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Original Articles

Land use in acid sulphate soils degrades river water quality – Do the biological quality metrics respond?

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ABSTRACT

Land use in the Acid Sulphate (AS) soils induces metal and acidity pollution of aquatic ecosystems in coastal areas worldwide. Increasing utilization of AS soils poses increasing risks for deterioration of water bodies. We studied the effects of the coverage of AS soils, together with other catchment land cover attributes, on aquatic assemblages of fish, diatoms and benthic invertebrates in 42 sites along 15 lowland rivers in Finland during three subsequent years. Low pH and increasing content of several metals in the river water were related to high amount of AS soils in the catchment. Especially increasing iron content and water color were correlated to amount of forested areas in the catchment, whereas lower water color values and higher arsenic, chromium and iron concentrations were associated with wetlands. The assemblage structure of all three biological groups was strongly spatially structured among rivers and varied less temporally. The spatial structure of fish and diatoms were strongly affected by the acidic water, whereas invertebrates were more affected by low alkalinity and increasing concentrations of organic matter and iron. Especially fish and benthic invertebrate bioassessment metrics demonstrated for AS soil induced degradation in acidity by responding to low pH and high acidity, while the response from the diatoms index was weaker. The high metal concentrations alone did not seem to add to the degradation in biometrics without further increase in acidification. Our results highlight the importance of recognizing AS soil areas in the catchment to target the mitigation effects. A holistic approach in the mitigation of the adverse effects from AS soils is needed, using several mitigation methods in the catchment, and directing main efforts and protection from human disturbance to catchment areas with the highest proportion of AS soils. Our results suggest that status assessment of AS rivers should be based on multiple biological quality elements and that their metrics could be improved for better detection of impacts from acidity and metal pressures. The effects of metals and their concentrations on aquatic assemblages should be further examined.

1. Introduction

Freshwater ecosystems are threatened worldwide, and their biodiversity is declining rapidly (Dudgeon et al., 2006; Woodward et al., 2010; Reid et al., 2019). The decline is typically a result of human-driven disturbances impairing biodiversity and ecosystem stability (Hautier et al., 2015). Catchment land use is one of the main causes for this development (Bayramoglu et al., 2020; Chen and Olden, 2020), and it is likely to accelerate when more and more marginal lands are taken into use (Popp et al., 2017; Chen et al., 2020).

There are about 170 000 – 240 000 km^2 acid sulphate (AS) soils in the world (Ritsema et al., 2000; Andriesse and van Mensvoort, 2002). Main areas of occurrence are in Africa, Australia, Asia and Latin America, typically in coastal and estuarine regions (Dent and Pons, 1995). AS soils are stable under anoxic conditions, but once they are oxidized, the sulfide minerals, mainly pyrites, form into sulfuric acid (Åström and Björklund 1996; Österholm and Åström, 2002).

Most of the AS soils In the Baltic Sea region result from the Litorina Sea stage some 7500 –4000 year ago when the salt content of the seawater was substantially higher than it is today (Tikkanen and

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Oksanen 2002). Sulfate-reducing microbes reduced the sulphates in seawater into sulphides, and as a consequence subsurface anoxic soils contain metal sulphides, mainly in the form of pyrites (Gupta & Germida 2021). Postglacial land uplift in the Baltic Sea area and human activities bring these sulphide bearing layers in contact with oxygen. Human activities involve especially drainage of soil for agriculture or forestry, where open ditches and subsurface pipes are conducted to lower the level of groundwater. As a result of soil drainage and concurrent oxidation of metal sulphides, sulfuric acid is produced (Åström and Björklund 1996). This leads to acidification of the soil, characterized by very low pH and extensive leaching of metals (Åström and Björklund, 1996; Boman et al., 2010). This toxic mix spreads into the environment, typically during heavy rain periods (Toivonen and Österholm, 2011; Nystrand and Österholm, 2013). The most visible associated sudden impacts are fish kills (Cook et al., 2000; Sutela et al., 2012; Sutela and Vehanen, 2017), but it is obvious that there are spatially and temporally variable impacts on the whole aquatic ecosystem (e.g., Corfield, 2000; Fältmarsch et al., 2008; Toivonen et al., 2020). The temporal and spatial distribution of the impacts are, however, poorly understood.

The AS soil problems culminate in the coastal and estuarine areas with intensive land use. This is true also for Finland, where the largest AS soil areas are located along the western and south-western coast (Ministry of Agriculture and Forestry and Ministry of the Environment, 2011). The total area of AS soils is estimated to be between 1000 and 3000 km^2, making Finland the country with most AS soils in Europe (Yli-Halla et al., 1999; Fältmarsch et al., 2008). These areas are well suited for agriculture, and a large proportion of the AS soils are under cultivation.

The European Water Framework Directive (WFD) has established indices based upon the Biological Quality Elements (BQEs) composition (e.g., fish, benthic diatoms, and macroinvertebrates) to assess ecological quality of freshwaters. The outcome of these indices has been intercalibrated among EU countries, i.e. within the quality element they indicate similarly results of the level of disturbance on the aquatic communities (Poikane et al., 2014). The WFD assessment methods measure biological degradation from undisturbed reference conditions. For the water bodies in Finland, the same type-specific reference conditions are used irrespective of AS soil cover in their catchment. The expectation is that the pressures from AS soils can be suppressed to the extent for the water bodies to reach good ecological status. The WFD methods are commonly a combination of multiple metrics aimed at reflecting the impact of most common pressures, like eutrophication and hydro-morphological degradation (Poikane et al., 2020). Only three countries have fish and benthic invertebrate methods targeted to detect the effects of acidification in WFD classification (Sweden, Norway, and UK; Poikane et al., 2020). There are, however, also other pressure-specific methods developed to detect the effect of acidity on biota in rivers (e.g. Juggins et al. 2016). Given the importance of the assessment outcomes to guide the necessary actions needed to mitigate the negative effects, it is important that they show the connection between the sources of disturbance and the true ecological conditions (Rapport and Hildén, 2013).

Aquatic community structures of fish, invertebrates and diatoms often show concordance with respect to environmental gradients (Jackson and Harvey, 1993; Kilgour and Barton, 1999; Soininen et al., 2009). In rivers these environmental gradients and aquatic communities are typically longitudinally arranged along the river continuum from headwaters to estuaries (Rosi-Marshall and Wallace, 2002; Cross et al., 2013; Sutela et al., 2020). However, the community concordance in not always consistent, as the structure of aquatic communities is a result of biogeographical processes acting at multiple habitat scales (Allen et al., 1999; Bae et al., 2011; Vehanen et al., 2020). Further, several other factors like dispersal and functional traits affect the assemblage composition (Grenouillet et al. 2008; Feio et al., 2017) and the concordance among aquatic communities in their response to disturbance can be weak (Carlisle et al., 2008; Pace et al., 2012). Therefore, the use of more than one biological quality element for the ecological impact assessments is recommended (Pace et al., 2012; Bae et al., 2014; de Morais et al., 2018).

Here we study 1) how the proportion of AS soils of the catchment area affects river water quality, 2) how the water quality impacts depend on the interactions between AS soils, land use and catchment characteristics 3) if the proportion of AS soils in the catchment affects spatio-temporal variation of the fish, benthic invertebrate and diatom assemblage structures, and 4) what is response of the national WFD indices of the biological quality elements to the disturbance from AS soils.

2. Material and methods

We sampled 15 lowland streams flowing to Baltic Sea in western and south-western coast of Finland during three subsequent years 2010–2012 (Fig. 1, Table 1). Mean flow of the streams ranged from 0.9 to 48.8 m^3 s^{-1} during the study period, thus representing small to mid-sized streams (Table 1).

From each river 2–6 swiftly flowing rapid reaches were sampled for water chemistry and biological communities (Fig. 1, Table 1). Landcover attributes and land use in the catchment area above each reach were determined using GIS analyses. Landcover attributes included agricultural area, forested areas, wetlands, area of surface waters (Corine Land Cover 2012) and the area of AS soils (Table 2). The area of AS soils was obtained from the digital data of the Geological Survey of Finland (GTK). GTK has created an interpretation map of the occurrence of acid sulfate soils in Finnish coastal areas up to the highest shoreline of the ancient Litorina Sea (https://gtkdata.gtk.fi/hasu/index.html). The interpretation is created using quantitative multivariable modelling based on spatial analysis. Interpretation map was used because all catchments above our study rapids were not physically sampled for AS soils (out of total of 42 rapids, 14 were not sampled from catchment above the rapid). We could, however, confirm the reliability of the interpretation by correlating the areas with sampling data with the interpretation data (Pearson correlation coefficient $r = 0.959$, $N = 28$, $p < 0.001$). The degree of land use pressure from agriculture and urbanization in each catchment was estimated by the area used for agriculture and the artificial surfaces (Table 2). All variables were calculated as proportion of the total area of the catchment above the reach (per km^2). The land use pressure from forestry was estimated by calculating the total length of ditches (km) in the catchment, i.e., drainage intensity per catchment area (Topographic database, National Land Survey of Finland) (Table 2).

Water quality samples were analyzed using standard methods by the Finnish Environmental Institute (https://www.syke.fi/methodsstandardization) and the data are stored in the open national database Hertta (https://wwwp2.ymparisto.fi/scripts/kirjaudu.asp). Yearly mean value was used for each water quality variable (mean number of samples per year and rapid = 6, median = 4, range 2–31). Water quality variables included metals (μg/l) (aluminum (Al), arsenic (As), cadmium (Cd), cobalt (Co), chromium (Cr), copper (Cu), lead (Pb), sodium (Na), nickel (Ni), iron (Fe) and zinc (Zn)), conductivity, pH, acidity (mmol/l), turbidity (FNU) and color (mg/l Pt) (Appendix 1). Environmental Quality Standards (EQS) for metal content in surface waters are listed for Cd, Pb and Ni in EU Directive 2008/105/EC. The directive listed priority substances for achieving good chemical status for water bodies in Europe. For the remaining metals, excluding Na, Finland recommends using Canadian Freshwater Metals Criteria (https://www.flowlink.ca/freshwater-metals-criteria).

Fish assemblages were sampled in each reach each year in August-September by electrofishing following the sampling procedure for WFD monitoring (Vehanen et al., 2010) Fish were captured using Hans Grassl Gmbh (Schönau am Königssee, Germany) 1G 200–2 electrofishing gear using pulsed (50 Hz) DC current with 400–600 V voltage. All captured fish were identified to species and counted. Total length (TL) of the narcotized fish was measured to the nearest 1 mm and individuals of

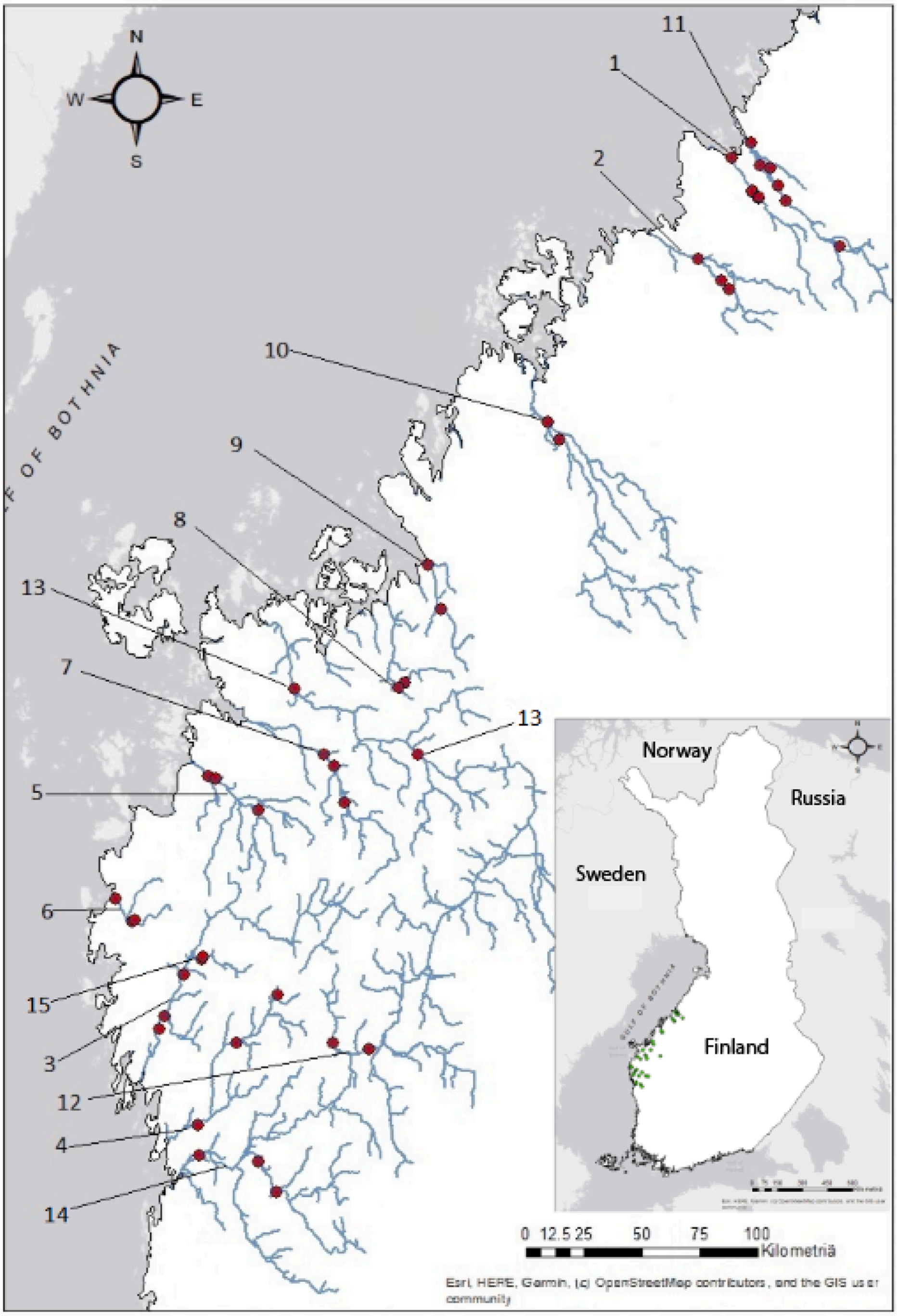

Fig. 1. Location of the 15 study rivers and rapids (2–6 in each river) used to study the effects of acid sulphate soils on water quality and aquatic assemblages.

each species were weighed to the nearest 0.1 g. Age-0 + brown trout, *Salmo trutta*, were recorded separately from older age classes. After recovery from anesthesia, the fish were released back to the stream.

Benthic diatoms were sampled using methods in accordance with the European standard (SFS-EN13946 2005) following the national sampling procedure for WFD monitoring (Järvinen et al., 2020). For each site sampled diatoms were brushed with a toothbrush from the surface of five randomly collected cobbles. The results were pooled into one composite sample and preserved in ethanol at the site. In the laboratory samples were treated with strong acid solution ($HNO_3 + H_2SO_4$; 2:1) and identified to species level with differential interference contrast (1000x magnification). Approximately 500 diatom valves were counted to determine the relative abundance of the diatom species.

Benthic macroinvertebrates were sampled and processed following the national sampling procedure for WFD monitoring (Järvinen et al., 2020). A composite 2-min kick-net sample was taken at each sampled reach using a net mesh size of 500 µm. The samples were preserved in 70% ethanol in the field. In the laboratory the samples were sorted, and all individuals were identified to the lowest possible taxonomic level, usually species or genus with the exclusion of Chironomidae (Diptera) and Oligochaeta. Identification was undertaken using national lists and keys.

WFD compliant biological assessment indices and their Ecological Quality Ratios (EQR), that are used to estimate the ecological status, were calculated for fish (Vehanen et al., 2010; Pont, 2011), macroinvertebrates (Aroviita et al., 2008) and diatoms following the current

Table 1
The 15 rivers studied and their characteristics. Sampled organism groups are also indicated.

River	Length km	Catchment area km^2	MQ m^3/s	HQ m^3/s	NQ m^3/s	Fish	Diatoms	Macro-invertebrates
Viirretjoki	14.0	195.4	1.4	191.0	0.0	X	X	X
Kälviänjoki	28.5	324.0	2.5	32.0	0.1	X	X	X
Närpiönjoki	76.5	991.9	9.0	135.4	0.2	X	X	
Tiukanjoki	60.0	500.0	4.9	98.0	0.1	X	X	X
Maalahdenjoki	27.5	677.2	4.4	52.0	0.1	X	X	X
Harrström	12.0	139.8	1.1	11.1	0.1	X	X	X
Laihianjoki	42.4	506.0	3.9	47.0	0.2	X	X	X
Vöyrinjoki	35.0	222.7	2.5	19.9	0.1	X	X	X
Kimojoki	18.4	196.2	2.2	17.6	0.1	X	X	X
Purmonjoki	68.6	864.3	8.7	22.4	1.0	X	X	
Lestijoki	99.9	1373.0	14.7	137.0	2.1	X	X	X
Kainastonjoki	23.8	424.2	3.5	30.8	0.5	X		
Kyrönjoki	131.7	4923	48.8	409.0	3.8	X		
Isojoki	52.4	693.2	13.3	199.0	1.4	X		
Lillån	13.9	100.8	0.9	12.0	0.1	X	X	X

Table 2
Catchment area and upstream catchment characteristics of the 42 rapids sampled in the 15 study rivers. The area of agriculture, AS soils, forests, wetlands, waters and artificial surfaces are given as percentage of the catchment area, forest ditches as kilometers per km2.

River name	Rapid name	Catchment area km^2	Agriculture %	AS soils %	Forests %	Ditches km per km^2	Wetlands %	Waters %	Artificial surfaces %
Viirretjoki	Tiinukoski1	166.8	14.9	16.4	76.6	10.3	5.9	0.1	2.5
	Tiinukoski2	166.9	14.9	16.4	76.6	10.3	5.9	0.1	2.5
	Alakoski	187.6	15.8	16.2	75.4	10.1	5.8	0.2	2.8
Kälviänjoki	Myllykoski	121	4.8	1.2	87.1	11.9	6.7	0.7	0.7
	Honkalankoski	131.4	5.5	2.2	86.8	11.6	6.3	0.7	0.7
	Keskusta	268.1	7.9	6.2	83.6	10.6	6.5	0.4	1.6
Närpiönjoki	Stenforsen	744.9	17.9	10.5	71.0	11.0	7.1	0.8	3.2
	Allmänningsf.	939.8	20.1	14.5	69.8	10.3	6.0	0.7	3.4
	Backforsen	944.4	20.3	14.6	69.6	10.2	6.0	0.7	3.5
Tiukanjoki	Tiukanjoki 3	22.1	11.3	0.0	84.2	17.8	3.2	0.0	1.8
	Tiukanjoki 2	280.5	22.7	12.9	69.6	12.3	3.3	0.0	4.4
	Puskamarkki	485.8	20.2	12.8	73.0	12.3	3.1	0.1	3.6
Maalahdenjoki	Sågkvarnsfors	133.6	11.1	13.2	81.8	9.9	5.2	0.1	1.9
	Kyrkbacken	427.3	14.2	19.2	79.9	9.9	3.2	0.1	2.5
	Maalahdenjoki 1	492.8	15.2	20.4	78.7	9.7	3.3	0.1	2.6
Harrström	Harrström 3	76.1	5.0	12.4	76.5	9.8	7.5	9.3	1.6
	Harrström 2	76.8	4.9	12.2	76.7	9.8	7.4	9.2	1.6
	Harrström bro	139.8	13.3	17.5	72.0	8.1	7.0	5.1	2.6
Laihianjoki	Laihianjoki 3	198.6	10.4	14.1	81.3	9.7	6.2	0.3	5.2
	Laihianjoki 2	298.7	17.8	20.4	74.7	7.7	4.6	0.3	2.7
	Yrjäälä	306.3	18.7	21.7	73.2	7.5	4.4	0.3	1.1
Vöyrinjoki	Vöyrinjoki 3	77.3	11.9	28.5	83.7	9.2	3.1	0.1	1.2
	Vöyrinjoki 2	96.9	16.6	31.5	78.9	8.0	2.8	0.1	1.5
Kimojoki	Kimojoki 2	90.3	19.4	5.5	65.4	4.3	7.3	5.1	2.9
	8-tien silta	204.8	20.1	8.9	69.3	5.3	4.8	2.7	3.0
Purmonjoki	Purmojoki 3	476.4	19.2	13.2	71.9	7.8	4.2	1.8	2.9
	Purmojoki 1	817.4	16.4	9.3	74.1	7.9	4.9	2.2	2.4
Lestijoki	Jäväjänkoski	1100.6	9.9	0.1	70.5	10.0	10.7	7.4	1.5
	Kuustonkoski	1291.8	10.5	2.3	71.1	9.9	10.1	6.4	1.9
	Niskankoski	1300.3	10.5	2.3	71.2	9.9	10.1	6.4	1.9
	Sämpilänkoski	1306.3	10.5	2.3	71.2	9.9	10.0	6.4	1.9
	Roukalankoski	1312.1	10.5	2.4	71.3	9.9	10.0	6.4	1.9
	Raumankoski	1386.9	10.7	2.8	71.7	10.0	9.6	6.0	1.9
Kainastonjoki	Pohjapato	130.2	29.0	3.8	61.3	10.8	6.8	0.0	2.8
	Nätynkoski	413.1	29.4	1.5	60.2	9.9	6.3	0.1	3.9
Kyrönjoki	Perttilänkoski	3896.6	22.7	6.0	65.1	8.6	6.3	1.5	4.4
	Voitila	4814	24.9	12.2	63.9	7.9	5.4	1.4	4.4
Isojoki	Nybrofors	1049.2	12.6	4.3	78.7	11.2	6.1	0.4	2.2
	Tuimalankoski	471.1	11.4	1.8	81.3	11.8	5.0	0.3	2.0
	Talvitienkoski	400	11.2	1.5	82.3	12.1	4.2	0.3	2.0
Lillån	Lillån 2	97.1	11.9	4.9	81.2	12.6	4.9	0.0	1.9
	Valtatie 8	97.5	11.9	5.0	81.1	12.6	4.9	0.0	1.9

national guidance (Aroviita et al., 2019). The fish index (FiFI) consists of five metrics: proportion of intolerant species, proportion of tolerant species, density of age-0 + brown trout and salmon, *Salmo salar*, density of cyprinid group individuals and number of species present. The macroinvertebrate assessment includes three metrics that measure compositional dissimilarity to reference conditions: number of stream type -specific taxa, number of stream type -specific EPT families (mayflies (Ephemeroptera), stoneflies (Plecoptera) and caddisflies (Trichoptera)) and PMA-index (Percent Model Affinity, Novak and Bode, 1992). The diatom assessment uses two metrics: number of stream type -specific taxa and PMA-index. We calculated the mean EQR (mean ± SD) for each of the sampled rivers (N = 15 for fish, 12 for diatoms, and 10 for benthic invertebrates) over years and study sites. For the diatoms we calculated also one pressure specific index, ACID index, especially developed in the same region (Sweden) to indicate acidic pressures (Andrén & Jarlman, 2008). The index consists of two parts. First is the ratio between the abundances of the species complex around *Achnanthidium minutissimum* (ADMI) and *Eunotia*-species (EUNO) (ADMI/EUNO ratio). The second part is the entire diatom community classified circumneutral (neutr) and alkalibiontic + alkaliphilous(alkbp) species, divided by acidobiontic + acidophilous (acibp) diatoms (Andrén & Jarlman, 2008).

2.1. Statistical analyses

Multivariate analyses were used to summarize the key indicators of water quality and their variability in the study sites, and examine their relationship to catchment landcover attributes. We also analyzed how the aquatic assemblages were structured temporally (years) and spatially (rivers), and which water quality and landcover attributes affected their structure. Principal component analysis (PCA) was used to reduce the number of water quality variables into mutually uncorrelated linear combinations (Abdi and Williams, 2010). PCA on water quality variables was computed by the base R-statistics package "prcomp", with centering so that variables are shifted to be zero centered and scaled to have unit variance before analysis. The calculation was done by a singular value decomposition of the centered and scaled data matrix, not by using eigen on the covariance matrix. PCA plots were done with "factoextra" package (Kassambara and Mundt, 2020). Horn's parallel analysis (Horn 1965) was used to determine the number of components to keep in the analysis. Statistical analyses were made using the statistical computing software R version 3.6.0 (R Core Team, 2019).

Canonical correlation analysis (CCA) explores to quantify and identify the interrelationships among sets of criterion variables and predictor variables (Weenink, 2003). CCA was used to examine the associations of water quality (the three first water quality principal components) to landcover attributes. CCA was computed and plotted with the R-package "yacca" (Butts, 2018). Canonical correlations were computed with rotated data. Both X and Y variables were scaled to unit variance, scaling the output of coefficients for the variables on each canonical variate. Rao's F approximation and Bartlett's Chi-squared test were used to test the significance of canonical correlations. Quantities of particular interest included the correlations between the original landcover attributes variables in each set and their respective canonical variates in water quality variables (structural correlations or loadings).

To explore the temporal and spatial similarity of aquatic assemblages Bray-Curtis dissimilarity indices were computed for fish, benthic invertebrate and diatom data using the vegdist function in the package "vegan" (Oksanen et al., 2019). Fish species densities (ind. per 100 m2) were used to analyze fish assemblage, relative abundance for diatoms and number of individuals per sample for benthic invertebrate species (Appendix 2). A dummy variable (1) was added to each sample in the original data prior to computing the dissimilarity indices to avoid fish samples with all zero scores. The dissimilarity indices were reduced to Principal Coordinates (PCo) using the betadisper function, which implements the PERMDISP2-procedure (Anderson, 2001). Permutation tests of the PCo's were performed with the ANOVA-like function permutest. Principal Coordinates were used to display the assemblage structure among rivers and years in ordination space. Finally, PERMANOVA (Anderson, 2001) was computed using the function adonis to analyze differences between the rivers and sampling years and their interaction in species assemblages. Rivers and years were treated as fixed factors in the PERMANOVA.

3. Results

There were clear gradients in the water quality of the study rivers (Appendix 1). The first three principal components of the PCA analysis explained 48.6 %, 14.7 % and 10.9 % of the variance in the water quality variables, respectively (Fig. 2). Horn's Parallel Analysis indicated to retain these three principal components, having eigenvalues above one, in the analysis. On principal component one, correlations between the original variables and principal components showed that content of several metals (Al, Cd, Co, Cu, Na, Ni and Zn) increased with increasing acidity and conductivity increased as the concentration of metal ions increased (Fig. 2). Second component mainly illustrates alkalinity, and, to a lower extent, Pb and turbidity, while Fe and color showed a negative correlation to these water quality metrics (Fig. 2). The main variables in the third principal component were water color, As and Cr, all having moderate positive correlations (Fig. 2).

In general, the average and the maximum metal contents in the river water of the study sites was higher than the EQS criteria (Table 3). The exception to this were As, Pb and Ni. In a revision of the EU Directive 2008/105/EC in 2013, the original Ni EQS (20 μg/l) has been revised to 4 μg/L bioavailable Ni. The variation in metal contents was relatively high, which could be expected given the range of AS soils (Table 2 and Table 3).

Significance tests on CCA showed statistical significance indicating a strong interrelationship between the two variable sets (Table 4). The shared variance on each of the three (1–3) canonical variates are 69.02%, 32.78%, 19.19%, respectively, the canonical variables (CV:s) showed a strong canonical correlation between landcover and land use attributes and water quality for CV1 (0.84), and moderate for CV2 (0.61) and CV3 (0.49). On CV1 structural correlations illustrated strongest correlations between PC1 water quality component with variables indicating low presence of AS soils and high coverage of ditches (Fig. 3A). The variance explained in PC1 was mostly due to these two variables (Fig. 3A). The structural correlations and the variance explained on CV2 showed a connection between PC3 and in the low existence of wetlands in the catchment (Fig. 3B). On the CV3, structural correlations were strongest between PC2 water quality component and higher presence of forested lands and low presence of artificial surfaces areas in the catchment (Fig. 3C). These two catchment variables also had the highest variance explained on PC2.

The assemblage structure of fish, benthic invertebrates and diatoms differed among the rivers, and river identity explained a major part of the variation in assemblage structure in all three biological elements (Table 5, Appendix 2). Also, the PCo ordinations indicated clear separation between the rivers in the assemblage structure for all biotic groups, whereas the assemblage variations among study years were largely overlapping (Fig. 4). This temporal variation, although significant in fish and diatoms, explained little of the overall assemblage structure of the three biological elements (Table 5).

Water quality component PC1 and the area of AS soils correlated with the ordination (assemblage sample spatial medians) of both fish and diatom assemblages on PCo dimension 1 (Table 6). Thus, the fish and diatom assemblage samples that had the least amount of ASS, and water quality least affected by ASS, were located to the left side of the PCo dimension 1 and those with high occurrence and impact to the right (Fig. 4). In addition, fish assemblage structure on PCo1 also correlated with PC2 and diatom assemblage structure with catchment forests cover. On PCo dimension 2, fish assemblages and especially diatom assemblages, were correlated with PC2 (Table 6). Consequently, to the higher end of the PCo dimension 2 were the sampling sites with water quality characteristics of higher alkalinity, turbidity and Pb content (Fig. 4). To conclude, the PCo ordination of fish and diatom assemblage samples were mostly affected by two water quality components, PC1 and PC2, and coverage of AS soils and forests in the catchment.

PCo on benthic invertebrate assemblage structure showed somewhat different main factors structuring the assemblage. The assemblage structure was most strongly correlated with PC2 (PCo dimension 1) and PC3 (dimension 2; Table 6). Thus, benthic invertebrate sampling sites from rivers with low alkalinity and turbidity, and high on color, Fe and Pb were placed on the positive end of horizontal axis (PCo dimension 1), while the ordination the vertical axis seemed to be based on several

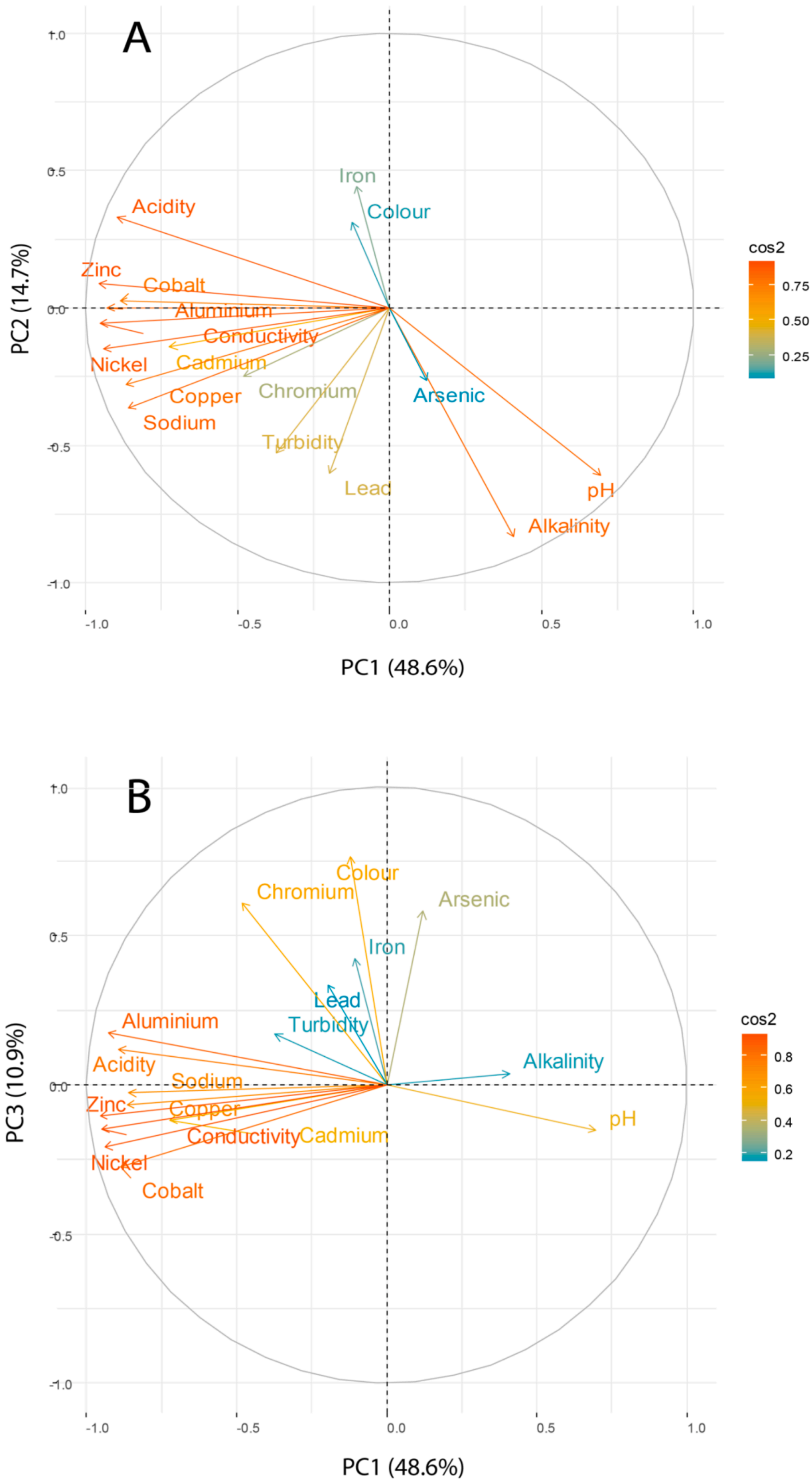

Fig. 2. Plot of the Principal Component Analysis (PCA) results on the water quality data (Appendix 1) of the 15 AS soil study rivers. PC components one and two (A) and one and three (B) are shown. Variation explained (%) by each component is given in parenthesis. The length and the color of the arrows indicate the most important water quality variables contributing to PC components. The squared cosine (cos2) shows the importance of a variable for a given observation: variables with a large value of cos2 contribute a relatively large portion to the PC.

Table 3
Mean yearly levels of metals (μg/l) in the study sites water samples 2010–2012 (N = 126). The Environmental Quality Standards (EQS) values for metal content are given in the last row. The coloring of the mean values refers to: red = numerous times higher than EQS, orange = around twice higher than EQS, yellow = higher than EQS and blue = lower than the EQS criteria. For Na there was no EQS value.

	Al	As	Cd	Co	Cr	Cu	Pb	Na	Ni	Fe	Zn
Mean	1536	0.9	0.140	6.5	1.7	4.3	0.5	6.5	14.4	1877	38.4
Maximum	3936	1.9	1.210	27.3	3.9	11.7	1.2	16.0	66.6	3730	135.0
Minimum	298	0.5	0.010	0.4	0.8	0.9	0.1	2.5	1.3	680	6.4
Std dev	886	0.3	0.191	5.6	0.6	2.5	0.2	3.9	13.4	617	28.9
EQS	100 *	5*	0.08**	4***	1***	2*	7.2**	-	20**	300*	30*

*Canadian Freshwater Metals Criteria – CCME, freshwater long term values.
**EU Directive 2008/105/EC, annual averages.
*** Canadian BC Water Quality Guidelines, freshwater long term values.

Table 4
Significance tests (Rao's F Approximation and Bartlett's Chi-Squared Test) of the canonical correlation analysis between catchment characteristics and water quality.

Canonical variate	Canonical correlation	Rao's F statistics	Num. df	Den. df	Prob. (>F)
CV1	0.831	13.664	21	333.64	<0.001
CV2	0.572	6.957	12	234.00	<0.001
CV3	0.438	5.605	5	118.00	<0.001
	rho^2	Bartlett's Chisq	Df		Prob. (>X)
CV1	0.690	212.958	21		<0.001
CV2	0.328	72.922	12		<0.001
CV3	0.192	25.465	5		<0.001

factors. The assemblage structure of benthic invertebrates also correlated with coverage of AS soils and forests in the catchment (Table 6).

Fish and invertebrate EQR-values were highest in rivers with the highest mean pH (mean river pH pooled over years and study sites, Fig. 5), and both EQRs had lowered along with the decreasing pH values (Spearman rank correlation, fish: $r_s = 0.525$, $p = 0.022$, $N = 15$, invertebrates: $r_s = 0.624$, $p = 0.027$, $N = 10$). Out of the metrics within the invertebrate EQR PMA-index ($r_s = 0.673$, $p = 0.017$, $N = 10$) and number of stream type -specific taxa ($r_s = 0.663$, $p = 0.018$, $N = 10$) were mostly affected by pH. Within the fish EQR the number of fish species present ($r_s = 0.757$, $p < 0.001$, $N = 15$), density of age-0 + salmonids ($r_s = 0.447$, $p = 0.048$, $N = 15$) and the density of cyprinid group individuals increased ($r_s = -0.709$, $p = 0.002$, $N = 15$, reversed metrics) with rising pH. Diatom EQRs were in general lower than those of fish or invertebrates, (Fig. 5), and the correlation between EQRs and pH values was not significant. The pressure specific diatom index (ACID) (index values, mean = 5.269 range = 3.161–7.609, N = 12) had a significant correlation with pH ($r_s = -0.681$, $p = 0.007$, $N = 12$), indicating relatively strong response by the index to changes in mean pH.

All three biological elements, fish, invertebrates, and diatoms had comparable trends in EQR's against water quality gradient in PC1 that combined the increase in concentrations of several metals to decreasing pH. The EQRs first rapidly decreased but increased in the two rivers with the highest PC1 values (Fig. 5). Because of this the correlation between EQRs and PC1 was significant only in fish (Spearman rank correlation, $r_s = 0.579$, $p = 0.012$, $N = 15$). Within the fish index the combination of rising pH with less metals changed the number of fish species present ($r_s = 0.600$, $p = 0.009$, $N = 15$), especially increased the proportion of intolerant fish species ($r_s = 0.623$, $p = 0.007$, $N = 15$), and also the densities in age-0 + salmonids increased ($r_s = 0.661$, $p = 0.004$, $N = 15$). The two rivers breaking the decreasing trend in EQRs (Rivers Laihianjoki and Maalahdenjoki) had the highest metal concentrations (Al, Cd, Co, Cu, Na, Ni, Zn, conductivity), but they were not the most acid rivers in the data (mean pH 5.6 and 4.9). The ACID index values did not correlate significantly with PC1 values (Spearman rank correlation, $r_s = 0.343$, $p = 0.138$, $N = 12$), the same two rivers (Rivers Laihianjoki and Maalahdenjoki) breaking the otherwise linear relationship.

4. Discussion

We observed a strong relationship between water quality and land-cover attributes, but more variable relations with biological quality elements. Several studies have demonstrated how catchment land use interacts with the soil types to impair water quality and often also the aquatic assemblages (Sliva and Williams, 2001; Donohue et al., 2006; Sutela and Vehanen, 2010; Valle Junior et al., 2015; Horak et al., 2020). Although catchment geology and soil types are the major factors determining overall ecology of streams (Hynes, 1975), it is evident that local aquatic assemblage structure is always a result of complex interactions between natural and human-induced environmental characteristics at multiple spatial and temporal scales (Allan, 2004; Varanka et al., 2015).

Our results underline that the key to understand the consequences of this complexity were the responses of the biological communities.. The area of AS soils affected water quality rather straightforwardly and rather much also biological quality. Biological metrics based on fish and invertebrates responded to decreasing pH in rivers with decreasing ecological quality ratios, while diatom metrics showed no significant response to pH. Metrics of all the three biological groups responded negatively to increasing metal concentrations up to moderately impacted rivers, but not in the two rivers with the highest metal concentrations and not the lowest pH. Thus, it may be that high metal concentrations without very low pH were not especially harmful to the assemblages sampled. Earlier AS river studies have shown that high metal levels (Al, Cd, Zn) may not induce ecotoxicity outside the most adverse acid surges, probably due to the simultaneous high Ca and DOC concentrations lowering metal bioavailability (Vuori 1995b). The level of metals in water quality samples generally surpassed EQS levels indicating lower than good ecological status in AS soils impacted rivers. The interpretation of the effect of metals is not, however, straightforward as their effects are dependent on the bioavailability as a function of several factors (Adams et al., 2020). Our study showed the effect of low pH on metals toxicity and the biological response.

The biological quality elements responded differently to the water quality impacts. While the fish and diatom assemblage structures were most strongly affected by the AS soil water quality changes, invertebrates were more structured according to the forestry-induced water quality changes, such as water color, turbidity and iron concentrations. Increased organic loading from the catchment can increase

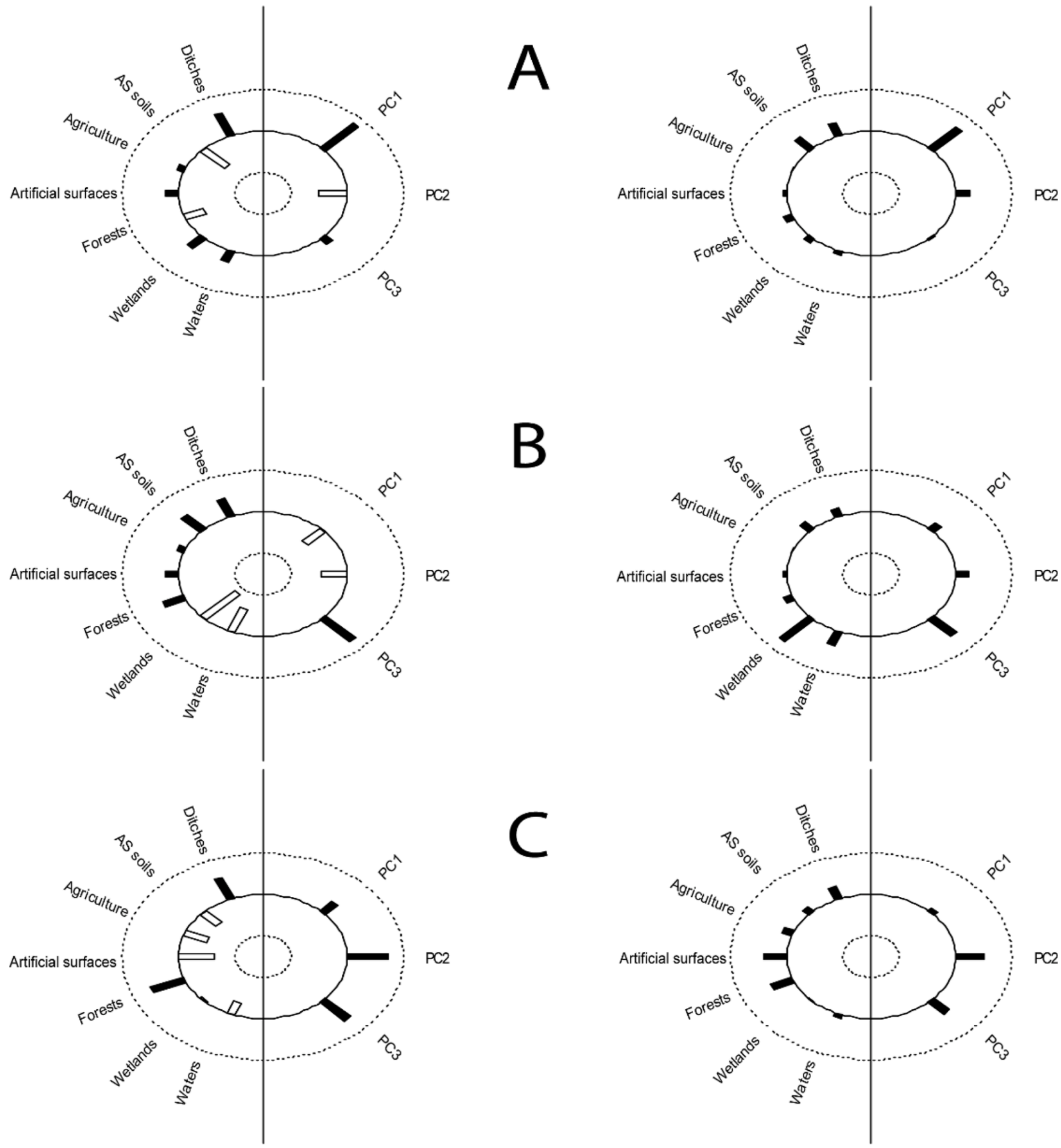

Fig. 3. The Canonical Correlation Analysis results of the associations between water quality (the three first water quality principal components, see Fig. 2) to landcover attributes in 15 AS soil rivers. The uppermost panel (A) shows the first Canonical Variable (CV), mid panel (B) is the second CV and the lowermost panel (C) is the third CV. The right panel shows the explained variance for by each variable (length of the black bar indicates the amount variance explained) and the left panel the structural correlations (black bars are positive correlations, white bars negative) for each variable for the CV in question.

especially the abundance of filter-feeding invertebrates (Karvonen, 1995).

The spatial variation in the aquatic assemblages among rivers was clearly higher compared to temporal variation among years. This suggests that the factors identified to cause the differences in the assemblages among the rivers, mainly the diffuse loading from AS soils (pH, metals) and forested areas (color, iron, alkalinity, turbidity), are in the long-term affecting the aquatic assemblages. Thus, to restore the ecological status of these rivers the restoration efforts should be directed to the catchment to diminish these diffuse loads. Previous research has highlighted the importance of mitigation efforts towards the acid leaching from agricultural lands by maintaining the groundwater levels high enough to avoid oxidation of AS soils, but clearly more reduction in acid loadings is needed to reach the target of good ecological status (Vintanen et al., 2016) Restoration of the disturbed freshwater ecosystems requires deactivating and mitigating the same mechanisms that have caused the ecosystem damage (Rapport and Whitford, 1999).

Our results demonstrate that the large area of AS soils had pronounced impacts on acidity and metal concentrations in rivers. Diffuse loading from agriculture on AS soils is the main source of leaching of metals to waters in Finland (Åström and Björklund, 1995). Often species diversity tends to decrease, and composition change in areas with elevated metal concentrations, but the mechanisms are not well known (Mayer-Pinto et al., 2010). According to Wallin et al. (2015) the concentration of metals in the AS soil river estuaries can be so high that harmful ecotoxicological impacts are likely to occur. For fish populations, the negative effect of environmental acidification is especially linked to aluminum (Al), as the combined effect of low pH and high Al level damages gill tissue (Youson and Neville, 1987; Muniz and Leivestad, 1980; Exley et al., 1991). Indeed, high Al levels combined with acidity in Finnish AS soil rivers were evaluated to affect fish assemblage structure and diminish species richness (Sutela & Vehanen 2017). In our study, elevated concentrations were not limited to Al, but also Cd, Co, Ni and Zn concentrations increased with increased proportion of AS soils and low pH. Overall, the combined impact of metals to aquatic assemblages remains poorly known. Given that more AS soils are increasingly taken to anthropogenic use (Smith et al., 2016), the metal pollution of surface and groundwaters is expected to accelerate in the future (Dent

Table 5
Summary of PERMANOVA statistics on Bray-Curtis dissimilarities of fish, diatom and benthic invertebrate assemblages among study rivers, study years and their interaction. The results are based on 999 permutations in each case.

Fish						
	Df	Sum. of sgs.	Mean sgs.	Pseudo-F	r^2	Prob. (>F)
River	14	21.264	1.519	10.925	0.565	0.001
Year	1	0.370	0.370	2.661	0.010	0.027
River*Year	14	2.638	0.188	1.355	0.070	0.042
Residuals	96	15.985	0.139		0.423	
Total	125	37.619			1.000	
Diatoms						
	Df	Sum. of sgs.	Mean sgs.	Pseudo-F	r^2	Prob. (>F)
River	12	15.419	1.285	8.594	0.522	0.001
Year	1	0.686	0.686	4.588	0.023	0.001
River*Year	12	2.070	0.172	1.154	0.070	0.138
Residuals	76	11.364	0.149		0.385	
Total	101	29.539			1.000	
Invertebrates						
	Df	Sum. of sgs.	Mean sgs.	Pseudo-F	r^2	Prob. (>F)
River	9	4.178	0.464	1.853	0.619	0.007
Year	1	0.169	0.169	0.675	0.025	0.756
River*Year	9	1.153	0.128	0.512	0.171	1.000
Residuals	5	1.253	0.250		0.185	
Total	24	6.753			1.000	

and Pons 1995; Hinwood et al., 2008; Enio et al., 2020); hence, effective biological assessment tools are needed.

The impacts of metals are not always directly related to acidification. In our study this was the case with Fe, Pb, As and Cr. Similar to our results, Åström and Björklund (1995) reported that concentrations of some metals like Al, Co, and Ni increase due to runoff from AS soils, but others, like Fe, do not increase above their baseline concentrations due to AS soils. The reason for this can be in oxidation–reduction processes, Fe, for example, can be rapidly immobilized by oxidation processes (Åström and Björklund, 1995). One plausible explanation is that these metals interact differently with humic compounds when water becomes more acidic. Vuori (1995a) observed a dramatic decrease of Fe concentrations during the acid surges, which was related to the co-precipitation of iron with humic compounds. These precipitates may increase mortality of invertebrates and fish embryos and induce indirect ecosystem changes (Vuori, 1995a). High concentrations of iron may also cause direct mortality: Myllynen et al. (1997) reported lower survival of river lamprey (*Lampetra fluviatilis*) larvae when total iron concentrations rose to high levels representing natural high flow conditions of an AS soil river. Fe has a prevalent role in ecosystem functioning in boreal freshwaters, and there is an indication that Fe concentrations have recently increased in boreal freshwaters, probably due to changes in precipitation and temperature (Heikkinen et al., 2022).

The most dramatic effects of agricultural AS soils emerge when heavy rainfall periods and elevated runoff are followed by prolonged dry periods with lowered groundwater levels enabling oxidation of AS soils and effective release of acidity (Toivonen and Österholm, 2011; Nystrand and Österholm, 2013). Such acid peaks have caused fish kills in several rivers in our study area (Sutela et al., 2012). During our study period there were no such sudden acidic peaks. Instead, rivers maintained their typical pH levels related especially to the quantity of AS soils, and degree of human disturbance. It is clear that acidity and metal

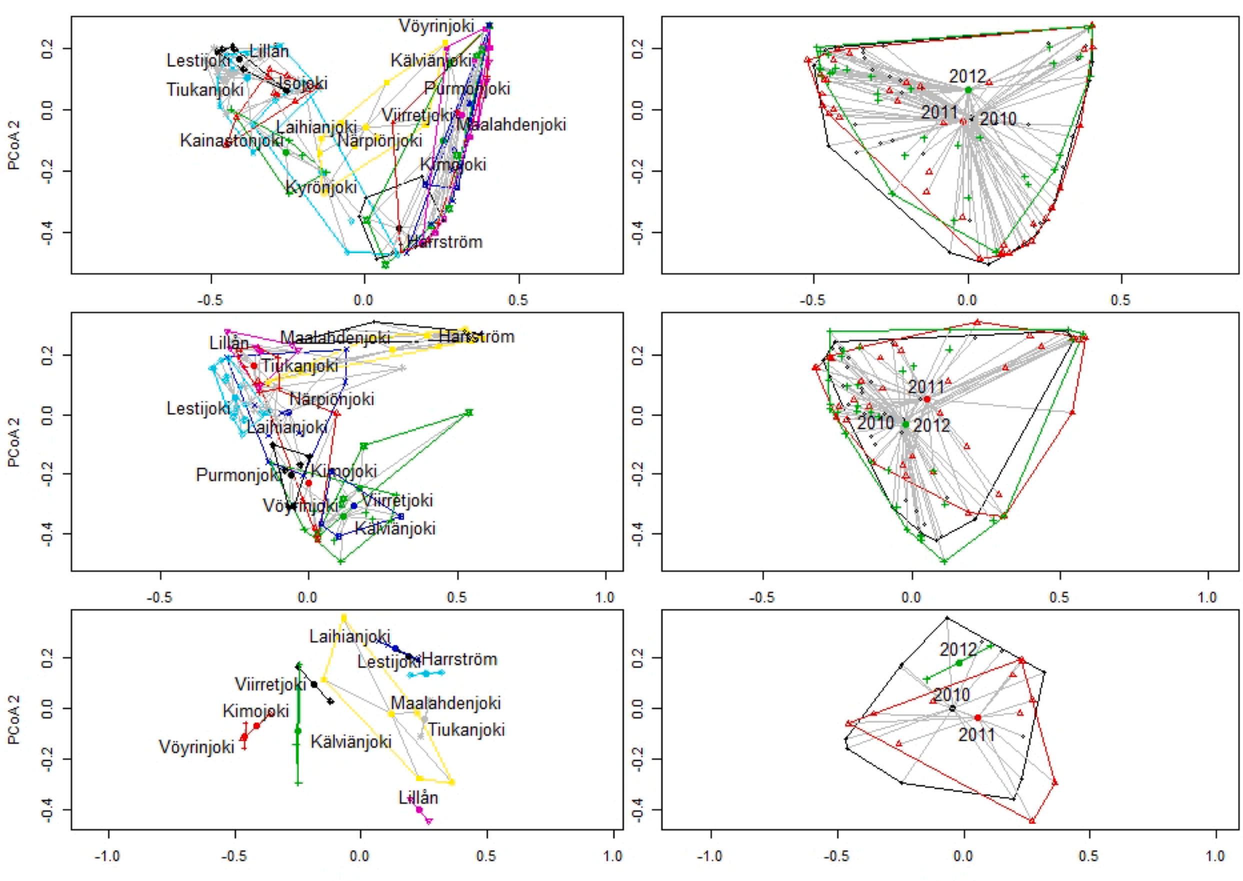

Fig. 4. Distances (Bray Curtis dissimilarities) between study rivers (left panel) and years (right panel) on Principal Coordinates Analysis (PCoA) dimensions one and two. The uppermost panel shows the results based on fish assemblage, mid panel based on diatom assemblage and the lowermost panel is based on invertebrate assemblage. River name or year shows the spatial median and the line covers the area of the samples for each group.

Table 6
Spearman rank correlation coefficients (r_s) between assemblage structure of fish, benthic invertebrates and diatoms and Principal Coordinates Analysis (PCoA) results with catchment and land use characteristics of the rivers studied. The spatial medians of the fish, diatom and benthic invertebrate samples were used for PCo dimension one and two. The most significant correlations ($p < 0.001$) are indicated by bold typeface.

Fish	PC1	PC2	PC3	Forests	Wetlands	Waters	AS soils	Ditches	Agriculture	Artificial surfaces
PCo dimension1	**−0.666**	**0.400**	0.254	0.278	−0.245	−0.101	**0.512**	−0.303	0.058	−0.071
Prob.	**<0.001**	**<0.001**	0.004	0.002	0.005	0.259	**<0.001**	0.001	0.517	0.428
PCo dimension2	−0.034	**−0.398**	0.242	**0.356**	−0.174	−0.218	−0.105	0.214	−0.225	**−0.350**
Prob.	0.703	**<0.001**	0.006	**<0.001**	0.051	0.014	0.243	0.016	0.011	**<0.001**
Diatoms										
PCo dimension1	**−0.504**	0.118	0.215	**0.466**	−0.207	−0.114	**0.373**	−0.221	−0.156	−0.230
Prob.	**<0.001**	0.236	0.030	**<0.001**	0.037	0.255	**<0.001**	0.026	0.118	0.020
PCo dimension2	0.160	**−0.667**	0.061	−0.044	0.003	−0.144	0.050	0.151	−0.031	0.174
Prob.	0.108	**<0.001**	0.546	0.664	0.977	0.255	0.619	0.130	0.759	0.081
Invertebrates										
PCo dimension1	0.196	**0.628**	0.134	−0.194	0.067	−0.260	−0.190	0.250	0.022	0.201
Prob.	0.479	**0.001**	0.522	0.347	0.751	0.209	0.363	0.228	0.918	0.334
PCo dimension2	−0.149	−0.299	**−0.466**	**−0.477**	0.050	0.424	**0.445**	−0.405	0.321	0.413
Prob.	0.479	0.149	**0.019**	**0.016**	0.814	0.035	**0.026**	0.045	0.118	0.040

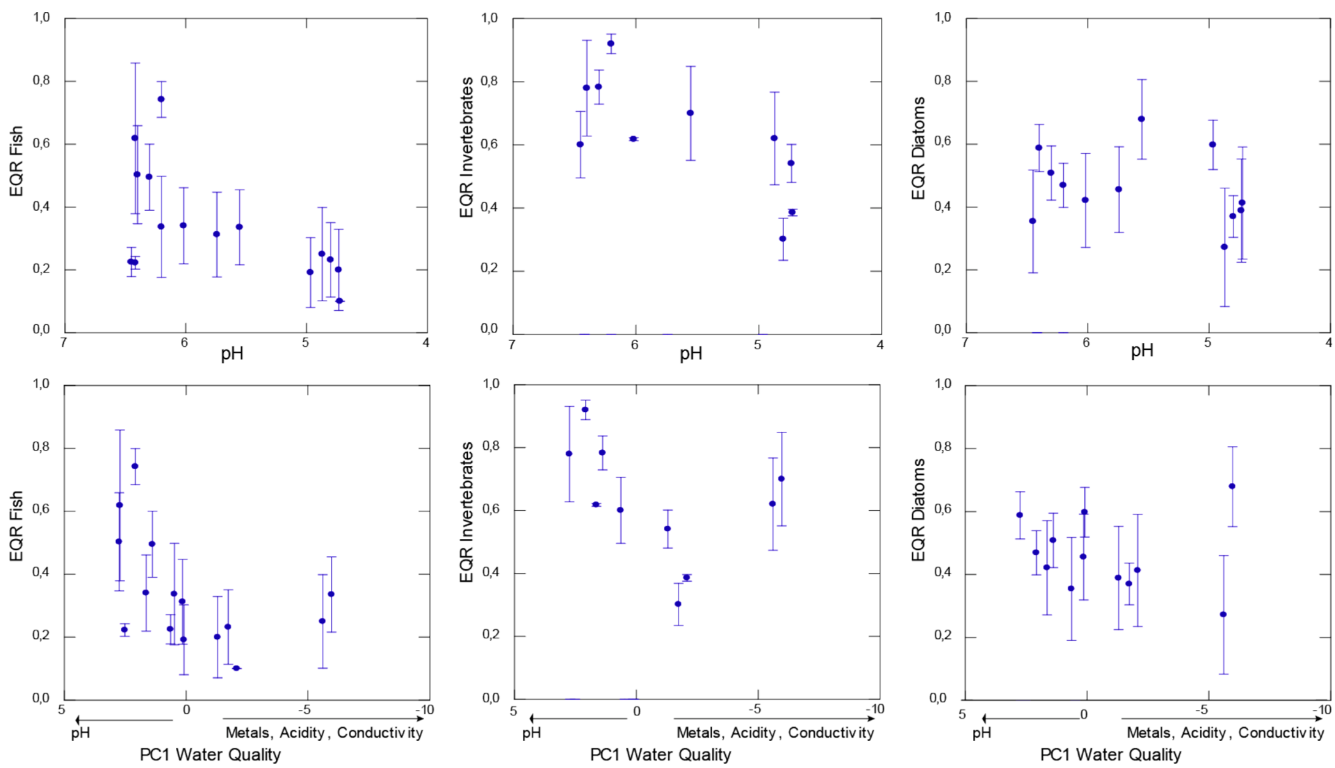

Fig. 5. Relationship between mean pH (upper panel) and water quality gradient (Principal Component one, lower pamel) to Ecological Quality Ratio calculated from fish, invertebrate and diatom data of the study rivers. Data is pooled over rivers and study years (2010–2012, mean ± SD).

load strongly vary spatially and temporally, depending on the amount of AS soils and their degree of oxidation which can be largely affected by land use, especially cultivation and drainage intensity (Vintanen et al., 2016). This variation was apparent also in our ecological quality assessment results.

Our results showed that the main drivers behind the ecosystem degradation in the study rivers were acidity pressures related to AS soils in the catchment. The national metrics used in this study where not acidity-specific, but were originally developed to respond to impacts of most common pressures, especially eutrophication and hydromorphological alteration (Vehanen et al., 2010; Aroviita et al., 2008; Aroviita et al., 2012). In our study fish and invertebrate metrics responded to pH gradient, while diatom metrics did not. To effectively target the mitigation measures it is important that biological indices respond to the key pressures of the area (Rapport and Hildén, 2013). If not, the obvious consequence should be to develop indices that are more specific to specific pressure impacts, as it is the case in the diatoms for which ACID index was developed by Andrén and Jarlman (2008). According to our results the ACID index responded well to the changes in pH in AS soils rivers. In the case of the effect of increasing metal concentrations the results were rather unified among the three biological metrics: the EQR values first steeply decreased as expected, but then slightly increased along the PC1 axis with metal concentration increase but also water pH decrease. It remains unclear whether in this case at the end of PC1 axis the signal of better ecological status was true, or falsely positive in failing to indicate potential stress from the high metal content.

The obvious reason for the diatom metrics not to respond to the effects of low pH is that the metrics (type-specific taxa and PMA) were applied for Finnish rivers to reflect mainly impacts of pressures such as nutrient leaching and organic pollution. Mykrä et al. (2019) reported that in streams with natural acidic environment nutrient enrichment did not increase diatom richness as it did in neutral environment. Hence the acidity may override eutrophication effects on diatom community. According to our results impacts from the AS soils altered the composition of invertebrate taxa compared to rivers with less acid pressures. Increased organic loading from the catchment can increase especially the abundance of filter-feeding invertebrates (Karvonen, 1995), which partly explain the observed partly irregular assemblage and metric patterns along water quality and pH gradient. Earlier studies have shown that invertebrates show species-specific differences in sensitivity to AS soil impacts (Vuori 1995b; Willner 2020). Runoff from AS soils has caused slower larval development and increased the occurrence of abnormalities among invertebrates (Vuori 1995b). Our fish results showed that acidity decreased the number of species present and ceased the reproduction of salmonids. The combination of decreasing pH and increasing metal content affected the fish community structure by decreasing the proportion of intolerant fish species. Somewhat similarly, many of the key fish species in Finnish rivers classified as intolerant in FiFI index (e.g., brown trout, grayling *Thymallus thymallus* and European bullhead *Cottus gobio*) do not tolerate acidity (Sutela and Vehanen, 2017) suggesting that FiFI index could be applicable with rivers disturbed by acidification. However, cyprinids are classified as tolerant species in FiFI though their tolerance to acidification is poor (Almer et al., 1974; Rahel and Magnuson, 1983). This was also confirmed by our results, as their density decreased with decreasing pH. In this aspect, the sensitivity of the metrics towards detecting acidification pressures could be further developed. Overall, our results support the conclusions of earlier studies on the necessity and added value to include several biological assemblages in the assessment of ecological impacts in rivers also when it comes to the effects from acid releases (Bae et al., 2011, 2014; Pace et al., 2012; de Morais et al., 2018).

Declaration of Competing Interest

The authors declare that they have no known competing financial interest or personal relationship that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ecolind.2022.109085.

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