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Spring Water pH in Forest Catchments Is Modified through Fluctuating Discharge under Climate Change

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Abstract: Over the course of industrialization in the 20th century, vast emissions of air pollutants have occurred. The exhaust gasses contain sulfur and nitrogen oxides, which are converted to sulfuric acid and nitric acid in the atmosphere. This causes acid rain to enter aquatic and terrestrial ecosystems, the most serious consequence of which is large-scale forest dieback across Europe and North America. However, through various political measures, the exhaust gasses have been reduced and, thus, acid rain and forest dieback were stopped. Nevertheless, the lingering effects of this pollution are still present today and are reflected in hydrochemistry. More recently, fluctuating precipitation regimes are causing additional stress to ecosystems in Central Europe. Climatic extremes are becoming more pronounced with climate change. Substantial differences between drought years and years with regular precipitation are directly altering the discharge of springs. Now, two overlapping and interacting syndromes of environmental pressures can be studied in these small catchments at a landscape scale: (1) acidification and (2) climate change. In this long-term study, the waters of 102 forest springs, located in two neighboring forest landscapes in north-eastern Bavaria, Germany (Frankenwald and Fichtelgebirge), were investigated over 24 years (1996 to 2020). By linking changes in pH values with changes in precipitation and spring discharge, we found that pH increases with decreasing discharge and decreasing precipitation. This effect was strongest in the Frankenwald compared to the Fichtelgebirge. We hypothesize that this temporal pattern reflects the longer residence time and, in consequence, the increased buffering of acidic interflow in small catchments during periods of drought. However, this should not be misinterpreted as rapid recovery from acidification because this effect fades in times of enhanced precipitation. We recommend that fluctuations in weather regimes be considered when investigating biogeochemical patterns throughout forest landscapes.

Keywords: acid rain; drought; helocrene springs; catchment acidification; climate change; Frankenwald; Fichtelgebirge

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1. Introduction

During the 20th century, unregulated industrial progress and accelerated socio-economic development created a legacy of severe air pollution and other environmental impacts. The local acidification of rainwater through emissions from coal-burning factories was first observed in Manchester by Robert Angus Smith [1] in the middle of the 19th century.

Yet, by the middle of the 20th century, it had become a widespread phenomenon across Central and Northern Europe [2,3]. With the rapid growth of industrial emissions during and after the Second World War, the problem of acidic precipitation reached a peak. Its consequences culminated in extensive forest decline ("Waldsterben"), which would become an emblematic grievance of environmental movements in the latter half of the 20th century [4–6].

In the 1960s, the discovery of the effects of acidic precipitation on the limnic systems of Swedish lakes led to the foundation of the Swedish Environmental Protection Agency [7,8]. The affected landscapes were characterized by siliceous bedrock and soils with low buffer capacity towards acidic waters. In Germany, forest decline due to acid rain was also aggravated in siliceous mountain ranges with humid climates and soils similarly unable to compensate for acidic depositions [9,10]. Evidently, the petrography of bedrock plays a significant role in soil buffering capacity [11,12].

Forest decline, as an apparent consequence of the deposition of acidic compounds, became a major topic by the end of the 1980s [6]. The effects of acidic precipitation and the precise ecological mechanisms of forest decline were too complex to be explained by existing knowledge at the time. The emerging threats to forest ecosystems inspired a bulk of ecological research. The acidification of forest soils and aquifers was found to negatively affect biodiversity, surface waters, groundwaters, soils, and entire forest ecosystems [10,13–16]. The mounting evidence of the devastating impacts of acid rain became a "game changer both scientifically and policy-wise" [17]. Eventually, acid rain became widely recognized as the greatest environmental threat of modern times, stimulating the development of less polluting technologies and their implementation. With the establishment of environmental regulations, measures, and policies in Europe and North America in the 1980s and 1990s, acidic precipitation was significantly reduced [18–20]. Today, there is far less deposition of sulfuric compounds, as Europe and Northern America have reduced their SO_2 emissions by 70–80% since 1990. [19,21]. Europe has reduced its SO_2 emissions from 55 Tg in 1980 to 15 Tg in 2004 [22]. However, this does not apply to nitrogen depositions, as emissions of NH_3 are still generally unregulated [23,24]. Furthermore, large parts of deposited compounds are still stored in soils and substrates. Complete ecological remediation cannot be expected in such a short period of time [10].

Research on water regimes in small, forested catchments has provided important contributions to the field of biogeochemistry in recent decades. In catchments of the northeastern United States, changes in pH and acid-neutralizing capacity (ANC) have been linked to the legacy of sulfuric deposition [25]. In the Hubbard Brook Experimental Forest, small catchments were used for treatments to better understand the recovery process from acidic precipitation [26]. Catchment-scale experiments included fertilization of the entire Hubbard Brook area using a mineral, wollastonite ($CaSiO_3$), with the intention of increasing pH, ANC, and the base saturation of soil solution and stream water, thereby reversing acidification and improving conditions for forest growth [27]. The results were positive and showed a decrease in inorganic monomeric aluminum and increases in calcium, silicic acid, pH, and ANC in soil solutions and stream waters [28]. Comparable results have also been observed in European forests with respect to the regeneration of forest ecosystems after acidification [29,30].

Currently, acid rain is no longer the most pressing environmental issue. Instead, forests and other ecosystems across the planet are increasingly under stress due to the various facets of climate change. Vegetation reacts more sensitively to fluctuations in precipitation regimes and to extreme weather events, than to long-term trends in mean annual temperatures. Extreme climatic events, such as the 2003 drought in Europe, have been shown to affect the hydrochemistry of small catchments [31]. The dense bedrock in the siliceous mountain ranges of Germany, composed primarily of metamorphic rocks, causes the lateral flow of water [32] and therefore shortens the residence time. Due to the shallow aquifers [10], the discharge of these small catchments is thus driven primarily by interflow within the surface near Periglacial slope deposits [32–34]. The shallow interflow is transported at a depth of 2 to 4 m. As the catchments are small, the maximum distance that is covered is in the range of 100 m. Thus, this shallow groundwater is closely linked to local precipitation regimes. This is why forest springs seem to react so quickly to changes in precipitation.

In this study, we aim to investigate landscape-scale disturbance interactions between two major environmental problems: (1) acidification and (2) climate change.

We hypothesize that reduced precipitation and discharge from catchments, related to periods of drought, will be reflected in increasing spring water pH values due to prolonged residence time within shallow aquifers.

2. Materials and Methods

2.1. Study Area

We investigated the influence of discharge fluctuations on spring water pH over three decades at 102 forest springs. The springs are located in Upper Franconia in two neighboring forested landscapes, Frankenwald and Fichtelgebirge (49.9°–50.4° N, 11.1°–12.2° E), which cover an area of about 780 and 550 km^2, respectively, and are characterized as siliceous low mountain ranges (Figure 1). The altitude of these two landscapes ranges from 260 to 1051 m. a.s.l., and the altitude of our spring sites from 388 to 909 m. a.s.l. The bedrock is relatively homogeneous in both areas. The bedrock composition of Frankenwald is mainly characterized by greywacke and slate, whereas Fichtelgebirge by phyllite and granite. Due to these differences in bedrock composition, the waters in the springs of Fichtelgebirge are considerably more acidic when compared to those in Frankenwald [35]. The dense metamorphic bedrock of low mountain ranges causes groundwater to flow close to the surface as so-called interflow. This leads to the emergence of numerous shallow springs, which, according to Thienemann's (1924) [36] morphological categorization of springs, belong to the helocrene type. They are distinguished by diffuse flow with low-to-medium discharge that generally ranges from 0.02 to 2 L/s. The catchments are covered by forest that is composed mainly of Norway spruce (*Picea abies* [L.] H. Karst.) but, in some areas, beech (*Fagus sylvatica* L.) and other broad-leaved species also prevail. Norway spruce would naturally only occur in the higher ranges of both study areas but is the main silvicultural tree in the area. The mean annual temperatures range between 5 and 7 °C, and the total annual precipitation between 750 and 1200 mm. In 2003 and 2018, this area, as well as large parts of Europe, were affected by severe drought, with the latter drought affecting forests even more severely than 2003 [37]. The years 2019 and 2020 were also very dry years, with groundwater levels having still not recovered from 2018.

Acidic deposition from industrial emissions, which peaked in the 1970s and 1980s, strongly affected the area. The low buffering capacity of siliceous bedrock contributed greatly to the acidification of the catchments. Since then, no significant signs of recovery have been observed [10].

2.2. Data Collection

In 1989, Beierkuhnlein and Durka [35] began studying the vegetation of springs in Frankenwald and Fichtelgebirge, respectively, with the aim of identifying bioindicators of certain hydrochemical conditions for long-term ecological monitoring. Spatial distribution, altitude, and climatic variation played the largest role in the selection of springs for long-term monitoring.

The springs evenly cover the entirety of the two forested landscapes of Frankenwald and Fichtelgebirge, boasting a range of different altitudes, climates, and local environmental factors.

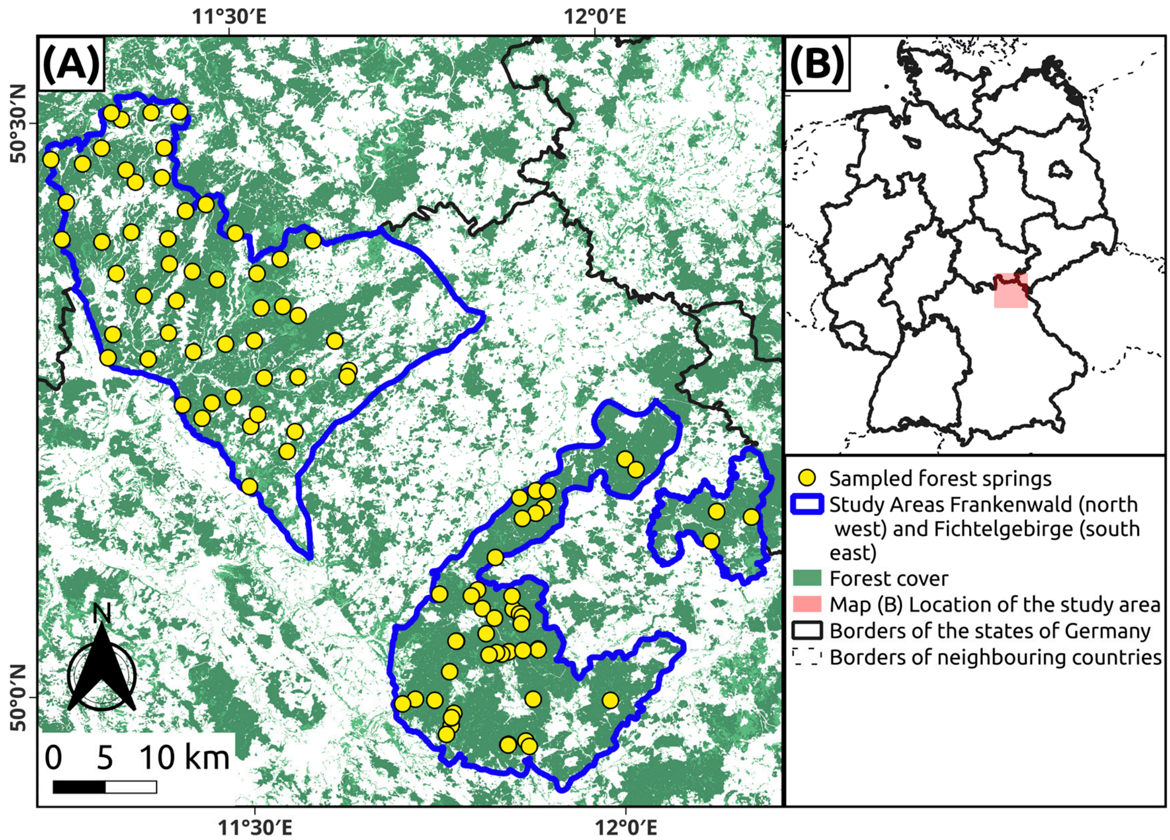


Figure 1. (**A**) The study areas of Frankenwald and Fichtelgebirge are located in northeastern Bavaria, Germany. The map shows the study areas based on the "Naturräumliche Gliederung Bayerns" [38] in blue as well as the locations of the sampled springs (yellow dots). In Frankenwald and Fichtelgebirge, 52 and 50 springs, respectively, were investigated as permanent sites since 1996. Forest cover is based on the Copernicus Forest Type 2018 product [39]. (**B**) The location of the study area in northeastern Bavaria within Germany. Thick, black lines represent the states of Germany, and dotted lines the neighboring country borders.

Samples for our analysis were collected at different periods over the years in autumn (September and October) from 1996 to 2020. In this period of about 24 years, springs were sampled 11 times at irregular intervals (Table 1). The spring sampling process from 1996 to 2020 remained unchanged. Water samples were taken from the highest point of the saturated area. Sampling was performed at the location where groundwater turns into surface runoff within the spring by digging a small hole and waiting for the water to clear, after which a measuring instrument was situated. pH was measured in situ. A pH cond 340i (WTW GmbH, Weilheim, Germany) device with a TetraCon 325 probe (WTW GmbH, Weilheim, Germany) was used for conductivity, and a SenTik81 (WTW GmbH, Weilheim, Germany) for pH and temperature measurements. Calibration of the probes was performed each day prior to sample collection. The approximate discharge was measured by placing a 100 mL graduated cylinder in a stream and measuring the time required to fill it. If, for some reason, cylinder placement was not possible, the discharge was determined based on one of the six categories shown in Table 2. A small number of springs could not be sampled because of either very low discharge or no discharge at all.

Table 1. Years and months in which the data used in this study were collected.

Year	1996	2003	2004	2005	2006	2007	2012	2013	2018	2019	2020
Month	September/ October	September	September	September/ October	September	September	September	September	September	September	September

Table 2. Descriptive classification of spring discharge.

Discharge Category	Approximate Discharge [L/s]
without discharge, water flow not visible, sampling not possible	0.00 L/s
seeping, water flow not visible, sampling hardly possible	0.02 L/s
very low, water flow visible, sampling sometimes possible	0.05 L/s
low, water flow visible and slightly turbulent, sampling usually possible	0.20 L/s
middle, water flow turbulent, sampling well possible	0.50 L/s
high, water flow strongly turbulent, sampling easily possible	1.00 L/s
very high, torrent-like flow	2.00 L/s

2.3. Data Analysis

Unless otherwise mentioned, all data preparation and analysis were carried out in R version 4.4 [40]. We used three datasets in our analysis: Frankenwald, Fichtelgebirge, and a combination of both regions.

We started our analysis by visualizing temporal trends in pH fluctuations in the springs of Frankenwald and Fichtelgebirge. We used annual precipitation data from DWD (Deutscher Wetterdienst) [41] and LWF (Bayerische Landesanstalt für Wald und Forstwirtschaft) [42] to create interpolation maps of local precipitation values in ArcGIS [43]. We then calculated the precipitation sum for each spring location 180 days before sampling. We calculated the differences in pH values, discharge, and precipitation between an initial year and all subsequent years for each spring that had been sampled in both years. This procedure was repeated for all years in the time series.

Because spring discharge is closely related to local precipitation, we first compared changes in pH to corresponding changes in local precipitation with linear regression. Next, with the expectation of finding a direct link between discharge and pH, we used boxplots to compare pH values at each level of discharge.

We fitted linear mixed effects models (LMMs) for the Frankenwald, Fichtelgebirge, and both regions combined with changes in pH as a response and changes in discharge as a predictor with fixed effects. Spring location was included as a random effect to directly account for variability in the environmental conditions of each spring. All LMMs were fitted using the “lme4” package [44] with the following formula:

$$\Delta\, pH \;\sim\; \Delta\, Discharge + (1|\; SpringID)$$

3. Results

Visualization of the pH fluctuations over time for the combined study regions (Figure 2a), Frankenwald (Figure 2b), and Fichtelgebirge (Figure 2c) revealed moderate peaks in pH values corresponding to the recent drought years of 2003 and 2018 in Central Europe. These peaks can be recognized in all three datasets but are most pronounced for the Frankenwald.

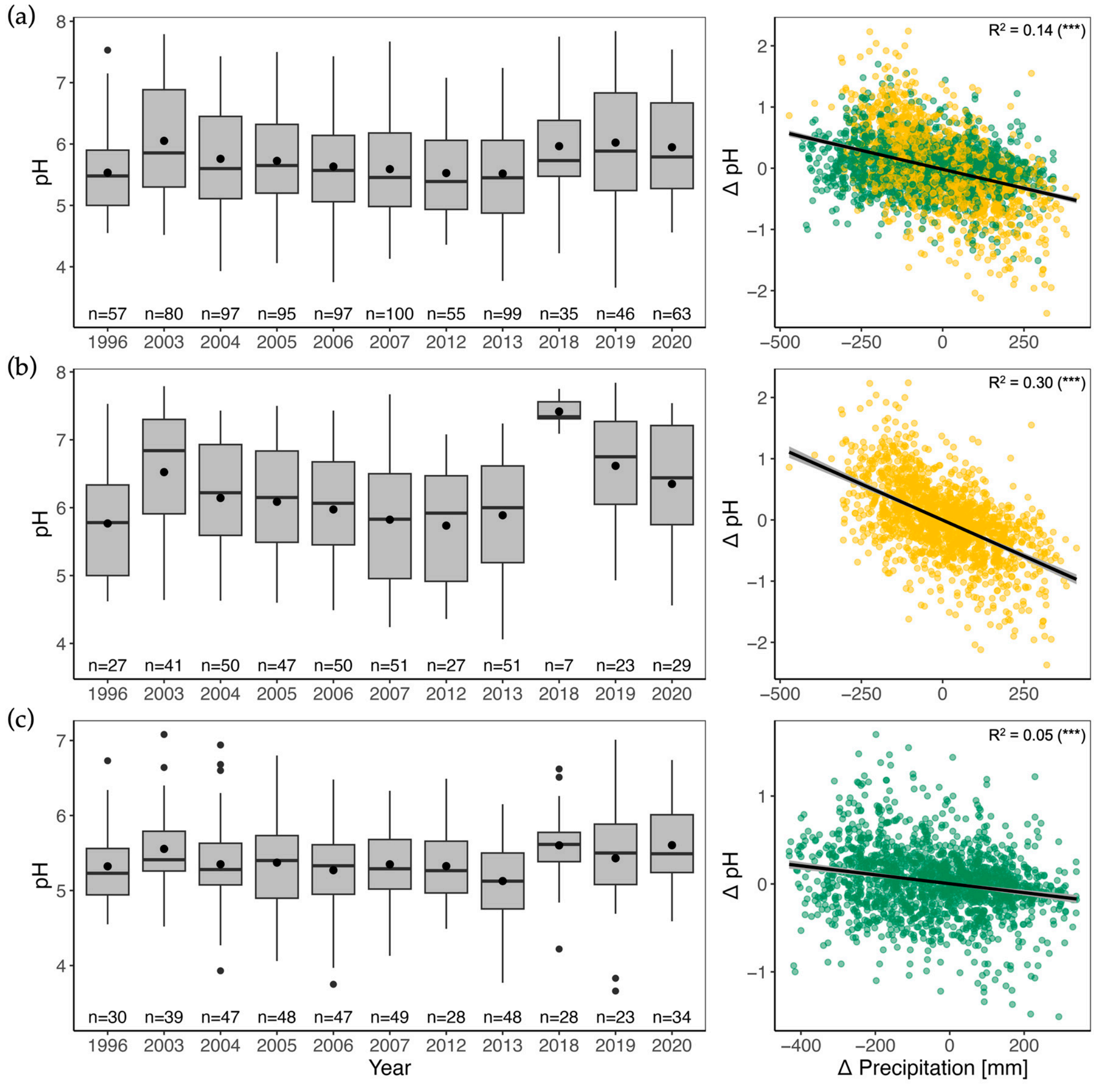
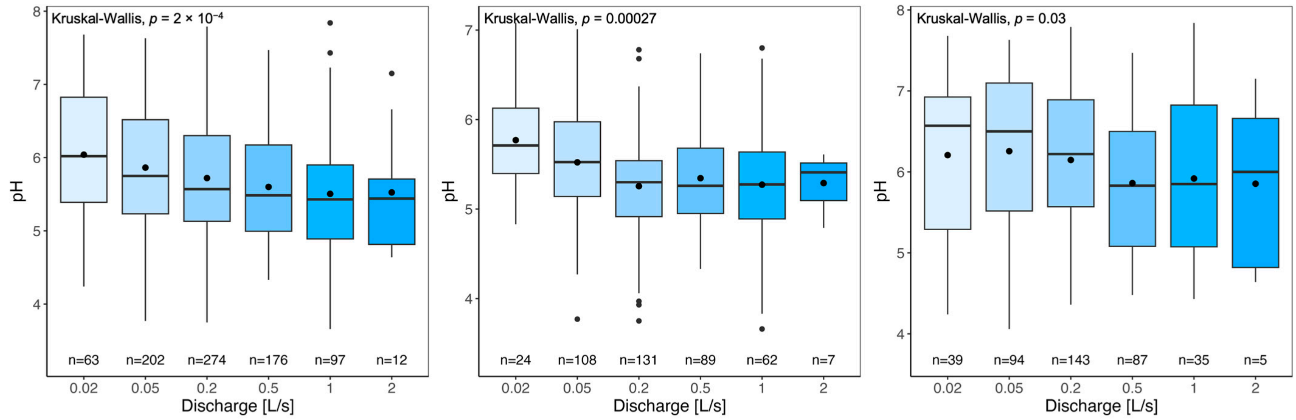


Figure 2. (**a**) Fichtelgebirge and Frankenwald combined; (**b**) Frankenwald; (**c**) Fichtelgebirge. Left panels depict pH fluctuations over time across the whole study period of 1996–2020 as boxplots. The gray box represents the interquartile range between the 25th and 75th percentile of the data, the vertical lines the minimum/maximum range, and black dots above/below the lines represent outlier values. The thick, horizontal line represents the median value, with the black dot next to it representing the mean. Right panels show scatter plots and linear regression results (black line) between changes in pH and changes in precipitation. Points in yellow refer to Frankenwald, while points in green to Fichtelgebirge. The R^2 and the significance level of the regression are noted in the top right corner (*** $p < 0.001$).

Linear regression analysis was conducted to examine the relationship between changes in pH and corresponding changes in discharge over the years. The analysis revealed significant responses of pH to precipitation fluctuations. This response was strongest in the Frankenwald region, where the relationship between Δ pH and Δ discharge demonstrated a strong negative correlation (R^2 = 0.30). In Fichtelgebirge, we also found a significant negative correlation, however, this effect was comparatively weaker than in the Frankenwald (R^2 = 0.05). When both regions were combined, we found a weak–moderate negative correlation between Δ pH and Δ discharge (R^2 = 0.14).

Next, we compared spring discharge with spring water pH irrespective of time in both study areas as well as in Frankenwald and Fichtelgebirge separately (Figure 3). When both areas were considered, the data showed a consistent decrease in pH values with increasing spring discharge (Figure 3a) and an average pH value of 5.4–6.0. When looking at individual areas, a decrease in pH with increasing spring discharge can still be observed, though the trends are not as linear. The mean pH values in Frankenwald were determined to be 5.8–6.3 and 5.2–5.7 in Fichtelgebirge.



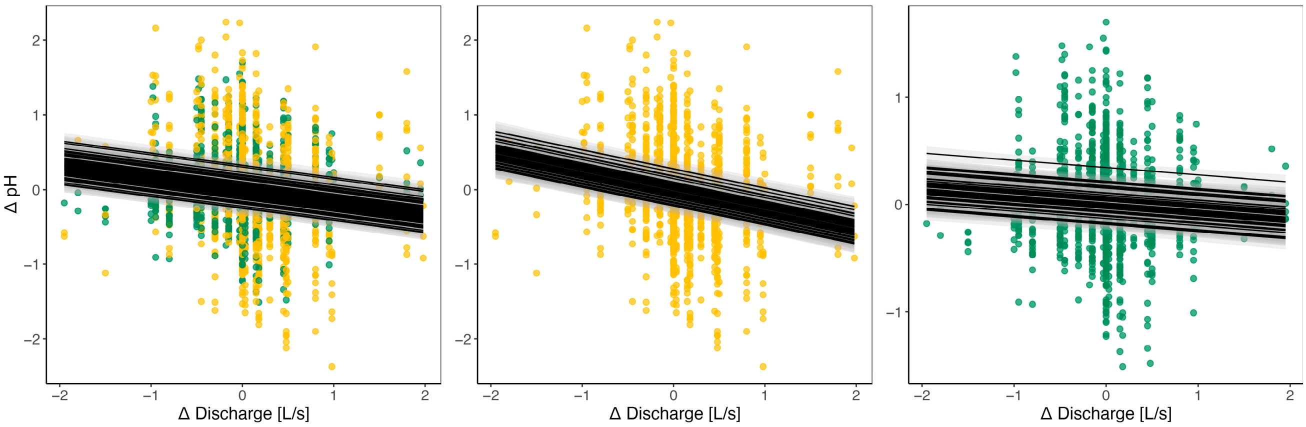
(**a**) (**b**) (**c**)

Figure 3. Comparison of spring discharge with the pH value of spring water presented as boxplots. The box represents the interquartile range between the 25th and 75th percentile of the data, the vertical lines the minimum/maximum range, and black dots above/below the lines represent outlier values. The thick, horizontal line represents the median value, with the black dot next to it representing the mean. Colors indicate different levels of discharge. The period of data collection lies between 1996 and 2020. The scaling of spring discharge is based on the descriptive classification of spring discharge from Table 2. The number of observations differs for each class. Springs with high discharge tend to be rare. In figure (**a**), the values of Frankenwald and Fichtelgebirge are combined; in (**b**) only Frankenwald and in (**c**) only Fichtelgebirge are considered.

All model parameters including effect sizes (β), standard error, and t-values of fixed effects as well as variation (σ^2) and standard deviation (σ) of random effects are presented in Table 3. Fitted LMMs for Δ pH against Δ discharge are shown in Figure 4, with spring location as a random intercept term. The fixed effect of Δ discharge was found to have a statistically significant influence on Δ pH for all three datasets. The model fitted for Frankenwald showed the strongest slope of −0.255, compared to −0.0677 for Fichtelgebirge and −0.163 for both regions. In general, we found that decreasing discharge was weakly to moderately associated with an increase in pH values.

Table 3. Model parameters for linear mixed effects models fitted for FRW (Frankenwald) and FGB (Fichtelgebirge) combined as well as for FRW and FGB separately.

	Fixed Effects	β	Std. Error	t-Value	Random Effects	σ^2	σ
FRW and FGB	Intercept	0.00854	0.0177	0.483			
	Δ Discharge	−0.163	0.0206	−7.92			
					SpringID	0.0215	0.147
					Residuals	0.240	0.490
FRW	Intercept	0.000356	0.0277	0.0130			
	Δ Discharge	−0.255	0.0353	−7.24			
					SpringID	0.0237	0.154
					Residuals	0.356	0.597
FGB	Intercept	0.0246	0.0217	1.13			
	Δ Discharge	−0.0677	0.0223	−3.03			
					SpringID	0.0177	0.133
					Residuals	0.138	0.372



(**a**) (**b**) (**c**)

Figure 4. Fitted linear mixed effect models of Δ pH for (**a**) Frankenwald and Fichtelgebirge combined; (**b**) only Frankenwald; and (**c**) only Fichtelgebirge. Points in yellow refer to Frankenwald, while points in green to Fichtelgebirge.

4. Discussion

The setting of small forest catchments with shallow groundwater transport (interflow) in Pleistocene solifluction layers enables detection of the interaction between fluctuating precipitation (and discharge) with the legacy of acidified substrates [31]. While policy changes have effectively reduced acid precipitation, sulfur compounds are still present in forest soils and enter the groundwater, leading to low pH values in helocrene springs [13]. Confounding influences such as agricultural land use or the contribution of old aquifers can be generally ruled out [35,45].

The purpose of our work was to determine whether spring water pH increases when precipitation and spring discharge decrease. We assumed that this link between pH and spring discharge is the result of longer residence time in the aquifer. Weathering bedrock leads to the presence of base cations such as calcium, magnesium, or potassium, which counteract and buffer acidic components such as nitrogen and sulfur bonds. Longer residence time in times of drought therefore allows for more buffering and neutralization of acid rain deposits, raising the pH value. To test this assumption, changes in the pH values of spring waters from 1996 to 2020 were correlated with corresponding changes in precipitation and spring discharge. We observed that pH tends to increase with a corresponding decrease in precipitation and spring discharge. This is consistent with our hypothesis that lower discharge leads to longer buffering times in the soil, thus leading to an increase in pH. The change in discharge, and consequently pH levels, is also clearly linked to drought conditions. This is particularly evident during the major droughts of 2003 and 2018 in Central Europe, when notable increases in pH levels were observed.

Springs in Frankenwald reacted with much stronger pH increases to corresponding decreases in discharge and precipitation compared to Fichtelgebirge. This difference could be explained by differences in environmental conditions between the two areas, particularly by variations in bedrock composition, with Frankenwald mainly characterized by greywacke and slate and Fichtelgebirge by phyllite and granite. Siliceous bedrock, such as granite, has been shown to have a low geogenic buffering capacity, which might further explain why pH increases were much weaker in the Fichtelgebirge [10]. Grain size differences in the rocks could also play a significant role in the observed regional discrepancies [46]. Due to the heterogenous soil conditions within the sampled catchments, the water percolates through before it is transported within the Pleistocene solifluction layers in 2–4 m depth below the surface; soil parameters around the sampled springs such as soil pH were excluded from our analysis as they do not inform about the conditions the water is exposed to on its way downhill.

Climate change is linked with emerging extreme climatic events that include periods of drought and periods of extensive precipitation, which are expected to cause significant effects in ecosystems [47]. In the recent past, changes in Central European precipitation regimes towards more pronounced periods of drought and intense precipitation have been observed [48–53]. On the other hand, the acidity of precipitation has strongly decreased, with the mean precipitation pH value measured in Fichtelgebirge by the Bavarian Environmental Ministry increasing from 3.5 within the forest because trees comb sulfur bonds out of the air and 4.0 outside of the forest in 1990 to 5 in 2013 [54], which undoubtedly also affects the pH of our sampled springs. In addition, this directly affects the spring vegetation, as precipitation pH affects the leaching of nutrients from plants [55]. While we were not able to account for pH value changes in precipitation throughout our study period due to the large spatial extent of our study area and the heterogenous distribution of precipitation, which made precipitation pH measures unfeasible, we have minimized seasonal variations by always sampling in the same time period each year.

Recently, a general close linkage between periods of drought and discharge of springs [56] as well as headwaters [57] has been documented. In forest catchments on dense siliceous rocks such as slate, greywacke, quartzite, schist, or phyllite in our investigated area in the Fichtelgebirge, the hydrological consequences of extreme fluctuations in precipitation regimes are even more pronounced. Due to the low porosity of the bedrock, the water can only circulate along thin fissures and fault, leading to the absence of a deep aquifer. The main aquifer is situated in the Pleistocene solifluction layers that cover the entire landscape with slope-dependent depths of 2–4 m. This layer is also the substrate of the Holocene soil formation. However, these current brown soils (Cambisols in WRB or Inceptisols in USDA Soil Taxonomy) [58] do not develop to depth beyond 50 to 80 cm. Rain water percolates through these soils and then is conducted in the dense base layer of the solifluction layer to the spring discharge at distances of 10 to 100 m within weeks or months, causing springs to reflect precipitation fluctuations quickly. Since we investigated springs in completely forested catchments in the low mountains of Central Europe, high fluctuations in annual precipitation were observed. This also presents one of the limitations of our dataset, which only contains seven datapoints for the exceptionally dry 2018 year [37,59], which caused most springs to fall dry. Nonetheless, the pH of the sampled springs offers a valuable insight into how this low discharge affects the acidity of these vulnerable communities

The natural vegetation and stenoecic biota of the springs are highly specialized and adapted to constant conditions in water supply and hydrochemistry [45,60,61]. Changes in these conditions are very likely to cause biodiversity loss. These forest landscapes are also still recovering from the effects of acidic precipitation in the 20th century [18,19]. Future challenges such as climate change-induced droughts as well as forest loss due to bark beetle outbreaks only further increase the vulnerability of these sensitive systems to biodiversity loss.

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References

1. Smith, R.A. *Air and Rain, the Beginnings of a Chemical Climatology*; Longmans Green: London, UK, 1872.
2. Cowling, E.B. Acid precipitation in historical perspective. *Environ. Sci. Technol.* **1982**, *16*, 110A–123A. [CrossRef]
3. Gorham, E. Acid deposition and its ecological effects: A brief history of research. *Environ. Sci. Policy* **1998**, *1*, 153–166. [CrossRef]
4. Roberts, L. Is acid deposition killing West German forests? *BioScience* **1983**, *33*, 302–305. [CrossRef]
5. Hinrichsen, D. The forest decline enignma. *BioScience* **1987**, *37*, 542–546. [CrossRef]
6. Pitelka, L.F.; Raynal, D.J. Forest decline and acidic deposition. *Ecology* **1989**, *70*, 2–10. [CrossRef]
7. Almer, B.; Dickson, W.; Ekström, C.; Hörnström, E.; Miller, U. Effects of acidification on Swedish lakes. *Ambio* **1974**, *3*, 30–36.
8. Almer, B.; Dickson, W. The discovery and early study of acidification of lakes in Sweden. *Ambio* **2021**, *50*, 266–268. [CrossRef]
9. Strohbach, M.; Audorff, V.; Beierkuhnlein, C. Drivers of plant species composition in siliceous spring ecosystems: Groundwater chemistry, catchment traits or spatial factors? *J. Limnol.* **2009**, *68*, 375–384. [CrossRef]
10. Schweiger, A.H.; Beierkuhnlein, C. The ecological legacy of 20th century acidification carried on by ecosystem engineers. *Appl. Veg. Sci.* **2017**, *20*, 215–224. [CrossRef]
11. Probst, A.; Party, J.P.; Fevrier, C.; Dambrine, E.; Thomas, A.L.; Stussi, J.M. Evidence of springwater acidification in the Vosges mountains (North-East of France): Influence of bedrock buffering capacity. *Water Air Soil Pollut.* **1999**, *114*, 395–411. [CrossRef]
12. Williard, K.W.J.; Dewalle, D.R.; Edwards, P.J. Influence of bedrock geology and tree species composition on stream nitrate concentrations in mid-Appalachian forested watersheds. *Water Air Soil Pollut.* **2005**, *160*, 55–76. [CrossRef]
13. Alewell, C.; Armbruster, M.; Bittersohl, J.; Evans, C.D.; Meesenburg, H.; Moritz, K.; Prechtel, A. Are there signs of acidification reversal in freshwaters of the low mountain ranges in Germany? *Hydrol. Earth Syst. Sci.* **2001**, *5*, 367–378. [CrossRef]
14. Stevens, C.J.; Gowing, D.J.G.; Wotherspoon, K.A.; Alard, D.; Aarrestad, P.A.; Bleeker, A.; Bobbink, R.; Diekmann, M.; Dise, N.B.; Duprè, C.; et al. Addressing the Impact of Atmospheric Nitrogen Deposition on Western European Grasslands. *Environ. Manag.* **2011**, *48*, 885–894. [CrossRef]
15. Lepori, F.; Keck, F. Effects of atmospheric nitrogen deposition on remote freshwater ecosystems. *Ambio* **2012**, *41*, 235–246. [CrossRef]
16. Garmo, Ø.A.; Skjelkvåle, B.L.; de Wit, H.A.; Colombo, L.; Curtis, C.; Fölster, J.; Hoffmann, A.; Hruška, J.; Høgåsen, T.; Jeffries, D.S.; et al. Trends in Surface Water Chemistry in Acidified Areas in Europe and North America from 1990 to 2008. *Water Air Soil Pollut.* **2014**, *225*, 1880. [CrossRef]
17. Grennfelt, P.; Engleryd, A.; Forsius, M.; Hov, Ø.; Rodhe, H.; Cowling, E. Acid rain and air pollution: 50 years of progress in environmental science and policy. *Ambio* **2020**, *49*, 849–864. [CrossRef]
18. Kopáček, J.; Hejzlar, J.; Stuchlík, E.; Fott, J.; Veselý, J. Reversibility of acidification of mountain lakes after reduction in nitrogen and sulphur emissions in Central Europe. *Limnol. Oceanogr.* **1998**, *43*, 357–361. [CrossRef]
19. Stoddard, J.L.; Jeffries, D.S.; Lükewille, A.; Clair, T.A.; Dillon, P.J.; Driscoll, C.T.; Forsius, M.; Johannessen, M.; Kahl, J.S.; Kellogg, J.H.; et al. Regional trends in aquatic recovery from acidification in North America and Europe. *Nature* **1999**, *401*, 575–578. [CrossRef]
20. Schaap, M.; Hendriks, C.; Kranenburg, R.; Kuenen, J.; Segers, A.; Schlutow, A.; Nagel, H.; Ritter, A.; Banzhaf, S. PINETI-3: Modellierung atmosphärischer Stoffeinträge von 2000 bis 2015 zur Bewertung der ökosystem-spezifischen Gefährdung von Biodiversität durch Luftschadstoffe in Deutschland. *Texte Umweltbundesamt* **2018**, *79*, 149.
21. Aas, W.; Mortier, A.; Bowersox, V.; Cherian, R.; Faluvegi, G.; Fagerli, H.; Hand, J.; Klimont, Z.; Galy-Lacaux, C.; Lehmann, C.M.B.; et al. Global and regional trends of atmospheric sulfur. *Sci. Rep.* **2019**, *9*, 953. [CrossRef]
22. Vestreng, V.; Myhre, G.; Fagerli, H.; Reis, S.; Tarrasón, L. Twenty-five years of continuous sulphur dioxide emission reduction in Europe. *Atmos. Chem. Phys.* **2007**, *7*, 3663–3681. [CrossRef]
23. Audorff, V. Vegetation Ecology of Springs: Ecological, Spatial and Temporal Patterns. Ph.D. Thesis, University of Bayreuth, Bayreuth, Germany, 2009.
24. Decina, S.M.; Hutyra, L.R.; Templer, P.H. Hotspots of nitrogen deposition in the world's urban areas: A global data synthesis. *Front. Ecol. Environ.* **2019**, *18*, 92–100. [CrossRef]
25. Palmer, S.M.; Driscoll, C.T.; Johnson, C.E. Long-term trends in soil solution and stream water chemistry at the Hubbard Brook Experimental Forest: Relationship with landscape position. *Biogeochemistry* **2004**, *68*, 51–70. [CrossRef]
26. Likens, G.E.; Driscoll, C.T.; Buso, D.C.; Mitchell, M.J.; Lovett, G.M.; Bailey, S.W.; Siccama, T.G.; Reiners, W.A.; Alewell, C. The biogeochemistry of sulfur at Hubbard Brook. *Biogeochemistry* **2002**, *60*, 235–316. [CrossRef]
27. Rosi-Marshall, E.J.; Bernhardt, E.S.; Buso, D.C.; Driscoll, C.T.; Likens, G.E. Acid rain mitigation experiment shifts a forested watershed from a net sink to a net source of nitrogen. *Proc. Natl. Acad. Sci. USA* **2016**, *113*, 7580–7583. [CrossRef]
28. Cho, Y.; Driscoll, C.T.; Johnson, C.E.; Blum, J.D.; Fahey, T.J. Watershed-Level Responses to Calcium Silicate Treatment in a Northern Hardwood Forest. *Ecosystems* **2012**, *15*, 416–434. [CrossRef]
29. Kauppi, P.E.; Mielikäinen, K.; Kuusela, K. Biomass and carbon budget of European forests, 1971 to 1990. *Science* **1992**, *256*, 70–74. [CrossRef]
30. Jandl, R.; Alewell, C.; Prietzel, J. Calcium Loss in Central European Forest Soils. *Soil Sci. Soc. Am. J.* **2004**, *68*, 588–595. [CrossRef]
31. Schweiger, A.H.; Audorff, V.; Beierkuhnlein, C. The acid taste of climate change: 20th century acidification is re-emerging during a climatic extreme event. *Ecosphere* **2015**, *6*, art94. [CrossRef]

32. Kleber, A.; Lindemann, J.; Schellenberger, A.; Beierkuhnlein, C.; Kaupenjohann, M.; Peiffer, S. Slope deposits and water paths in a spring catchment, Frankenwald, Bavaria, Germany. *Nutr. Cycling Agroecosyst.* **1998**, *50*, 119–126.
33. Kleber, A. Periglacial slope deposits and their pedogenic implications in Germany. *Palaeogeogr. Palaeoclimatol. Palaeoecol.* **1992**, *99*, 361–371. [CrossRef]
34. Semmel, A. Hauptlage und Oberlage als umweltgeschichtliche Indikatoren; Hauptlage und Oberlage als umweltgeschichtliche Indikatoren; Solifluction layers ("Hauptlage" and "Oberlage") as indicators of environmental history. *Z. Fuer Geomorphol.* **2002**, *46*, 167–180. [CrossRef]
35. Beierkuhnlein, C.; Durka, W. Beurteilung von Stoffausträgen immissionsbelasteter Waldökosysteme Nordostbayerns durch Quellwasseranalysen. *Forstw. Cbl.* **1993**, *112*, 225–239. [CrossRef]
36. Thienemann, A. Hydrobiologische Untersuchungen an Quellen. *Arch. Hydrobiol.* **1924**, *14*, 151–190.
37. Schuldt, B.; Buras, A.; Arend, M.; Vitasse, Y.; Beierkuhnlein, C.; Damm, A.; Gharun, M.; Grams, T.E.E.; Hauck, M.; Hajek, P.; et al. A first assessment of the impact of the extreme 2018 summer drought on Central European forests. *Basic Appl. Ecol.* **2020**, *45*, 86–103. [CrossRef]
38. Naturräumliche Gliederung Bayerns—Bayerisches Landesamt für Umwelt. Available online: https://www.lfu.bayern.de/natur/naturraeume/index.htm (accessed on 19 July 2024).
39. Forest Type 2018—Copernicus Land Monitoring Service. Available online: https://land.copernicus.eu/en/products/high-resolution-layer-forest-type/forest-type-2018 (accessed on 19 July 2024).
40. R Core Team. *R: A Language and Environment for Statistical Computing*; R Foundation for Statistical Computing: Vienna, Austria, 2024. Available online: https://www.R-project.org/ (accessed on 19 July 2024).
41. DWD. Climate Data Center (CDC): Grids of Monthly Averaged Daily Air Temperature (2m) over Germany, Version v1.0. 2021. Available online: https://opendata.dwd.de/climate_environment/CDC/grids_germany/monthly/air_temperature_mean/ (accessed on 19 July 2024).
42. Bayerische Waldklimastationen, Bayerische Landesanstalt für Wald und Forstwirtschaft. Available online: https://www.lwf.bayern.de/wks (accessed on 19 July 2024).
43. ESRI. *ArcGIS Desktop: Release 108.2*; Environmental Systems Research Institute: Redlands, CA, USA, 2024.
44. Bates, D.; Maechler, M.; Bolker, B.; Walker, S. Fitting Linear Mixed-Effects Models Using lme4. *J. Stat. Softw.* **2015**, *67*, 1–48. [CrossRef]
45. Audorff, V.; Kapfer, J.; Beierkuhnlein, C. The role of hydrological and spatial factors for the vegetation of Central European springs. *J. Limnol.* **2011**, *70*, 9. [CrossRef]
46. Dill, H.G.; Buzatu, A.; Kleyer, C.; Balaban, S.I.; Pöllmann, H.; Füssel, M. A natural GMS Laboratory (Granulometry-Morphometry-Situmetry): Geomorphological-sedimentological-mineralogical terrain analysis linked to coarse-grained siliciclastic sediments at the basement-foreland boundary (SE Germany). *Minerals* **2022**, *12*, 1118. [CrossRef]
47. Jentsch, A.; Kreyling, J.; Beierkuhnlein, C. A new generation of climate-change experiments: Events, not trends. *Front. Ecol. Environ.* **2007**, *5*, 365–374. [CrossRef]
48. Boergens, E.; Güntner, A.; Dobslaw, H.; Dahle, C. Quantifying the Central European Droughts in 2018 and 2019 With GRACE Follow-On. *Geophys. Res. Lett.* **2020**, *47*, e2020GL087285. [CrossRef]
49. Mohr, S.; Wilhelm, J.; Wandel, J.; Kunz, M.; Portmann, R.; Punge, H.J.; Schmidberger, M.; Quinting, J.F.; Grams, C.M. The role of large-scale dynamics in an exceptional sequence of severe thunderstorms in Europe May–June 2018. *Weather Clim. Dynam.* **2020**, *1*, 325–348. [CrossRef]
50. Zeder, J.; Fischer, E.M. Observed extreme precipitation trends and scaling in Central Europe. *Weather. Clim. Extremes* **2020**, *29*, 100266. [CrossRef]
51. European Environment Agency (EEA). *Europe's Changing Climate Hazards*; Publications Office: Copenhagen, Denmark, 2021; ISBN 1977-8449.
52. Moravec, V.; Markonis, Y.; Rakovec, O.; Svoboda, M.; Trnka, M.; Kumar, R.; Hanel, M. Europe under multi-year droughts: How severe was the 2014–2018 drought period? *Environ. Res. Lett.* **2021**, *16*, 34062. [CrossRef]
53. World Meteorological Organization (WMO). *State of the Global Climate 2021: WMO Provisional Report*; WMO: Geneva, The Switzerland, 2021.
54. 25 Jahre Versauerungsmonitoring. Available online: https://www.lfu.bayern.de/wasser/25_jahre_versauerungsmonitoring/niederschlag/index.htm (accessed on 2 September 2024).
55. Tukey, H.B. The leaching of substances from plants. *Annu. Rev. Plant Physiol.* **1970**, *21*, 305–324. [CrossRef]
56. Staśko, S.; Buczyński, S. Drought and its effects on spring discharge regimes in Poland and Germany during the 2015 drought. *Hydrol. Sci. J.* **2018**, *63*, 741–751. [CrossRef]
57. Vlach, V.; Ledvinka, O.; Matouskova, M. Changing Low Flow and Streamflow Drought Seasonality in Central European Headwaters. *Water* **2020**, *12*, 3575. [CrossRef]
58. IUSS Working Group WRB. *World Reference Base for Soil Resources. International Soil Classification System for Naming Soils and Creating Legends for Soil Maps*, 4th ed.; International Union of Soil Sciences (IUSS): Vienna, Austria, 2022.
59. Buras, A.; Rammig, A.; Zang, C.S. Quantifying impacts of the 2018 drought on European ecosystems in comparison to 2003. *Biogeosciences* **2020**, *17*, 1655–1672. [CrossRef]

60. Beierkuhnlein, C. Räumliche Analyse der Stoffausträge aus Waldgebieten durch Untersuchung von Waldquellfluren. *Die Erde* **1991**, *122*, 291–315.
61. Schweiger, A.H.; Beierkuhnlein, C. Water temperature and acidity regime shape dominance and beta-diversity patterns in the plant communities of springs. *Front. Biogeogr.* **2014**, *6*, 132–143. [CrossRef]