Abstract

The uptake of carbon dioxide (CO$_2$) from the atmosphere through photosynthesis is accompanied by an inevitable loss of water vapor through the stomata of leaves. The rate of leaf-level CO$_2$ assimilation per unit stomatal conductance, i.e. intrinsic water-use efficiency (WUE$_i$), is thus a key characteristic of terrestrial ecosystem functioning that is central to the global hydroclimate system. Empirical evidence and theory suggest a positive response of forest WUE$_i$ to increased CO$_2$ levels globally. Although evidence exists for a positive effect of ecosystem nitrogen (N) inputs on WUE$_i$, it is not clear how trends in atmospheric N deposition have affected WUE$_i$ in the past. Here we combine twentieth-century climate and nitrogen deposition with stable isotope signature in tree rings and document a WUE$_i$ trend reversal at two sites in Switzerland, that matches the timing of a trend reversal in atmospheric N deposition. Using generalized additive models (GAMs), we fitted observed WUE$_i$ time series to multiple environmental covariates. This suggested N deposition to have a significant effect on long-term WUE$_i$ at the site that was exposed to higher N deposition levels. The ratio of the increase in WUE$_i$ in response to increase in CO$_2$ ($d$WUE$_i$/dCO$_2$) declined by 96% after 1980 (from 0.53 to 0.02) in the beech forest and declined by 72% in the spruce forest (from 0.46 to 0.13) concurrent with a sharp decline in N deposition. Using the GAM model for two scenarios, we show that had N deposition levels not declined after 1980, WUE$_i$ would have increased more strongly in response to increasing CO$_2$. Although the increase in N deposition was limited to the 1950–1980 decades and the signals have declined with improvements in air quality across Europe, the role of atmospheric pollution must be reconsidered in interpretation of tree ring studies and for building environmental proxies that are pivotal to understanding future sink capacity of terrestrial ecosystems in response to climate change.

1. Introduction

Intrinsic water-use efficiency (WUE$_i$), or the ratio of photosynthesis to stomatal conductance determines the balance between carbon gain and water loss through stomatal pores and is a key characteristic of terrestrial ecosystem functioning (Beer et al 2009). A large body of evidence shows a steadily increasing WUE$_i$ trend over the past decades inferred from multiple types of observations including atmospheric and ecosystem flux measurements, and tree-ring studies (Keenan et al 2013, Frank et al 2015, Keeling et al 2017, Guerrieri et al 2019, Belmecheri et al 2020, Mathias and Thomas 2021). The increasing trend in WUE$_i$ is consistent with theory that predicts a strong positive effect of rising CO$_2$ in forests, particularly because CO$_2$ is a limiting factor to the functioning of the carboxylation pathway in C3 plants (Farquhar et al 1989, Frank et al 2013). In addition to CO$_2$, changes in WUE$_i$ are sensitive to any environmental factor that affect the rate of photosynthesis or stomatal conductance. To date, understanding how
centennial WUE\textsubscript{i} is affected by long-term climate and atmospheric changes has focused predominantly on climatic factors such as precipitation patterns, temperature, and atmospheric CO\textsubscript{2} concentrations (e.g. Keenan et al 2013, Saurer et al 2014, Frank et al 2015, Belmecheri et al 2021) and considerably fewer studies have explored the role of N deposition (but see Leonard et al 2012, Levesque et al 2017, Adam et al 2021) despite the importance of N supply for assimilation and plant response to atmospheric CO\textsubscript{2} (Oren et al 2001).

Empirical evidence shows that N deposition can have a significantly positive effect on WUE\textsubscript{i} (Wallin et al, Höberg et al 2003, Brooks and Mitchell 2011, Guerrero et al 2011, Yan et al 2014, Jennings et al 2016) through increased assimilation or decline in stomatal conductance (Ward et al 2015, Savard et al 2020). Although at the leaf level, N fertilization can increase investment in enzymes resulting in increased assimilation (A) for a given stomatal conductance (g\textsubscript{s}), at the plant and ecosystem level effect of N deposition on WUE\textsubscript{i} can be negative via enhancing leaf area and concurrently transpiration and compensating leaf-level water saving effects (Zhu et al 2016, Lu et al 2018, Liang et al 2020). Increasing leaf area and productivity can lead to concomitant increase in tree water uptake, unless its regulation changes proportionally through decreased canopy conductance per unit leaf area (i.e. stomatal conductance). The response of trees and their WUE\textsubscript{i} to N deposition are further complicated by the interaction with concomitantly increasing air temperatures, evaporative demand, and atmospheric CO\textsubscript{2} concentrations (Fernández-Martínez et al 2014, Grossiord et al 2020), which all can lead to stomatal closure and thus increasing WUE\textsubscript{i} (Hatfield and Dold 2019). Plant water loss is affected by increase in air temperature and evaporative demand on two opposing directions: in one direction increase in evaporative demand directly increases transpiration, and on the other hand increase in evaporative demand indirectly reduces transpiration due to stomatal closure (Massmann et al 2018).

Human activity is a large contributor to atmospheric N deposition (Tian et al 2020), and the interaction of the N cycle with climate and the C cycle is becoming increasingly important for predicting the future response of the Earth’s system to global change, and defining the planetary boundaries (Rockström et al 2009, Liu et al 2013). N deposition, however, and its consequences for the carbon–water balance are less frequently investigated over the past century (compared to CO\textsubscript{2} and climate), despite its significant interactions with the hydro-climatic changes in the 20th century (Marvel et al 2019) and its relevance for improving global terrestrial carbon sink estimates (Gais et al 2019). This may be due to the lack of long-term observational N deposition data (Simpson et al 2014, Engardt et al 2017).

Since the beginning of the last century, atmospheric CO\textsubscript{2} concentrations have been increasing as a result of fossil-fuel combustion (figure 1) (Keeling et al 1995). At the same time, also N deposition increased due to fossil fuel combustion and agricultural emissions (Galloway et al 2008, Yao et al 2020). While CO\textsubscript{2} concentrations continue to increase, N deposition started to decline in Europe after 1980 as NO\textsubscript{x}, NH\textsubscript{3}, and N\textsubscript{2}O emissions declined by 49%, 18%, and 38%, respectively following policies that enforced measures in transport, fuel switching, production industries, agriculture, and waste management European environment agency (EEA 2014, Engardt et al 2017). This however has not reduced the significance of N deposition for functioning of the ecosystems (Robbin and Hettelingh 2011).

Here, we document and analyze the contributions of N deposition, CO\textsubscript{2}, and climate (temperature and precipitation) on centennial time series of WUE\textsubscript{i} for two temperate forests in Switzerland: a low-elevation forest dominated by European beech (Fagus sylvatica) and a subalpine evergreen forest dominated by Norway spruce (Picea abies). The two species of study are among the most economically viable tree species found in Europe (FOREST EUROPE 2020). We use long-term (from 1900 to 2012) tree-ring stable carbon isotope (δ\textsubscript{13}C) chronologies and atmospheric CO\textsubscript{2} concentration records to calculate carbon discrimination (Δ\textsubscript{13}C) and WUE\textsubscript{i}. Stable isotope signatures in tree rings have been shown to mirror gas exchange at the leaf level and can provide substantial information on tree physiology (Wieser et al 2018). We test the contribution of climate and N deposition to WUE\textsubscript{i} using multiple linear and general additive models (GAMs) and test the hypothesis that N deposition positively affects WUE\textsubscript{i}.

2. Materials and methods

2.1. Site description
Two contrasting forest stands located in Switzerland were selected for this study, a mixed deciduous forest in the Jura Mountain range at the Lägeren site (CH-Lae), and an evergreen coniferous forest in the eastern Swiss Alps at the Davos-Seehornwald site (CH-Dav). The forest at Lägeren is dominated by Fagus sylvatica L the forest at Davos by Picea abies (L) Karst. Mean annual precipitation is 1211 mm in Lägeren and 1046 mm in Davos, while mean annual temperature is 8.7 °C in Lägeren and 3.5 °C in Davos (supplementary figure 1 (available online at stacks.iop.org/ERL/16/114036/mmedia)). Further details about the sites are given in table 1.

2.2. Climate, CO\textsubscript{2} concentrations and N deposition
Monthly total precipitation and mean temperature data were extracted from nearby MeteoSwiss stations which showed good agreement with site measurements (supplementary figure 2), for the period
Figure 1. Time series of annual CO$_2$ concentrations (ppm), N deposition (kg N ha$^{-1}$ yr$^{-1}$), mean summer (June–August) precipitation ($P_{\text{summer}}$ (mm yr$^{-1}$)) and mean summer air temperature ($T_{\text{summer}}$ (°C)) between 1900 and 2012 at the Lägeren (mixed deciduous forest dominated by European beech) and Davos (coniferous evergreen forest dominated by Norway spruce) sites. $P_{\text{summer}}$ showed no significant change over this period ($p > 0.01$), while $T_{\text{summer}}$ showed a significantly increasing trend at both sites ($p < 0.001, r_{\text{Lägeren}} = 0.3$ and $r_{\text{Davos}} = 0.4$).

between 1900 and 2012 and were aggregated to seasonal and annual values (figure 1). Spring was defined as March–May, summer as June–August. Recently compiled timeseries of atmospheric CO$_2$ concentrations were extracted from Belmecheri and Lavergne (2020). Total atmospheric N deposition (kg N ha$^{-1}$ yr$^{-1}$), i.e. the sum of wet and dry deposition of NO$_3^-$, NH$_4^+$, NH$_3$, NO$_2$, HNO$_3$, was estimated using a modeling approach for Switzerland that combines monitoring data, spatial interpolation methods, emission inventories, statistical dispersion models, and inferential deposition models for the period 1990–2010 with a 5 years temporal resolution (Rihm and Kurz 2001, Rihm 2016). The validation of the emission-based model with actual deposition measurements at Lägeren and Davos for 2013–2017 showed comparable estimates of total N deposition. For a detailed description of this comparison, see Thimonier et al (2019). N deposition during 1880–1985 were based on 1990 values and rescaled using data by Schöpp et al (2003). Annual N deposition was estimated from 5 year values using a linear interpolation to be comparable with the temporal resolution of the climate and tree ring data (see supplementary figure 3).

2.3. Tree-ring isotope analysis

At each site, we established a circular plot (Nehrbass-Ahles et al 2014, Babst et al 2014) where we mapped all trees with a diameter at breast height >5.6 cm and subsequently took two increment cores of each tree. For tree-ring isotope analysis we selected
seven (Lägeren) and five (Davos) dominant trees to avoid age effects for these two shade tolerant tree species, related to changes in light availability, e.g. due to competition (Klesse et al. 2018). For both species, full tree rings were considered, using both earlywood and latewood. We separated individual rings formed during the 1900–2012 study period with a razor blade under a microscope and transferred them into Teflon filter bags (Ankom Technology, Macedon, NY, USA) for a three step cellulose extraction: (a) lignin was removed with NaClO2 in an ultrasonic bath for 24 h (24 g sodium chloride and 8 ml in acetic acid in 2 L deionized water; the solution was renewed every 3 h followed by an overnight solution with 72 g NaClO2 at 70 °C). (b) Fats, resins, oils, tannins and hemicellulose were removed by washing with distilled water and soaking in a sodium hydroxide solution (150 g NaOH in 1 L water) for 45 min. (c) The solution was neutralized with HCl (3%) for 45 min in an ultrasonic bath, and the cellulose was washed in distilled water until neutral pH was achieved. The cellulose material was then dried at 50 °C in a cabinet drier for 1 d before transferring to Eppendorf flasks and soaked in distilled water for 2 d for subsequent ultrasonic homogenization (Hielscher Ultrasonics GmbH, Teltow, Germany), and dried by lyophilisation. The cellulose samples were weighed (0.5–1.0 mg) into silicon capsules to determine the C13/C12 ratio (δ13C) by pyrolysis at 1450 °C in an elemental analyzer (PYROcube, Elementar, Hanau, Germany) linked via a variable open split interface (CONFLO III) to an IRMS (Delta Plus XP; Thermo Finnigan Mat, Bremen, Germany). Precision was ±0.12‰ for δ13C. The δ13C signal was corrected for a dampening of the signal due to memory effects from the pyrolytical process (Weigt et al. 2015) by applying a linear correction. This was determined from double measurements with pyrolysis or combustion of a subset using the following equation:

\[ \delta^{13}C_{\text{corr}} = 1.219 \delta^{13}C_{\text{pyro}} + 5.3545 \]  

(1)

where \( \delta^{13}C_{\text{corr}} \) represents the corrected values, and \( \delta^{13}C_{\text{pyro}} \) refers to pyrolysis measurements (after correction with internal standards). Isotope values are expressed in the δ-notations as relative deviations from the international standard, V-PDB (\( \delta^{13}C = (\delta^{13}C/\delta^{12}C \text{ sample})/(\delta^{13}C/\delta^{12}C \text{ standard})-1 \)); δ13C values are expressed as \( 10^3 \times \delta \) corresponding to the traditional (%o), in accordance with mUr (Brand and Coplen 2012).

2.4. WUEi

WUEi was calculated from tree-ring δ13C chronologies, averaged by site and year, between 1900 and 2012. Following Farquhar et al. (1982), the isotope discrimination against 13C(Δ) during photosynthesis can be defined in the simplified version as:

\[ \Delta = a \frac{c_i - c_a}{c_a} + b \frac{c_i}{c_a} = a + (b - a) \frac{c_i}{c_a} \]  

(2)

where \( a \) is the fractionation occurring due to diffusion in air (~4.4‰), \( b \) is the net fractionation during carboxylation (27‰), and \( c_i \) and \( c_a \) are the CO2 concentrations of the intercellular spaces and atmospheric air, respectively. The discrimination can also be defined as:

\[ \Delta = \frac{\delta^{13}C_a - \delta^{13}C_{\text{sample}}}{1 + \delta^{13}C_{\text{sample}}/1000} \approx \delta^{13}C_a - \delta^{13}C_{\text{sample}} \]  

(3)

where \( \delta^{13}C_a \) is the isotope value of atmospheric CO2 and \( \delta^{13}C_{\text{sample}} \) that of the sample, in our case, tree rings. Combining equations (3) and (4), \( c_i \) can be calculated as:

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Table 1. Characteristics of the two study sites Lägeren (mixed deciduous forest) and Davos (coniferous evergreen forest). Reference period for mean annual air temperature, mean annual precipitation is 2004–2011 in Lägeren and 1997–2011 in Davos. Normal N nutrition range is according to Mellert and Göttlein (2012).

|                         | Lägeren, CH-LAE | Davos, CH-DAV |
|-------------------------|-----------------|---------------|
| Altitude (m a.s.l.)     | 682             | 1639          |
| Latitude                | 47° 28’ 42.0” N | 46° 48’ 59” N |
| Longitude               | 8° 21’ 51.8” E  | 9° 51’ 25” E  |
| Mean annual air temperature (°C) | 8.7          | 3.5           |
| Mean annual precipitation (mm) | 1211        | 1046          |
| Dominant tree species   | Fagus sylvatica | Picea abies (L) Karst |
|                        | Fraxinus excelsior | —            |
|                        | Picea abies (L) Karst | —            |
|                        | Abies alba      | —             |
| Tree age range for sampled trees (year) | 130–164    | 139–164       |
| Mean foliage N concentration (mg g⁻¹) | 22.4        | 11.6          |
| Normal N nutrition range (mg g⁻¹) | 18.7–23.2   | 14–17.5       |
| Max leaf area index (m² m⁻²)    | 1.7–5.5        | 3.9           |
| Soil type               | Rendzic leptosols, | Chromic cambisols, |
|                        | Haplic cambisols | Rustic podzols  |
| Soil pH                 | 4.0–7.5        | 3.5–4.5       |
Recently compiled timeseries of \( \delta^{13}C_a \) were extracted from Belmecheri and Lavergne (2020).

Finally, the WUE\(_i\) can be calculated as the ratio of photosynthesis (\( A \)) to the conductance for water vapor (\( \gamma_{H_2O} \)):

\[
WUE_i = \frac{A}{\gamma_{H_2O}} = \frac{(\epsilon_a - \epsilon_i)}{1.6}.
\]

Combining equations (5) and (6) yields WUE\(_i\) as:

\[
WUE_i = \frac{\epsilon_a b - \delta^{13}C_a + \delta^{13}C_{\text{sample}}}{b - a}.
\]

We consider the role of photosynthesis on carbon isotope discrimination to be minimal in this study, given that the effect on \( \Delta^{13}C \) is 0.004‰ ppm\(^{-1}\) over the range of 285–400 ppm at 25 °C (Lavergne et al 2019), while in our case the mean air temperature is significantly lower (supplementary figure 1). For more details regarding the data collected in this study, see Tomlinson (2015).

2.5. Statistical analysis

For each site, WUE\(_i\) was calculated from a bi-weight robust mean of the tree-ring \( \delta^{13}C_{\text{sample}}\). Between-tree variability is shown in supplementary figure 4. We used a Mann–Kendall test (\( r_s \)) for trend analysis, and a Welch t-test and a Tukey HSD test to compare the means (at \( \alpha = 0.05 \)). We used GAMs to investigate the effects of climate variables, CO\(_2\) concentrations and N deposition on long-term WUE\(_i\) and compared this with a multiple linear regression model. For comparison of different models, we used the akaike information criterion (AIC), and used a step-wise approach (i.e. compared the full model with a model where variables were dropped one by one) to identify the most important variables. The theoretically expected linear dependency of WUE\(_i\) on CO\(_2\) was removed by using a CO\(_2\)-corrected WUE\(_i\) (1.6 × WUE\(_i\)/\( \epsilon_a \) ≈ \( b - \delta^{13}C_a + \delta^{13}C_{\text{sample}} (b - a) \)) as the dependent variable. We used a GAM multivariate analysis since GAMs are nonlinear and nonparametric regression techniques that do not require \textit{a priori} functional relationship specifications between dependent and independent variables (Hastie and Tibshirani 1986). The GAM type model involves the sum of smooth functions of covariates (Hastie and Tibshirani 1986) and was applied using the mgcv package in R (Wood 2011). For each model (one model per site), residuals were checked for autocorrelation. We used 50% of the dataset for training the models, and assigned 50% for testing, after shuffling the full dataset to remove any temporal autocorrelations. The testing dataset was only used for cross-validation and was not used for model fitting.

Shift in slope of change of WUE\(_i\) in response to changes in CO\(_2\) (dWUE/dCO\(_2\)) was assessed based on the parameters of a linear regression model in two separate periods; between 1950–1980, and after 1980 when N deposition started to decline significantly (figure 1). We used the GAM model to test two main scenarios: (a) a ‘constant climate’ scenario for which summer temperature and summer precipitation were kept unchanged after 1950 at a value observed at this time (18.5 °C and 303 mm in Lägeren, and 12 °C and 384 mm in Davos). (b) A ‘constant N’ scenario for which N deposition was kept unchanged after 1950 at a value observed at this time (17.2 kg ha \( \text{yr}^{-1} \)) in Lägeren and 10.2 kg ha \( \text{yr}^{-1} \) in Davos. We used the values observed in 1950 as the basis value for each scenario, because this was the time when N deposition started to increase sharply at both sites.

3. Results

3.1. Long-term changes in climate, CO\(_2\) concentrations and N deposition

Since 1900, atmospheric CO\(_2\) concentrations have increased continuously (figure 1), while N deposition rates increased concomitantly with largest growth rates after 1950 (figure 1). After the 1980s, N deposition started to decrease at both sites. Overall, N deposition rates were considerably higher at Lägeren (between 10.4 and 34.8 kg N ha \( \text{yr}^{-1} \)) than at Davos (between 8.2 and 17.5 kg N ha \( \text{yr}^{-1} \)) which is located at 1639 m a.s.l., due to Lägeren forest’s proximity to intense agricultural activities on the Swiss Plateau. Results of the Mann–Kendall trend analysis showed that summer temperatures increased significantly at both sites after 1980 \( (p < 0.001) \), although with a less pronounced trend at Lägeren \( (r = 0.3, p < 0.05) \), compared to Davos \( (r_s = 0.4, p < 0.05) \) (figure 1). In contrast, summer precipitation, constituting the largest fraction of annual precipitation (supplementary figure 1), remained relatively constant over the last century, albeit with large inter-annual variations \( (p > 0.05, \text{figure 1}) \).

3.2. Long-term WUE\(_i\)

The spruce trees at Davos had consistently higher WUE\(_i\) compared to the beech trees at Lägeren \( (p < 0.001) \) (figure 2). Between 1900 and 2012, WUE\(_i\) of Norway spruce at Davos increased continuously by 37%, from 80 \( \mu \text{mol mol}^{-1} \) (during the 1st decade) to 110 \( \mu \text{mol mol}^{-1} \), while WUE\(_i\) of beech at Lägeren increased only by 20% overall, from 72 \( \mu \text{mol mol}^{-1} \) to 90 \( \mu \text{mol mol}^{-1} \) (figure 2). WUE\(_i\) of beech trees at Lägeren increased mainly between 1950 and 1980 and reached the peak in the early 1980s. N deposition also reached its peak in 1980, with an increase of 100%
since 1950 at Lägeren and 72% at Davos, while CO$_2$ concentrations during the same time increased only by 8% (figure 1). After 1980, N deposition declined until 2012 by 41% at Lägeren and by 29% at Davos, while CO$_2$ concentrations continued to increase by 16%. Nevertheless, WUE$_i$ increased only by a further 3% for beech and 10% for spruce trees between 1981 and 2012. Overall, the ratio of intercellular to atmospheric CO$_2$ concentrations ($c_i/c_a$) was higher in beech trees at Lägeren compared to $c_i/c_a$ in spruce tree at Davos. $c_i/c_a$ of the beech trees was relatively constant between 1900 and 1950, but started to decline from 1950 until reaching its minimum around 1980 (figure 3). These minimum $c_i/c_a$ values (0.55 for beech and 0.51 for spruce) were observed at the time when N deposition values were at their peak (34.8 kg ha$^{-1}$ yr$^{-1}$ at Lägeren and 17.5 kg ha$^{-1}$ yr$^{-1}$ at Davos, in the early 1980s). After 1980 $c_i/c_a$ ratio started to increase again to pre-1950 levels at both sites (figure 3).

### 3.3. Effects of climate, CO$_2$ concentrations, and N deposition on WUE$_i$

Mean monthly air temperature was higher and precipitation was lower at Lägeren than at Davos (supplementary figure 1). At both sites, summer precipitation constituted the major part of annual precipitation (supplementary figure 1).

Building a GAM model of WUE$_i$ based on the most important drivers revealed that N deposition (44% rel importance), CO$_2$ concentrations (26%), and summer precipitation (14%) had the strongest effects on WUE$_i$ of the beech trees in Lägeren, while CO$_2$ concentrations (47% rel importance) and summer temperature (22%) explained most of the variance in WUE$_i$ of the spruce trees in Davos (table 2). As expected, WUE$_i$ declined with increasing summer precipitation and increased with increasing summer temperature or N deposition (supplementary figure 5). CO$_2$ concentration, N deposition, and climate together explained 75% of the modeled
Table 2. Results of the GAM of CO$_2$-corrected WUE$_i$ for beech (at Lägeren) and Norway spruce (at Davos). GAM model performance on the training dataset was $r = 0.79$ for Davos and $r = 0.77$ in Lägeren, and $r = 0.79$ for Davos and $r = 0.75$ for Lägeren on the test dataset. On the full dataset (1900–2012) performance of the GAM model was $r = 0.83$ in Lägeren, and $r = 0.80$ in Davos. AIC of the full model (i.e. all predictors included) was $-370$ for Davos, and $-306$ for Lägeren. AIC for each variable is the AIC of the full model excluding that variable (larger AIC means more important predictor), and edf is the estimated degree of freedom for each smooth term.

| Training smooth terms | edf | p-value | AIC | rel. importance | edf | p-value | AIC | rel. importance |
|-----------------------|-----|---------|-----|-----------------|-----|---------|-----|-----------------|
| $s (P_{\text{summer}})$ | 2.1 | $< 0.05$ | -299 | 14% | 1 | ns | -363 | 2% |
| $s (T_{\text{summer}})$ | 1 | ns | -306 | 9% | 1 | $< 0.05$ | -354 | 22% |
| $s (P_{\text{spring}})$ | 1 | ns | -308 | 1% | 1.8 | ns | -363 | 7% |
| $s (T_{\text{spring}})$ | 1 | ns | -307 | 6% | 1 | ns | -364 | 4% |
| $s (\text{CO}_2)$ | 1 | $< 0.05$ | -296 | 26% | 3.0 | $< 0.001$ | -335 | 47% |
| $s (\text{nitrogen})$ | 4.7 | $< 0.001$ | -305 | 44% | 1 | ns | -362 | 18% |

Figure 4. Change in WUE$_i$ with increase in atmospheric CO$_2$ concentrations before 1980 (1950–1980) and after 1980 (1981–2012), and the linear regressions for each period.

The response of WUE$_i$ to CO$_2$ in both the beech and the spruce trees declined after 1980, albeit more strongly for the beech trees (figure 4). The ratio of the increase in WUE$_i$ in response to increase in CO$_2$ (dWUE$_i$/dCO$_2$) declined by 96% after 1980 (from 0.53 to 0.02) in beech trees and declined by 72% (from 0.46 to 0.13) in spruce trees (figure 4). The strength of the relationship between measured WUE$_i$ and CO$_2$ also declined after 1980 from $r^2 = 0.5$ to $r^2 = 0.005$ in Lägeren and from $r^2 = 0.72$ to $r^2 = 0.34$ in Davos (figure 4).

3.4. Modeled WUE$_i$ with N deposition and climate scenarios
For the deciduous beech trees, testing a scenario with the GAM model where N deposition remained unchanged after 1950 showed that WUE$_i$ would have been significantly lower than the observed magnitudes, had N deposition not increased after 1950 (figure 5). Under a constant N scenario, WUE$_i$ of beech trees would have increased by 10% between 1900 and 2012 as opposed to the 30% increase that was observed. The constant climate scenario (for which summer temperature and summer precipitation were kept unchanged after 1950) did not affect WUE$_i$ significantly, and WUE$_i$ showed a decline in rate of increase after 1980, similar to that of the
measured WUE$_i$ (figure 5). For the coniferous spruce trees in Davos, in both scenarios (constant N and constant climate) regardless of whether nitrogen deposition or climate remained unchanged after 1950, WUE$_i$ continued to increase after 1980 in parallel to increased CO$_2$ concentrations (figure 5).

4. Discussion

We observed a clear regime shift in long-term forest WUE$_i$ over the past century and identified an important relationship between N deposition and WUE$_i$ trends at the site with greater deposition values. Our observations were collected from sites dominated by two widespread European species (*Fagus sylvatica* and *Picea abies*) in Switzerland, and with very different deposition levels: one mixed forest close to agriculture production sites at 682 m a.s.l. (maximum N deposition of 35 kg ha$^{-1}$ yr$^{-1}$) and one less polluted subalpine coniferous forest at 1639 m a.s.l. (maximum N deposition of 17.5 kg ha$^{-1}$ yr$^{-1}$). Based on our observations, we highlight the importance to include N deposition trends in combination with climate, in future analysis of tree rings that aim to understand long-term carbon–water relation in forests (Rinne *et al* 2010, Rayback *et al* 2020).

4.1. CO$_2$ effect on WUE$_i$

The increase in WUE$_i$ over the past century has been predominantly attributed to increased CO$_2$ concentrations (i.e. the CO$_2$ fertilization effect) (Frank *et al* 2015, Weiwei *et al* 2018, Molina *et al* 2019), particularly in long-term (i.e. tree ring) studies (Silva and Horwath 2013). In contrast to most records that show a proportional increase in WUE$_i$ with CO$_2$ increase, we found a weakening rate of change in WUE$_i$ after 1980 that was concurrent with a clear regime shift in N deposition (figure 4), albeit with a differences between the two forests that had a considerable difference in N deposition loads.

Recently, a diminishing rate of WUE$_i$ change with CO$_2$ in the 2nd half of the 20th century was reported based on a global meta-analysis of tree ring $\delta^{13}C$ (Adams *et al* 2020) and similarly in a study across temperate forests in the northeastern USA (Belmecheri *et al* 2021). The latter was explained with changes in precipitation regimes, showing that particularly in the long-term, climatic factors act on WUE$_i$ in opposite directions as CO$_2$, and have a significant effect on the CO$_2$ response of forests. While leaf-level studies show that N deposition could potentially affect leaf photosynthetic capacity (Liang *et al* 2020) and reduce sensitivity of CO$_2$ assimilation towards higher concentration (de Kauwe *et al* 2016), establishing a clear link would require further testing with a larger number of observations across species and site conditions.

4.2. N deposition effect on long-term WUE$_i$

We identified an important relationship between N deposition and WUE$_i$, in the study site where N deposition levels were high (peak of 34.8 kg ha$^{-1}$ yr$^{-1}$) that echoes findings of fertilization experiments and long-term observations that identified a significant effect of N deposition on WUE$_i$ and tree ring carbon isotope discrimination (see for...
Aboveground uptake of N from the atmosphere contributes 20%–40% of the requirement for growth and unlike uptake through the roots that is metabolically regulated, N uptake via the canopy is not limited by any mechanisms (Harrison et al 2000, Burkhardt et al 2012). Adapted to more nutrient-poor shallow soils at high elevations, the conifers have a higher capacity for N uptake via the crown as compared to deciduous beech that presumably relies more on root N uptake and tree-internal N cycling (e.g. Bauer et al 2000, Jussy et al 2004) which could underpin some of the differences observed in response to N between the two sites, while noting that there is significantly lower N deposition loads at the coniferous site in this study and at higher elevations in general (EEA 2014).

The higher WUEi, that we observed in the spruce forest in Davos is a trait typical of conifers compared to broadleaved species (Frank et al 2015). This is mainly explained by the more sclerophyllous foliage architecture in conifers and a greater coupling with the atmosphere and changes in the surface humidity (Jones et al 1992, Niinemets et al 2011). Conifers have a vascular system that is more susceptible to hydraulic failure but have a more isohydric stomatal response that leads to a relatively constant leaf water potential (lower risk of embolism) but a larger decline in stomatal conductance (gs) in response to reduced soil water potential. This increases their overall WUEi relative to deciduous trees (Gharun et al 2020).

### 4.3. Disentangling climate versus N effect

Increase in atmospheric CO2 concentrations is known to enhance photosynthetic rate of trees (Gunderson and Wullschleger 2011), constrain transpiration as stomata tend to close under elevated CO2 (Peñuelas et al 1995), and enhance WUEi (Battipaglia et al 2013). But also increased N deposition can positively affect WUEi via increases in foliar N-induced photosynthetic capacity in N-limited ecosystems (e.g. temperate forests) (Brueck 2008, Guerrieri et al 2011). There is also evidence that reports adverse effects of high atmospheric N deposition on plant growth and foliar C gain in forest ecosystems leading to N saturation (Aber et al 1995, Magill et al 2000), suggesting that the effect of increased N deposition on WUEi in forest ecosystems is less clear than that of elevated CO2. Dynamics of N effect on carbon–water relations can be complex and make it difficult to infer a clear relationship. For example, N deposition is well known to enhance leaf N status and intrinsic WUEi but have a more isohydric stomatal response that leads to a relatively constant leaf water potential (lower risk of embolism) but a larger decline in stomatal conductance (gs) in response to reduced soil water potential. This increases their overall WUEi relative to deciduous trees (Gharun et al 2020).

Strategies of trees in their gas exchange have been conceptualized by three general patterns in how ci/c3 varies with increasing CO2 (Sauer et al 2004): (a) ci remains constant or (b) the ratio of ci/c3 remains constant, or (c) the difference of ci – c3 remains constant. Between 1900 and 1950, we observed a constant ci/c3 ratio in Norway spruce, indicating a proportional regulation of A and gs (figure 3). The mean ratio of ci/c3 of the beech trees in Lägeren declined significantly between 1950 and 1980 (from 0.61 to 0.59, p < 0.05) (Rezaie et al 2018), while N deposition increased. This indicates an increase in A while gs would remain constant (Wieser et al 2018). After 1980 and with a declining N deposition, the ci/c3 ratio also started to increase to pre-1950 levels that could indicate a stronger stomatal regulation compared to A (presumably due to increase in Tsummer also at this time, figure 1).

e.g., Leonardi et al 2012, Adams et al 2021). These results emphasize the relevance of N deposition for analysis of centennial WUEi trends, particularly for forests growing across distinct climatic gradients with potentially different local trends and availability of N deposition (Etzold et al 2020).

The increase in WUEi in response to N deposition is evidence of a N-fertilization effect that happened particularly at the lowland Lägeren forest between 1950 and 1980. Evidence from leaf-level studies and N-addition experiments shows that N fertilization can significantly enhance photosynthesis per unit leaf area (Liang et al 2020). Since 1980, N deposition levels have declined, however it is possible that where deposition is high, N remains available even after decline, due to increased soil N and particularly increased mineralization in more recent decades when temperatures have continuously increased (Bagherzadeh et al 2008). The response of different tree species to changes in N deposition depends also on the shift in resource availability, not just at the leaf level, but also belowground, e.g. by changing the rate of organic matter decomposition (Janssens et al 2010). Multiple changes could happen in response to increased N, e.g. shift in allocation between fine and coarse roots (Högberg et al 2003, Piñeiro et al 2017), that would in turn affect carbon allocation and hydraulic conductivity of the plant, access to soil moisture, and response of the stomata which would directly affect plant gas exchange dynamics (Damour et al 2010).

The interaction between increased N, whole plant productivity, changes in the root:shoot ratio, and plant conductivity can lead to diverse effects from N on stomatal conductance, and ultimately on plant water use efficiency (WUE). For example, N deposition is known to enhance photosynthetic rate of trees (e.g. known to enhance leaf N status and intrinsic WUEi (Gunderson and Wullschleger 2011), constrain transpiration as stomata tend to close under elevated CO2 (Peñuelas et al 1995), and enhance WUEi (Battipaglia et al 2013). But also increased N deposition can positively affect WUEi via increases in foliar N-induced photosynthetic capacity in N-limited ecosystems (e.g. temperate forests) (Brueck 2008, Guerrieri et al 2011). There is also evidence that reports adverse effects of high atmospheric N deposition on plant growth and foliar C gain in forest ecosystems leading to N saturation (Aber et al 1995, Magill et al 2000), suggesting that the effect of increased N deposition on WUEi in forest ecosystems is less clear than that of elevated CO2. Dynamics of N effect on carbon–water relations can be complex and make it difficult to infer a clear relationship. For example, N deposition is well known to enhance leaf N status and intrinsic WUEi but have a more isohydric stomatal response that leads to a relatively constant leaf water potential (lower risk of embolism) but a larger decline in stomatal conductance (gs) in response to reduced soil water potential. This increases their overall WUEi relative to deciduous trees (Gharun et al 2020).

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of N on stomatal conductance ($g_s$), carbon isotope discrimination, and WUE$_i$, particularly when combined with drought (Levesque et al 2017, Rayback et al 2020). In our study however, mean annual climatic water balance, CWB (precipitation–potential evapotranspiration) was positive throughout the past century (mean annual 523 ± 14 mm in Davos and 463 ± 17 in Lägeren) and did not have a significant trend, hence water availability was not a limitation (supplementary figure 6). However, the prevalence of drought would have changed our conclusions would have to be tested across a larger number of sites with diverse water-limitation levels.

When reflected at the ecosystem level, differences in adaptation of gas exchange across sites will have strong impacts on the ecosystem energy balance, resulting in a warmer and drier surface today than would exist without such vegetation-climate feedback. By maintaining or reducing transpiration, forests enhance partitioning of available energy into sensible heat thereby increasing surface temperatures (Teuling et al 2010, Graf et al 2020). Thus, it could be expected that although temperatures are generally lower in the subalpine coniferous forest, these ecosystems are more rapidly shifting towards warmer and drier conditions due to an increased WUE$_i$ and a tighter vegetation-climate feedback that amplifies surface heating. Studies that combine long-term gas exchange (e.g. from tree rings) with ecosystem fluxes of energy and heat exchange are further needed to test the climate forcing from tree physiological response to changes in the climate and anthropogenic emissions.

5. Conclusion

Our analysis of WUE$_i$ trends at two contrasting forest sites in Switzerland revealed that trends in WUE$_i$ covaried strongly with trends in nitrogen deposition over the 20th century. This suggests that a better understanding of nutrient and carbon cycle interactions and the degree of N limitation is key for understanding past WUE$_i$ trends and for making reliable projections in response to future climate change. Trends in WUE$_i$ and stomatal conductance modify the energy, water, and CO$_2$ exchange between the land surface and the atmosphere and should thus be considered for understanding feedbacks between the biosphere and climate.

Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.

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Conflict of interest

The authors declare no competing interest.

Author contributions

M G, N B, R S designed the study. M G, G T, B R, S K collected the data. M G analyzed the data and all authors helped draft the manuscript

ORCID iDs

Mana Gharun © https://orcid.org/0000-0003-0337-7367

Nina Buchmann © https://orcid.org/0000-0003-0826-2980

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