrück, Hochwald and Idarwald) and Adenau (North Eastern Eifel), where long and consistent time-series were available (see map insert Fig. 1). Plots have been monitored since 1983 and the yearly investigations were based on the standardized protocols outlined in Tarricone et al. (2015) and Rautio et al. (2020). Non-destructive assessments of the vitality (crown condition, de-foliation) were done in July on all trees in a permanent monitoring plot of 50 x 50 m. Needle sampling took place after the vegetation period (winter months November to March) on other trees than those used for crown condition assessments and considered a uniform height and canopy position. Twigs were harvested from marked trees by helicopter and after 2006 tree climbers were involved in the sampling. Needle and shoot length were measured on selected side and main branches since 1997. The seventh whorl was used for the assessments and the next younger whorl was chosen, when there was not enough needle material. Here, we only considered the originally selected main branches but addressed all the up-to-seven age classes present at the times of assessment. For each measurement, we knew in which year it was performed and in which year the shoot/needles were formed. We could thus determine the age of the measured organs and follow how the mean needle and shoot length changed in consecutive years.

For the chemical analyses, needles from the current terminal first-year (c+0) and third-year (c+2) shoots were sampled. Here, we will refer to the samples as cohorts of one year and three-year-old needles that were collected as alive green organs. A detailed overview of the procedures of the forest monitoring and the results from all plots are given by Greve et al. (2016), but the findings from later than the year 2013 have not been analyzed in detail.

We also considered the dead needles that were collected in the annual litterfall since 1997. Originally, litter samples were gathered from twelve single collectors and were taken every month covering a year from November to November. Four samples were combined to one for the element analyses. We had additional information on total masses per hectare, needle mass and area and derived from these, specific leaf area (SLA). Apart from needles, litterfall was further sorted into the fractions, cones, twigs and the rest.

All the samples were stored both as dry intact and milled samples under dark, dry and temperature-controlled conditions in a NATO Bunker in the Palatinate region. Sub-samples for the retrospective analyses in our study were taken in early 2025. An aliquot of 1g of the up to 15 individual tree samples was taken, combined and thoroughly mixed prior to the analyses. In addition to the milled samples, we obtained a sub-set of samples from intact needles, which we milled in our lab. Chemical analyses performed by FAWF were available for all the samples of the mentioned litterfall fractions and the alive needles. To reduce the effort in our lab, samples were pooled to one sample per year, resulting in a total of 167 composite samples.

Chemical analyses in the first years of the study were done using acid digestion (HNO_3) followed by flame atomic absorption spectrometry (FAAS), which was later replaced by Inductively Coupled Plasma atomic emission spectrometry (ICP-AES). After 2014 all analyses were made using ICP-MS. NIST 1575 Pine needle standards were used to calibrate and check the analyses.

To calibrate our approach, we re-analyzed Pb and hoped to come up with the same results that had been obtained in previous analyses. If the numbers differed, a “sample ageing” could be the reason that would affect chemical composition. However, Hg cannot evade when bound to organic material and all the samples were stored und dry, dark and cool conditions.

Analyses of Hg, Pb and the rare earth elements (REE) cerium, (Ce), lanthanum (La) and neodymium (Nd) took place at the Hohenheim Core Facility (CFH) after VDLUFA (2011, 2014). 0.2 g of the milled needles were

digested in HNO_3 using an UltraClave III microwave (MLS Leutkirch, Germany). The heavy metals and the REE were then determined by inductively coupled plasma mass spectrometry (ICP-MS) applying a NexION 300 X system (PerkinElmer, Rodgau, Germany). NIST Standards 1575a and NIST 1573a were used for quality assurance.

Near-infrared spectrometry (NIRS) analyses were performed using the Bruker MPA (Bruker Corporation, Billerica, MA). The ground needle samples were measured in diffuse reflection with an RT-PbS detector. The resolution was set to 8 cm^{-1}, and 32 scans were co-added for both the sample and the background. Because some samples contained unground needle fragments, the material was not entirely homogeneous. To account for this, each sample was measured three times, and care was taken to measure only ground material.

For each sample, the replicate spectrum was averaged, and the standard deviation across the replicates was calculated at every wavelength and averaged over the spectrum. Dividing this average standard deviation by the mean absorbance of the sample gave its coefficient of variation (CV). Two samples were dropped as they had markedly higher CVs than the other samples, Sample 34 (CV = 7.8 %) and Sample 103 (CV = 6.5 %) compared to the set median of CV = 0.35 % and the next highest sample with CV = 1.3 %. These two samples are therefore not part of the subsequent analysis of the spectra.

Before modelling, the remaining spectra were corrected for light-scatter effects. Two standard scatter corrections, Standard Normal Variate (SNV) and Multiplicative Scatter Correction (MSC), were applied separately and compared. Each was optionally followed by a Savitzky–Golay first-derivative filter with an 11-point window and a second-order polynomial. For each target, the preprocessing was selected within the cross-validation described below. In addition to the full recorded range (782–2779 nm), a small number of literature-based absorption windows in the combination-band and first-overtone regions (1389–2500 nm) were considered as candidate variable subsets.

Quantitative calibrations for the continuous targets (sampling year and the compositional parameters) were built by partial-least-squares regression (PLSR), the established chemometric method for NIR data. The categorical targets (needle age class and site) were treated by the analogous PLS discriminant analysis. The number of latent variables was the only structural setting of the models; it was searched over 1 to 12 and selected by cross-validation, and for the reported models always remained well below the number of calibration samples.

The current-year, older and senescent needles collected at one site each year share the same stand, growing season and laboratory batch and cannot be regarded as statistically independent. All validation therefore kept the needles of a site-year collection together as a single unit that was used either entirely for calibration or entirely for validation. Both the preprocessing and the number of latent variables were selected using only the calibration samples of each calibration-validation split, so that the reported errors refer to genuinely unseen collections rather than to samples the model had already partly seen.

Every figure of merit reported for the calibrations, and every point in the predicted-versus-measured plots (Fig. 7), is based on cross-validated predictions that were obtained in the following four steps.

1. The 65 site-year collections were partitioned into ten folds of roughly equal size, each collection kept intact together with its age siblings.
2. Each fold in turn was held out as the test set while the remaining nine folds formed the calibration set, so that every collection was held out exactly once.
3. From the calibration set alone the model was chosen by a further, internal five-fold cross-validation over the same site-year collections. Each of the 288 candidate combinations (the candidate spectral regions and preprocessing pipelines explained above each tried with 1 to 12 PLS latent variables) was scored by its predictions on the internally held-out samples, and the combination with the highest internal R^2 was kept.
4. This single combination was refitted on the whole calibration set and used to predict the held-out samples; those predictions are the points plotted for that fold.

Repeating steps 2 to 4 for each of the ten folds gives exactly one predicted value per sample. The R^2, ratio of performance to deviation (RPD) and Ratio of Performance to Inter Quartile distance (RPIQ) annotated on each panel are computed from precisely this pooled set, so the points shown in Fig. 7 and the figures of merit quoted for them are one and the same result. The region, preprocessing and number of latent variables chosen in step 3 may differ from fold to fold. Where a single configuration is quoted, as in Table 1, it is the modal one, i.e. the combination selected most often across the ten folds.

Predictive performance is reported by unit-free measures only, so that constituents with different units remain comparable. These are the cross-validated coefficient of determination R^2, the RPD (the standard deviation of the reference values divided by the root-mean-square error of prediction) and the RPIQ (the interquartile range divided by the same error), the latter being more robust to skewed reference distributions. For the categorical targets, balanced accuracy is reported against the majority-class baseline. The statistical significance of every model was checked by a label-permutation test, in which the reference values were randomly reassigned and the whole procedure was repeated. All models discussed below were significant at $p<0.01$.

Analysis of stable isotopes ^{13}C and ^{15}N: approximately 2 mg of a milled plant sample were weighed into tin cups for stable isotope ratio analysis. The samples were pyrolyzed (950 °C) and oxidized in the element analyzer Vario ISOTOPE select (Elementar Langenselbold, Germany) using He as a carrier gas. The Vario ISOTOPE select is linked with the isotope ratio mass spectrometer (Elementar Langenselbold, Germany), isotopic ratios of N_2 and CO_2 were determined and calibrated using suited reference materials. The sample isotope ratios were compared to those of pure cylinder gases injected directly into the IRMS before and after sample peaks. The isotopic ratio is expressed in parts per thousand as $\delta^{13}C$ (VPDB) and $\delta^{15}N$ (Air).

CN elemental analyses were performed on the samples via an element analyzer Vario ISOTOPE select (Elementar Langenselbold, Germany) by catalytically combusting the samples with pure oxygen at high temperatures and quantitatively reducing them to molecular nitrogen and SO_2.

Results and discussion

Climatic conditions and trends over time

In present study, we considered data from long time series collected at the two FAWF long-term monitoring plots Idar-Oberstein (Hunsrück) and Adenau (North Eastern Eifel), see map insert Fig. 1. Observations stemmed from unlimed forest inventory plots that had been studied since the year 1983. Microclimate data from the plots were available from 1988 to 2016 and were compared to data from the DWD reference station Trier. Trends (data not shown) were not obvious in the temperature data acquired within the montane forest plots, probably because data stretched only until 2016 and missing or wrong data due to malfunctions of the climate stations could not be ruled out. We therefore extracted time series from the Deutscher Wetterdienst (DWD) hydrometeorological raster dataset (HYRAS, 5 x 5 km) that were based on modelling temperatures and precipitation for each of the sites considering the eight nearest stations from the DWD national network. According to these data, mean temperatures were slightly lower at the Idar-Oberstein plot compared to Adenau, latter place being situated at a slightly lower altitude (Fig. 1 upper panel). Due to more gradient rainfall, precipitation was significantly higher in the Western Hunsrück mountains than in the Eastern Eifel. The modelled HYRAS data confirmed both the altitudinal temperature gradient and the global warming over time. Accordingly, the climate data measured at the DWD station Trier (80 km from both stations) for the period 1983 to 2023 shows a linear trend in temperatures (R^2 0.48; +0.4°C per decade) and a slight reduction of precipitation (R^2 0.09, -30 mm per decade).

In order to better focus on the climate of the growing season of the current first needle class that was sampled along with the third needle class in the winter, we calculated growing degree days (GDD, sum of daily temperatures above 0°C) and precipitation sums for the months April to November using the HYRAS data. We hypothesized that the seasonal climate (day of the year, DOY 91 to DOY 334) better explains the biological responses of the studied alive and dead organs than the yearly means also covering the unproductive winter months. Temperature and precipitation sums (data not shown) at the two sites showed more pronounced changes between 1980 and 2020 than the yearly averages. During the times series, GDD at Idar-Oberstein increased by 12.8 °days (R^2 0.52) and at Adenau by 10.1 °days (R^2 0.44) per year, whereas seasonal precipitation sums decreased by 2.2 and 2.5 mm per year, respectively. In line with the higher GDD, needle sprouting was advanced by 7 days per decade (R^2 0.5, data not shown) at Reichenbach (DWD site 09968, data available from 1980 to 2018), which is situated close to Idar-Oberstein. Unfortunately, long-term data for a location close to Adenau was not available in the phenological database of the DWD, but the advancement of sprouting of new needles should also be traceable there. As has been demonstrated by weekly radial growth measurements by Bose et al. (2025), the earlier onset of the vegetation period, however, did neither boost nor compensate the seasonal growth of spruce and other tree species.

While the increasingly drier atmospheric conditions may explain plant (eco)physiological changes, (reduced) air pollution and global brightening (less particles and soot) may also have directly or indirectly contributed to biological and leaf compositional changes. PM10 (data not shown), NO_2 and SO_2 levels have much decreased during the last four decades, while the annual means of tropospheric ozone have steadily increased over time (Fig.

1 lower panel). Since the ozone precursor concentrations have declined, the main reason for the higher photooxidant levels can be assumed to be the increased global radiation (data not shown), which parallels the elevated temperatures, and which can interact with the plant-water relations of trees. We assume that the ongoing CO_2 fertilization effect and the reduced acidification (rising rainfall pH, data not shown) will also indirectly affect the nutrition, health and growth of forests. pH of the rainfall may furthermore have direct effects on the wash-off of adhering particles and contaminants as well as the buffering capacity of soils.

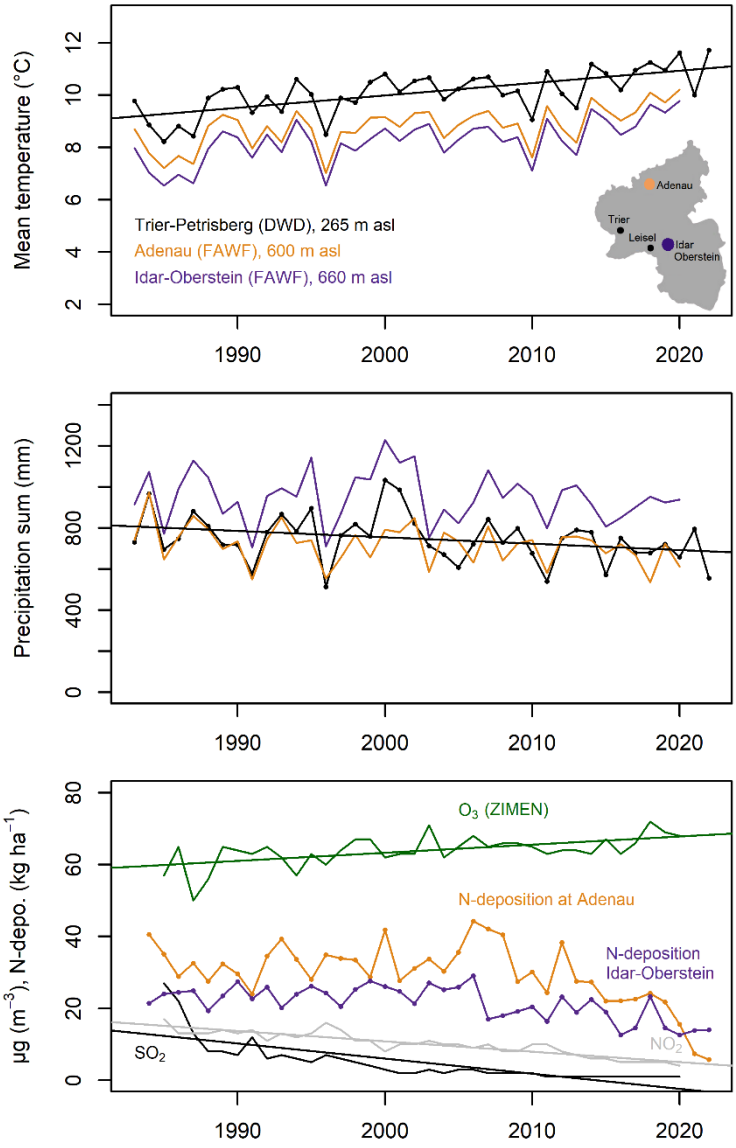


Figure 1. Climate and air pollution recorded at the two forest monitoring sites Idar-Oberstein (•) and Adenau (•) over 40 years. Above panel: temperatures representing annual data from the DWD-weather station Trier and the modelled HYDRAS data for the two plots. Insert shows the shape of the Federal Land Rhineland-Palatinate and the locations of sites considered here. Central panel shows the precipitation sums measured at Trier and those modelled for the two permanent plots. Below panel: Measured nitrogen deposition at the two forest sites and air pollution data (SO_2, NO_x and O_3) measured within the ZIMEN network (https://luft.rlp.de/zentrales-immissionsmessnetz-zimen).

Litterfall and trends over time

Litterfall, i.e. the sum of the fractions twigs, needles, cones and rest, was higher at Adenau as compared to Idar-Oberstein, probably because of lower annual growth rates and productivity at latter site and its higher elevation. The data on needle mass in the litter showed some consistencies at the two sites, with slightly decreasing masses over time (Fig. 2). Shed twig mass showed an increase in recent years, indicating an impaired tree health which was also shown in the yearly assessments of defoliation (see Table S1 supplementary). The peak twig and needle

mass shed in the year 1990 in Idar-Oberstein probably relates to the impact of the winter storm "Wiebke", whereas the cyclone "Lothar" in the end of 1999 did not leave an imprint. In the Adenau plot, litterfall showed a slightly inverse relationship to the HYRAS precipitation sums of the preceding year, indicating that more dead material had been shed from the trees after dry years. However, this trend may be confounded by the fact that with the ageing of trees in a drier environment the vitality and growth may generally have come under pressure. In the wetter and cooler Idar-Oberstein plot, litterfall was almost unaffected by the drought experienced during the years before. The share of dead needles to total litter mass (data not shown) varied from 40 to 90% at both sites and showed similar trends over time. It seemed to be unaffected by climatic parameters, but since the year 2005 the share of needles to total litter mass had declined in Adenau.

After 2004, biometric parameters of the dead needles were studied and showed that 1000 needle mass and area (data not shown) did not change over time. On the contrary, specific leaf area (SLA) of the needles from the litter slightly decreased over time (R^2 0.26), suggesting that needles became more compact over time. This was, however, not directly related to climatic changes or year-by-year variation of the seasonal climate. Since needles shed as litter comprise of different age classes, climatic effects of single years on the needle biometry cannot be identified. It may also be that the higher mass to area ratio (inverse of SLA) related to tree ageing or a lower degradation of the material e.g. due to the general trend to drier conditions. Further assessments of eventual structural and composition changes of the needle material will be made in chapter 3.5.3 (NIR spectra).

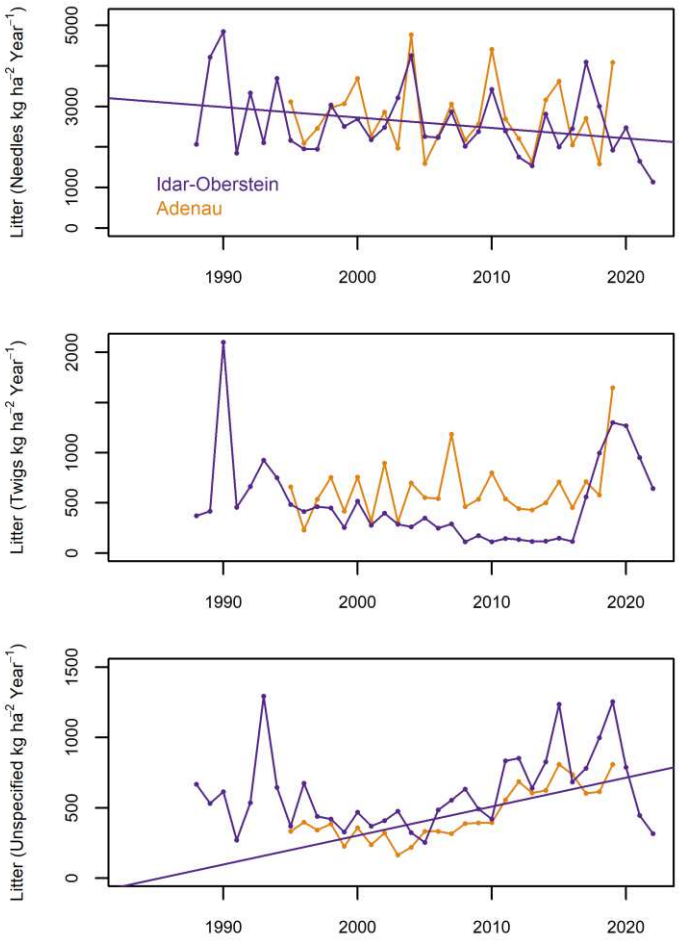


Figure 2. Litterfall at the forest monitoring plots Idar-Oberstein (•) and Adenau (•), specified after the three fractions (decreasing in mass): dead needles (above), twigs (centre) and unspecified rest (below).

Biometry of needles and length and defoliation of 1- and 3-year-old shoots

Besides the analytical results from the needles, we had additional information on the biometric properties of the organs that were considered every year at the two forest monitoring sites. In these additional samples, needle and shoot length were recorded in up to seven age classes. Here we mostly focus on the first-year and third-year needles, which were also subjected to chemical, NIRS and isotopic analyses. Since we had no information on water

contents of alive needles, we refer here to results from one-year old shoots that were sampled in the nearby Warndt Forest (Saar) in the German environmental specimen banking (Umweltprobenbank, UPB). The database also reports mean values for element concentrations in the formerly highly polluted region, which we will use as a reference. While thousand needle mass (data not shown) did not change between 1985 and 2022, water contents decreased during this time (R^2 0.38). Latter finding confirms the effects of the above-mentioned stronger atmospheric drought in recent years as compared to some decades ago.

Needles may adapt their shape, surface to volume ratios and surface characteristics. The adaptation of specific leaf area (SLA) could be shown in the dead needles (see above) that were recovered in the litter. Accordingly, Hesse et al. (2024) showed that in dry years spruce needles will become smaller and that the reduction in total leaf area will probably reduce the growth of a tree. Latter may be regarded as a strategy to cope with prolonged and repeated stress. At the same time, the different mass and volume of needles may somewhat modify the accumulation of elements. In dry years, one might observe concentration effects e.g. of Ca, while in moist years, a dilution of elements (and accumulated pollutants) may occur.

When referring to the heat map on average needle length (see Table S1 supplementary), we can identify several years (see diagonals and bold numbers), in which short or long needles/shoots were formed. The warm years, e.g. 2000, 2004, 2006, 2011 and 2014, all featured very compact needles, while precipitation, both expressed as annual or seasonal sums, only showed a weak positive relationship to the needle and shoot length. This temperature effect could best be seen in the year of the formation of needles/shoots and the size of the effect proved to differ between sites. Strongest negative effects of annual mean temperatures, less so the seasonal GDD, were found on shoot length at Idar-Oberstein (R^2 0.45), while at Adenau needle length of the current year decreased by 0.22 cm per 1° C (R^2 0.26). With time, these initial effects were partially compensated for, but the conserved effect of warm years on the length of organs can still be seen in the diagonal patterns in the color matrix.

Overall, needle length was comparable between the two sites (grand mean of 1.39 cm), but the mean length of needles measured in a certain age class differed (see diagram S1 left, supplementary). In the study on foliar chemistry, only first-year and third-year-old needles were used. While current or first-year needles were of the same length (presumably size), the third-year needles were somewhat longer (larger) on average at the Idar-Oberstein plot. At the same time, shoots were longer on average in each age class at the Adenau site. Trees at latter site were 30 years older; in 2019 142 vs. 112 years at the Idar-Oberstein site. There may be a combination of age and density related, edaphic and genetic reasons for the differences in needle length and shoot, but climate has probably a larger imprint on these variables.

In our analysis, we used the needle and shoot length of the first and third age classes as a biometric variable. It cannot be ruled out that differences in growth between sites and years will affect the uptake of air pollutants and the demand for soil-borne nutrients. Contrasting acquisition of resources and the production of biomass may be responsible for dilution or concentration of nutrients and absorbed pollutants. If in a certain year small needles or shoots are formed these will hence stay small in the following years (see diagrams S1 left and centre), which will then probably also affect the accumulation of airborne pollutants and the quality of the material in the following seasons. Moreover, the needle loss each year will interact with the continuing ab- and adsorption of pollutants. The increase in mean needle length of a specific year over the different measurements of the yearly samplings at both sites does not necessarily mean that needles were getting longer year by year. It only reflects that the spectrum of needles moves to longer needles, i.e. a loss of small (ineffective and damaged) needles and a prolonged survival of the longer, probably more resilient needles.

Data on shoot defoliation gives further insight into the changes in vitality over time. More than 50% of the needles were shed after four years (diagram S1 right), but needle loss (inverse of retention) did not differ much between the sites. We also did not find clear effects of the climate of a single year on the defoliation. Still, it tended to be lower in the moist years at the Idar-Oberstein site, whereas at the Adenau site, defoliation was generally slightly higher. After seven years, over 90% of the needles had been shed at both locations. Needles sampled in the litterfall mainly consist of material that was at least four years old. We have no indication whether needles that fell off each year were more contaminated than the remaining needles. Nevertheless, heavy metal concentrations were much higher in the dead as compared to the alive needles (refer to Fig. 3). Interestingly, needle loss of the 2 and 3-year-old shoots became more pronounced after the dry years 2003 and 2004. Before, it was less than 10%, while later it increased to over 25%, except in the year 2009. The premature and stronger loss of photosynthetic organs in one season due to preceding dry years has been related to a reduced resource storage under drought stress. For the region under study, this has also been confirmed for deciduous tree species and the conifers spruce and pine

(Dietrich et al. 2026). Underlying mechanisms for smaller leaves and shoots and an increased defoliation in the following season may be that more energy and assimilates are being used to reduce stress and that less nutrients are taken up due to a largely reduced transpiration stream. Defoliation (the inverse of foliation) in the first- and third-year needles will also be used to discuss the results of element concentrations, NIR spectra and stable isotopes.

While we saw only slight differences between the sites, Fröhlich (1969) suggested that variations in needle length are determined individually and therefore do not overlap the differences between the localities of origin. The absolute values, however, are greatly influenced by environmental conditions. As a rule, and as stated above, shortened needles will develop in the growth period following a dry year. A grand mean of 1.5 cm was found in the study of Fröhlich (1969), surpassing the mean length of 1.39 cm in present study.

Interestingly, our analysis shows a slight positive relationship between needle loss and N concentrations (data presented in chapter 3.4) of third-year needles. This may suggest that N is remobilized from dying organs to the remaining needles to sustain their photosynthetic activity. In the growing buds, i.e. the youngest organs of Douglas fir, most of the nitrogen comes from the soil as has been shown in the $\delta^{15}N$ study by Qubain et al. (2021). Also, Greve et al. (2016) addressed the remobilization of nutrients from older to younger needles and discussed differences between different cations and anions. These relate to their solubility and transport mechanisms in the xylem and phloem. While rare earth metals will be mobile to a certain extent within the tree, only small fractions of heavy metals will translocate between needles, so that older needles will always have higher concentrations of these elements (see below). One reason behind the continued accumulation of heavy metals is that these elements will be bound firmly to sulfhydryl groups (SH-) of membrane associated proteins.

Up to the 3rd needle class, we did not observe differences in defoliation between the sites (see Figure S1 right, supplementary), but in the older shoots, relatively more needles were lost at the drier Adenau as compared to the Idar-Oberstein site. This may also relate to slightly different resource efficiency in the two studied forest ecosystems. Contrasting expectations, Fröhlich (1969) found that on "good" sites needle longevity is shorter than on "bad" sites, where resources must be dealt with efficiently.

Besides nitrogen, also C-acquisition may be impaired under drought conditions. In *Picea engelmannii* × *glauca* in British Columbia, basal area increment (BAI) declined in dry years and over time (Wiley et al., 2018). Drought also created "carbon stress" so that less starch and stronger discrimination of $\delta^{13}C$ could be recorded in the needles. We will further discuss along these lines in chapters 3.5.2 and 3.5.3 to see whether there are indications of climate signals on C contents, $\delta^{13}C$ and NIR spectra.

Nitrogen, sulfur and lead concentrations determined in the original analyses

Following results and discussion are based on the original analyses the FAWF contracted each and every year when litter and needle samples had been taken at the monitoring sites. The data represents the averages over up to 15 sub-samples that had been gathered from the trees. We only present here exemplary data on nitrogen (N), sulfur (S) and lead (Pb), which are representative of the nutrition and pollution history of the sites. However, the original data includes other nutrients (e.g. P, K, Mg) and various metals, which will be presented in the correlation analyses.

The chemistry of the litter and the alive needle samples from both sites showed marked differences between the materials and sites and exhibited changes over time. As expected, C:N ratios of the woody branches (data not shown), were higher than in the dead and alive needles and decreased between 1988 and 2016. We assume that the increased N deposition in the 1990s (eutrophication and acidification) was an important driver of these changes, but it cannot be ruled out that increasing tree age slightly interacted with these findings. In the beginning of the study (1983) the stands were already 76 and 106 years old. However, the effects would show the opposite direction, since in a larger dataset Greve et al. (2016) found a negative relationship between tree age and the N and S needle concentrations. The higher availability of N and the widespread N-saturation of ecosystems not only create nutrient imbalances in plants but may eventually lead to growth impairments and adjustments in nutrient acquisition. At the same time, climatic factors may also explain part of the variation in growth and nutrient levels. As can be seen in Fig. 3, N concentrations over time in twigs and needles show very similar courses and of ups and downs at both sites suggesting the existence of a mesoclimatic component. However, N concentrations in twigs increased more in the Idar-Oberstein compared to the Adenau samples, whereas at latter site N concentrations in the dead needles increased more over time than in those from Idar-Oberstein. This may indicate that the remobilization of N from dying needles was less efficient and probably not necessary in the more eutrophied site at Adenau and that this effect became more pronounced over time.

Changes in the nutrient levels in twigs and needles have also been addressed experimentally with *Pinus pinea* by Balekoglu et al. (2023). According to the authors, drought affects the acquisition and allocation of C (sugars, starch) and N (proteins) to different plant organs. We will discuss this in greater detail in latter chapters when analyzing the NIR spectra and isotopic ratios. We will then also present and discuss the C:N ratios in the dead and alive needles.

Both the twigs and dead needles collected in the litterfall of each year, constitute of material, which was produced in the years before. The samples can thus be regarded as an environmental archive, while the (fresh) alive needles collected every year represent the actual ecophysiology. The increase in N levels of alive needles at both sites contradicts the lowering of NOx levels (Fig. 1) but may e.g. be related to higher background levels of ammonia (NH_3) in the study regions. However, we only have data for the station Adenau and indeed, NH_3 concentrations slightly increased between 1998 and 2017 (https://fawf.wald.rlp.de/index.php?id=12482). In the final years of the investigation, the total N deposition (2022) went down again partly due to the reduced interception of the canopy and approached the UN-ECE critical load for conifer forests of 7 kg N ha^{-1} y^{-1} (Fig. 1).

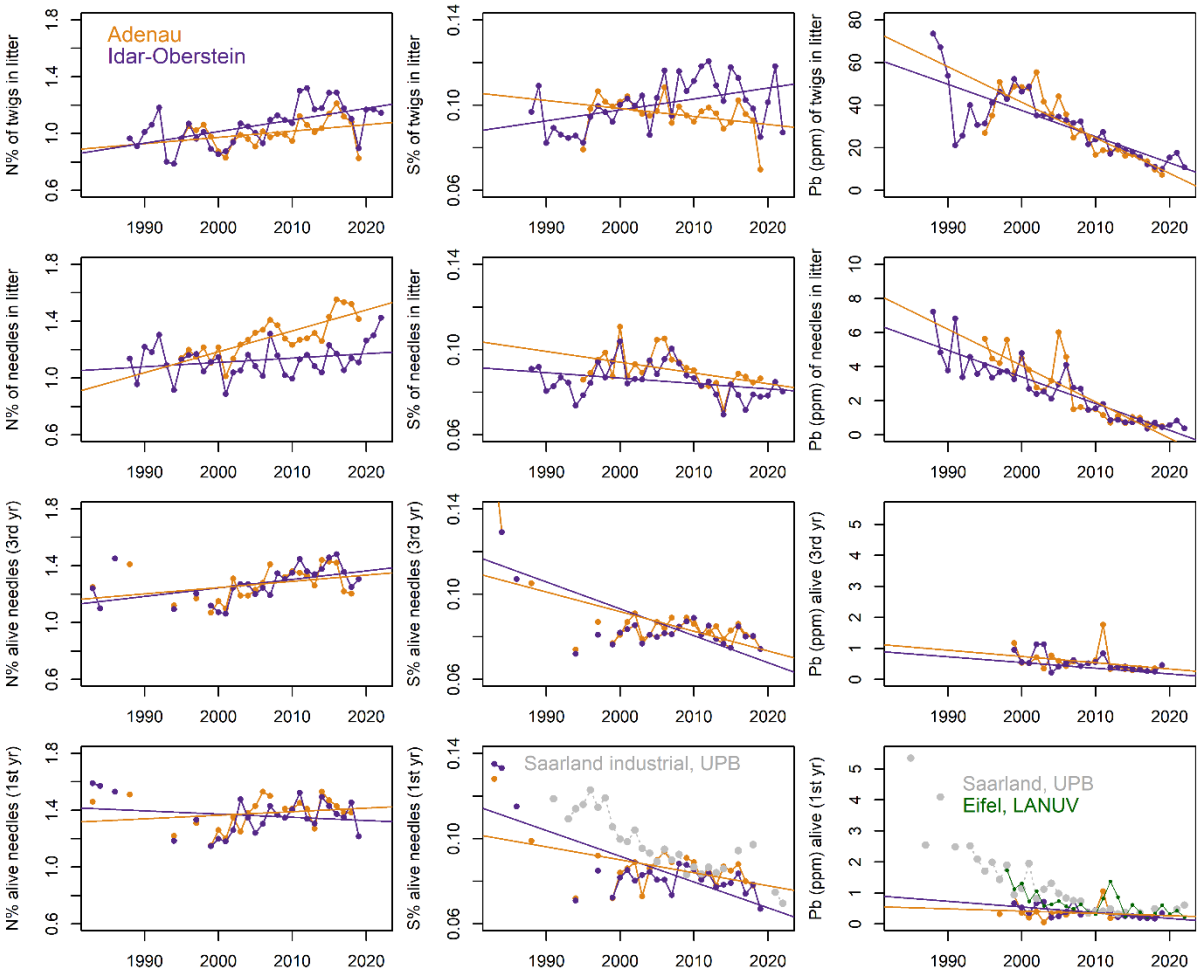


Figure 3. Time series of the nutrients N (left) and S (centre) and the heavy metal Pb (right) in different materials (from above to down: twigs and dead needles in litter, alive and green needles from the third and first year), which were collected at Idar-Oberstein (●) and Adenau (●). Gray (●) dots: The data series refers to the S and Pb concentrations in first-year spruce shoots, which were collected within the framework of the biannual National Environmental Specimen Bank (UPB, www.umweltprobenbank.de, UBA) in the formerly heavily industrialized Saar region. Green (●) dots: refer to Pb-concentrations in standardized grass cultures exposed in the Northern Eifel by LANUV (Northrhine-Westfalia State Agency for Nature and Environment, https://www.opengeodata.nrw.de/produkte/umwelt_klima/luftqualitaet/wirkungsdauermessprogramm/)

Generally, the altered N supply due to the deposition of nutrients and acids may have caused long lasting changes in the quality and degradability of plant materials. Carbon incorporated in the litter and humus, may be released much more rapidly in the form of gaseous emissions (CO_2 and CH_4) or in the case of N, via N_2O emissions or DON in the runoff. At the same time, rising temperatures will increase the speed of the degradation of materials

and thus add to the fluxes of C and N into the atmosphere. Likewise, the recent German forest inventory (Bundeswaldinventur 2022, BMEL 2024) confirmed that carbon releases from forests are actually surpassing the annual sequestration rates due to drought and pest related calamities and part of this comes from higher fluxes of C from the pedosphere. Berg & Lönn (2022) have studied the effects of a different needle chemistry and temperatures and rainfall on the decomposition rates of spruce and pine needles and found strong positive effects of temperatures in the first stage, in which nutrients and starch are being released while in the second stage, where also lignin is being degraded, precipitation proved to have a larger impact.

Interestingly, C:N of twigs from the plot in Idar-Oberstein was also slightly related to the ozone concentrations at the nearby Leisel station (see Fig. 1), while temperature did not explain much of the variation of C:N at this plot (data of needles presented in chapter 3.5.2). It has been shown in many studies that photooxidants and the formation of reactive oxygen species (ROS) reduce the productivity of trees, create premature senescence and interact with the secondary metabolism (e.g. lignin biosynthesis) of plants (Agathokleous et al. 2022; Cheesman et al. 2024). At the same time, the "CO_2 fertilization effect" has been discussed to aggravate the nutritional status of forests (Craine et al. 2018; Peñuelas et al. 2020). The "progressive nutrient limitation" (PNL) or "oligotrophication" may be due to the enhanced growth (dilution of nutrients) or due to the reduced uptake of nutrients associated with stomatal closure under elevated concentrations of CO_2. Furthermore, increased soil drought may reduce nutrient flows.

When comparing the observed needle nutrient levels to the threshold values for N (1.3%) and S (0.1%) for Norway spruce (*Picea abies*) in Germany that have been given in Göttlein (2015), Talkner et al. (2019) and Wellbrock & Bolte (2019), it may be suggested that S-concentrations of the alive needles have recently approached levels indicating a slight deficiency. In Fig. 3, we have included data on S-needle concentrations from a site that was once heavily affected by industrial emissions (coal burning and steel manufacturing in the Saar region). After the introduction of clean air technologies and the shut-down of big polluters, the S-concentrations of alive needles have meanwhile approached low levels at all sites. Interestingly, S-concentrations in the branches, which were collected in the annual litter, still show the legacy of SO_2 pollution due to the high share of older material.

Likewise, the observed N levels are in the lower range of values that have been found in other German forests despite the slight increments observed during the past decades. This is in line with the findings of Riek et al. (2017), who identified elevated levels of the nutrient N in the BZE II plots from Rhineland-Palatinate. When looking jointly at the nutrient N and S concentrations of old material collected in the litter and one-year and three-year old fresh needles, we can observe the following. S and N concentrations in the twigs collected in the litter at the plots showed an upward trend and a similar pattern (not for the S concentrations at Adenau). The decrease in S at Adenau may reflect an earlier downward trend in regional S emissions, while the Idar-Oberstein plot was probably still affected to some extent by emissions from the nearby Saar-Lorrainian industrial region (Fig. 3). As stated above, the increasing trend over time at Idar-Oberstein suggests that the "flush" of eutrophication and acidification from the 1990s is still being preserved in the old woody material. It may also be that despite the decreasing deposition, "old" N and S were remobilized for several seasons from the branches and older needles to the younger needles. At the same time, SO_4-S- concentrations in soil water are still higher in Idar-Oberstein as compared to Adenau (data not shown).

N and S-concentrations in the alive one-year and three-year old needles do not show a large variation between the plots suggesting that site (edaphic) factors do not play a large role. The levelling off of S pollution can best be demonstrated by the concentrations of the youngest needles, whereas the older material still conserved the higher contamination levels.

Differences in the pollution history and the successful European air pollution control, e.g. the Lead-in Petrol Act (2000), were probably best mirrored in the steep decline in concentrations of the non-essential heavy metal lead. In the litter fractions twigs and old needles, the levels of Pb showed a marked decline at both sites (Fig. 3, right-hand panel). Highest concentrations of over 60 ppm were observed in the early 2000s in the twig samples from Idar-Oberstein. This may be related to the proximity to the Saar region, where until the early 2000s the steel manufacturing industry and coal burning played a big role. High pollution levels in this region are also confirmed by the environmental specimen banking performed in the Saar region (grey data series, Fig. 3). Pb-levels in spruce shoots were much higher here than in alive needles from the two mountain sites, but after 2008 went down to comparable levels.

The dead needles collected in the annual litterfall also featured elevated levels of Pb, which only after 2010 approached those of the fresh needle samples. While Pb levels of the three-year old needles were still slightly

higher than those of the first year, Pb concentrations have declined to levels of lower than 1 ppm in the past decade. An exception were the levels from the year 2011 at the Adenau site, but no explanation for the elevated values can be given. Also grass culture biomonitors exposed in the Northern Eifel mountains by LANUV featured elevated levels in the years 2011 to 2013.

Since Pb is immobile and cannot be taken up in large quantities via the roots, Pb-accumulation in twigs and needles have mainly occurred via the atmospheric route. Most of the Pb will have been deposited to forest canopies with particulate matter (PM). The heavy metal containing dust particles will be primarily adsorbed to the plant surface. Since twigs have a rough surface, more dust and dust-associated heavy metals may accumulate as compared to conifer needles, where wash-off plays a bigger role.

Re-analyses of dead and alive needles

Since we were interested in other elements (Hg and selected REE), stable isotopes and the NIR spectra, which had not been determined in the original analyses, we combined and mixed aliquots of the archived subsamples to have composite samples for each year. In the re-analyses, we only focused on needles not on woody material. A total of 167 samples were hence available consisting of milled needles from the litter and first and third-year needles. While latter material stemmed from alive green organs, the needles from the litter were already dead at the time they were collected. We assume that most of those needles were formed more than four years before the sampling (compare Figure S1 supplementary). As has been shown above, the old dead needles had higher concentrations of lead than the younger alive material because much of the material was formed when air pollution levels were still higher. It may also be that the loss of water-soluble compounds, e.g. sugars and amino acids, from the disintegrating needles have produced concentration effects of e.g. lignin or fiber-associated elements. Tree health and the age of the litter play a role in the chemical release during degradation of leaf or needle material and heavy metals and REE will preferentially be retained in the solid litter material (Montemagno et al., 2022). The structural quality of dead needles (e.g C:N and ash) from the litter as compared to intact alive needles will be addressed later in the NIRS section.

To test for the validity and representativity of our approach, we first re-analyzed the lead concentrations. There was a high match between the old and new results (R^2 0.9, data not shown) suggesting that storing the samples up to 40 years under dry, cool and dark conditions had not altered the composition of the material with regard to heavy metals. At the same time, good agreement between the data confirms that the mixing of composite samples was effective.

From our analyses of isotopic signatures by IRMS, we were able to also derive N and C concentrations, which could be compared to the original data obtained by FAWF. We assume that there were no errors in either the original analyses (element analyzer) or the re-analyses (derived from IRMS analyses). While for N, we ended up with a complete side-by-side comparison, in the case of the C-analyses, a fourth of the values had to be discarded due to inaccurate recovery rates. We therefore also performed C and N elemental analysis seperately to get a better insight into potential differences.

For N, the agreement between the original and the re-analyses, was much lower than for lead. Originally determined N concentrations showed a low relationship to the data derived from IRMS (R^2 0.37) and a slightly stronger relationship to the data that were reanalyzed using CN elemental analysis (R^2 0.58). Since about 2005, N contents that were re-analyzed in the stored samples were often up to 0.5% lower than the N-concentrations that were originally obtained by FAWF year by year. It may thus not be ruled out that the samples lost some nitrogen over time. However, the older samples showed comparable values in both data sets.

While for C:N there was a good agreement (R^2 0.67) between the old and new data sets, the C concentrations from the original and re-analyzed data were only loosely related, but the re-analyses showed clearer differences between the different needle types (alive 1 and 3 year needles and dead needles from the litter). Interestingly, the original data indicated a general increase of C-content overtime (see Fig. 5), but the opposite was observed in the re-analyses of stored samples. Again, we assume that both the original analyses and the re-analyses yielded exact and correct results. However, the original analyses were performed every year and over the 40 years different labs and equipment were involved. In general, the differences indicated a maximum loss of only 5% of the carbon overtime, which may well be due to analytical imprecision. Since the samples were stored airtight in a dry, cool and dark environment degradation and loss of volatile components will have been kept to a minimum. Nevertheless, the somewhat downward trend in the re-analyzed values over time and the increasing difference between old and new results could indicate that needles had a different chemistry in more recent years, e.g. more VOCs, as compared to

earlier years and that in recent years the loss of C during storage was higher than in the earlier years. We refer the reader to chapter 3.5.3 for further results and interpretations.

REE and mercury

The analyses of mercury and the REE cerium, lanthanum (data not shown) and neodymium confirmed downward trends from the 1980s to the year 2020. Again, element concentrations were higher in the (dead) needles that were collected in the litter than in alive first- and third-year needles. Over the past 40 years, concentrations of the REE more than halved, whereas Hg levels did not change much over time. A much steeper gradient for the reduction in Hg-concentrations was observed in one-year-old shoots in the industrial Saar region (Fig. 4, above, green data series, data from the Umweltprobenbank).

Like the heavy metal lead, also the REE concentrations in spruce needles can best be related to particulate industrial emissions and car exhaust. Despite Pb was used as an anti-knock agent up to the 1990s, Ce, La and Nd are still being used in catalytic converters. With the increasing use of the elements e.g. in electric vehicles (EV) and wind turbines, environmental levels of REE might be increasing in the future also in remote areas. Our investigation into archived biological samples may thus be used as a benchmark for emerging pollution from certain REEs. While our analyses suggest a downward trend for REE from 1983 to 2020, the deposition measurements performed in Bavaria show significantly increased deposition of cerium and lanthanum in rural areas between 2014 and 2023 (LfU Bayern 2025). However, the deposition of REE in urban areas was twice as high as in rural areas, confirming the presumed impact of EVs in metropolitan areas. Our conifer analyses compare well to the data from Gautam et al. (2023), who reported REE concentrations in shed needles (litter) to be 0.163 ppm for La, 0.236 ppm for Ce and 0.096 ppm for Nd. However, these values refer to needle collections from 1978 performed in Southern Sweden, a region with lower industrial emissions but higher geogenic contents of REE. Linear increases in REE concentrations with needle age were previously shown by Wyttenbach et al. (1994) in spruce samples collected at nine Swiss forest sites. Levels were not related to the geogenic background confirming the impact of their deposition with particulate (transboundary) air pollutants. REE were most strongly related to Si.

In contrast to dust-associated heavy metals, mercury (Hg) primarily deposits to vegetation canopies as a gas (Hg^0). Latter fraction may be taken up into the needle via the stomata and may not be washed off again. Hg-concentrations in needles have been shown to increase over time, so that old needles will generally present higher concentrations than younger needles (e.g. Wohlgemuth et al. 2022; Franzaring et al. 2024). Provided using the same age class of spruce needles, spatial monitoring can prove regional differences in Hg pollution and deposition. One-year old needles were also studied in the dense Austrian spruce needle network, with concentrations ranging from 0.005 to 0.66 ppm in the remote and urban areas, respectively (Fürst 2007). These values are very much in line with our findings from remote sites and those from the industrial Saar region.

As expected, we observed decreases of Hg levels over time, but the downward trend was not as pronounced as those reductions in the air concentration and wet deposition data reported for the remote mountain stations Schmücke and Schauinsland by the Federal Environmental Agency (UBA, https://ebas-data.nilu.no). Also, in the study of Zhang et al. (2025), there was a limited response of needle and litterfall Hg concentrations to the decreasing deposition. Their study referred to a boreal forest ecosystem in Sweden and addressed the period from 1987 to the year 2000 only, whereas our study covered 20 years more. Reasons for discrepancies between emission inventories and measured Hg concentrations in air, precipitation and biota are currently being discussed (e.g. Feinberg et al. 2024) and it is not yet clear whether re-emission of deposited mercury to the atmosphere plays an important role. Another uncertainty relates to the function of vegetation as a scavenger of gaseous compounds and wet deposition throughfall.

It has been shown in a two-year pilot by König et al. (2024) in Germany and by Navrátil et al. (2024) in a long-term study (1994-2018) in the Czech Republic that Hg deposition with litterfall is of a much greater importance than the wet deposition. While König et al. (2024) measured a range from 94 to 246 mg ha^{-1} Hg per year that were deposited with the litter at three forest plots in Germany, Zhang et al. (2025) came up with 112 mg ha^{-1} annually for a site in Northern Sweden. In the study of Navrátil et al. (2024) in Czechia, much more Hg was deposited with the litterfall, namely 510 mg per hectare.

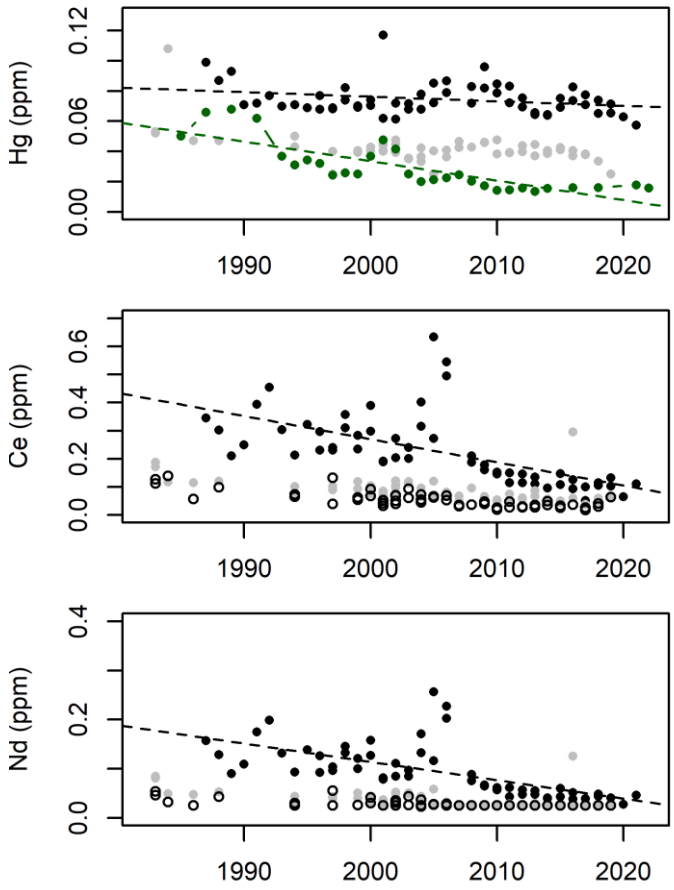


Figure 4. Levels of mercury, cerium and neodymium in spruce needles from the litter (●), third-year- needles (●) and first-year needles (○) from the two monitoring sites. (●) represents the results of Hg concentrations in one-year old shoots collected in the industrialized Saar region (Data from the Umweltprobenbank). Trendline (dashed) represents the linear downward trend calculated from the needles collected in the litter. Note: Hg-concentrations of one-year old needles were all below 0.02 ppm and are not shown in the graph.

When multiplying the Hg concentration with the annual litterfall in present study, we come up with a range of 94 in the year 2021 to 392 mg ha^{-1} (1989) of mercury that deposited with the yearly needle fall. The number would be somewhat higher if we knew the concentrations of Hg in the other litter constituents, i.e. twigs and cones.

An assessment of Hg concentrations for different litter components has been presented by Navrátil et al. (2019) for the time series 2003 to 2017 at two Czech mountain sites. Needles contributed with 46%, being followed by twigs (22%), cones (9 %), other material (8%), bark (5%), and lichen (2%). In the study of Zhang et al. (2025) needles made up a comparable 44% of the Hg-deposition. Also, in present study, litterfall consisted of about 50% out of needles.

The critical load for the protection of ecosystems from mercury is set at 1 g per hectare and year (UBA 2024) and does not consider the deposition of the element that is previously absorbed by plant surfaces. It would probably be exceeded if we considered needles and the other litter components as well as the wet and dry gaseous and particulate atmospheric deposition that will deposit directly. In a two-year study in Switzerland by Huang et al. (2023), non-needle litterfall (also the attached epiphytic liches) accounted for 86% of the total Hg litterfall, so indeed we would end up with much higher Hg deposition if we had the information on other components. To the end, 7 g per hectare of Hg alone were scavenged with the yearly needle fall in Idar-Oberstein in the years 1987 to 2021 and 4.5 g of Hg were accumulated between 1996 and 2018 at the Adenau site. Most of the deposited Hg will remain associated with organic matter in the topsoil layer and will not be mobile within the water cycle.

In order to characterize the potential changes in emissions and sources over time, Navrátil et al. (2024) addressed the Hg:S, Hg:N and Hg:C ratios (mg/mg) in the different materials collected in the litter. In the needles, they found values of 167, 9.3 and 0.2, respectively, for the three ratios. At the Idar-Oberstein site, which has a slightly higher mercury pollution than the Adenau site, we found the mean Hg:S, Hg:N and Hg:C ratios to be 87.6, 6.8 and 0,14,

respectively, while at Adenau the values were 79.8, 5.6 and 0.14. The ratios were very similar in 1-year and 3-year needles from both sites but were higher in 3-year as compared to 1-year needles (data not shown). In contrast to Navrátil et al. (2024), temporal changes at both sites were absent for the Hg:S ratios, suggesting that the regional pollution patterns and potential local sources had not changed much. S and Hg concentrations in the earlier years of monitoring should have been interlinked due to the common pollution sources (coal burning, steel manufacturing), but there are also biological reasons for the association of these elements, namely the binding of the metal to SH-groups. While shifts in Hg:S ratios were not important, we found decreasing Hg:N ratios over time at the Adenau site, which points to the rising importance of atmospheric N pollution.

Stable isotopes

Analyses of stable isotopes can give wealthy insights into the responses of plants to changes in the nitrogen (NUE) and water use efficiency (WUE). While ^{15}N has often been used as a tracer in agronomic fertilization studies, changes in the "natural" abundance of the heavier isotope over time have rarely been addressed in environmental and forest monitoring programs. Also, the $\delta^{13}C$-signatures of leaves and needles are not being studied on a regular basis, although they might serve as a proxy for water supply and drought stress and thus indicate the effects of climate change over time.

Our investigation using archived needle materials from a forest monitoring program is probably the first, in which multi-decadal changes of stable isotopes in leaf organs were performed. Comparable studies, however, have relied on tree rings as an environmental archive (e.g. Treydte et al. 2001; Píšová et al. 2008; Schäfer et al. 2017; Wieloch et al. 2018; Bassett et al. 2023 and Llanos-Campana et al. 2025)

^{13}C

^{13}C analyses reflect the balance between the demand and the supply of CO_2 to the photosynthetic organs and also mirror the loss of water due to transpiration. Photosynthetic discrimination of the heavier ^{13}C isotope relative to the atmospheric CO_2 is influenced by stomatal conductance and the enzymatic carboxylation, while post-photosynthetic discrimination is due to the metabolic fractionation inside the leaves, the transport of assimilates out of the leaves to growing tissues and a further fractionation due to respiration, i.e. loss of lighter $^{12}CO_2$ (Cernusak et al. 2013). While leaf analyses incorporate photosynthetic discrimination mainly, glucose, cellulose and lignin-based measurements from dated tree rings also address the post-photosynthetic discrimination. This has to be recognized when comparing leaf/needle and tree-ring $\delta^{13}C$ data. We must also consider that the needles from our study were alive one or three-year-old organs and the needles collected with the litter were dead organs that were made up from up to seven age classes.

To analyze in greater detail the $\delta^{13}C$ data, we had to first consider the "Suess" effect, i.e. the decrease of the ratio of ^{13}C to ^{12}C in the atmosphere due to the release of carbon from fossil fuels. We took the data from the Scripps CO_2 Program (https://scrippsco2.ucsd.edu) that integrates air measurements from Mauna Loa (Hawaii) and the Antarctic South Pole. Detrending was done by subtracting the annual average for atmospheric $\delta^{13}C$ (source) from the values we obtained from the spruce needle material (product) to isolate climate and pollution signals. These were hence regarded as $\Delta^{13}C$ values.

Figure 5 (upper row) compares the isotopic discrimination of dead needles and the alive one and three-year old needles that were collected every year. While signatures in the dead needles showed a clear continuing trend towards further discrimination at both sites (R^2 0.92 for Adenau and R^2 0.75 for Idar-Oberstein), a larger scatter of data between years and lower coefficients of determination for the linear increase were observed in the alive needles. The larger year-by-year variation and similar patterns of $\Delta^{13}C$ at the sites and in the one and three-year-old needles indicates that climate had some effect on the gas exchange (discrimination) of trees. The smoother increment in discrimination over time in the dead needles derives from the mixing of different age classes that leads to a blurring of the signature. The climate and air pollution trends were thus better conserved in the dead needles, which integrate the responses of several years.

Generally, the alive needles at the warmer Adenau site discriminated ^{13}C more strongly (more negative $\Delta^{13}C$) than those at the cooler Idar-Oberstein although the C concentrations of alive and dead needles were very similar at the two sites (Fig. 5, row 5). This may be due to the warmer and drier conditions and presumably more pronounced stress (higher VPD) than in Idar-Oberstein. Interestingly, the dead needles showed the contrary, i.e. higher discrimination at the latter site, and also featured higher discrimination than the alive needles. A reason may be that relatively more of the lighter ^{12}C was remobilized from the old and dying needles to younger organs, trapping more of the heavier isotope in structural carbohydrates and lignin. An explanation for differences between the sites

may be that at Idar-Oberstein needles became older and thus could discriminate longer, while at Adenau needles shed before carbon and nitrogen could be translocated to the younger leaves. Also, the different partitioning between alive needles in the crown and dead needles from the shade may lead to changes in isotopic signatures. Indeed, the defoliation data (see above) point into this direction (needle longevity) and also N levels remained higher in the dead needles from Adenau (Figure 5, row 4), while in the alive needles N concentrations were very similar. After the year 2015, however, $\Delta^{13}C$ in the dead needles was very comparable, suggesting similar growth and stress conditions at both sites.

Correlation analyses (see Supplementary S 2) confirmed several associations between $\Delta^{13}C$ (discrimination) and climatic/air quality parameters, N deposition, needle and shoot length and nutrient concentrations. These were generally more pronounced at the drier Adenau site than at Idar-Oberstein and were more evident in the dead and three year-old needles than in the youngest needles. Latter finding indicates that it may not be single years that evoke a series of stress cascades, but rather the sequence of several unfavorable years. While we can assume that the mentioned associations point to a reduced fitness of spruce trees, we cannot disentangle single factors responsible for changes in isotopic signatures. During the last decades, both air quality and climate changed and jointly altered the growth conditions and nutrient acquisition of spruce.

When comparing our results to ^{13}C analyses of one-year old shoots of spruce from the Umweltprobenbank (Figure 5), we can observe that signatures were in the same range at a northern German site (Belau Lakes) but largely differed from a site in the Bavarian Alps (Wimbachtal). Needles at latter site discriminated much less against the heavier isotope probably due to more humid atmospheric conditions and a shorter vegetation period at higher altitudes. Unfortunately, data from the environmental specimen bank only contains a few sites and is based on biannual analyses starting after 1998 only. Nevertheless, the comparison between needles and shoots may be regarded as well suited, since Gebauer & Schulze (1991) found a very high agreement between these organs. Interestingly, latter authors found larger variations in $\delta^{13}C$ between different crown positions as compared to different age-classes and at the same time, ^{13}C was discriminated more at a polluted site. It is thus advisable to always use the same tree cohorts and crown positions for forest monitoring, and this was the case in present monitoring programme.

Since we did not find other long term data series on C-isotopes in conifer needles from specified sites, we refer here also to investigations of $\delta\ ^{13}C$ in dendrochronological studies, in which the wood of tree rings or the cellulose therein was considered. Compared to present data, such studies often consist of longer time-series (>100 years) and hint to the existence of "pointer years", which provide evidence of certain historical climatic extremes. Treydte et al. (2002) and Píšová et al. (2008) presented data from the 20th century and showed a stronger discrimination of the heavier isotope after the 1980s. They suggested that air pollution and associated changes in soil chemistry were responsible for these changes in growth and isotopic responses. Potential climate change signals were not yet evident and discussed at those times. As has been shown by Schäfer et al. (2017), Wiley et al. (2018) and Vadeboncoeur et al. (2020), the stand characteristics (mono-specific or mixed) as well as the moisture regime, tree height and canopy position can largely affect the results, so that many trees must be sampled to average out these effects. In the same study region like ours (Eifel mountains), Thomas et al. (2018) sampled spruce tree cores along a soil moisture gradient. $\Delta^{13}C$ did not vary much between gleysols and cambisols and like in present study isotopic discrimination increased after 1980.

We suggest that collecting needles or leaves is probably much easier to yield more representative and well dated samples than taking tree cores because photosynthetically active organs give a much better account on the seasonal ecophysiological responses to climate and nutrition. Nevertheless, $\delta\ ^{13}C$ signatures will remain difficult to interpret even when long and complete data series are available. Besides climatic and edaphic factors also the rising levels of atmospheric CO_2 (1980: 330 ppm vs. 414 ppm in 2020) will have had effects on the growth, morphology, stomata density and intrinsic water use efficiencies of spruce confounding the isotopic fractionation (refer to the considerations in Wieser et al. 2016).

^{15}N

Several studies have shown that over time, tree rings in Northern temperate forests have become depleted in ^{15}N during the last decades. The underlying reason is the widespread impact and transport of regional nitrogen oxide emissions, that derive from the combustion of fossil fuels. While "thermal NOx" has the same isotopic signature than air, the formation of "fuel NOx" during the combustion leads to highly negative $\delta^{15}N$. The dry/wet and gaseous/particulate deposition of these emissions will lead to more negative signatures in the upper soil horizon, while the gaseous releases of the lighter ^{14}N (N_2O, NOx) and its preferential uptake by plant roots will furthermore

decrease these values. Increased discrimination of $\delta^{15}N$ over a century has been shown in Czech forests by Oulehle et al. (2022) and over seven decades in Swedish spruce and pine trees the same effect was observed by Bassett et al. (2023). In both studies, emissions from the traffic and industry as well as the speeding up of N cycles in a warmer world have been made responsible for stronger discrimination of the heavier ^{15}N. Nitrification will also favor the lighter isotope, while the heavier isotope may eventually drain into deeper soil layers or ground waters.

Our results (Figure 5, second row) confirm these findings and represent the first study that made use of needle samples from an environmental archive. Needles from both sites and from three age classes, i.e. alive 1 and 3-year-old needles and dead needles that were shed annually, all featured increased depletion of ^{15}N (more negative $\delta^{15}N$) over time. However, we observed differences between the two sites and the three age classes. In line with the higher N-deposition at Adenau as compared to Idar-Oberstein (see Figure 1) and a presumably higher input of ^{15}N depleted nitrogen, a stronger discrimination of the heavier isotope was found in the dead needles at the former site. Interestingly, the trend of increasing discrimination at the Adenau site was reverted after the year 2008, suggesting that during this depression relatively more ^{15}N was taken up by the trees after a sequence of drier years after the extremely dry year 2003 and a generally decreasing N-deposition. It may well be that following the extreme year 2003 fine roots had to explore deeper soil horizons to access water and that this indirectly favored the uptake of nitrate and ammonium that was less depleted in ^{15}N. Vertical gradients of $\delta\ ^{15}N$, namely less discrimination i.e. relatively more ^{15}N in deeper soil layers and marked differences during the decomposition have been shown in various studies (Sah et al. 2008, Craine et al. 2015, Gautam et al. 2024 and Högberg et al. 2024), but we do not have further information on the N cycling and vertical distribution of $\delta^{15}N$ at the studied sites. In the years from 2009 to 2016, $\delta^{15}N$ signatures were comparable at the two sites, while in the final years of the observation, ^{15}N discrimination in dead needles was again higher at the Adenau site.

In contrast to the dead needles that were collected each year and that consisted of material from up to seven years, the alive one- and three-year old needles showed stronger inter-annual variation in $\delta^{15}N$, especially at the drier and probably N-saturated Adenau site. The higher fluctuation as compared to the blurring/smoothing of data in needles from the litter most probably derives from distinct ecophysiological responses of the trees over time. Compared to data from the Umweltprobenbank, $\delta^{15}N$ of one year old spruce shoots from Belau Lakes were in the same range than our results (see Figure 5), while in the Bavarian Alps (Wimbach), a much stronger discrimination was found, probably due to lower N mineralization and N deposition rates.

To explain these fluctuations, we related $\delta^{15}N$ in one- and three-year-old needles to the climatic parameters mean annual temperature (MAT), precipitation sum, VPD and growing degree days (GDD). While climatic data from the Adenau site could only explain a maximum of 20% of the variation, for the cooler Idar-Oberstein site a stronger association between seasonal GDD and $\delta^{15}N$ (R^2 0.42 for one-year and 0.38 for three-year old needles) could be observed. However, the stronger discrimination of ^{15}N at the cooler and moister alpine site Wimbach indicates the opposite and the extensive data collection from Caldararu et al. (2022) generally points to more discrimination at lower temperatures and higher precipitation. One must however note that the effects of N deposition cannot be separated from the climatic component in the N acquisition process.

Despite the differences in $\delta^{15}N$ and $\Delta^{13}C$ observed between the two forest plots, the concentrations of C, N and C:N (Figure 5) followed the same temporal patterns in the dead and alive one- and three-year old needles, confirming that overall, the N-assimilation over the years followed similar patterns. Since climatic factors explained less than 30% of the variation of the overall increasing carbon and nitrogen contents, we may assume that the carbon dioxide fertilization effect, i.e. the increasing concentrations of atmospheric CO_2 and changes in the N deposition could have been overall drivers for the C and N acquisition and isotopic discrimination during the past four decades. The stronger increase in N-concentrations at the Adenau site after the year 2000 (Figures 3 and 5, fourth row) in the dead material, may on the one hand be indicative for the N saturation caused by the prolonged N-deposition, but the N-concentrations of alive needles do not reflect these changes anymore. It could thus well be that after ca. the year 2000 the needles shed at the Adenau site indeed retained more N than those at Idar-Oberstein (see above). This may have been caused by either an ineffective and incomplete internal remobilization of N from older, senescent to younger needles or/and a higher share of younger needles to the total mass of needles shed every year (see above).

Unfortunately, we do not have further information on edaphic and soil nutrition factors that may interact with or even overrun the observed effects, but as can be seen in Figure 5 (last row), the availability of nutrients e.g. magnesium differs between the sites and is much higher at the Adenau site.

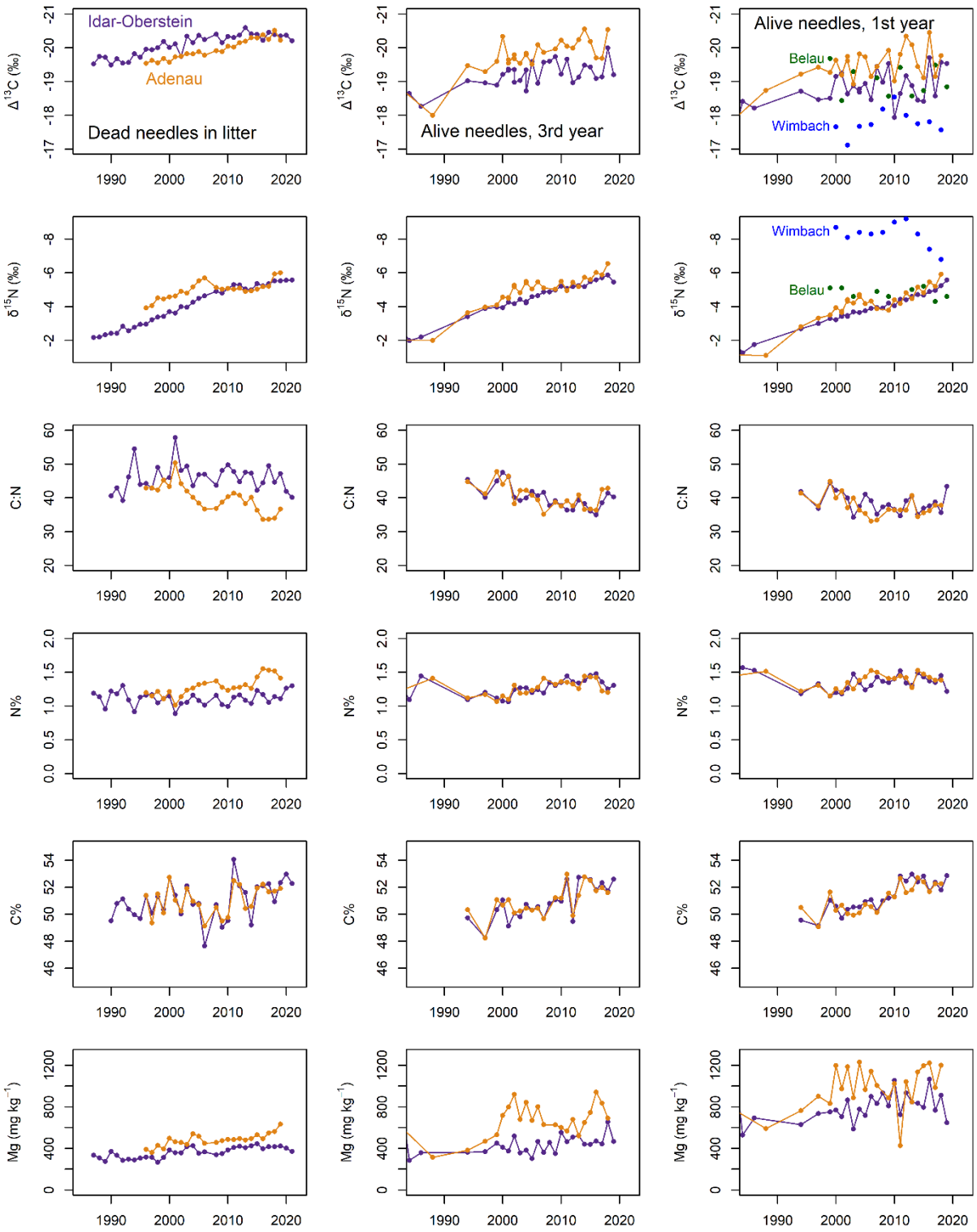


Figure 5. $\Delta^{13}C$, $\delta^{15}N$, C:N, concentrations of nitrogen, carbon and magnesium (from top to bottom) determined in the dead (left) and alive three (centre) and one-year-old (right) needles from Idar-Oberstein (●) and Adenau (●). (●) denotes results from one-year-old spruce shoots from Northern Germany and (●) from the Bavarian Alps (downloaded from www.umweltprobenbank.de).

As mentioned above, N and S-concentrations in needles from present study are relatively low despite the still high N deposition values for nitrogen. Since N and S are both important elements in amino acids, the reduced deposition and availability of sulfur can overall mean that N concentrations will not further increase. Also, the lack of the other essential elements P, Mg and and K will have effects on the N nutrition. It will thus take longer to revert N-

saturation and acidification of forest ecosystems. Lower nitrogen and nutrient levels, a decline in $\delta^{15}N$ signatures under increasing levels of CO_2 over time have been suggested to be indicators of a global progressive nitrogen limitation (PNL, Luo et al. 2004). Indeed, nutrient impoverishment in forests and an "oligotrophication" in unfertilized terrestrial ecosystems have been claimed by several authors (Craine et al. 2018, Peñuelas et al. 2020, Bassett et al., 2026). While in Central Europe the more extreme climatic conditions and beetle infestations will furthermore decrease the annual growth and demand for nutrients of spruce, the increasingly longer vegetation periods and enhanced nutrient cycling in Northern Europe may create a different future.

Using measured ^{15}N data from the literature and N concentrations in tree leaves from a large European database, Caldararu et al. (2022) failed to capture ongoing nitrogen limitation in a land surface model. The authors stated that an *"ideal data set for assessing changes in ecosystem N limitation in time would be a consistent time series of observations at the same sites, including measurements of soil and leaf $\delta^{15}N$ following a common protocol, similar to the kind of information available from the ICP Forests database."* In combination with long term data on soil ^{15}N, stored leaf or needle samples from forest monitoring programs like ours could be a valuable source for deepening such investigations.

NIR spectra

In the final step of our exercise, we recorded the NIR spectra of all ground samples and arranged them after the two sites and the three needle ages. Here, we aimed to first address the overall biochemical similarity, i.e. material quality, among the samples. Besides the potential differences between geographical origins (edaphic and microclimatic site effects) and photosynthetically active vs. dead needles, we were also interested in changes of the spectral outputs over time. However, we could not clarify whether these were driven by the environmental conditions the intact needles experienced in the forest or whether the ageing of the ground samples in the storage systematically altered the material over time. As stated above, the samples were stored in dry, dark, cool and airtight conditions, so that over the years the chemistry and structure of the powder should not have changed much. But in the case of C, repeated analyses showed marked differences between the old results and the re-analyses (see above). Another flaw might be that the samples were ground unevenly. Some of the samples contained larger particles. The uneven grinding might be the reason why the samples differ in CV as described in Materials and Methods.

When looking at the needle spectra (Figure 6), we could visualize differences between alive and dead needles at both sites on the one hand and a general shift of spectra over time on the other. It appeared that in the last approximately ten years absorbance was higher in the wavelength bands >1900 nm, while in the alive needles, it was lower in the third overtone range in samples collected after 2010. Overall, the difference between different needle types and years were much bigger than the differences between the sites, although at Idar-Oberstein alive needles showed much bigger variability of absorbance than at the warmer Adenau site, especially in the third overtone region.

In a similar study with different conifer species along an altitudinal gradient, Richardson et al. (2004) found larger differences between species and crown positions than between elevations. Also, Espinoza et al. (2012) made use of dry ground needle powders of various conifers to differentiate true species from hybrids. The authors confirm that the method delivers robust results and that using dry ground samples yields more accurate results than leaf scans from intact alive samples. However, the mentioned studies did not use additional parameters derived from wet chemistry and genetical analyses to verify the results. In another relevant study, Champagne et al. (2020) tried to predict the terpene concentrations of five conifer species using NIRS. Model predictions were better for those phytochemicals that were present at higher concentrations and likewise macronutrients will be easier to predict than micronutrients. To further investigate the suitability of NIRS to describe the material quality of spruce needles we will use a large data set with chemical reference data, which we can link to the recorded spectra by partial least squares regression (PLSR) and machine learning studies. First calibrations for selected constituents are presented below, while the full analysis will follow in a separate paper.

Among the compositional parameters, the organic and structural constituents were the most accessible to NIR (Table 1). Total ash was the best-predicted constituent (R^2=0.39), followed by the carbon/nitrogen ratio, nitrogen and carbon. Carbon and nitrogen are bound in the C–H and N–H groups that give rise to NIR absorption, whereas ash is inorganic and is most likely captured indirectly through its co-variation with the organic needle matrix. The macronutrient calcium reached a comparable level, and magnesium and sulfur were likewise predicted with modest but statistically significant skill ($R^2 \approx 0.19–0.21$; not shown). Predicted-versus-measured plots for the two best-determined nutrient parameters, total ash and nitrogen, are given in Fig. 7.

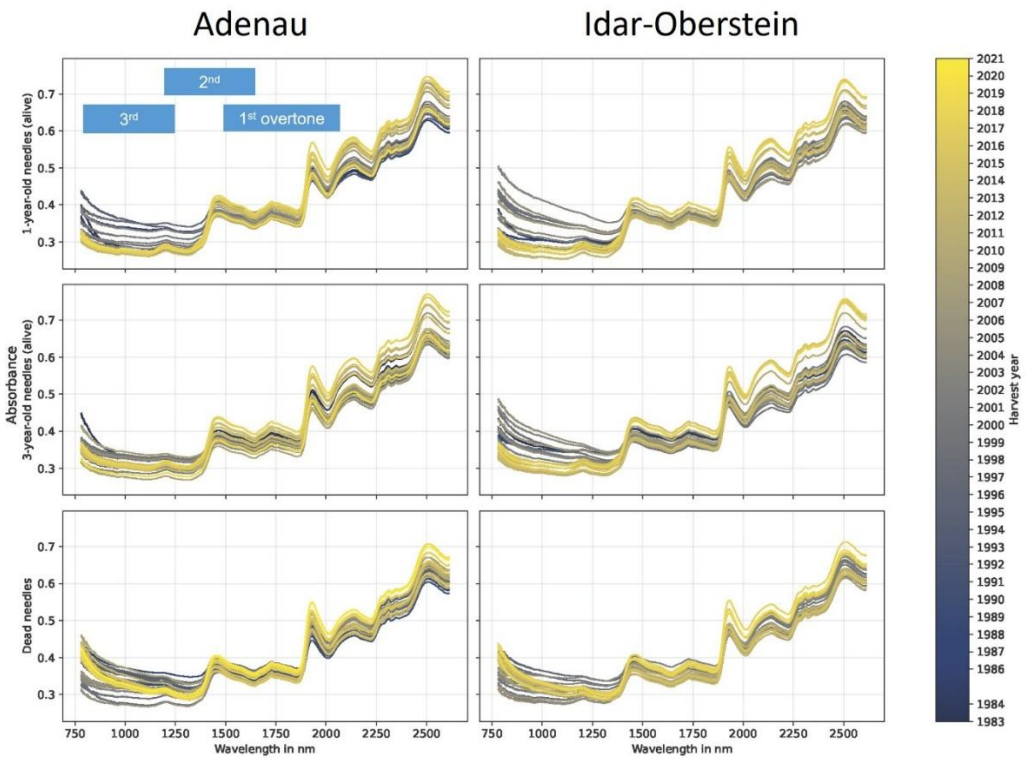


Figure 6. Near infrared (NIR) spectra (absorbance, λ, along wavelength) of ground needles of spruce (*Picea abies* L.) collected between 1983 and 2021 at the monitoring sites Adenau (left) and Idar-Oberstein (right). Each spectrum represents a sampling year (color palette) and data are arranged after alive 1-year (top) and 3-year-old (centre) and dead (shed) needles, that were collected in the litter (bottom). The upper left diagram includes a representation of prominent "overtones" representing regions where certain chemical bonds are excited.

Table 1. Preliminary PLS calibrations for selected, chemically interpretable needle properties, evaluated by grouped cross-validation over site-to-year collections. All figures of merit are unit-free, so the rows are directly comparable. R^2 is the cross-validated coefficient of determination, RPD and RPIQ are the ratios of the reference standard deviation and interquartile range to the prediction error. The Region, Preprocessing and LV (number of PLS latent variables) columns report the modal configuration and describe the typical model rather than one fitted value. All models were significant at $p<0.01$ (label-permutation test).

Property	R^2	RPD	RPIQ	Region	Preprocessing	LV
Total ash	0.39	1.28	2.46	Full spectrum	SNV	4
C:N ratio	0.24	1.15	1.60	Organic core	MSC	10
Nitrogen	0.19	1.11	1.60	Full spectrum	MSC	8
Carbon	0.17	1.10	1.66	Full spectrum	SNV + 1st deriv.	2
Calcium	0.23	1.14	1.62	O–H/N–H comb.	SNV	7

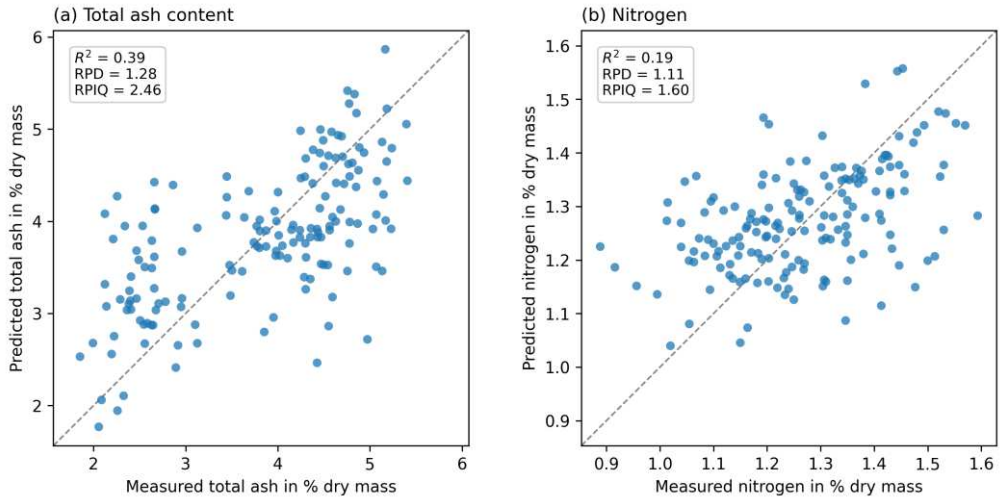


Figure 7. Cross-validated predicted versus measured values for two nutrient parameters central to the study: (a) total ash content and (b) nitrogen. Points are pooled out-of-fold predictions from the nested cross-validation (grouped by site-year collection); the dashed line is the 1:1 relation.

To see which parts of the spectrum carry the compositional information, the Pearson correlation between each (SNV-preprocessed) wavelength and the reference value was computed for every constituent, with the low-signal channels at the two ends of the recorded range excluded. For total ash and nitrogen for example (Fig. 8) the correlation is modest at any single wavelength (peak $|r| \approx 0.4$) and spread across broad regions rather than concentrated in one sharp band. This is consistent with the screening-level accuracy of the calibrations and demonstrates the need for a multivariate model that pools many weakly informative channels. Nitrogen correlates most strongly in the C–H overtone region near 1110 nm and total ash in the short-wavelength region near 810 nm.

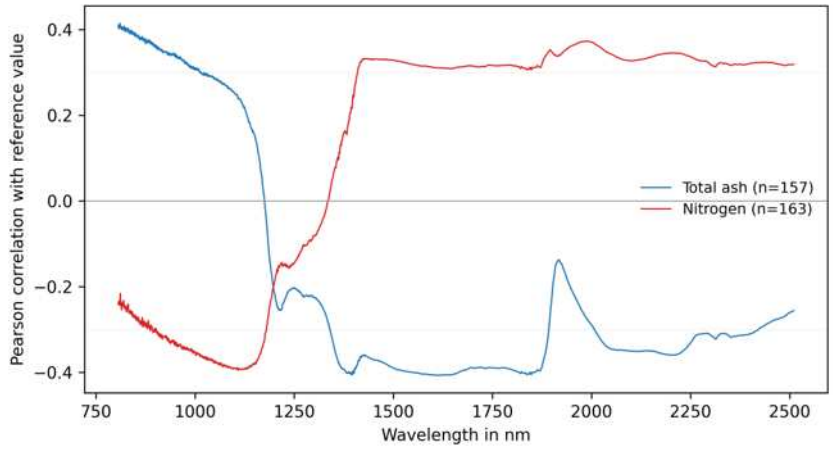


Figure 8. Per-wavelength Pearson correlation of the SNV-preprocessed spectra with the reference values of total ash and nitrogen. Low-signal channels at the extreme ends of the recorded range are excluded; dotted lines mark $|r|=0.3$.

Extended to all measured constituents (Fig. 9), the correlations concentrate on the same few organic absorption regions, namely the C–H second-overtone region (~1105–1205 nm), the O–H/N–H first-overtone region (~1361–1429 nm) and the O–H combination region (~1835–1961 nm) rather than on constituent-specific features. This indicates that NIR accesses these constituents largely through their co-variation with the organic needle matrix that dominates the spectrum. The correlation spectra are univariate and hence only indicative. Because the PLS models combine wavelengths, a channel with a low individual correlation may still contribute in combination.

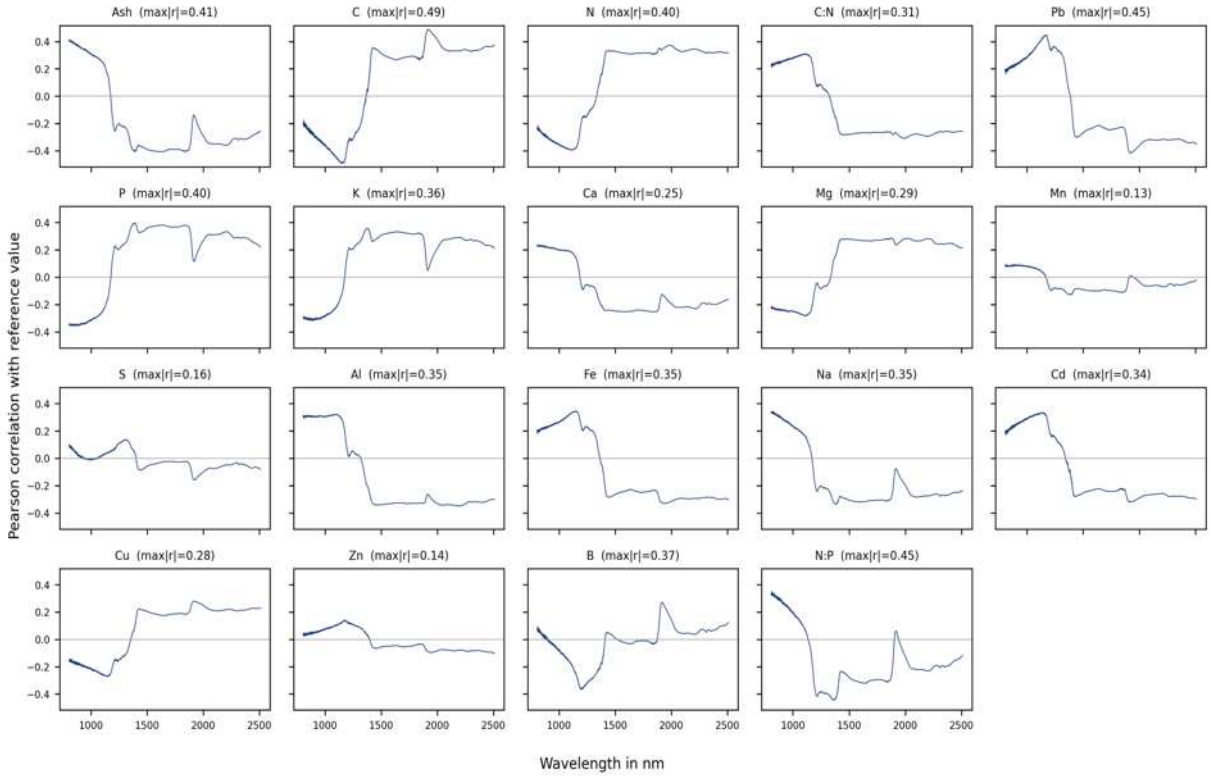


Figure 9. Per-wavelength correlation spectra for all measured constituents (SNV-preprocessed, edge channels excluded, shared axes); each panel gives the peak absolute correlation. The correlations concentrate on the organic C–H, O–H and N–H bands common to all constituents rather than on element-specific features. The peak correlation is an indicative guide to how strongly a constituent is expressed in the spectra.

Sampling year is the most strongly expressed of the three (peak $|r|=0.63$), and its correlation lies outside the non-significant band over almost the entire spectrum. Consistently, sampling year could itself be predicted by PLSR with $R^2=0.70$ under the grouped cross-validation. It is positive throughout the combination and first-overtone regions above about 1430 nm, with its sharpest maximum near 1920 nm at the O–H combination band of water, and negative in the region that includes the C–H second overtone (~1100–1350 nm). This agrees with the higher absorbance above 1900 nm in recently collected needles visible in Fig. 6. Senescent needles differ clearly from both live classes (peak $|r|=0.49$ against current-year and 0.37 against three-year-old needles), with lower relative absorbance above about 1350 nm and higher relative absorbance below about 1110 nm. The contrast between the two live classes follows the same pattern but remains weak ($|r|\leq 0.23$) and leaves the non-significant band only in a few narrow regions, in agreement with the differences between live and dead needles visible in Fig. 6. Needle age class was recognized by PLS discriminant analysis with a balanced accuracy of 0.70, well above the majority-class baseline of 0.34. Site, by contrast, leaves no detectable univariate trace, as its correlation stays inside the non-significant band over the whole spectrum ($|r|\leq 0.14$). This matches the discriminant analysis, which separated the two sites only slightly better than the majority-class baseline (balanced accuracy 0.63 against 0.56). The correlation spectra thus confirm quantitatively that the spectra differ far more between needle types and sampling years than between the two sites.

The year and age curves change sign across the spectrum and are nearly flat within broad regions. They therefore reflect a change in the overall shape of the normalized spectrum rather than isolated absorption bands, in the same way as the constituent correlations. The age contrasts run opposite in sign to the year curve, so needles from early collection years deviate from recent ones in the same spectral direction in which senescent needles deviate from

live ones. Since the three age classes span the same range of years, this resemblance is not an artefact of an uneven age composition over time. It is consistent with the storage effect discussed above, although it does not prove it.

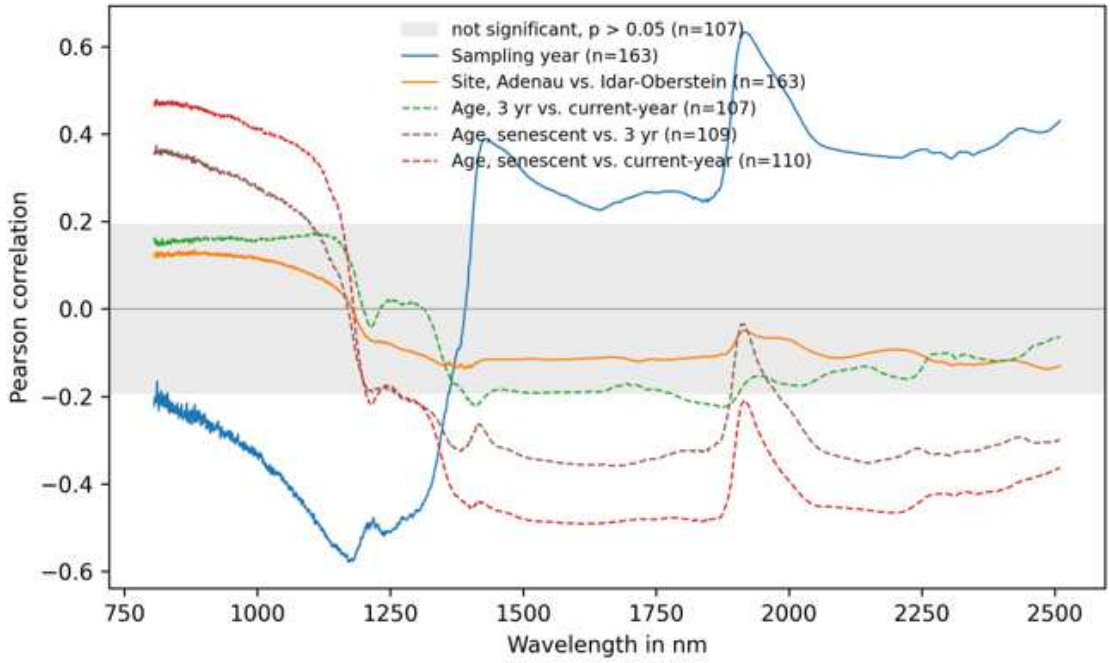


Figure 10. Per-wavelength Pearson correlation of the SNV-preprocessed spectra with the collection metadata. Sampling year is used directly. Site and needle age are expressed as two-class contrasts (point-biserial correlation), with needle age split into its three pairwise comparisons. A positive value means higher absorbance in the first-named class or in more recent samples. The shaded band marks |r| values that are not significant at p=0.05 for the smallest sample set shown; low-signal channels at the extreme ends of the recorded range are excluded.

Compared to other NIRS studies on plant materials, the predictive value of spectral information for chemical constituents of the dried leaves was rather low, probably due to the ageing of the material, being it alive one- or three-years old needles or shed needle mass that was collected every year from the two forest stands under study. In an investigation of herbarium samples using scans of the whole leaves, Kühn et al. (2024) found that storage duration and standard conservation treatments do not significantly alter the NIR spectral data of the same herbarium collections of three species. However, their samples were stored only for three years while ours were kept under presumably inert conditions for up to 40 years. Still, Lee et al. (2026) suggest that PLSR models trained on younger specimens can give robust estimates of leaf functinal and chemical traits from older specimens. In a deeper analysis, we will address in greater detail the differences in spectra between needle age classes, forest sites, sampling years as well as the potentially overriding effects of samples ageing.

Conclusion

Leaf samples from environmental archives are a useful source for retrospective analyses of inorganic elements like heavy metals and rare earth elements but for organic compounds, the aging of the material may create problems. We found that changes in air quality, eutrophication and acidification all could be discerned in the samples and that these drivers and the changes in climate jointly altered the growth conditions, isotopic discrimination and nutrient acquisition of spruce, which complicates the interpretation of monitoring results.

NIR spectra of the archived spruce needles carry systematic information on needle age, sampling year and the composition of the needles. Under a validation that held out entire site-year collections, total ash, the C:N ratio, nitrogen, carbon and calcium were predicted with modest but statistically significant skill (R^2 between 0.17 and 0.39), and needle age class was recognised with a balanced accuracy of 0.70 against a majority-class baseline of 0.34. The prediction errors remain large compared with the spread of the reference values (RPD between 1.10 and 1.28), so the calibrations are of screening-level accuracy. The correlation spectra show that the compositional information lies in broad organic absorption regions shared by all constituents, so NIR accesses the constituents largely through their co-variation with the organic needle matrix. The two sites could only barely be distinguished in the spectra. Sampling year, in contrast, was predicted considerably better (R^2=0.70), and needles from early

collection years deviate from recent ones in the same spectral direction as senescent needles deviate from live ones. With the present data, a genuine long-term change in needle composition cannot be separated from ageing of the stored material, so the temporal signal has to be interpreted with caution. A full analysis of all measured parameters will follow in a separate paper.

Declarations

Funding: no funding was obtained
Conflicts of interest/Competing interests (include appropriate disclosures): none
Ethics approval (include appropriate approvals or waivers): not applicable
Consent to participate (include appropriate statements): not applicable
Consent for publication (include appropriate statements): not applicable
Availability of data and material (data transparency): the complete data on which this article is based will be made available by the authors upon request.
Code availability (software application or custom code): not applicable
Authors' contributions: JF developed the idea and was responsible for the data collection, curation, statistical analysis, and writing of the original manuscript. MG made available the samples, gave information on the monitoring programme and provided historical data from the two sites. He was involved in the evaluation and discussion of the experimental approach, assisted in the development of the project idea and the review of the manuscript. FB conducted chemical and isotopic analyses and AlS and TNL performed, graphically represented and evaluated the NIRS analyses. AnS helped to review, discuss and improve the manuscript.

References

Agathokleous E, Feng Z, Saitanis CJ (2022) Effects of Ozone on Forests. In: Akimoto H, Tanimoto H (eds) Handbook of Air Quality and Climate Change. Springer, Singapore. https://doi.org/10.1007/978-981-15-2527-8_24-1

Anders T, Hetzer J, Knapp N, Forrest M, Langan L, Tölle MJ, Wellbrock N, Hickler T (2025) Modelling past and future impacts of droughts on tree mortality and carbon storage in Norway spruce stands in Germany. Ecological Modelling. https://doi.org/10.1016/j.ecolmodel.2024.110987

Balekoglu S, Caliskan S, Makineci E, Dirik H (2023) An experimental assessment of carbon and nitrogen allocation in *Pinus pinea* populations under drought stress and rewatering treatment. Environmental and Experimental Botany. https://doi.org/10.1016/j.envexpbot.2023.105334

Bassett KE, Östlund L, Gundale MJ, Fridman J, Jämtgård S (2023) Forest inventory tree core archive reveals changes in boreal wood traits over seven decades. Science of The Total Environment. https://doi.org/10.1016/j.scitotenv.2023.165795.

Bassett KR, Hupperts SF, Jämtgård S et al (2026) Rising atmospheric CO_2 reduces nitrogen availability in boreal forests. Nature 650: 629–635. https://doi.org/10.1038/s41586-025-10039-5

Berg B, & Lönn M (2022) Long-Term Effects of Climate and Litter Chemistry on Rates and Stable Fractions of Decomposing Scots Pine and Norway Spruce Needle Litter—A Synthesis. Forests. https://doi.org/10.3390/f13010125

BMEL (2021) Bodenzustandserhebung im Wald (BZE II) – Ergebnisse der bundesweiten Bodenzustandserhebung. https://www.fva-bw.de/daten-tools/monitoring/bodenzustandserhebung-bze/ergebnisse-der-bze-ii

BMEL (2024) Der Wald in Deutschland. Ausgewählte Ergebnisse der vierten Bundeswaldinventur. 60 S. Bundesministerium für Ernährung und Landwirtschaft (BMEL). https://www.bundeswaldinventur.de/fileadmin/Projekte/2024/bundeswaldinventur/Downloads/BWI-2022_Broschuere_bf-neu_01.pdf

Boonen K, Shetti R, Navrátil T, Nováková T, Rohovec J, Lehejček J (2025) Atmospheric mercury pollution recorded in conifer tree rings: Disentangling the effects of tree-ring width, water content, and climate on mercury concentrations. Dendrochronologia. https://doi.org/10.1016/j.dendro.2025.126370

Bose AK, Etzold S, Meusburger K, Gessler A, Baltensweiler A., et al (2025) Decreasing stem growth in common European tree species despite earlier growth onset. Global Change Biology. https://doi.org/10.1111/gcb.70318.

Braun S, Tresch S, Hopf SE, Schindler C. (2025) Four Decades of Forest Development in the Context of Nitrogen Eutrophication and Climate Change. In: Lüttge, U., Cánovas, F.M., Risueño Almeida, M.C., Leuschner, C., Pretzsch, H. (eds) Progress in Botany, vol 86. Springer, Cham. https://doi.org/10.1007/124_2025_94

Caldararu S, Thum T, Yu L, Kern M, Nair R, Zaehle S (2022) Long-term ecosystem nitrogen limitation from foliar δ15N data and a land surface model. Global Change Biology. https://doi.org/10.1111/gcb.15933

Cernusak LA, Ubierna N, Winter K, Holtum JA, Marshall JD, Farquhar GD (2013) Environmental and physiological determinants of carbon isotope discrimination in terrestrial plants. New Phytologist. https://doi.org/10.1111/nph.12423

Champagne E, Bonin M, Royo AA, Tremblay J-P, Raymond P (2020) Predicting terpene content in dried conifer shoots using near infrared spectroscopy. J Near Infrared Spectrosc. https://doi.org/10.1177/0967033520950516

Cheesman AW, Brown F, Artaxo P et al (2024) Reduced productivity and carbon drawdown of tropical forests from ground-level ozone exposure. Nat Geosci. https://doi.org/10.1038/s41561-024-01530-1

Craine JM, Brookshire ENJ, Cramer MD (2015) Ecological interpretations of nitrogen isotope ratios of terrestrial plants and soils. Plant Soil. https://doi.org/10.1007/s11104-015-2542-1

Craine JM, Elmore AJ, Wang L et al (2018) Isotopic evidence for oligotrophication of terrestrial ecosystems. Nat Ecol Evol. https://doi.org/10.1038/s41559-018-0694-0

Dietrich V, Wambsganss J, Greve M (2026) Foliar nutrient composition, fructification and previous years' climatic conditions explain changes in defoliation of temperate tree species. Ecol Indicat. https://doi.org/10.1016/j.ecolind.2026.114672

Espinoza JA, Hodge GR, Dvorak WS (2012) The potential use of near infrared spectroscopy to discriminate between different pine species and their hybrids. J of N Infr Spectr. https://doi.org/10.1255/jnirs.1006

Feinberg A, Selin NE, Braban CF, Chang K, et al (2024) Unexpected anthropogenic emission decreases explain recent atmospheric mercury concentration declines. Proc Natl Acad Sci. https://doi.org/10.1073/pnas.2401950121

Ferretti M, Cools N, Dörner M, Michel A., et al (2025) On the pulse of European forests. 40 years of pan-European forest monitoring: from air pollution to climate change. ICP Forests 40th Anniversary Report under the UNECE Convention on Long-range Transboundary Air Pollution (Air Convention). https://doi.org/10.3220/253-2025-21

Franzaring J, Holz I, Zipperle J, Fangmeier A (2010) Twenty years of biological monitoring of element concentrations in permanent forest and grassland plots in Baden-Württemberg (SW Germany). Environ Sci Pollut Res. https://doi.org/10.1007/s11356-009-0181-x

Franzaring J, Haneke J, Sannino A, Radermacher G, Schweiger A (2024) Effects of legacy mining on mercury concentrations in conifer needles and mushrooms in northern Palatinate, Germany. Env Poll. https://doi.org/10.1016/j.envpol.2024.124406

Fröhlich HJ (1969) Untersuchungen über Benadelungsverhältnisse an Fichten. Theoret. Appl Gen. https://doi.org/10.1007/BF00281976

Fürst A (2007) Quecksilber in Fichtennadeln als Immissionsmarker. Forstschutz Aktuell. https://bfw.ac.at/400/pdf/fsaktuell_41_7.pdf

Gautam MK, Berg B, Lee KS, Nilsson T, Shin HS (2023) Dynamics of trace and rare earth elements during long-term (over 4 years) decomposition in Scots pine and Norway spruce forest stands, Southern Sweden. Front Environ Sci. https://doi.org/10.3389/fenvs.2023.1190370

Gautam MK, Berg B, Lee KS (2024) Carbon ($\delta^{13}C$) and Nitrogen ($\delta^{15}N$) Isotope Dynamics during Decomposition of Norway Spruce and Scots Pine Litter. Forests. https://doi.org/10.3390/f15081294

Gebauer G, Schulze ED (1991) Carbon and nitrogen isotope ratios in different compartments of a healthy and a declining Picea abies forest in the Fichtelgebirge, NE Bavaria. Oecologia. https://doi.org/10.1007/BF00325257

Göttlein A (2015) Grenzwertbereiche für die ernährungsdiagnostische Einwertung der Hauptbaumarten Fichte, Kiefer, Eiche, Buche. AFZ. http://www.sauerlaender-verlag.com/CMS/uploads/media/_03__G%C3%B6ttlein_6273.pdf

Greve M, Block J, Schröck HW, Schultze J, Werner W, Wies K (2016) Nährstoffversorgung rheinlandpfälzischer Wälder. Mitteilungen aus der Forschungsanstalt für Waldökologie und Forstwirtschaft Rheinland-Pfalz Nr. 76/16, 268 pp. https://fawf.wald.rlp.de

Hesse BD, Hikino K, Gebhardt T, Buchhart C, Dervishi V, Goisser M, Pretzsch H, Häberle KH, Grams TEE (2024) Acclimation of mature spruce and beech to five years of repeated summer drought – The role of stomatal conductance and leaf area adjustment for water use. STOTEN https://doi.org/10.1016/j.scitotenv.2024.175805

Högberg P, Lucas RW, Högberg MN, Skyllberg S, Egnell G, Larson J, Binkley D (2024) What happens to trees and soils during five decades of experimental nitrogen loading. For Ecol Manag. https://doi.org/10.1016/j.foreco.2023.121644

Huang JH, Berg B, Chen C, Thimonier A, Schmitt M, Osterwalder S, Alewell C, Rinklebe J, Feng X (2023) Predominant contributions through lichen and fine litter to litterfall mercury deposition in a subalpine forest. Env Res. https://doi.org/10.1016/j.envres.2023.116005

Hüttl RF (1992) Die Blattanalyse als Diagnose- und Monitoringinstrument in Waldökosystemen. Freiburger Bodenkundl Abhandlungen. https://www.bodenkunde.uni-freiburg.de/de/publikationen/fba/inhalt_28

König N, Krinninger M, Geppert F, Sanders TGM (2024) Messung der nassen Quecksilberdeposition unter dem Kronendach von Wäldern. Vergleich von drei Standorten mit unterschiedlicher Belastung. TEXTE 135/2024,

Umweltbundesamt, Dessau. https://www.umweltbundesamt.de/publikationen/messung-der-nassen-quecksilberdeposition-unter-dem

Kühn P, Proß T, Römermann C, Wesche K, Bruelheide H (2024) Using near-infrared spectroscopy to predict nitrogen and phosphorus concentrations of herbarium specimens under different storage conditions. Plant Meth. https://doi.org/10.1186/s13007-024-01146-x

Lee AK, Van der Esch L, Oong J, Fredericksen B et al (2026) Robust estimation of key leaf traits from reflectance spectroscopy of herbarium specimens. Meth Ecol Evolut. https://doi.org/10.1111/2041-210x.70353

LfU (2018) Dioxine, Furane und PCB: Dauerhaft stabil - nicht immer von Vorteil - 20 Jahre Biomonitoring in Bayern. Bayerisches Landesamt für Umwelt, Augsburg. 118 pp. https://www.lfu.bayern.de/luft/schadstoffe_luft/organische_schadstoffe/fichten/index.htm

LfU (2025) Hintergrundwerte der atmosphärischen Deposition. Jahresmittelwerte 2004 – 2023. Bayerisches Landesamt für Umwelt, Augsburg. https://www.lfu.bayern.de/luft/schadstoffe_luft/schwermetalle/ergebnisse/doc/hintergrundwerte_atmosphaer_depo.pdf

Llanos-Campana DM, Kern Z, Popa I, Perşoiu A (2025) Stable carbon and oxygen isotope ratios in Norway spruce (*Picea abies* (L.) Karst.) tree rings along an elevation gradient in the Rarau Mts. (Romania). Dendrochronologia. https://doi.org/10.1016/j.dendro.2025.126365

Lorenz M, Fischer R, Becher G, Granke O, Roskams P, Nagel HD, Kraft P (2008) Forest Condition in Europe: 2008 Technical Report of ICP Forests and EU. https://www.icp-forests.org/pdf/ER2008.pdf

Luo Y, Su B, Currie WS, Dukes JS, Finzi AC, Hartwig U et al (2004) Progressive nitrogen limitation of ecosystem responses to rising atmospheric carbon dioxide, Bioscience. https://doi.org/10.1641/0006-3568(2004)054[0731:PNLOER]2.0.CO;2

McLagan DS, Biester H, Navrátil T, Kraemer SM, Schwab L (2022) Internal Tree Cycling and Atmospheric Archiving of Mercury: Examination with Concentration and Stable Isotope Analyses. Biogeosciences. https://doi.org/10.5194/bg-19-4415-2022

Michel AK., Haggenmüller K, Kirchner T, Prescher A-K, Schwärzel K, Wohlgemuth L (2024) Forest Condition in Europe: The 2024 Assessment; ICP Forests Technical Report under the UNECE Convention on Long-range Transboundary Air Pollution (Air Convention). Eberswalde: Thünen Institute of Forest Ecosystems, 99 p., ICP Forests Techn. Rep 2024, https://www.icp-forests.org/pdf/ICPForests_TR2024.pdf

Monaci F, Baroni D (2025) Leaves and Tree Rings as Biomonitoring Archives of Atmospheric Mercury Deposition: An Ecophysiological Perspective. Plants. https://doi.org/10.3390/plants14091275

Montemagno A, Hissler C, Bense V, Teuling AJ, Ziebel J, Pfister L (2022) Dynamics of rare earth elements and associated major and trace elements during Douglas-fir (*Pseudotsuga menziesii*) and European beech (*Fagus sylvatica* L.) litter degradation. Biogeosciences. https://doi.org/10.5194/bg-19-3111-2022

Navrátil T, Nováková T, Roll M, Shanley JB, Kopáček J, Rohovec J, Kaňa J, Cudlín P (2019) Decreasing litterfall mercury deposition in central European coniferous forests and effects of bark beetle infestation. STOTEN. https://doi.org/10.1016/j.scitotenv.2019.05.093

Navrátil T, Rohovec J, Nováková T, Roll M, Cudlín P, Oulehle F (2024) Quarter century of mercury litterfall at a coniferous forest responding to climate change, Central Europe. Env Sci Poll Res. https://doi.org/10.1007/s11356-024-33555-9

Offenthaler I, Weiss P (2008) Metalle und Nährstoffe in Fichtenholz Entwicklung ab dem 18. Jahrhundert und heutige Situation. Umweltbundesamt Österreich. https://www.umweltbundesamt.at/fileadmin/site/publikationen/REP0173.pdf

Oulehle F, Tahovská K, Ač A, Kolář T, Rybníček M, Čermák P et al (2022) Changes in forest nitrogen cycling across deposition gradient revealed by $\delta^{15}N$ in tree rings. Env Poll. https://doi.org/10.1016/j.envpol.2022.119104

Peñuelas J, Fernández-Martínez M, Vallicrosa H (2020) Increasing atmospheric CO_2 concentrations correlate with declining nutritional status of European forests. Commun Biol. https://doi.org/10.1038/s42003-020-0839-y

Píšová L, Svoboda M, Šantrůček J, Šantrůčková H (2008) Can ^{13}C stable isotope record of Norway spruce tree rings display the effect of environmental conditions? J For Sci. https://doi.org/10.17221/816-JFS

Qubain CA, Yano Y, Hu J (2021) Nitrogen acquistion strategies of mature Douglas-fir: a case study in the northern Rocky Mountains. Ecosphere. http://dx.doi.org/10.1002/ecs2.3338

Rautio P, Fürst A, Stefan K, Raitio H, Bartels U (2020) Part XII: Sampling and Analysis of Needles and Leaves. Version 2020-3. In: UNECE ICP Forests Programme Co-ordinating Centre (ed.) Manual on methods and criteria for harmonized sampling, assessment, monitoring and analysis of the effects of air pollution on forests. Thünen Institute of Forest Ecosystems, Eberswalde, Germany, 16 p. + Annex, http://www.icp-forests.org/Manual.htm

Richardson AD, Reeves JB, Gregoire TG (2004) Multivariate analyses of visible/near infrared (VIS/NIR) absorbance spectra reveal underlying spectral differences among dried, ground conifer needle samples from different growth environments. New Phytol. https://doi.org/10.1046/j.1469-8137.2003.00913.x

Riek W, Talkner U, Dammann I, Kohler M, Meiwes KJ, Göttlein A (2017) Situation der Waldernährung in Deutschland. AFZ. https://www.nw-fva.de/fileadmin/nwfva/publikationen/pdf/riek_2017_situation_der.pdf

Sah SP, Brumme R, Lamersdorf N (2008) Natural abundance of ^{15}N of a spruce forest ecosystem under acid rain and manipulated clean rain field conditions. J For Sci. http://jfs.agriculturejournals.cz/pdfs/jfs/2008/08/05.pdf

Schäfer C, Grams TEE, Rötzer T, Feldermann A, Pretzsch H (2017) Drought stress reaction of growth and $\Delta^{13}C$ in tree rings of European Beech and Norway Spruce in monospecific versus mixed stands along a precipitation gradient. Forests. https://doi.org/10.3390/f8060177

Seim A, Marquer L, Bisson U, Hofmann J, Herzig F et al (2022) Historical Spruce abundance in Central Europe: A Combined Dendrochronological and Palynological Approach. Front Ecol Evol. http://dx.doi.org/10.3389/fevo.2022.909453

Talkner U, Riek W, Dammann I, Kohler M, Göttlein A, Mellert KH, Meiwes KJ (2019) Nutritional status of major forest tree species in Germany. In: Status and Dynamics of Forests in Germany. Ecol Stud. https://doi.org/10.1007/978-3-030-15734-0_9

Tarricone K, Wagner G, Klein R (2015) Toward standardization of sample collection and preservation for the quality of results in biomonitoring with trees – A critical review. Ecol Ind. https://doi.org/10.1016/j.ecolind.2015.05.012

Thomas FM, Rzepecki A, Lücke A, Wiekenkamp I, Rabbel I, Pütz T, Neuwirth B (2018) Growth and wood isotopic signature of Norway spruce (*Picea abies*) along a small-scale gradient of soil moisture, Tree Physiol. https://doi.org/10.1093/treephys/tpy100

Treydte, K.S., Schleser, G., Schweingruber, F. Winiger, M. (2001) The climatic significance of $\delta^{13}C$ in subalpine spruces (Lötschental, Swiss Alps). Tellus B. 53B: 593–611. https://doi.org/10.3402/tellusb.v53i5.16639

UBA (2024) Critical Loads für Schwermetalle.https://www.umweltbundesamt.de/themen/luft/wirkungen-von-luftschadstoffen/wirkungen-auf-oekosysteme/critical-loads-fuer-schwermetalle#was-sind-critical-loads

UN/ECE (2023) ICP Forests Manual. International Co-operative Programme on Assessment and Monitoring of Air Pollution Effects on Forests. https://www.icp-forests.net/monitoring-and-research/icp-forests-manual

Vadeboncoeur MA, Jennings AP, Asbjornsen H (2020) Correcting tree-ring $\delta^{13}C$ time series for tree-size effects in eight temperate tree species. Tree Physiol. https://doi.org/10.1093/treephys/tpz138

VDLUFA (2011) Methodenbuch Band VII Umweltanalytik, 2.2.3.1: Bestimmung von ausgewählten Elementen in Misch- und Mineralfutter- sowie Düngemitteln mittels Massenspektrometrie mit induktiv gekoppeltem Plasma (ICP-MS). Available under: https://www.methodenbuch.de/produkt/methodenbuch-band-vii-umweltanalytik/ (12 July2024)

VDLUFA (2014) VDLUFA-Methodenbuch 2.2.3.2 Bestimmung von Quecksilber mittels Massenspektrometrie mit induktiv gekoppeltem Plasma (ICP-MS). Available under: https://www.methodenbuch.de/produkt/methodenbuch-band-vii-umweltanalytik/ (12 July 2024)

Weiss P (1999) Elementgehalte von Fichtennadeln, Papel- und Ahornblättern. Eine tabellarische Zusammenstellung von Literaturdaten. Umweltbundesamt Österreich. https://www.umweltbundesamt.at/fileadmin/site/publikationen/be143.pdf

Wellbrock N, Bolte A (2019) Status and Dynamics of Forests in Germany. Results of the National Forest Monitoring. Ecol. Stud. https://link.springer.com/book/10.1007/978-3-030-15734-0

Wieloch T, Ehlers I, Yu J et al. (2018) Intramolecular 13C analysis of tree rings provides multiple plant ecophysiology signals covering decades. Sci Rep. https://doi.org/10.1038/s41598-018-23422-2

Wieser G, Oberhuber W, Gruber A, Leo M, Matyssek R, Grams TEE (2016) Stable Water Use Efficiency under Climate Change of Three Sympatric Conifer Species at the Alpine Treeline. Front Plant Sci. https://doi.org/10.3389/fpls.2016.0079

Wiley E, Rogers BJ, Griesbauer HP, Landhäusser SM (2018). Spruce shows greater sensitivity to recent warming than Douglas-fir in central British Columbia. Ecosphere. https://doi.org/10.1002/ecs2.2221

Wohlgemuth L, Rautio P, Ahrends B, Russ A, Vesterdal L, Waldner P et al (2022) Physiological and climate controls on foliar mercury uptake by European tree species. Biogeosciences. https://bg.copernicus.org/articles/19/1335/2022/

Wyttenbach A, Schleppi P, Bucher J, Furrer V, Tobler L (1994) The accumulation of the rare earth elements and of scandium in successive needle age classes of Norway spruce. Biol Trace Elem Res. https://doi.org/10.1007/BF02917214

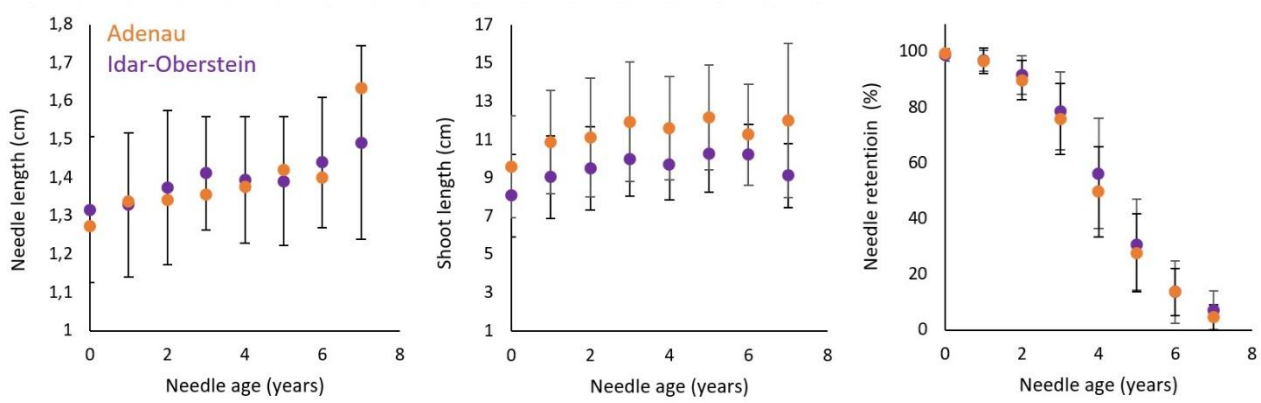
Zhang X, Peng H, Osterwalder S, Bishop K, Nilsson MB, Peichl M, Björn E, Zhu W (2025) Limited response of boreal forest litterfall mercury deposition to declines in atmospheric mercury concentrations (1987–2000). Env Poll. https://doi.org/10.1016/j.envpol.2025.126901

Supplementary

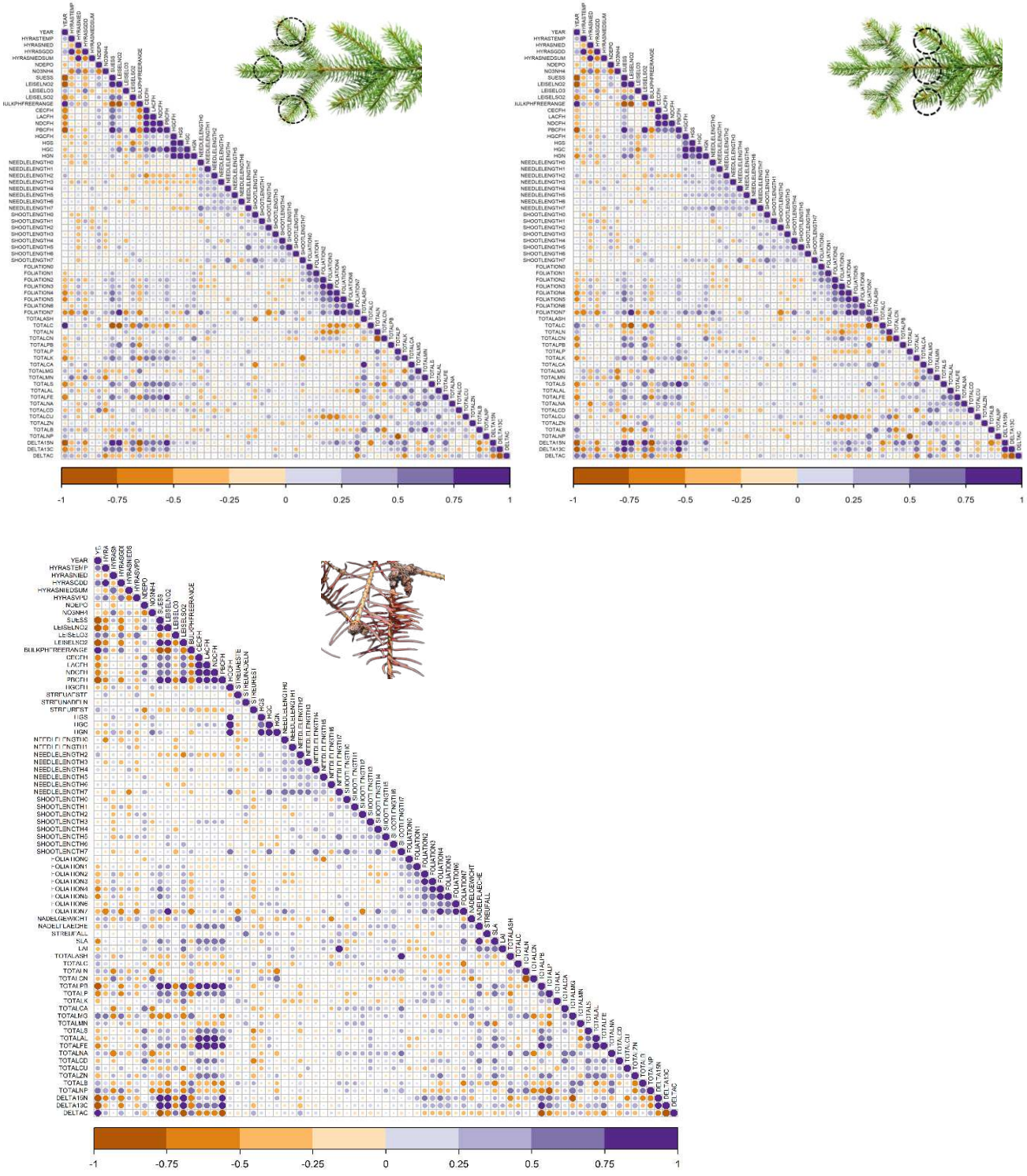
Table S1: Heat maps for measurements of needle/shoot lengths and foliation assessments of up to seven age classes of selected main shoots.

				Needle Length (cm) at main branch								Shoot length (cm) at main branch								Foliation (%), inverse of needle loss							
				Age classes								Age classes								Age classes							
Idar-Oberstein		Temp	Prec	0	1	2	3	4	5	6	7	0	1	2	3	4	5	6	7	0	1	2	3	4	5	6	7
1994	101	9,071	952																								
1995	101	8,215	1143																								
1996	101	6,543	710,4																								
1997	101	8,165	869,9	1,35	1,33	**0,98**	1,33	1,37	1,24	1,2		7,97	7,5	**6,13**	8,63	8,8	9,3	10,2		100	99,3	98	84	52,7	37	23,3	
1998	101	7,881	1047																								
1999	101	8,325	1036	1,24	1,18	1,31	1,43	1,19	1,31	1,5	1,25	10	12,2	10,6	11	**7,99**	11	12,5	8,11	100	100	100	97,8	88,3	49,4	24,4	12,5
2000	101	8,729	1228	**1,06**	1,29	1,44	1,42	1,62	1,34	1,53		**6,67**	8,57	12,9	11,2	10,5	**8,78**	11,4	11,1	100	100	100	100	70	22,5	0,5	0
2001	101	8,246	1118	1,4	**1,18**	1,57	1,47	1,66	1,73	1,42		10,2	**7,57**	9,08	10,5	7,96	8,63	**6,68**		97,8	100	96,7	88,9	70	33,9	30	
2002	101	8,686	1150	1,29	1,27	**1,16**	1,36	1,29	1,52	1,49	1,5	5,78	7,44	**7,28**	8,27	12,1	10,2	10	**8**	100	97,8	97,8	96,7	87,8	59,4	22,2	16,7
2003	101	8,908	752,6	1,11	1,14	1,26	**1,19**	1,31	1,29	1,52		7,66	11,7	12	**10,4**	11,6	14,8	11,5		100	98,9	94,4	78,9	73,9	39,4	9,38	
2004	101	7,805	889,5	**1,14**	1,4	1,43	1,54	**1,24**	1,53	1,46		**7,63**	11,3	14	14,1	11	13,3	11,7		100	100	100	92,5	71,3	42,5	9	
2005	101	8,301	824	1,5	**1,24**	1,18	1,27	1,4	**1,3**	1,4		10,5	**8,36**	10,3	12,6	11,7	10,2	11		97,2	89,4	82,8	73,9	40	21,1	7,22	
2006	101	8,722	924,8	1,08	1,49	**1,01**	1,31	1,27	1,4	**1,2**		**6,86**	9,83	**6,46**	11,6	11,8	11,7	11,5		99	95,8	80	71,3	53,8	14,4	3,13	
2007	101	8,793	1082	1,5	**1,13**	1,63	1,53	1,21	1,43	1,45		**5,34**	**5,61**	9,26	**8,69**	7,39	10,8	11,3		90,6	90,6	78,1	72,5	38,8	43,3	16,7	
2008	101	8,206	947,2	1,66	1,39	1,44	1,61	1,39	1,46	1,48	1,9	10,9	**8,48**	**8,94**	10,4	**9,58**	11,6	13,2	11,8	100	97,8	95,6	80	75	45,6	28,9	10
2009	101	8,403	1016	1,23	1,42	1,34	1,27	1,44	1,27	1,26		9,21	12,7	**7,96**	**7,16**	10,7	**9,88**	10,3		100	100	98,9	98,9	92,2	67,2	42,2	10
2010	101	7,105	955,8	1,5	1,53	1,66	1,5	1,36	1,38	1,18		11,1	10,1	12,2	**7,44**	**8,44**	9,25	8,58		99,4	99,4	92,2	68,8	45	18,8	5	
2011	101	9,107	799	1,24	1,48	1,47	1,4	1,29	1,26	1,5		**4,69**	10,9	10,6	11,2	10,4	9,97	10,3		100	97,2	81,7	53,6	22,7	14	5	
2012	101	8,245	983,6	1,58	1,3	1,49	1,53	1,71	1,74	1,8		9,03	**7,86**	10,9	9,75	10,6	9,08	8,41		94,4	89,6	88,3	64,3	50	24,4	5	
2013	101	7,715	1008	1,56	1,58	1,56	1,48	1,49	1,56	1,4		8,97	8,14	**6,11**	12,3	11,2	13	9,38		100	98,9	90,6	68,9	37,6	18,8	5,25	
2014	101	9,477	916,7	**1,43**	1,76	1,69	1,48	1,6	1,47			**7,42**	11	8,92	**7,33**	11,2	10,6	11,3		98,9	96,7	87,2	57,9	44,3	9,91	7,5	
2015	101	9,072	805,5	1,33	**1,03**	1,34	1,31	1,19	1,26	1,5		6,97	**5,53**	10,6	11,1	**6,09**	10,5	8,75		99,4	97,2	86,7	65,3	38,6	14,2	13,7	
2016	101	8,483	849,9	1,48	1,46	**1,26**	1,61	1,67	1,25	1,58		10,1	8,82	**6,96**	11,5	10,5	**6,79**	9,73		100	96,1	93,3	75,3	50,3	13	20	
2017	101	8,792	900,4	1,07	1,31	1,47	**1,11**	1,39	1,2	1,28	1,5	10,7	10,8	8,15	**6,99**	10,7	9,32	**7,57**	9,23								
2018	101	9,65	952,8	1,07	1,39	1,47	1,68	1,39	1,59	1,8	1,6	3,5	9,33	9,76	8,6	**6,34**	11	9,95	**7,91**	98,8	99,3	92,6	92,5	34,2	35,1	1,18	0
2019	101	9,34	925,2	1,15	0,94	1,09	1,23	1,21	1,1	1,3	1,2	6,56	5,23	10,1	9,24	7,31	**5,7**	9,42	7,78	100	89,2	90,5	69,5	45	18,6	6,67	0,31
Adenau																											
1994	106	9,405	727,9																								
1995	106	8,746	740,5																								
1996	106	7,02	553,7																								
1997	106	8,593	654,5	1,23	1,3	1	1,1	1,23	1,18	1,36		9,97	8,47	8,67	10,7	11,3	11,1	11,5		100	100	98	82	60,8	46,4	31,4	
1998	196	8,563	767																								
1999	106	9,142	657,4	1,24	1,29	1,31	1,47	1,27	1,42	1,4	1,8	12	14,6	11	11	8,81	11,9	10,5	12,3	100	100	94,4	82,2	66,4	54,3	10	2,5
2000	106	9,16	792,8	**0,96**	1,27	1,04	1,24	1,26	1,28	1,25		**6,17**	8,06	11,1	10,8	8,67	7,78	11,7		100	100	100	84,4	44,4	18,9	2,22	5
2001	106	8,796	779,8	1,13	**1,1**	1,2	1,28	1,23	1,49	1,2		9,66	**10**	10,2	14,4	9,63	10,1	8,23		100	100	95,6	86,7	70	40,6	18,9	
2002	106	9,312	849	1,24	1,39	**1,2**	1,34	1,33	1,37	1,57		7,06	9	**8,83**	9,42	11,5	9,87	9,51		100	100	93,9	82,2	63,9	34,4	2,86	
2003	106	9,362	586,2	1,11	1,21	1,43	**1,27**	1,51	1,4	1,55		12,7	14,5	14,8	12,3	12,1	15,8	9,4		100	100	88,9	84,4	60	23,9	13	
2004	106	8,357	777,9	**1,1**	1,4	1,34	1,47	**1,21**	1,49	1,43	1,33	**6,61**	10,4	8,5	8,33	**7,67**	9,78	12,6	10,6	100	100	100	97,8	76,7	56,7	20	10,6
2005	106	8,865	734,8	1,56	**1,1**	1,43	1,34	1,42	1,4	1,48		9,44	**7,89**	15	17	13,3	12,8	10,9		98,9	92,2	84,4	65,6	43,3	20	9,44	
2006	106	9,219	631,3	1,35	1,69	**1,21**	1,4	1,43	1,65	1,27		7,19	9,9	**7,44**	13,8	12,5	11,9	8,63		93,2	85	75,5	61,5	43,5	15	2,5	
2007	106	9,401	807,7	1,4	1,42	1,6	**1,18**	1,36	1,39	1,41		11,4	11,6	11,1	**9,97**	15,2	17,1	15,5		98,9	88,3	76,7	66,7	50,6	31,7	15,6	
2008	106	8,754	640,8	1,66	1,39	1,44	1,61	1,39	1,46	1,48	1,9																
2009	106	8,917	723,9	1,26	1,34	1,37	1,32	1,53	1,25	1,38		14,1	15,6	12,1	14,2	11,6	11,4	14,8		100	91,1	98,9	95,6	69,4	38,3	24,4	
2010	106	7,619	741,2	1,43	1,34	1,41	1,52	1,4	1,44			13,7	14,2	16,9	11,3	10,1	10,8	9		100	98,3	85	54,1	22,5	13,3		
2011	106	9,584	580,6	**0,78**	1,23	1,34	1,38	1,38	1,53			**5,58**	15,3	17,1	16,1	14,8	14	11,5		98,3	96,7	88,9	62,2	26,3	10		
2012	106	8,715	753,7	1,8	1,59	1,46	1,47	1,51	1,67	1,8		7,89	**8,19**	12,9	12,8	12	11,7	12,7		100	98,9	88,9	68,9	47,2	29,2	22,5	
2013	106	8,192	759,1	1,6	1,52	1,6	1,5	1,53	1,55	1,2		11,4	7,25	**5,78**	19,4	17,1	16,2	11,5		100	97,2	84,7	78,3	47,1	18,7	12	
2014	106	9,909	740,9	**1,15**	1,48	1,42	**1,11**	1,42	1,5			7,12	11,9	10,2	**6,77**	15,3	13,2	12,6		99,4	97,8	86,7	60,3	26,9	16,5	5	
2015	106	9,437	677,1	1,24	**1,27**	1,57	1,62	**1,13**	1,41	1,47		8,51	8,96	13,3	10,7	**8,51**	17,5	14,8		99,4	92,8	87,2	65,7	33,4	22,2	21,7	
2016	106	9,03	721,9	1,34	1,36	**1,33**	1,43	1,51	**1,26**	1,45		11	8,82	7,94	11,8	10,1	**8,27**	15,7		100	99,4	87,2	72,3	58	22,9	12,6	
2017	106	9,344	668,7	1,15	1,37	1,23	**1,3**	1,6	1,38	**1,2**	1,5	12,8	12,2	9,56	9,83	13,8	10,6	**6,04**	17,4								
2018	106	10,11	535,9	0,98	1,04	1,24	1,11	**1,24**	1,32	1,3		7,66	11	9,99	8,29	8,06	11,7	8,07	**7,8**	100	99,4	91,7	90,3	33,1	13,5	8,33	0
				0	1	2	3	4	5	6	7	0	1	2	3	4	5	6	7	0	1	2	3	4	5	6	7
				Mittelwerte								Mittelwerte								Mittelwerte							
				101	1,32	1,33	1,37	1,41	1,39	1,39	1,44	1,49	1,39	8,08	9,05	9,51	9,99	9,72	10,3	10,2	9,13	9,49	98,8	96,8	91,7	78,6	56,3	30,6	13,6	7,07	59,2
				106	1,27	1,34	1,34	1,36	1,38	1,42	1,4	1,63	1,39	9,6	10,9	11,1	11,9	11,6	12,2	11,3	12	11,3	99,4	96,7	89,8	75,9	49,7	27,7	13,7	4,51	57,2
				SDs								SDs								SDs							
				101	0,19	0,19	0,2	0,15	0,17	0,17	0,17	0,25		2,16	2,15	2,19	1,94	1,85	2,01	1,6	1,66		2,32	3,78	6,88	14	19,9	16,4	11,3	6,88	
				106	0,25	0,16	0,16	0,15	0,13	0,12	0,15	0,26		2,66	2,71	3,1	3,13	2,7	2,75	2,66	4,03		1,58	4,55	7,13	12,8	16,3	14	8,5	4,52	

S1 Supplementary Diagrams



S1 Mean needle length (left), shoot length (centre) and degree of needle retention (right) after age classes at the two monitoring sites at Idar-Oberstein (●) and Adenau (●). Error bars indicate the standard deviation.



S2. Correlation matrices for the variables that had been addressed in present study for the alive one-year-old (upper left), three-year old needles (upper right) and dead needles that were collected in the litter (lower left). Apart from the chemistry and isotopic data, climatic and biometric data were included in the analyses not separating after the two sites. Note: colors from orange to purple represent correlation coefficients from -1 to +1 (highly positive correlations) and not the sites.