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Recovery of Streams in the Harz National Park (Germany)—The Attenuation of Acidification

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Abstract: Between 1995 and 2022, 19 measuring points in small and medium sized streams in the Harz National Park, Germany, were sampled. The samples were evaluated in terms of their macroinvertebrate (MI) biology and hydrochemistry. Nearly all streams showed a natural hydromorphology, and low values of biological oxygen demand (BOD) characteristic for rivers not contaminated by organic matter. Nevertheless, in the 1990s, most streams were still only settled by a small number of MI species. However, by 2022, the MI species number had doubled or tripled in most cases, with a maximum increase from 14 to 52. There is a clear correlation between species number and pH. At 15 of the 19 sampling sites, the acidity class has gotten better by at least one value. Thus, acid-sensitive species, mainly from the taxonomic orders Trichoptera, Plecoptera, and Ephemeroptera, have been able to settle higher altitudes, as well as formerly acidic reaches. In general, the streams contain a very specific macroinvertebrate fauna that emphasizes the conservation value of the Harz National Park. Attenuation of acidification has not only influenced the MI diversity. Along with the increase in pH, fish populations have recovered, and formerly fish-free stream sections have been recolonised. The biological recovery of the streams has also been fostered by the breakdown of spruce forest monocultures in the surroundings, the natural development of deciduous trees on the banks, and increasing levels of DOC (dissolved organic carbon).

Keywords: acidification; mountain streams; forest change; macroinvertebrates

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1. Introduction

Acid deposition, resulting from the atmospheric transport of acidifying compounds emitted during the incineration of fossil fuels, particularly of sulphur-rich fuels, has historically resulted in both chronic and episodic acidification in many mountain streams [1,2]. Prolonged deposition has depleted watershed reservoirs of the base cations associated with the acid neutralizing capacity (ANC) [3]. ANC is the ability to buffer the effects of acid inputs and is determined by the balance between the concentrations of anthropogenic and geological acidic anions (i.e., sulphate SO_4^{2-}, nitrate NO_3^-, nitrite NO_2^-, and chloride Cl^- ions) and base cations provided by a watershed's underlying bedrock (i.e., calcium Ca^{2+}, magnesium Mg^{2+}, potassium K^+, and sodium Na^+ ions). Stream acidification has been shown to result in emigration, decreased biomass, and reduced recruitment of fish, as well as decreased fish and macroinvertebrate (MI) species diversity [4–8]. In the 1990s, we found that acidic streams of the Harz National Park had about 75% less MI species compared to non-acidic ones [8].

Thus, for several decades, surface water acidification has been recognized as a major environmental problem in many parts of Europe and North America. However, studies that have been performed from 2000 onwards have often provided evidence for (at least a partial) recovery from acidification in response to decreasing emissions of acidifying pollutants [9–14]. In Europe, recovery of surface waters was most significant in the Czech Republic and Slovakia, moderate in Scandinavia and the UK, but comparatively weak in Germany [10]. A widespread decrease in SO_4^{2-} and aluminium (Al^{3+}), as well as an increase in the ANC, basic cations (especially Ca^{2+}), and pH has been observed. It was also found that the recovery from acidification in Europe and North America is very different and depends on a range of factors, including the magnitude of deposition changes and catchment characteristics [13]. Most regions showed decreasing SO_4^{2-} concentrations and improvement in at least one indicator of chemical recovery (alkalinity, ANC, or pH). Nitrate remained largely unchanged, and dissolved organic carbon increased significantly in half of the regions [15]. Besides chemical monitoring, long-term recovery of the MI fauna is less frequently determined. Thus, the University of Applied Sciences Magdeburg-Stendal has conducted hydrochemical and hydrobiological research of running waters since 1994. This monitoring program has demonstrated the lengthwise development of acidification in selected streams and assessed the MI communities and their relationships to the water quality over a prolonged period [8,16].

This paper summarizes the main results of these monitoring programmes until 2022, with a special focus on aquatic MI. Conclusions are drawn for setting priorities for further protection and development.

2. Materials and Methods

2.1. Study Area

With almost 25,000 hectares, the Harz National Park is one of the largest national parks in Germany. It is located on the former inner German border in what are now the federal states of Saxony-Anhalt and Lower Saxony (Figure 1). The highest point is the Brocken Mountain at 1141 m. The natural heritage was acknowledged by the foundations of the Hochharz National Park (Saxony-Anhalt) in 1990 and the Harz National Park (Lower Saxony) in 1994. Since 2006, both areas have formed the Harz National Park.

Originally, 97% of the area was covered with deciduous and coniferous forests, as well as rocks, bogs, and mountain streams. Due to its high elevation, the Brocken region is normally an area of high precipitation. The annual precipitation is about 1600 mm per year [17]. However, in recent years, hard drought periods, storms, and pests (bark beetles) have led to the death of large areas of the spruce monocultures, and also, to a lesser degree, of near-natural forests (Figure 2).

The Harz National Park is part of the watershed between the River Elbe (with its Kalte Bode and Holtemme tributaries) and the River Weser (with its Ilse, Ecker, Radau, and Oder tributaries). The sampling area covers mostly the upper reaches of these streams. These waterbodies are characterized by natural hydromorphology without anthropogenic disturbances, dominant coarse mineral bottom substrates, and by more or less high flow velocities up to 2 m/s. Until the year 2000, at elevations of 800 m, their water temperature never exceeded 8 °C, and at 420 m very infrequently 12 °C [8]. However, as a result of climate change and deforestation, temperatures are increasing, and in summer can episodically reach more than 20 °C.

The most common type of bedrock in the upper Harz region consists of electrolyte-poor granite, which makes the area particularly susceptible to acidification.

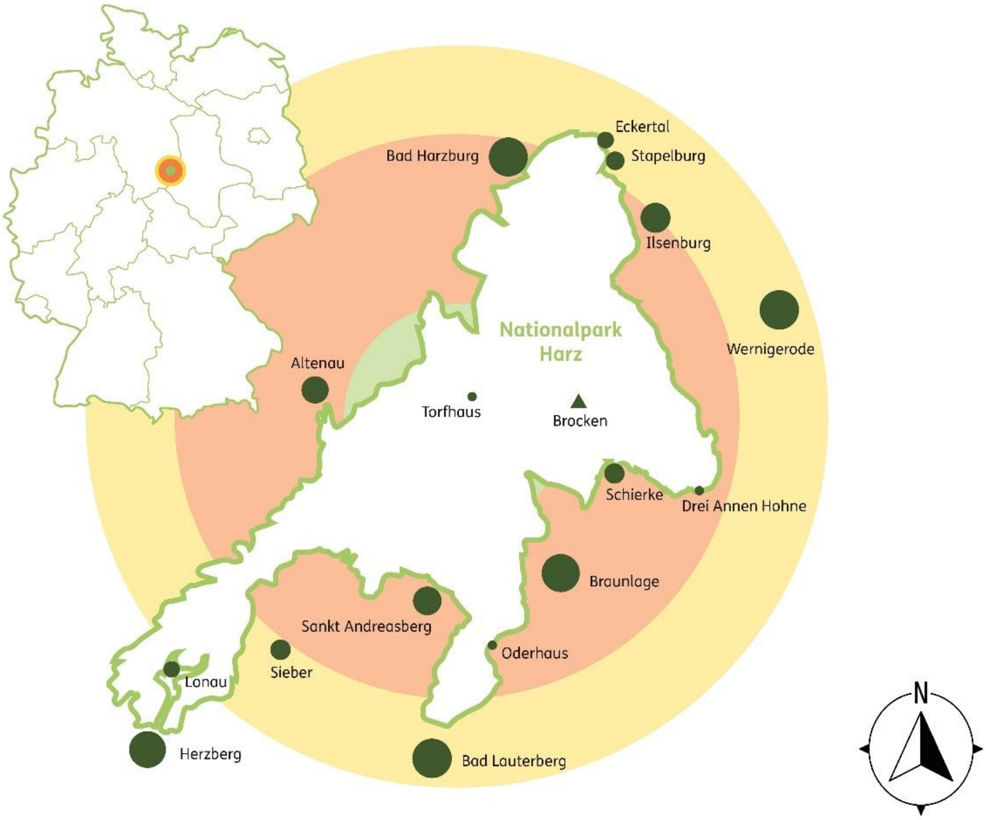


Figure 1. Location of the National Park and the adjacent towns and villages. The yellow, red, and green circle is the official symbol of Harz National Park. (Picture: Mandy Gebara, National Park Harz).

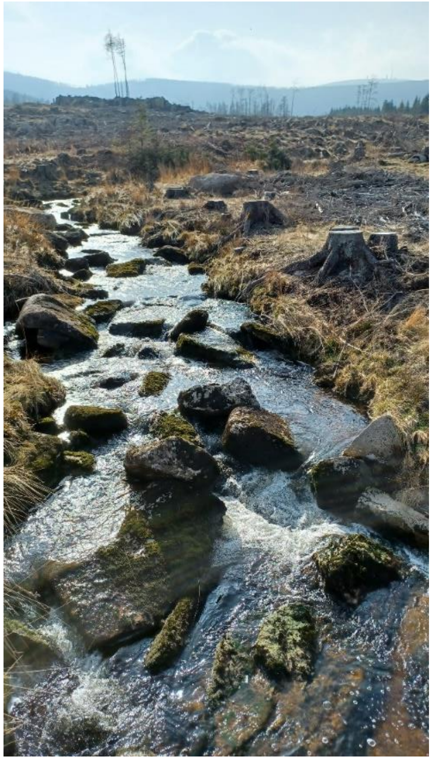
From 1994 to 2022, a total of 19 watercourse sections (Figure 3, Table 1) were investigated in the context of different research questions. These included the influence of tourism, such as hikers and the historic steam-driven narrow-gauge railway, the influence of acidification, and the impacts of heavy precipitation events [8,16]. Today, changes due to temperature increases, forest breakdown, and forest conversion pose additional and new challenges. Therefore, the water bodies have been sampled with different intensities in selected years.

2.2. Macroinvertebrates–Sampling and Indication

MI specimens were collected twice during sampling years (in April and June) using an extended version of the multihabitat sampling technique [8,18,19]. This technique includes all microhabitats, including mineral and organic bed substrates, submerged and emerged aquatic plants, and roots and woody debris. To ensure the detection of rare species, an area of approximately 10 m^2 was sampled at each site using a hand net with a mesh size of 0.5 mm. We combined kick sampling with a hand net, sieving of gravel, and hand collection, covering all substrate types. The abundances as well as the density of species were classified on a scale from one to seven (1 = one individual, 2 = rare (2–10 individuals), 3 = rare to common (10–30 individuals), 4 = common (30–100 individuals), 5 = common to frequent (100–300 individuals), 6 = frequent (300–1000 individuals), 7 = abundant, predominant (>1000 individuals). All collected organisms, except those easily estimable species that were directly identified on site, were preserved and brought into the lab for further microscopical estimation.

The organisms were determined down to the species level (some Diptera only to the genus level) by means of the literature listed in the Supplementary Materials. Because we mostly estimated to the species level, we use the term MI-species number.

Sampling site 12: Holtemme in 2006



Sampling site 12: Holtemme in 2022

Sampling site 19: Wormke in 2009

Sampling site 19: Wormke in 2022

Figure 2. Photos showing the changes in shading for selected sampling sites due to forest dieback. The locations and details of the sampling sites are given below. (Pictures: Uta Langheinrich).

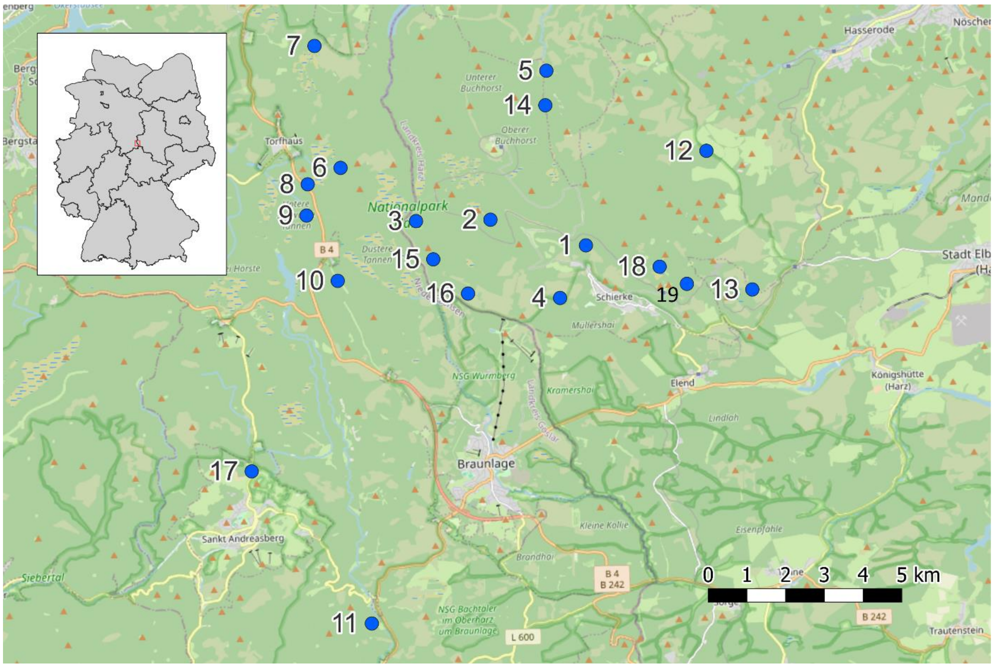


Figure 3. Map showing the locations of the 19 sampling sites on different streams (Source: Q-GIS Version 3.34.1, changed).

Table 1. Sampling sites in streams of the Harz National Park.

Stream	Site Number	Altitude (m)	Substrate Type, Vegetation	Coordinates *	
				Latitude (N)	Longitude (E)
Stream near Brocken street	1	830	gravel, CPOM **, no vegetation	51°46′56.0″	10°38′54.1″
Schluftwasser	2	890	rocks, gravel, sparse reeds	51°47′05.3″	10°37′02.3″
Ecker (near spring)	3	880	gravel, sand, CPOM, reeds, mosses	51°47′25.6″	10°35′05.8″
Kalte Bode (Schierke)	4	654	rocks, gravel, mosses, sparse reeds	51°46′07.6″	10°37′50.0″
Ilse	5	556	rocks, gravel, sand, mosses, sparse reeds	51°49′42.6″	10°38′03.4″
Abbe/Abbetränke	6	780	rocks, gravel, sand, mosses	51°48′07.1″	10°33′27.3″
Radau	7	545	rocks, gravel, CPOM, no vegetation	51°49′49.3″	10°32′56.3″
Bog drainage	8	810	gravel, sand, CPOM, reeds, mosses	51°47′59.3″	10°32′46.1″
Flörichshaier Graben	9	810	gravel, sand, CPOM, reeds, mosses	51°47′29.4″	10°32′39.9″
Oder (Oderbrück)	10	795	rocks, gravel, sand, CPOM, sparse reeds, mosses	51°46′41.4″	10°33′35.2″
Oder (Oderhaus)	11	432	rocks, gravel, mosses	51°41′45.6″	10°33′56.1″
Holtemme	12	582	rocks, gravel, mosses	51°48′04.9″	10°41′26.1″
Wormsgraben	13	650	rocks, gravel, sparse reeds	51°46′17.4″	10°42′38.1″
Ilse (concealed section)	14	665	Rocks, gravel, mosses	51°48′55.9″	10°38′04.8″

Table 1. *Cont.*

Stream	Site Number	Altitude (m)	Substrate Type, Vegetation	Coordinates *	
				Latitude (N)	Longitude (E)
Kalte Bode near Königsberger Weg	15	851	rocks, gravel, sand, mosses	51°46′49.0″	10°35′29.4″
Kalte Bode below Sandbeek junction	16	708	gravel, sand, sparse reeds	51°46′19.7″	10°36′14.9″
Sonnenberger Graben	17	712	gravel, sand, mosses	51°43′55.1″	10°31′18.7″
Wormke (Glashüttenteich)	18	806	gravel, sand, CPOM	51°46′37.9″	10°40′27.9″
Wormke (Spinne)	19	770	rocks, gravel, no vegetation	51°46′24.0″	10°41′11.0″

* coordinate system WSG84 (degrees° Min′ Sec″). ** CPOM = coarse particulate organic matter.

2.3. Ecological Status Assessment

The ecological status of the water bodies as indicated by the MI was assessed using PERLODES (https://gewaesser-bewertung-berechnung.de/index.php/home.html, accessed on 6 March 2023), which is the current standard assessment tool in Germany, in agreement with the EU Water Framework Directive (WFD) [20]. The current biocoenosis is compared with a given reference biocoenosis. Accordingly, the difference between the current and reference biocoenosis is indicated as the ecological status. The comparison is carried out using stream-type-specific metrics describing the biocoenosis (Table 2). For this, the metrics are combined in modules. The ecological status (Ecological Quality Ratio—EQR) according to MI was attributed according the principle “one out all out”, using among the three modules (see Table 2) the lowest EQR value. This was represented as an EQR class, ranging from bad (5) to poor (4), moderate (3), good (2), or very good (1).

Table 2. Modular assessment according the German PERLODES system (manual for calculation of metrics see in https://gewaesser-bewertung-berechnung.de/index.php/home.html, accessed on 6 March 2023); in agreement with the EU Water Framework Directive (WFD) [20]. (E—Ephemeroptera, P—Plecoptera, T—Trichoptera, ac—abundance class).

Module	Stream Type 5 Metrics
Organic pollution	Saprobic Index
General degradation	German Fauna Index % EPT (ac) Rheo-Index
Acidification	Acidity class

All streams in this study were, according to the WFD, coarse material-rich, siliceous low mountain streams (stream type 5).

To detect changes within the biocoenoses, the variables “percentage of mayfly, stonefly and caddisfly larvae based on abundance classes” (% EPT (ac)) and the “Shannon–Wiener index” were also used. EPTs are generally indicators of good status. However, they react very differently to acidification, depending on the species [2]. The Shannon–Wiener Index describes the diversity of the data under consideration and takes into account both the number of different data categories (e.g., the number of species) and the abundance (number of individuals per species) [21].

2.4. Hydrochemical and Physicochemical Methods

Water temperature, conductivity, pH, and oxygen concentration/saturation were measured directly at the sampling sites using appropriate sensors (WTW, Germany). Biological oxygen demand (BOD) after 5 days incubation was measured in the laboratory using the same WTW oxygen sensor. Composite samples were taken mid-stream using a beaker attached to a pole and filled into either plastic (for total phosphorous, calcium, magnesium, and BOD) or glass (for all other parameters) bottles. These were completely filled so that there was no headspace. Samples for total nitrogen and total organic carbon analyses were acidified using a few drops of concentrated HCl. Samples for iron and aluminium analyses were acidified using a few drops of concentrated sulfuric acid. The remaining samples were not treated. All samples were transported cooled back to the laboratory for immediate analysis following standardised methods. Please refer to Supplementary Table S1 in the Supplementary Materials for a full overview of these methods plus measurement details.

2.5. Statistical Analysis Methods

We calculated species richness and the Smith and Wilson evenness index [22] for the different sites sampled over different years. Species richness and evenness were correlated with the water pH using the Pearson correlation coefficient and tested for significance ($p < 0.05$).

Ordination techniques can help explain community variation and assess temporal and spatial trends. We used Detrended Correspondence Analysis (DCA) [23] to analyse the species composition (based on species density) of all sampling sites for each survey year (the codes are the site number followed by the sampling year). The coordinates on the first and second DCA axes for each of these samples were correlated with the pH using the Pearson correlation coefficient and tested for significance ($p < 0.05$).

The water body samples coordinates and species coordinate for axes I and II have been graphically presented.

3. Results

3.1. Water Chemistry

Table 3 below shows a summary of the key water quality parameters for each of the sites. Figure S1A,B in the Supplementary Materials shows the temporal trends in selected water quality parameters for site 4 on the Kalte Bode and site 5 on the Ilse River. These were the sites with the highest sampling resolution and were thus selected to illustrate temporal changes in the water chemistry. The complete data for these sites are summarized in Tables S2 and S3, and, being similar to the levels measured at the other sites, as shown in Table 3, are representative.

Water temperature showed a consistent seasonality (see Figure S1), with the highest values being recorded in summer. A long-term trend between 1994 and 2022 is not evident, likely due to the measurements being taken to coincide with the biologically active period between spring and autumn rather than throughout the year. As expected, given the obviously high flow velocities and turbulences, the waters were always well-aerated, with oxygen concentrations varying around the saturation value (see Figure S1 and Tables S2 and S3).

Table 3. Summary (mean, minimum, and maximum) of the key water quality parameters for all the sampling sites.

		Site 1: Stream near Brocken Street	Site 2: Schluftwasser	Site 3: Ecker (near Source)	Site 4: Kalte Bode (Schierke)	Site 5: Ilse	Site 6: Abbe/Abbetränke	Site 7: Radau	Site 8: Moorabfluss	Site 9: Flörichshaier Graben	Site 10: Oder (Oderbrück)	Site 11: Oder (Oderhaus)	Site 12: Holtemme	Site 13: Wormsgraben	Site 14: Ilse (Concealed Section)	Site 15: Kalte Bode near Königsberger Path	Site 16: Kalte Bode Below Sandbeek Junction	Site 17: Sonnenberger Graben	Site 18: Wormke (Glashüttenteich)	S19: Wormke Spinne
Temp.	**Mean**	**7.5**	**7.2**	**6.6**	**7.9**	**8.8**	**7.6**	**8.8**	**7.2**	**7.8**	**7.8**	**9.6**	**9.5**	**10.3**	**8.9**	**7.9**	**8.1**	**8.5**	**11.5**	**9.0**
(°C)	Min	0.8	0.2	2.8	0.9	1.1	2.1	0.7	3.0	2.6	2.2	1.8	3.3	5.0	3.7	4.7	4.7	5.6	4.5	4.5
	Max	12.5	15.4	12.0	15.0	18.0	12.3	13.9	11.7	12.5	13.5	17.1	19.3	22.2	13.4	10.2	10.4	11.2	16.6	11.3
pH	**Mean**	**5.35**	**4.76**	**5.43**	**6.34**	**5.52**	**4.89**	**6.96**	**4.89**	**5.31**	**5.04**	**6.72**	**6.41**	**7.15**	**5.35**	**5.87**	**6.13**	**6.06**	**5.11**	**6.93**
	Min	4.31	3.80	4.09	4.16	4.10	3.96	4.49	3.94	4.00	3.68	5.71	5.88	6.56	4.52	5.44	5.53	5.55	4.25	6.11
	Max	6.69	6.22	6.60	8.46	6.95	6.61	8.22	5.87	7.54	6.75	8.30	6.91	7.62	6.48	6.23	6.52	6.74	5.71	7.60
O_2	**Mean**	**10.349**	**10.785**	**11.025**	**10.891**	**11.185**	**10.388**	**10.508**	**7.835**	**9.698**	**10.444**	**11.139**	**10.494**	**10.436**	**10.581**	**10.785**	**10.811**	**11.087**	**9.156**	**10.780**
(mg/L)	Min	6.880	7.180	6.600	7.180	5.250	6.980	7.220	3.850	6.350	6.600	8.300	7.310	6.890	7.280	10.200	10.200	10.260	5.260	8.190
	Max	13.800	15.100	15.000	14.800	16.000	14.300	14.500	11.900	13.300	14.400	15.000	12.210	12.370	12.200	11.570	11.860	12.550	11.670	12.340
NO_3^-	**Mean**	**1.271**	**0.978**	**1.835**	**1.381**	**1.391**	**1.317**	**1.475**	**1.728**	**1.653**	**1.488**	**2.271**	**3.064**	**3.600**	**3.055**	**2.162**	**2.324**	**11.785**	**5.645**	**5.599**
(mg/L)	Min	0.428	0.258	1.130	0.317	0.299	0.390	0.357	0.596	0.596	0.506	0.790	0.270	0.578	0.615	0.970	0.729	9.470	2.720	1.380
	Max	7.750	4.130	5.940	9.250	8.260	4.500	9.040	7.320	5.380	6.280	13.200	14.800	15.700	6.590	3.920	5.470	14.100	18.400	14.600
o-PO_4^{3-}	**Mean**	**0.010**	**0.005**	**0.006**	**0.006**	**0.005**	**0.007**	**0.006**	**0.007**	**0.008**	**0.006**	**0.011**	**0.006**	**0.005**	**0.007**	**0.006**	**0.006**	**0.010**	**0.035**	**0.013**
(mg/L)	Min	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.003	0.010	0.010	0.010
	Max	0.050	0.014	0.015	0.050	0.015	0.015	0.012	0.018	0.016	0.010	0.116	0.010	0.010	0.010	0.010	0.013	0.013	0.181	0.020
Total P	**Mean**	**0.022**	**0.021**	**0.024**	**0.017**	**0.013**	**0.018**	**0.019**	**0.019**	**0.021**	**0.014**	**0.010**	**0.008**	**0.012**	**0.009**	**0.008**	**0.006**	**0.013**	**0.045**	**0.033**
(mg/L)	Min	0.008	0.008	0.003	0.003	0.005	0.005	0.005	0.006	0.008	0.003	0.003	0.003	0.003	0.005	0.006	0.003	0.010	0.016	0.010
	Max	0.090	0.063	0.114	0.050	0.030	0.079	0.128	0.051	0.063	0.030	0.032	0.017	0.024	0.013	0.009	0.013	0.018	0.095	0.096
Al^{3+}	**Mean**	**0.442**	**0.435**	**0.254**	**0.162**	**0.399**	**0.309**	**0.181**	**0.236**	**0.308**	**0.266**	**0.150**	**0.296**	**0.201**	**0.442**	**0.253**	**0.166**	**0.158**	**0.885**	**0.300**
(mg/L)	Min	0.238	0.176	0.010	0.023	0.142	0.106	0.020	0.060	0.108	0.071	0.023	0.188	0.066	0.138	0.042	0.048	0.033	0.576	0.060
	Max	1.040	0.776	0.772	0.548	0.793	0.688	0.624	0.458	0.646	0.714	0.500	0.576	0.612	0.700	0.980	0.338	0.344	1.338	0.582

A seasonal pattern in pH was also observed, with the lowest values generally being recorded in spring and autumn, and an increase of up to more than two pH units during the summer months. For Site 5 on the Ilse River (see Figure 4A), there was a positive correlation between pH and temperature. However, this was not as pronounced for Site 4 on the Kalte Bode. The minimum pH values measured per annual sampling campaign also showed an increasing trend over the study period (see Figure S1). For example, during the earlier sampling years, the lowest overall pH values were recorded. Here, minimum annual values were all below around pH 5, sometimes even reaching as low as pH 4. In contrast, for the later sampling times, the minimum pH values were all higher than around 5.

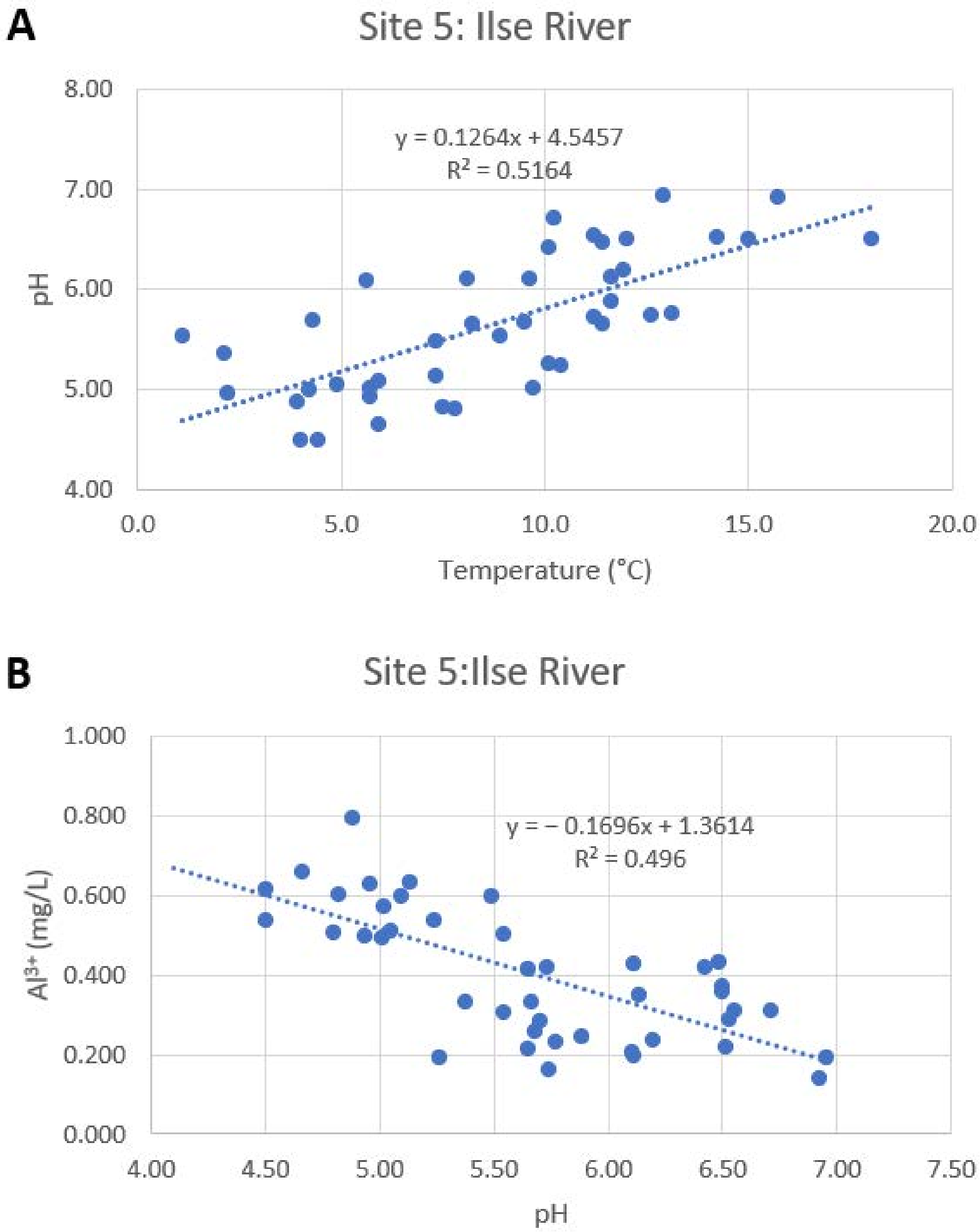


Figure 4. Correlations between (**A**) temperature and pH and (**B**) pH and dissolved aluminium (Al^{3+}, mg/L) for Site 5 on the Ilse River.

The remaining dissolved water constituents remained relatively consistent throughout the study periods and did not show any trends over time.

From 1994 to 2007, nitrate concentrations (NO_3^-) were all at low levels (below 2 mg/L) and remained relatively constant throughout the study period. Interestingly, significantly higher values of 7.57 and 8.26 mg/L were measured during the last sampling period in 2022. Ammonium (NH_4^+) was also measured, but at much lower concentrations, and was often below the method limits. Both ortho-phosphate (o-PO_4^{3-}) and total phosphorous were measured, but the latter was only determined during the earlier sampling times. The levels of o-PO_4^{3-} were low and relatively consistent, with a mean concentration of 0.008 (range 0.004 to 0.015) mg/L (see Table S3). However, the levels that were measured were often below the method limits.

3.2. Macroinvertebrate Settlement

A total of 220 species were recorded during the whole sampling period (from 1994 to 2022). The complete list can be found in the Supplementary Materials (Table S4, Part1–4). At all sites, MI-species numbers increased from the middle of the 1990s to 2022. At the same time, at most sites, we calculated an increasing Ecological Quality Ratio (EQR) to a good or very good status. Only Site 9 remained more or less stable with a moderate status (Table 4).

Table 4. Changes in macroinvertebrate-species number, Ecological Quality Ratio-class (EQR-class), pH, percentage of Ephemeroptera, Plecoptera, and Trichoptera in accordance with abundance class (% EPT ac), and Shannon–Wiener Index in streams of the Harz National Park; site description in Table 1 (** no data).

Scheme	Year	Species Number	EQR-Class	pH Mean	%EPT (ac)	Shannon–Wiener Index
1	1994_96	16	moderate	5.29	43.8	2.46
	2022	35	good	6.10	58.1	3.14
2	1994_96	12	moderate	4.71	75.8	1.80
	2022	33	good	5.81	74.5	2.90
3	1994_96	11	poor	5.56	64.5	2.14
	2005	15	moderate	5.23	78.8	1.97
	2022	35	good	5.44	72.3	3.08
4	1994_96	30	good	6.93	71.2	2.52
	2006	30	good	**	75.3	3.01
	2008	42	good	6.18	74.7	2.52
	2017	42	good	**	76.2	3.40
	2022	59	good	6.24	75.8	3.50
5	1994_96	14	moderate	5.43	65.0	1.82
	2008	29	good	5.98	82.9	2.88
	2017	36	moderate	**	67.9	3.08
	2022	52	good	6.25	66.9	3.17
6	1994_96	8	poor	4.94	77.3	1.73
	2022	38	good	5.96	73.9	3.20
7	1995_96	41	good	7.23	57.7	2.43
	2010	44	very good	**	80.0	3.35
	2013	50	very good	**	78.9	3.42
	2022	68	very good	7.41	73.4	3.75
8	1995_96	7	poor	4.79	76.2	1.13
	2022	24	good	5.64	58.0	2.36

Table 4. *Cont.*

Scheme	Year	Species Number	EQR-Class	pH Mean	%EPT (ac)	Shannon–Wiener Index
9	1995_96	9	poor	5.66	66.7	1.88
	2010	20	moderate	**	70.0	2.51
	2022	27	moderate	5.83	58.8	2.66
10	1995_96	9	moderate	5.02	33.3	1.47
	2010	26	moderate	5.17	62.2	2.53
	2022	47	good	6.25	69.1	3.19
11	1995_96	25	good	6.93	51.3	2.76
	2010	52	very good	6.98	75.4	3.38
	2022	70	Very good	6.97	75.3	3.82
12	2003_04	22	moderate	6.27	51.6	1.92
	2006	23	good	6.87	57.6	2.83
	2022	45	very good	6.63	68.3	3.26
13	2003_04	30	good	7.17	69.5	2.85
	2022	41	good	7.09	69.0	3.28
14	2008	**	**	5.09	**	**
	2022	24	good	5.87	86.9	2.71
15	2006	17	good	**	70.9	2.23
	2008	29	good	5.86	79.7	1.93
	2022	42	very good	5.99	73.7	3.11
16	2008	36	good	6.11	82.6	2.90
	2022	51	very good	6.41	71.1	3.34
17	2013	36	good	6.02	71.6	3.23
	2022	45	very good	6.14	71.3	3.38
18	2009	28	good	5.05	58.2	2.59
	2022	33	good	5.24	57.3	2.75
19	2009	40	very good	6.95	86.5	3.05
	2022	65	very good	6.89	76.8	3.54

Ephemeroptera, Plecoptera, and Trichoptera (EPT) were detected with high percentages at all sites. According to the WFD, results higher than 60% correspond to a very good status and higher than 50% to a good status. However, within this context, increases and decreases, as well no change in these percentages, were all observed. An increase in species diversity was also detected, as shown by the increase in the Shannon–Wiener Index at all sites.

For all the samples, we correlated species richness with the pH and found a significant relationship between these variables ($r_{50} = 0.52$, $p < 0.001$; Figure 5). However, the relationship of pH with evenness was not significant ($r_{50} = 0.06$, N = 50, p = non-significant).

Over the decades, we found a clear co-development of species numbers and pH (Figure 6) towards higher, i.e., better values. This is illustrated in the summarized examples for sites 1–11 and 14–19.

When site coordinates of DCA axis I were correlated with pH, this revealed a significant relationship ($r_{50} = 0.70$, $p < 0.001$). However, axis II coordinates were not related with pH ($r_{50} = 0.21$, p = non-significant) (Figure 7). Some samples were related with higher pH, such as Sites 7 and 13, located at the left of the bidimensional space at lower values of the coordinates. In contrast, others, depending on the year, were related with lower pH, such as samples 3, 12, or 18 (Figure 7). This all indicates that pH had an effect on the species composition of the streams.

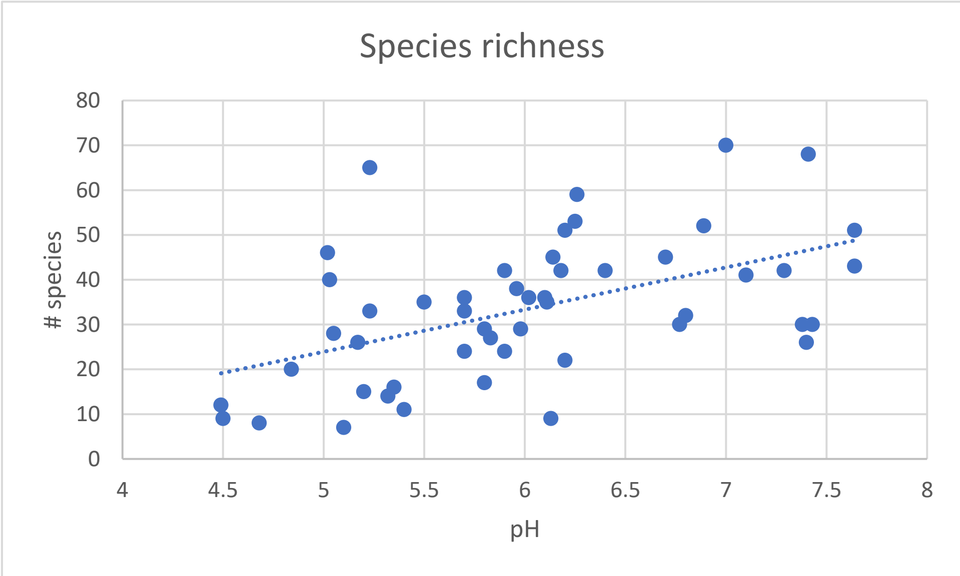


Figure 5. Relationship between species richness of MIs and pH.

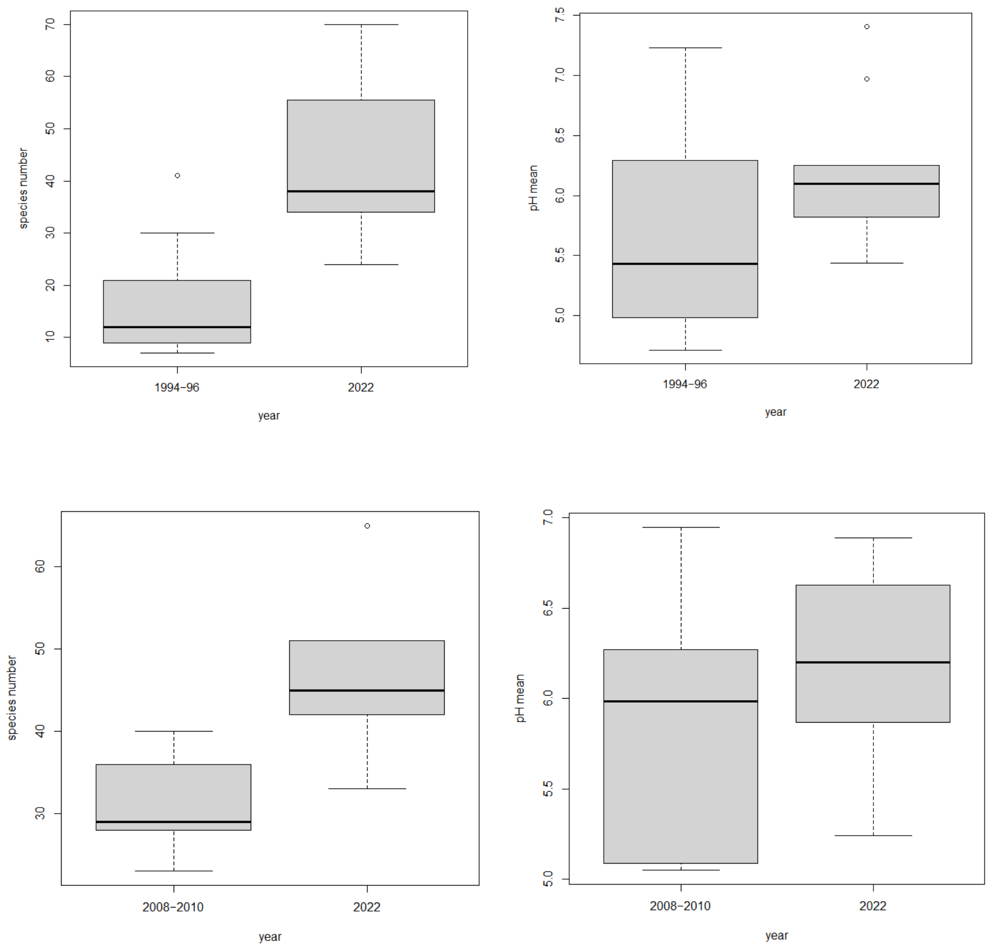


Figure 6. Top: Development of species numbers (**left**) and pH mean (**right**) for 11 sampling sites (1–11) that were sampled between 1994 and 1996 and again in 2022. **Bottom**: Development of species numbers (**left**) and pH mean (**right**) for sampling sites 14–19 that were sampled between 2008 and 2010 and again in 2022. (○ outlier).

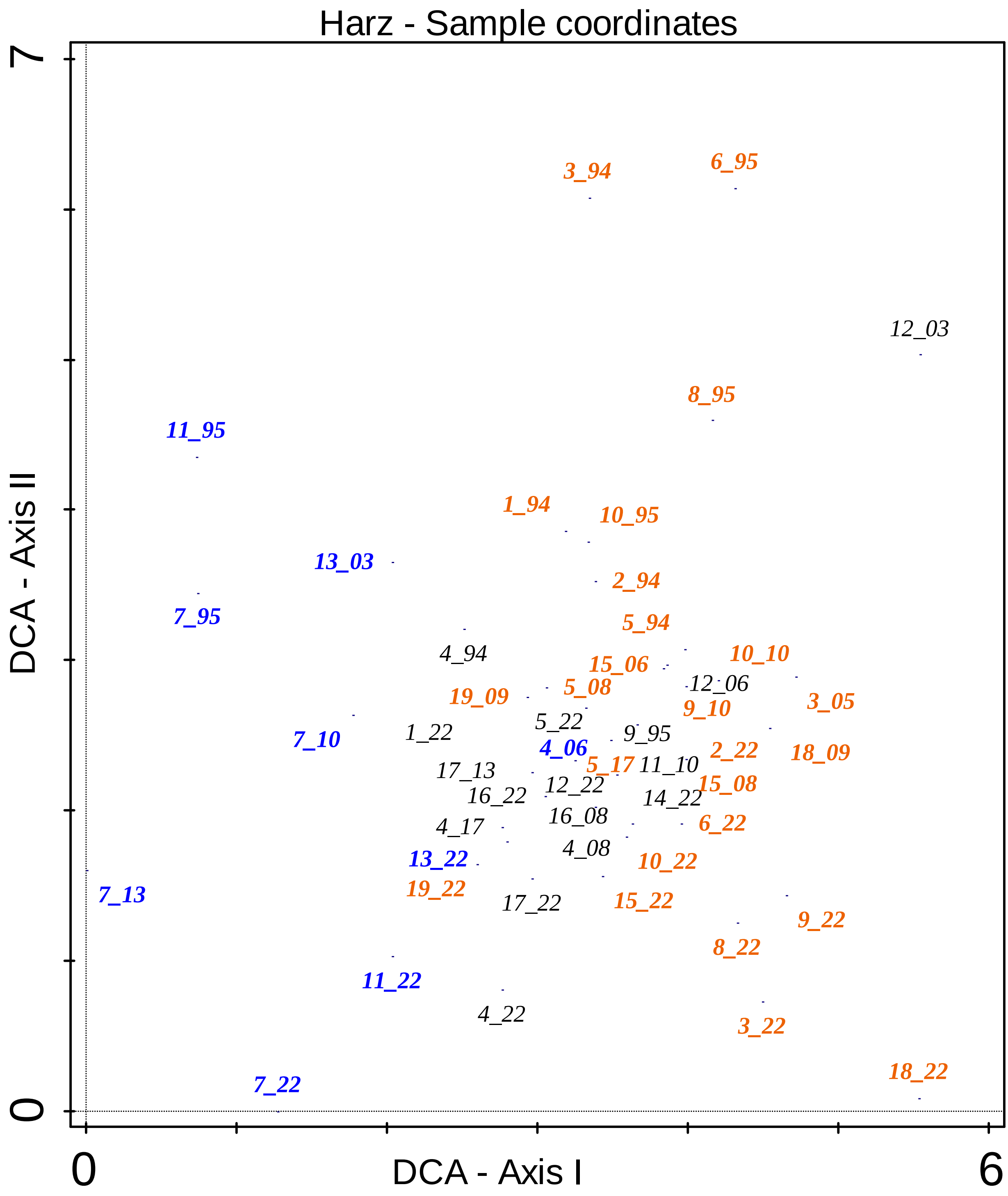


Figure 7. Stream sample site scores in the space defined by axes I and II of the Detrended Correspondence Analysis (DCA) based on the matrix density of the species. Acidified sites are on the right side and neutral ones on the left (sites with pH over 7 are indicated in blue, while sites with pH below 6 are indicated in orange). The first number is the site, while the second number (followed by the underscore) is the sampling year, the first sampling year in case this took place over several years (see Table 4).

The MI communities in the sampled streams were dominated by Ephemeroptera, Plecoptera, and Trichoptera species. Our sampling reaches were very representative for streams in the National Park because we found 30 out of 33 Ephemeroptera and 44 out of 47 Plecoptera species that have ever been found in the National Park (Table 5).

Table 5. Number of EPT species that have been found in the Harz mountains in general as well as in the Harz National Park and in streams of our studies.

Species Number	Ephemeroptera	Plecoptera	Trichoptera	Source
Harz Mountains	66	56	188	[24]
National Park	33	47	120	[25]
Study area	30	44	67	own studies

Nine of the found MI species, including aquatic Coleoptera, are endangered to different degrees and included in the German Red Lists (Table 6) [26–29].

Table 6. MI results 2022: Species of German Red Lists in sampled streams (category 2 = endangered, category 3 = vulnerable).

Group	Species	Category
Coleoptera	*Hydroporus longicornis*	3
	Hydroporus longulus	3
Ephemeroptera	*Ameletus inopinatus*	2
	Rhithrogena hercynia	3
Plecoptera	*Leuctra rauscheri*	3
	Nemoura mortoni	3
Trichoptera	*Drusus discolor*	3
	Grammotaulius submaculatus	3
	Pseudopsilopteryx zimmeri	3

4. Discussion

Changes in the relative importance of stressors are the main drivers for shifts in biocoenoses. Recently, more rigorous air purification policies have significantly reduced the emission of acidifying pollutants. Between 1990 and 2008, the emissions of oxidized sulphur compounds were lowered by 91%, of nitrogen oxides by 52%, and of ammonia by 13% [30,31]. Nevertheless, nitrogen inputs, resulting in equal parts from fuel combustion (traffic and power plants) and emissions in agriculture, presently remain at a high level [32–34]. Thus, the total acid input still exceeds the tolerance and neutralization capacity of many ecosystems [30,35,36]. Obviously, restoration of terrestrial and aquatic ecosystems from acidification is a slow process. Even in 1998, in German low mountain ranges, stream water quality with respect to pH, nitrogen, sulphate, and aluminium generally did not show a positive development, despite decreasing acid deposition [37]. Acidification even during this phase led to a further deficit of alkaline cations (sodium, magnesium, potassium, calcium), affecting root growth and activity and eventually leading to a decrease in the remediation functions of the soil and plants [38]. The recovery of the water bodies in the Harz mountains started approximately 10 years after the drastic reduction in acid deposition [16]. These trends began in other regions like the Black Forest earlier than in the Harz mountains, with a slight improvement of the biological conditions in some streams already observed before 2000 [2]. That study showed that the number of the most acidic sites (class 4) decreased from 32 in 1992 to 25 in 1998, a reduction of 37%. During the same period, the number of class 3 streams declined from 49 to 31, also a reduction of about 37%. In general, the investigated streams in Germany have responded in an unexpectedly rapid manner to the reduction in anthropogenic acidic deposition since the mid-1980s. However, the extent of recovery from acidification varies over time, between regions and between sites within regions, depending on a range of factors, including the magnitude of the change in deposition and the catchment characteristics. Generally, the streams experiencing the highest deposition also demonstrated the largest observed changes [39]. Those regions which were formerly subjected to very high sulphur and nitrogen deposition (e.g., Ore Mountains, Harz Mountains), have responded to the marked reductions in this deposition with a distinct improvement of their acidification status.

The main result of our long-term monitoring of streams in the Harz National Park is the steady increase of MI-species, specifically of EPT, and the improvement of ecological status shown by EQR-classes. In terms of the MI populations, the decrease of acidification is relevant, as such low pH events are critical for the survival of sensitive species even if these minima are only temporary [8,30]. At 15 of the 19 sampling sites, the acidity class got better by at least one value. Thus, acid-sensitive species were able to settle higher altitudes, i.e., formerly acidic reaches. These include, e.g., *Cloeon dipterum*, *Gammarus fossarum*, *Glossosoma conformis*, *Halesus digitatus*, *Isoperla goertzi*, *Leuctra aurita*, *L. albida*, *Nemura flexuosa*, *Perlodes microcephalus*, and *Protonemura nimborum.* Most of the species found in streams belong to the groups of Trichoptera, Ephemeroptera, and Plecoptera. These taxonomic orders are, in general, indicators of good water quality and other features, such as hydromorphological structures [39]. Meanwhile, the group of Odonata that is normally also important for aquatic bioindication only plays a subordinate role in running waters. Many species only occur in ponds and bogs and were not found during the sampling for this study. Nevertheless, the higher altitudes of the Harz Mountains are the main, and possibly only, habitat in Saxony-Anhalt for endangered raised bog dragonfly species such as *Aeshna subarctica*, *Somatochlora alpestris*, and *Aeshna juncea* [40,41]. We have also found them during other campaigns.

One interesting observation for the explanation of increased MI diversity was that the levels of dissolved aluminium generally showed a negative relationship with pH, which was particularly evident for Site 5 on the Ilse River (see Figure 4B). This implies that (i) the highest dissolved aluminium concentrations occurred in spring and autumn, in line with the seasonality in pH, and (ii) there was a decrease in the maximum dissolved aluminium concentrations attained each year. The latter is due to the trend of increasing minimum pH values discussed above. It is well established that increased acidification of aquatic ecosystems leads to increased mobilization of this metal, which is toxic, particularly to plants, but also to aquatic MI in acid water bodies [42].

Species richness was correlated with pH, revealing a larger number of species in line with higher pH values. In the case of species composition, pH could also discriminate between the different water body samples and years. Therefore, pH is a determinant for both species richness and composition, but the effects of pH showed a great variation between different water bodies. Since acidity is not the only environmental factor affecting the composition of the MI communities in the studied area, it is quite challenging determining the effects of the attenuation of acidification within such a multi-stressor environment. For example, even seemingly stressor-specific macroinvertebrate indices can be confounded by the presence of other stressors [43]. Therefore, recovery from previous disturbances such as acidification might be masked by the effects of currently ongoing environmental changes like global warming [44].

Attenuation of acidification did not only influence the MI diversity in the National Park. Along with the increase in pH, fish populations also recovered, and formerly fish-free stream sections have been recolonised [45]. Formerly acid-impacted streams are now inhabited by healthy populations of different rheophilic fish species [46], without having had to resort to active restoration methods such as stocking or watershed liming.

It is not only the emission situation that has an influence on acidity status. The most important catchment factor is the type of vegetation. Numerous studies have shown that concentrations of acids below spruce are much higher than below beech stands [47–49]. This so-called "combing effect" (atmospheric acids and needle-bearing trees) is considerable [2]. Careful selection of tree species can lead to tighter element cycles, thus decreasing acidification and leaching of base cations [50]. Until 2018, the common spruce (*Picea abies*) has been the dominant tree species in the National Park. However, since 2018, more than 300,000 hectares—more than 2.5% of the Germany's total forest area—have died because of a combination of mass population development of bark beetles and drought fueled by a warming climate [51]. With regards to the Harz National Park, during a long-term drought, successive waves of bark beetles have killed more than 10,000 hectares of spruce stands. The disappearance of spruce trees from the banks and the near surroundings of streams is a promoting factor for increasing water quality [16]. Reduced shading allows more light to reach the bottom of the streams and promotes the development of biofilm as a resource for grazers and scrapers among the MI community.

Measured NO_3^- concentrations were low and typical for this watershed. Other measurements in the same rivers and streams showed concentrations in the headwaters and forested sections of the catchment below 10 mg/L, often even below 5 mg/L [52]. Here, the highest levels were recorded under high flow conditions, which might provide an explanation for the increased NO_3^- concentrations measured in 2022 in this study. Moreover, the high concentrations in the last sampling year also coincide with freely accessible data from the State of Saxony-Anhalt. An increase in NO_3^- concentrations in several streams of the Harz mountains from 2018 onwards is apparent [53], which can be traced back to the extensive dying of spruce due to bark beetle infestation. The potential release of NO_3^- after such an event is well documented [54–56].

Despite an increase in recent years, NO_3^- levels were still well below the threshold level of 50 mg/L set, for example, in the WFD. However, with respect to maintaining a good ecological status, even this value is too high for natural rivers and streams. Total nitrogen thresholds of 1 to 2.5 mg/L [57] and 0.8 to 2.4 mg/L [58] have been proposed for small rivers with low salinity at medium altitudes. Given that nitrate accounted for the major fraction of nitrogen found in the waters (see Tables S2 and S3), the concentrations from this study are close to this suggested range for maintaining a good ecological status. Increased nitrogen concentrations, in combination with other factors, can trigger a marked shift in macroinvertebrate communities in low mountain streams [44].

Currently, around two thirds of rivers in Germany do not achieve a good ecological status due to high phosphorous levels [59]. In the waters of the Harz National Park without any anthropogenic phosphorous inputs, the values remain below the suggested range for maintaining a good ecological status (0.032–0.090 mg/L for reactive phosphorous and 0.047–0.070 mg/L for total phosphorous [57,58]).

Another factor influencing species number and density of MI is food availability. Dissolved organic carbon (DOC) is an indirect source of MI nutrition. This represents a broad classification for organic molecules of varied origin and composition in aquatic systems. The main source of DOC is leaching of decomposed organic matter from soils into stream water. DOC is an important source of carbon and energy for microorganisms that form biofilms and also plays an important role in many chemical and photochemical reactions and transformations. Increases in stream water DOC concentrations occurred in most of the analysed streams in the Harz mountains [15]. The processes responsible for the increased DOC concentrations are complex and not entirely understood [60,61]. More mineralisation due to climate change and higher temperatures can lead to an increased release of DOC from forest soils, especially from fens and bogs [11,62]. Reduced DOC oxidation can also be accompanied by a decrease in nitrate (15].

A reverse effect on the diversity of MI or a further restructuring of the community composition could be caused in the future by increasing water temperatures. At Site 13 (Wormsgraben), we already measured an extremely high temperature of 22 °C in June 2022, which is 8 degrees higher than 10 years ago. In addition, at sampling Site 12 in the larger stream Holtemme (Figure 2, top right), 19 °C was recorded. These extreme water temperatures were caused by the lack of shading since dead spruce had been removed by the forest management in these areas at the fringe of the Harz National Park. In 2022, no adverse biological effects of this warming were apparent. The reason could be that mountainous species mainly emerge in early spring when the water is still cold. However, other studies have already observed community shifts in low-mountain ranges due to increasing water temperatures [44,63]. Therefore, shading should be enhanced again by promoting the resettlement of the stream banks by deciduous trees in order to reduce maximum water temperatures.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/ecologies6010013/s1, Table S1: Sample preparation and analytical methods used for measuring the various water quality parameters; Table S2: Water quality parameters measured at Site 4: Kalte Bode (Schierke). Levels below method detection limits were not included in the summary statistics and have been designated as "<" and "nd" means not determined. Temp. is the water temperature, conduct. is the conductivity, BOD5 is the biological oxygen demand measured after 5 days and TOC is total organic carbon; Table S3: Water quality parameters measured at Site 5: Ilse. Levels below the method detection limits were not included in the summary statis-tics and have been designated as "<" and "nd" means not determined. Temp. is the water temperature, conduct. is the conductivity, BOD5 is the biological oxygen demand measured after 5 days and TOC is total organic carbon; Table S4: Total species list of MI. The numbers are the highest abundances of the respective species found in the study year. ID-no: name of the species in the operational taxa list of the Perlodes assessment system; Figure S1: Temporal trends in selected water quality parameter for (A) Site 4: Kalte Bode and (B) Site 5: Ilse river. Refs. [64–89] are cited in the supplementary file.

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