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Dynamics of surface water quality changes in model headwater areas of the Czech Republic

(Dynamika změn kvality povrchových vod v modelových povodích České republiky)

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Abstrakt: Prameny řek mají vysokou ekologickou hodnotu. Bohužel biogeochemické procesy v pramenných oblastech v kontextu různých srážko-odtokových podmínek a specifického půdního pokryvu nebyly dosud plně prozkoumány. Tato studie se zaměřuje na změny korelací 16 biogeochemických parametrů souvisejících s různými typy srážko-odtokových událostí a podmínkami půdního pokryvu pro osm pramenných povodí ve střední Evropě. Vícenásobné metody jako lineární regrese, Spearmanova pořadová korelace, analýza hlavních komponent a hysterezní smyčky C/Q odhalily hlavní vztahy. Přítomnost rašelinišť a podmáčených smrčin měla rozhodující vliv na biogeochemii (především pro $CHSK_{Mn}$, huminy, Fe, P-PO_4^{3-} TP a N-NO_3^-). Nejsilnější pozitivní korelace organických látek ($CHSK_{Mn}$) a Fe byla zastoupena v povodí s největší plochou poškozeného lesa (70 %), ale s menším podílem mokřadů (8 %). Vysoké průtoky ovlivňují uvolňování většího množství organických látek a N-NO_3^-.

Klíčová slova: pramenné oblasti – organické látky – podmáčené oblasti – rašeliniště – srážko-odtokové události – kvalita vody – měrná elektrická vodivost

Abstract: River headwaters have a high environmental value. Unfortunately, the biogeochemical processes in headwaters in context of different rainfall-runoff conditions and specific land cover have not been fully examined. This study focuses on changes in correlations of 16 biogeochemical parameters related to different types of rainfall-runoff events and land cover conditions for eight headwater catchments in Central Europe. Multiple methods as linear regression, Spearman rank correlation, Principal Components Analysis and C/Q hysteresis loops revealed main relationships. Presence of peatlands and waterlogged spruce forests had decisive influence on the biogeochemistry (mainly for COD_{Mn}, humins, Fe, P-PO_4^{3-} TP, and N-NO_3^-). The strongest positive correlation of organic matter (CODMn) and Fe is represented in a catchment with the largest area of damaged forest (70%), but with a smaller proportion of wetlands (8%). High flow rates influence the release of greater amounts of organic matter and N-NO_3^-.

Keywords: headwater areas – organic matter – waterlogged areas – peatbogs – rainfall-runoff events – water quality – electric conductivity

1. Introduction

Headwater streams are important both for the local aquatic ecosystem and for ecosystem goods and services. They are also very sensitive to any pollutant inputs or climate change and can therefore be assumed to be an early indicator of such changes. Currently, increasing temperatures and increased risk of extreme rainfall-runoff events are leading to changes in surface water biogeochemistry. In particular, the increased risk of elevated concentrations of organic matter, which could have negative effects on human health due to the possible formation of disinfection by-products after water treatment. The study of changes in water quality in relation to different conditions in the catchment is necessary to develop appropriate strategies for maintaining water quality.

2. Study areas and data sources

The study was carried out in two headwater localities of the Elbe River basin in south and west part of Czechia – Šumava Mts.(Fig. 1) and Krušné hory Mts. (Fig. 2). The area of study catchments ranged from 0.14 km^2 (ROK2) to 22.4 km^2 (SLA). Long-term specific discharges (2008–2013) ranges from 29.3 $l \cdot s^{-1}.km^{-2}$ (BRE) to 41.2 $l \cdot s^{-1}.km^{-2}$ (ROK2) in Šumava Mts. (Vlček et al. 2016) and about 14–15 $l \cdot s^{-1}.km^{-2}$ (ROL, SLA) in Krušné hory Mts. Large parts of catchments occupy wetland areas with ratio from 83% (ROK2) to 3% (SLA) of catchment area according to Base map of the Czech Republic 1:10 000, Czech Office for Surveying and Cadastre. Five land cover categories (as possible drivers of water quality changes) were derived for the study catchments – healthy spruce forest (HSF), damaged forest (DF), decayed forest with partly regeneration (DFR), meadow (M) and peatbog (PB), Fig.3.

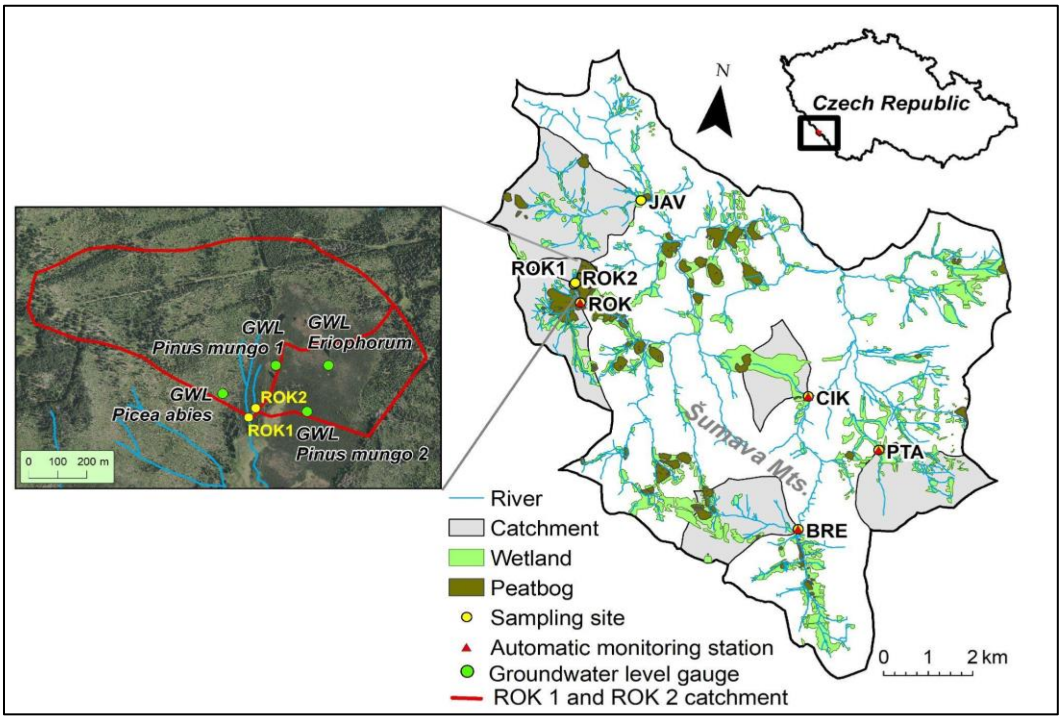

Fig. 1 Locations of the studied catchments in the Šumava Mts. Ptačí Brook (PTA), Javoří Brook (JAV), Cikánský Brook (CIK), Březnický Brook (BRE), Rokytka Brook (ROK), ROK1, Rokytka Brook left tributary (ROK2). Source: ARCČR 500, DIBAVOD, KVES, © AOPK ČR, WMS – Orthophoto.

Two main data sources were used to analyse changes in surface water quality in headwater areas. The first data source included seasonal field measurements and water samples for laboratory analyses at selected sites in headwater areas collected between October 2013 and November 2019. The second data source was collected between 2013 and 2022 using a network of automatic water quality and gauging monitoring stations of the Department of Physical Geography and Geoecology, Charles University.

3. Methodology

The dependency of 15 physico-chemical parameters and specific discharge in 6 catchments in the headwater area of the Šumava and in 2 catchments in the headwater area of the Krušné hory Mts. was analysed by correlation analysis using Spearman's r coefficients (Spearman 1904). Missing data were deleted pairwise. Principal component analysis (PCA) was performed in Excel using XLSTAT software (Addinsoft 2018) for 16 physicochemical parameters, 8 catchment characteristics and discharge. Simple C/Q hysteresis loops for electric conductivity (*EC*) and *pH* were examined to assess changes in water chemistry during different rainfall-runoff events.

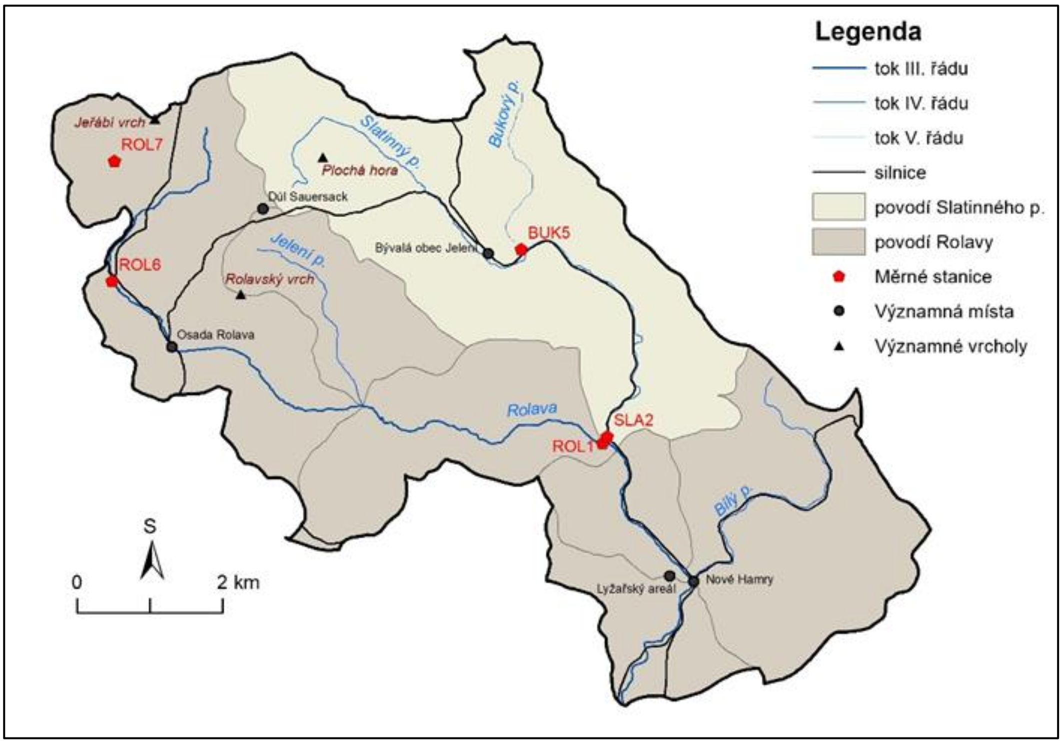

Fig. 2 Locations of the studied catchments in the Ore Mts. – Rolava River (ROL1), upper Rolava R. (ROL6, ROL7), Slatinný Brook (SLA2), Source: ARCČR 500, DIBAVOD, VÚV T.G.M., ČÚZAK.

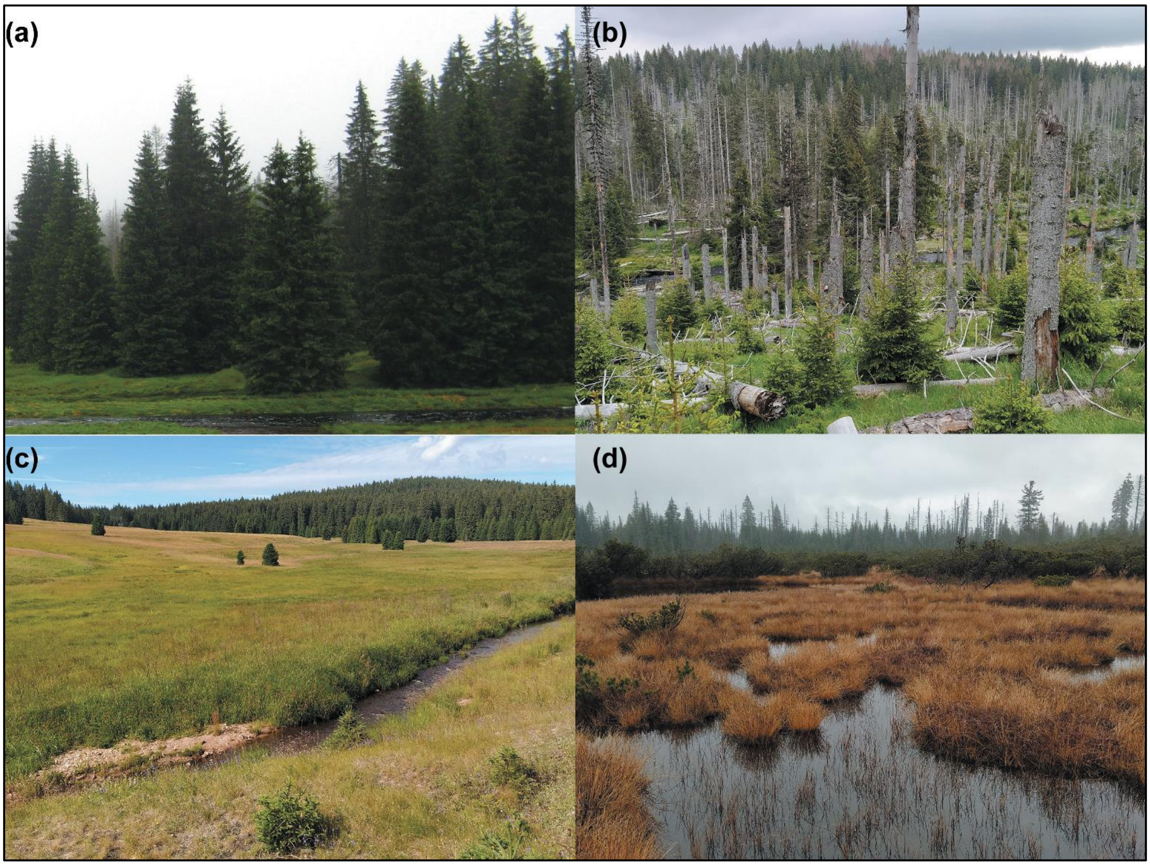

Fig. 3 Land-cover categories as possible drivers of water quality changes in the study catchments. (a) Healthy spruce forest (HSF). (b) Decayed forest with partial regeneration (DFR). (c) Meadow (M). (d) Peatbog (PB).

4. Results

Using PCA, it is possible to see the main relationships between each profile, individual parameters and catchment characteristics (Fig. 4). The first two factors explain together 66.02% of the variance among the 16 physicochemical parameters, 8 catchment characteristics and discharge. The 21 variables are well represented on the plane under consideration, either by the first component (EC, DO, Ca^{2+}, COD_{Mn}, N-NO_2^-, N-NO_3^-, P-PO_4^{3-}, Fe, TP, humins, TH, WL, M, Area, Slope, Discharge) or by the second (water temperature, *pH*, ANC4.5, BNC8.3, DF). The sampling sites can be roughly divided into two groups. Group A includes sampling sites with < 20% wetland cover and comprises two subgroups. The first subgroup - the upper Rolava catchment (ROL and SLA) is defined mainly by higher concentrations of DO and slightly higher values of EC, but lower values of other parameters, that corresponds with the box-plots and is related to lower mean temperatures and larger catchment area, steeper slopes and larger area of meadows and healthy spruce forest. The second subgroup comprises profiles in upper Vydra catchment (PTA, JAV, BRE), which exhibit higher pH possibly due to less wetland cover (< 15%) than other profiles in upper Vydra. Group B includes sampling sites with > 20% wetland cover and higher concentration of organic compounds. Profiles ROK2 and CIK are represented by the slightest catchment slope with lowest *pH*, higher CODMn, humins, Fe and P-PO_4^{3-}, which corresponds with the results that mean slope has been considered as the strongest (negative) determinant of organic matter (Parry et al. 2015).

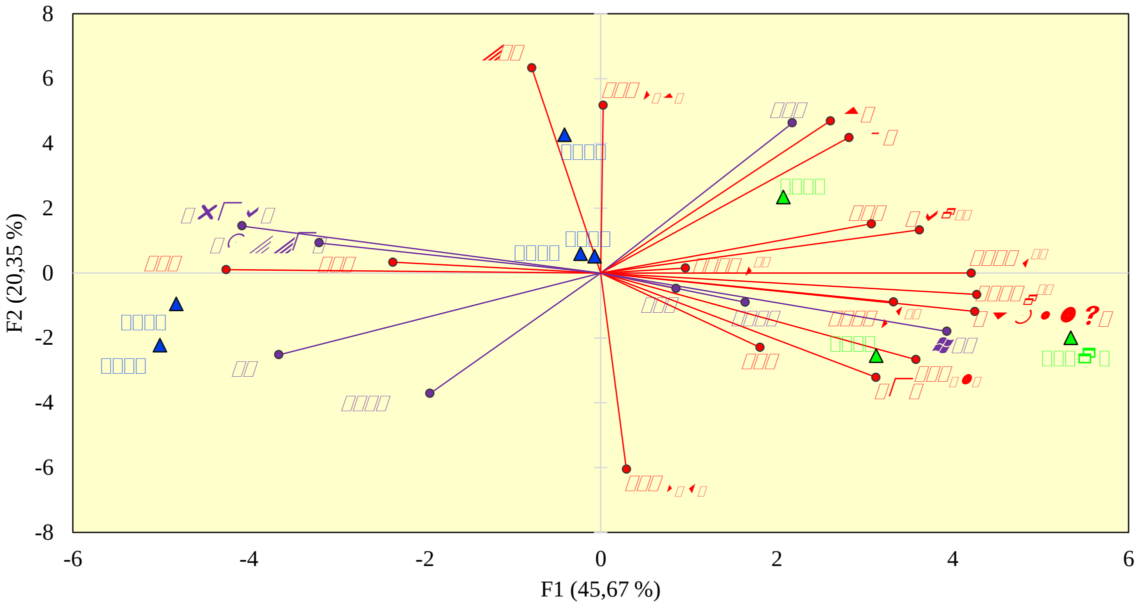

Fig. 4 Principal component analyses (PCA) of measured parameters, catchment characteristics and discharge in 8 catchments (2013–2019). Individual profiles: Filled blue triangles (< 20% wetlands), filled green triangles (>20% wetlands). EC = electric conductivity, t = water temperature, DO = dissolved O2, TH = total hardness, TP = total phosphorus, Fe, CODMn = chemical oxygen demand, ANC4.5 = acid neutralization capacity, BNC8.5 = base neutralization capacity, HSF = healthy spruce forest, DF = damaged forest, DFR = decayed forest with partly regeneration, M = meadow, WL = wetlands, PB = peatbog, q = discharge.

Discharge and catchment conditions before rainfall-runoff events have a fundamental impact on the behaviour of water quality parameters (Erlandsson et al. 2008; Köhler et al. 2008; Fučík et al. 2017). Even the rainwater is relatively low in dissolved minerals (Holko et al. 2006; Cano-Paoli et al.2019), decrease of *EC* with increasing discharge was registered only at SLA profile in upper Rolava (Fig. 5) and JAV in upper Vydra in our study. Both catchments have ≤ 10% wetland cover. Positive linear correlation was observed at other profiles (CIK, ROK2) or there was no relationship. Positive relationship of discharge and *EC* may be related to revitalization measures at the CIK monitoring site in the Šumava Mts. Increased *EC* values have been recorded in the outflow in revitalized water-logged forests in the Šumava Mts. which is consistent with the study Bufková et al. (2010). The most marked negative impact of discharge on *pH* can be observed in catchments with greatest wetland cover at CIK and ROK2 sites ($p < 0.05$; Figs. 6, 7), corresponding to Kocum et al. (2016).

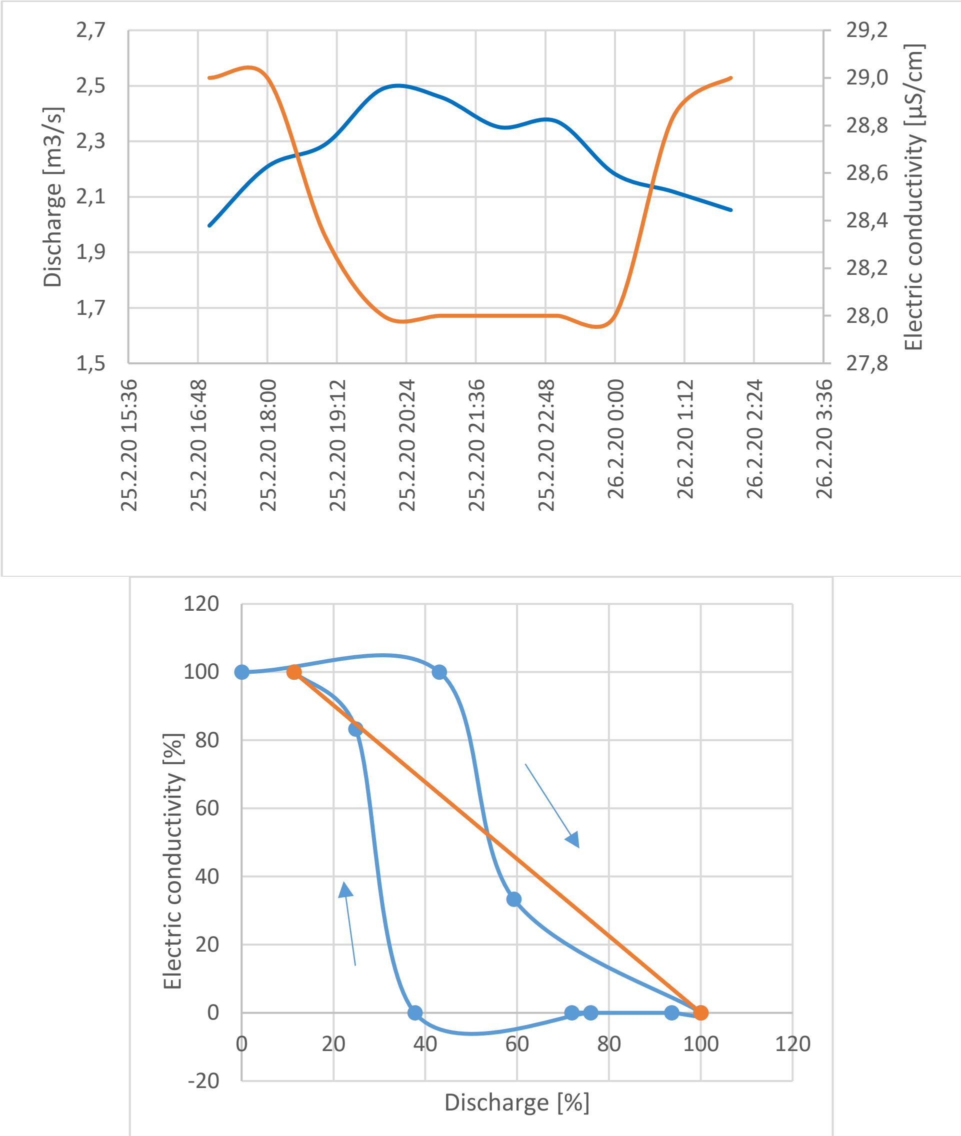

Fig. 5 Trend of electrical conductivity and discharge, event 25. 2. 2020 for SLA2 profile and hysteresis loop for electrical conductivity-discharge relationship.

Discharge is considered as one of the most important factors contributing to changes in organic matter concentrations. For example, Erlandsson et al. (2008) note a strong positive correlation between CODMn and changes in discharge. Our results show that CODMn increases with increasing discharge. The changes of humins concentration with increasing discharge are similarly to CODMn (Fig. 6). The greatest linear increase in humins was observed at the BRE and CIK sampling sites (*slope* > 0.9), the coefficient of determination indicates a medium relationship (*R2* > 0.5). Using Spearman's rank correlation coefficient, a significant relationship (*p < 0.05*) between humins and discharge was determined at JAV, CIK, BRE, ROK, ROK2 sites with the strongest relationship (*p* < 0.01) at CIK and ROK2 sites with the greatest wetland cover. The greatest release of organic matter is also related to iron reduction/oxidation cycles (Grybos et al. 2009; Knorr 2013). Coefficient of determination indicated positive correlation between CODMn and Fe in all catchments with the strongest correlation at JAV (*R2* > 0.7). This was also confirmed by Spearman's correlation coefficient (*p* < 0.05) at all sites with the exception of CIK and ROK2 (Fig. 6).

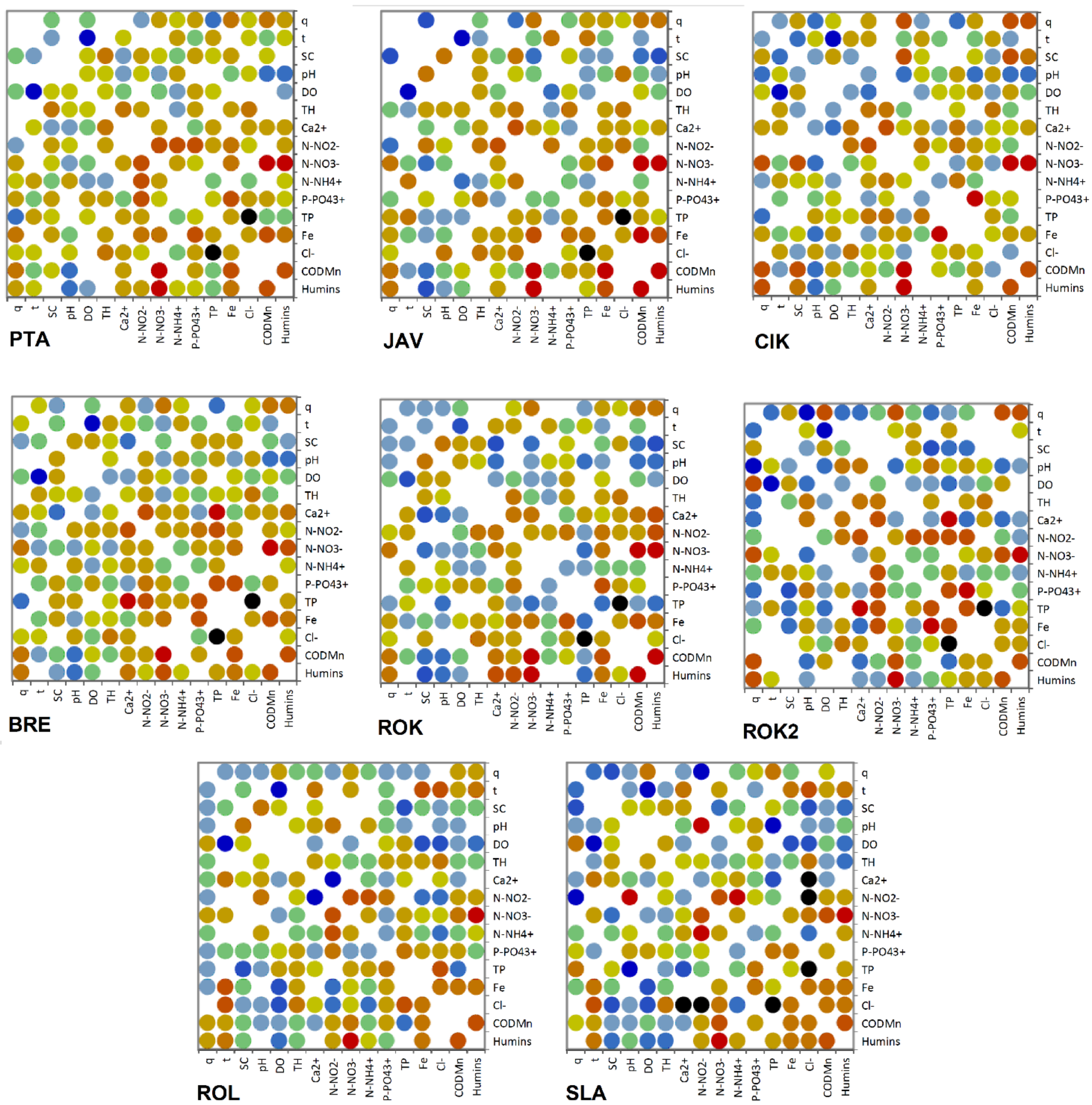

Fig. 6 Correlation maps of Spearman's rank correlation; The blue colour corresponds to a correlation close to −1 and the red colour corresponds to a correlation close to 1. Green corresponds to a correlation close to 0. Individual sites: Upper Vydra: Ptačí Brook (PTA), Javoří Brook (JAV), Cikánský Brook (CIK), Březnický Brook (BRE), Rokytka Brook (ROK), Rokytka Brook left tributary (ROK2); upper Rolava: Rolava (ROL), Slatinný Brook (SLA). q = specific discharge, t = water temperature, EC = electric conductivity, DO = dissolved O2, TH = total hardness, TP = total phosphorus, CODMn = chemical oxygen demand measured using the permanganate method.

At most of the monitoring sites, there was also an increase in N-NO_3^- during higher rate of discharges. This relationship was observed at sites in the upper Vydra catchment (Fig. 6) with significant correlation ($p < 0.05$) at JAV, CIK, BRE, ROK, ROK2 sites. In the upper Rolava catchment and the JAV profile, the increase of N-NO_3^- was not significant ($p > 0.05$). Increased concentrations of N-NO_3^- in small montane streams after rainfall events may also be caused by increased organic matter in study areas or atmospheric deposition and soil microbial response to N deposition, resulting in greater export of humic material (Peterson et al. 2001; Findlay 2005). A strong positive correlation between the concentration of N-NO_3^- and humins was found at all monitoring sites ($p < 0.01$).

Linear regression or Spearman's rank correlation coefficient did not confirm any relationship between $N\text{-}NH_4^+$ and discharge. In case of $N\text{-}NO_2^-$, the change is not clear as well, because it is a highly reactive compound; under aerobic conditions it oxidizes quite easily into nitrates (Pitter 2009).

Slight positive correlations ($p < 0.1$) of iron concentrations and discharge have been observed only at PTA and JAV sampling sites (Fig. 3). At SLA and ROL sites, higher concentrations of Fe were not positively correlated with higher discharge, but rather with higher temperatures, corresponding to Sarkkola et al. (2013).

Increased phosphorous concentrations have been associated with higher discharge, although in summer after long dry periods, significant increases in phosphorous concentrations in streams have also been observed as in studies of Jennings et al. (2009), Ockenden et al. (2016). At our study sites, the $P\text{-}PO_4^{3-}$ concentrations are generally very low, especially during spring and autumn. At the ROK2 site, the highest concentrations of this compound were found during the lowest discharge ($0.06\ mg \cdot l^{-1}$). Values of *TP* are the highest mainly in winter and during low discharge (PTA, CIK, ROL).

Even though the release of iron from peat soils could be related to acidic conditions, only a slight negative correlation between pH values and iron concentrations ($R2 > 0.25$) were observed at PTA, CIK, BRE and JAV using linear regression. This correlation was confirmed by the Spearman's correlation coefficient only at CIK profile. Sarkkola et al. (2013) also found that water pH was not a significant factor explaining Fe concentrations, but rather the water temperature. A significant positive correlation of temperature and Fe was confirmed only at upper Rolava (Fig. 6).

EC behaviour and the shape of hysteresis loops during rainfall-runoff events often differ greatly (Evans and Davies 1998), while pH hysteresis loops are more often similar. However, many factors influence the final shape of hysteresis loops (Whitfield and Schreier 1981). Based on an analysis of events at each sampling site, six different C/Q hysteresis loop types were identified. These types can be classified as belonging to one of four basic loop shapes (clockwise, counter-clockwise, eight-shaped, and mixed).

The dominant type of hysteresis loop of *EC* in the upper Vydra catchment was type 2 (counterclockwise); in the upper Rolava catchment, the dominant type was type 1 (clockwise) which also corresponds with the results of linear regression. Similar types of hysteresis loop of *EC* were identified at sampling sites in the upper Vydra catchment especially during consecutive summer rainfall-runoff events (particularly type 2 counter-clockwise loops). These findings correspond with those of an earlier study (Su et al. 2017) investigating rainfall-runoff events at PTAms, BREms, and ROKms in 2011–2014. During individual events, dissolved ionic compounds were released from the soil into streams; once baseflow conditions returned, *EC* values decreased to their initial values. This behaviour was primarily caused by the effect of peatbogs. The situation was slightly different in BRE catchment, where 80% of forest cover has been decayed with only small part of regenerated area. During the onset of each rainfall-runoff event, an initial decrease in *EC* values occurred (resulting in an eight-shaped loop), but then *EC* values developed following the same pattern observed at other sampling sites. The same behaviour was also observed in study Su et al. (2017). The study site in the upper Rolava catchment (SLAms) behaved differently during consecutive summer rainfall-runoff events (resulting in type 1 clockwise loops for *EC*). During these events, stream water was diluted with water poor in dissolved ionic compounds. Catchment in the upper Rolava behaved similarly during snowmelt (resulting in type 1 clockwise loops), when water poor in dissolved ionic compounds diluted stream water. In the upper Vydra catchment, *EC* also decreased at the onset of events; hysteresis loop shape was type 3 – counter-clockwise. The CIKms sampling site demonstrated completely different behaviour during a snowmelt event (type 2), during which ion-rich water was released from the soil. After long dry periods, the findings from the upper Vydra catchment were like those made during other rainfall-runoff events (ROKms and BREms, eight-shaped; CIKms and PTAms counter-clockwise), whereas findings from the upper Rolava catchment differed. The first rainfall event after a long dry period led to increased *EC* with increased discharge and decreased *EC* after the end of the event (type 2). During the subsequent rainfall event, *EC* figures remained constant at first, but as the event subsided and discharge decreased, *EC* values began to increase and remained higher (type 6 – mixed).

Very interesting are also events where it was possible to perform analyses simultaneously on multiple profiles and follow their different reaction to increased flow, which most likely came from the same sources. As example it is a short event in the Rolava catchment that started in the morning 8. 9. 2022 and stretched to 9. 9. 2022. The discharge and electrical conductivity during the event are shown in Fig. 7. On both profiles, there was an increase in discharges at the same time, around 7:00 a.m., followed by an increase in flow. The increase was lower on the ROL1 than on SLA2 profile. The peak of the flow occurred at a very similar time, namely around 1 p.m. on the same day. The drop-in flow rates to the original values were again faster for the SLA2 profile, while it was slower for the ROL1 profile. Electrical conductivity reacted similarly on both profiles, with a reduction that corresponded to the rate of increase in flow. For the ROL1 profile, the decrease in electrical conductivity was relatively steep, and the lowest conductivity occurred long before the peak flow rate. The SLA2 profile also had the lowest electrical conductivity values before the peak flow rate, but significantly later than the ROL1 profile.

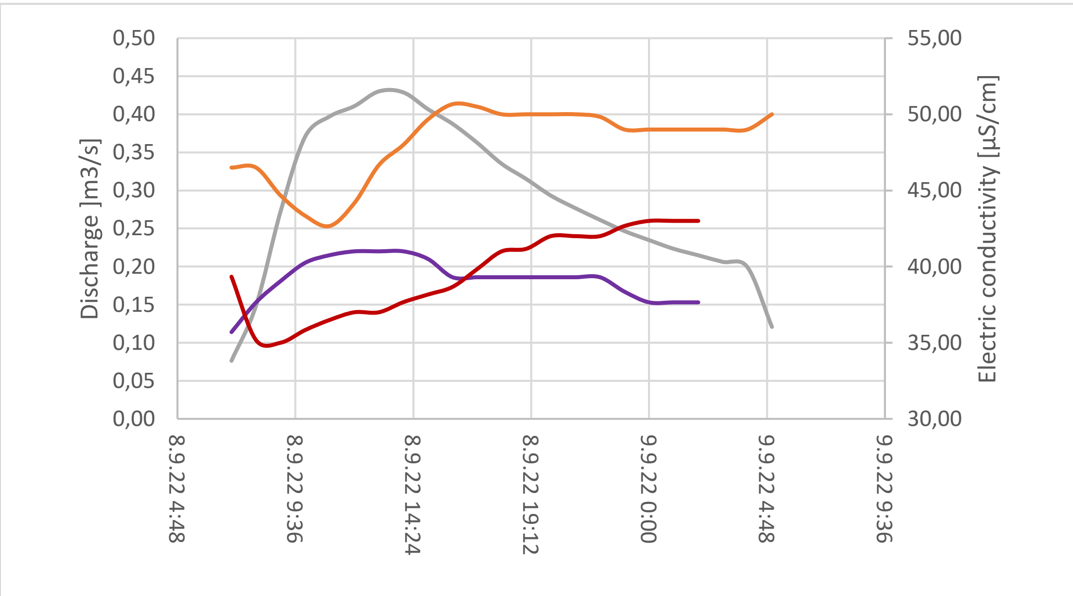

Fig. 7 Running Q and EC during the event in the Rolava catchment from 8th to 9th September 2022 for SLA2 and ROL1 profiles. EC – red colour, discharge SLA2 – green colour, discharge ROL1 – violet.

In contrast, *EC* mainly increased during rainfall events after long dry periods at most of the sampling sites, which is primarily related to greater mineralization when groundwater levels drop, as well as the subsequent washing out of these materials after rain. Considering the ongoing effects of climate change, increasing air and water temperatures, and increased occurrence of extreme meteorological events (longer dry periods, flash flooding), this behaviour may have a fundamental impact on ecosystems (Worrall et al. 2004; Jennings et al. 2009; Broder et al. 2017).

The *pH* changes during rainfall-runoff events were represented mainly by type 1 (clockwise) C/Q hysteresis loop with its highest concentration on the rising limb. This was an expected outcome, because the *pH* of groundwater is more neutral than the event water components (Carrol et al. 2007), but the velocity of decreasing of *pH* were different. The decrease of *pH* was much more rapid during consecutive summer rainfall-runoff events than during a snowmelt event and after a long dry period.

5. Conclusions

This study shows results of an analysis of 16 physicochemical parameters in 8 headwater catchments with presence of wetlands and peatbogs. Increased concentrations of organic matter (represented mainly by CODMn and humins) and their higher release during greater discharges were observed in catchments with > 20% of wetlands dominated by peat. Catchments with higher wetland cover were represented by higher TP, N-NO_3^- and a significant decrease in *pH* during high streamflow rates. Higher mean concentrations of Fe were also detected, but discharge was not the main driver of higher release of Fe in catchments with > 20% of wetlands.

Concentration of Fe was correlated with CODMn concentration more than with *pH* or discharge. Iron and organic matter (more CODMn, less humic substances) mobilization in catchments was influenced by wetland area, but the strongest correlation of Fe and CODMn was noticed in the catchment with a relatively small proportion of wetlands (8%) and peatbogs (2.3%), but with 70% of damaged forest cover in the catchment.

The analysis of *EC* and *pH* changes during rainfall-runoff events showed that the type of rainfall-runoff event affects the velocity of pH changes. The decrease of pH was much more rapid during consecutive summer rainfall-runoff events than during a snowmelt event and after a long dry period. The changes of EC were controlled not only by the type of rainfall-runoff event, but also by the hydrological preconditions of the catchment.

Overall, considered as a drinking water source, higher concentration of natural organic matter is the main issue in Šumava and Krušné hory headwaters, because of the possible formation of disinfection by-products after water treatment. Not only wetlands and peatbog areas affect the concentration of organic substances, but also the total area, mean slope, and hydrological precondition of the catchment. In contrast, values of *pH*, BNC8.3 or ANC4.5 did not have any connection to natural organic matter in our study. Restoration of drained peatland in one catchment appeared considerably problematic from the geochemical point of view, especially when associated with extreme rainfall-runoff events.

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