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Changes and dynamics of headwaters chemistry on the boundary of nature protected areas: Example of upper Blanice River catchment, Czechia

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ABSTRACT Changes of biogeochemical parameters in the context of long-term trends and different rainfall-runoff conditions were examined with a special focus on various catchment characteristics. The study area is situated in the upper part of the Blanice River catchment, where more than 77% of the area belongs to a Protected Landscape Area and is unique for the most abundant population of the critically endangered freshwater pearl mussel (*Margaritifera margaritifera*) in Central Europe. The Mann-Kendall test revealed a decrease of nitrogen and phosphorus compounds at the catchment outlet since 2003. The principal component analysis divided nine study catchments into three main groups according to biogeochemical composition (natural, partly anthropogenically influenced, subsurface drainage). Changes of biogeochemical parameters during different runoff conditions revealed a higher release of aluminium, $\mathrm{COD_{Mn}}$, dissolved organic carbon and total phosphorus during heavy precipitation event, which could have a negative effect on the vulnerable ecosystem including freshwater pearl mussel.

KEY WORDS Blanice River – water chemistry – drainage – trends – freshwater pearl mussel

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1. Introduction

The surface water quality in headwaters is important both for the local aquatic ecosystem, which is often represented by various fauna and flora, and for ecosystem goods and services (e.g. drinking water extraction). Unfortunately, studies focused on the biogeochemical processes in headwaters are however relatively rare mostly due to data deficiency. In general, headwater areas are valuable as there is often small direct anthropogenic impact and is possible to find areas of some degree of protection and endangered species there. Areas of conservation and conservation programs have positive impact on biodiversity and water quality (Helin et al. 2013). However, such ecosystem is very sensitive to any kind of disturbance. Acidification of European headwaters in 1970s/1980s, which was caused by acidic precipitation, is one of the examples (Kolář et al. 2015, Oulehle et al. 2016). The acidification of precipitation has significantly affected the composition of soils. As a result, increased soil acidity reduces the microorganism's activity, causes calcium leaching and has negative effect on both plant resistance and consequently water quality (Oulehle et al. 2021). Since the early 1990s, water quality in Czechia has improved due to changes in industrial and municipal practices (Langhammer 2010; Chalupová, Havlíková, Janský 2012). Recently, climate change appeared to have gradually increasing effect on water resources in headwaters (Soulsby et al. 2001, Bates et al. 2008).

Rising air temperature results in the concentration increase of natural organic matter (NOM) (Evans, Monteith, Cooper 2005; Oulehle, Hruška 2009) and in an increase in liquid and a decrease in solid precipitation (Hynčica, Huth 2019), and an increase in winter runoff (Kliment et al. 2011, Blahušiaková et al. 2020). A decrease in snow cover and earlier onset of snowmelt leads to a higher probability of spring floods (Middelkoop et al. 2001) and decreased availability of water in summer (Hynčica, Huth 2019; Blahušiaková et al. 2020), which affects negatively not only the quantity, but also the quality of water. Especially during storm rainfalls after a long period of drought, there is an increase in organic matter in the stream water (Ockenden et al. 2016; Broder, Knorr, Biester 2017).

Although land cover has obvious impact on water quality and it is possible to observe some general correlations (Gove, Edwards, Conquest 2001), in general, the relationship is not uniform (Baker 2006; Selle, Schwientek, Lischeid 2013). While Kändler et al. (2017) detected a relatively tight correlation between water chemical composition and the land use in the upper Nisa catchment in Czechia and Germany, Staponites et al. (2019) found out that the spatial position and terrain of the land can govern the conveyance of reactive or unstable water quality parameters, whereas the proportions of land use are dominant factors for predicting more stable chemical data in headwater catchments in South Bohemia.

Besides NOM, nitrogen (N) and phosphorus (P) are responsible for a large proportion of the surface water pollution across the globe and in some areas is registered an increase (Torrent, Barberis, Gil-Sotres 2007; Whitehead, Crossman 2012). One of the main sources of soil nutrient loss and increased leaching N and P into the surface waters is agriculture drainage system (Moloney, Fenton, Daly 2020). Nevertheless Kvítek et al. (2009) concluded that the proportion of drained land in the catchment after grassing had no marked influence on nitrate nitrogen concentration in surface waters, while the proportion of ploughed land in the catchment played the most important role in nitrate pollution. Later study (Fučík et al. 2015) observed a positive impact in the nitrate-nitrogen leaching decrease after grassing in recharge area of the drainage system, but with lag time approximately one year. Cattle and sheep grazing could cause water quality deterioration, especially by increased values of undissolved substances, nutrients (inorganic and organic forms of phosphorus and nitrogen) and pathogens flowing into the stream water (Hubbard, Newton, Hill 2004; Torrent, Barberis, Gil-Sotres 2007). The annual N, P, K excretion depends on the total annual intake and total annual retention of the animal. Important factors influencing the nutrient load into surface waters are treatment of livestock production waste and management of pastures, number of livestock units and access of livestock to water sources. Therefore, farming practices and adopted measures within a catchment area have a fundamental role (Fučík, Novák, Žížala 2014).

The study area, upper Blanice River catchment has very low population density around 2 inhabitants per square kilometre according to Czech Statistical Office (2020) with many natural areas characterized by different degrees of protection (Wanner, Simon, Kladivová 2012). The area is also important for freshwater pearl mussel protection (*Margaritifera margaritifera*), which is on the IUCN Red List (Preston, Keys, Roberts 2007) and needs specific habitat conditions including very clean oligotrophic water (Simon et al. 2015). The upper Blanice River catchment is one of the most important localities of this critically endangered bivalve mollusc in Central Europe with preservation of a high genetic diversity (Absolon, Hruška 1999; Machordom et al. 2003; Bílý, Simon 2007; Simon et al. 2015). In the Blanice River catchment, water chemistry has been monitored since 1988 (Švanyga et al. 2013). Water quality has been monitored together with the implementation of the Freshwater Pearl Mussel Rescue Program since 1999 (Simon et al. 2018).

This study assesses the development and current condition of water quality in the Blanice River headwaters which represents an ecologically unique area. Different types of evaluation were chosen regarding to the character of the data.

The present study aims in particular at:

1. Trend analyses of selected biogeochemical parameters
2. Evaluating the current state of biogeochemical parameters in small subcatchments with different degrees of protection, land use and anthropogenic impact

3. Analysing the suitability of water quality for freshwater pearl mussel (*Margaritifera margaritifera*)
4. Calculating the influence of different rainfall-runoff conditions on water chemistry.

2. Data sources and methods

2.1. Study sites

The upper part of the Blanice River catchment (85.5 km²) is located in Southern Bohemia (Fig. 1) in the Šumava Mts. and its foothills. Altitudes range from 743

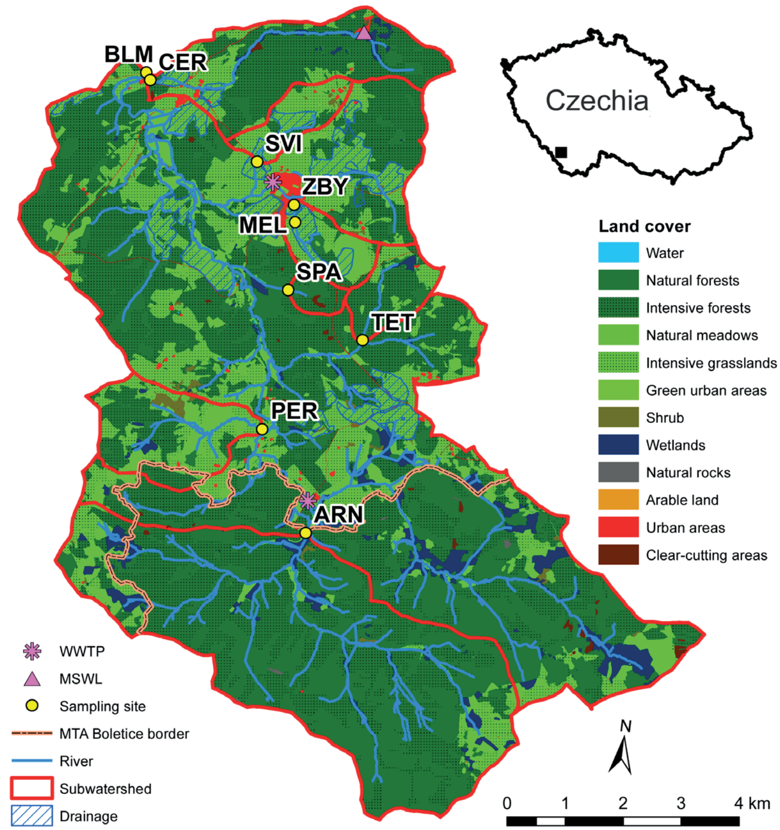

Fig. 1 – Location of sampling sites. Source: CGS (2019), VUV (2019), NCA CR (2013), VUMOP (2019), adjusted. Reference system – S-JTSK. WWTP – Wastewater treatment plant, MSWL – Municipal solid waste landfill.

Table 1 – Land cover changes between 1992–2000

Class	Corine Land cover	1992 [%]	2000 [%]
112	Discontinuous urban fabric	1.3	0.3
211	Non irrigated arable land	5.7	0.3
231	Pastures	25.3	27.7
243	Land principally occupied by agriculture	6.7	3.9
311	Broad-leaved forest	0.2	0.8
312	Coniferous forest	41.9	61.2
313	Mixed forest	7.2	2.3
324	Transitional woodland-scrub	12.6	3.4

Note: Grey background highlights main changes. Source: CORINE (COoRdination of INformation on the Environment, European Environment Agency) land cover map layer 1992 and 2000.

Table 2 – Nature protected areas in the catchment

Site		NNM and NM	Protected Landscape Area	Bird Area	Special Area of Conservation	NNM and NM	Protected Landscape Area	Bird Area	Special Area of Conservation
		[km²]	[km²]	[km²]	[km²]	[%]	[%]	[%]	[%]
1	ARN	1.03	20.54	18.81	20.54	5.00	100.00	91.62	100.00
2	PER	0.91	3.71	3.08	3.71	24.44	100.00	82.81	100.00
3	TET	0.00	0.00	0.00	1.63	0.00	0.00	0.00	100.00
4	SPA	0.00	0.38	0.38	0.55	0.00	68.99	69.60	100.00
6	ZBY	0.00	0.00	0.00	1.52	0.00	0.00	0.00	100.00
7	SVI	0.01	0.01	0.00	1.40	0.63	0.69	0.00	100.00
8	CER	0.00	0.78	0.00	3.32	0.00	13.71	0.00	58.18
9	BLM	5.99	66.05	50.30	82.89	7.01	77.27	58.85	96.97

Note: NNM and NM – National Nature Monument and Nature Monument. Grey background – more than 50% of catchment area. Source: State Administration of Land Surveying and Cadastre (CUZK 2020).

to 1,236 m a.s.l., the average annual air temperature varies around 6.4 °C with an annual rainfall amounts of about 850 mm. Geology is dominated by high-grade metamorphic rocks (granulite) and sediments. Soils are generally Cryptopodzols (41.8%) or Cambisols (32.2%), with hydromorphic soils covering 31.6% of the entire catchment. From the historical point of view, this area has registered extensive land use changes (Hintnaus 2008), especially with a decrease in farmland area and an increase in forested area (more in Table 1), which reflects historical trends in the land management as well as the impact of social and political changes on the environment in the region (Measom 2019). According to the Consolidated Layer of Ecosystems (NCA CR 2013; Hönigová, Chobot 2014), the catchment is covered mainly by forest (69%) concentrated primarily in the upper part of the catchment with a mixture of Norway spruce (*Picea abies*), European beech (*Fagus sylvatica*)

Table 3 – Basic characteristics of sampling sites

Profile	Profile, river	Abbrev.	Area	Hydromorphic soil	Drainage	Urban areas	Green urban areas	Arable land
number			[km²]	[%]	[%]	[%]	[%]	[%]
1	Arnoštov, Blanice	ARN	20.55	17.92	0.00	0.02	0.00	0.00
2	near freshwater pearl mussel breeding location, Blanice left tributary	PER	3.72	43.14	0.00	0.24	0.00	0.00
3	Tetřívčí brook	TET	1.63	37.05	0.00*	0.53	0.00	0.00
4	Spálenecký brook	SPA	0.55	38.43	0.00	1.25	0.00	0.00
5	Drainage to Zbytinský brook	MEL		74.24	—	0.00	0.00	0.00
6	Zbytinský brook left tributary	ZBY	1.52	30.19	29.76	3.52	0.00	0.00
7	Sviňovický brook	SVI	1.40	26.70	19.49	1.52	0.00	0.11
8	Černý brook near Blažejovice	CER	5.71	37.74	4.28	2.07	0.00	0.00
9	Blanický mlýn, Blanice	BLM	85.49	31.57	0.45	0.95	0.03	0.00

Note: Urban areas (Transport units, Discontinuous urban fabric, Industrial and commercial units, Dump and construction units); Green urban areas (Parks, gardens, cemeteries, Recreation and sport areas); Natural meadows (Alluvial meadows, Mesic meadows, Heaths); Intensive forests (Intensive coniferous forests, Intensive broad-leaved forests, Intensive mixed forests); Natural forests (Beech forests, Alluvial forests, Bog forests, Spruce forests, Dry pine forests, Ravine forests); Shrub (Introduced shrub vegetation, Natural shrub vegetation); Wetlands (Swamps, Macrophyte vegetation of water bodies, Wetlands and littoral vegetation, Peatbogs and springs); Water (Ponds, Natural water courses). *In Tetřívčí brook catchment is present ditching 7.36 $km.km^{-2}$. Source: CGS (2019), CUZK (2021), Kalkus (2012), NCA CR (2013), VUMOP (2019).

and Scots pine (*Pinus sylvestris*). The rest of the catchment consists mainly of meadows (19%) and wetlands (7%).

Nearly 80% of the area belongs to the Šumava Protected Landscape Area, which was declared as a UNESCO biosphere reserve in 1990. In 2005, almost the entire area was declared as a part of the Natura 2000 protected areas system, both Bird Areas and Special Areas of Conservation – Šumava and Boletice (Table 2).

Despite the near-natural character of the landscape, some anthropogenic activities which directly affect water quality can be found in the river catchment. The most important anthropogenic factors influencing the water quality in the catchment are: (1) subsurface drainage systems in the central and lower parts of the catchment (Table 3, Fig. 2) and ditching at Tetřívčí (TET) site created during the main wave of building drainage measures in this area in the second half of the 20th century, (2) settlement (municipality of Zbytiny is the biggest village with population of 322 inhabitants in 2020, another village is Křišťanov with 93 inhabitants in 2020), (3) agriculture, mainly cattle and sheep pastures (Fig. 2), (4) municipal solid waste landfill Libínské sedlo.

There were also some measures, which should contribute to water quality improvement in the upper Blanice catchment. The wastewater treatment plant (WWTP) with two low-loaded stabilization ponds was built for the Zbytiny

	Intensive grassland	Natural meadows	Intensive forests	Natural forests	Shrub	Wetlands	Water (water bodies and water courses)	Natural rocks	Forest clearcutting area
	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]	[%]
1	5.11	4.78	47.98	36.56	0.23	4.72	0.42	0.18	0.04
2	30.01	20.49	39.14	3.37	3.88	2.56	0.30	0.00	0.00
3	20.72	2.50	65.18	7.87	0.02	2.98	0.21	0.00	0.00
4	0.00	0.00	60.66	37.77	0.00	0.20	0.12	0.00	4.29
5	51.60	31.46	11.04	3.05	0.00	2.09	0.76	0.00	0.00
6	38.75	28.55	23.67	4.62	0.15	0.48	0.25	0.00	0.00
7	72.08	4.42	19.15	0.58	1.93	0.00	0.22	0.00	0.00
8	20.96	1.78	65.39	5.43	0.29	3.80	0.26	0.02	0.49
9	19.20	8.13	46.47	19.97	0.69	4.02	0.46	0.08	0.25

municipality in 2008 projected for 450 population equivalents (PE), with a designed discharge of Q24 67.5 m^3 per day (Wanner, Simon, Kladivová 2012). 450 PE refers to 27 kg BOD_5, 5.4 kg N and 0.7 kg P per day, after treatment efficiency measured by Wanner, Simon, Kladivová (2012) it is 0.5 kg BOD_5, 1.2 kg N and 0.03 kg P per day. Outlet load is therefore 8 $mg.l^{-1}$ for BSK5, 18.4 $mg.l^{-1}$ for N and 0.5 $mg.l^{-1}$ for P.

WWTP Křišťanov was built as a part of Freshwater Pearl Mussel Rescue Program in the upper part of the catchment in 2016 for 60 PE. WWTP Křišťanov was constructed with membrane filter technology, reliable and highly efficient in contrast to the sludge activation method, where there is a risk of accidents.

Fig. 2 – Subsurface drainage causes brown colouring and increased matter flow at SVI (left). Cattle and sheep grazing is the main agriculture activity in the catchment (right).

Membrane technology does not physically allow sludge to overflow and is very effective at phosphorus (95%) and nitrogen (80%) removing. Another step is the ground filter (biological treatment) and seepage in the floodplain (Beleco 2016). Restoration of the Sviňovický brook, which is a right tributary of the Blanice River, was conducted in 2006. However, even after restoration, increased values of COD_{Mn}, conductivity and nitrate nitrogen were observed (Kliment et al. 2008).

Švanyga et al. (2013) presented the concentration of total phosphorus (TP) in the river main stream, as well as eutrophication and erosion rates of some tributaries as fundamental problems causing water quality degradation. On the contrary, concentration of Ca, organic pollution (represented by COD_{Cr} in this case) and dissolved O_2 did not represent a problem in the river catchment.

The menace to water quality is vegetation stress, especially forest disturbances, and improper forest management. Improper forest management led to increased phenols, phosphorus and ammonia contents in the past and it still represents one of the main threats to water quality (Simon et al. 2018), as well as the use of toxic xenobiotics – e.g. RoundUp (Švanyga et al. 2013).

2.2. Data sources

Our study comprises water quality data from three different sources.

Long term data from Povodí Vltavy, State Enterprise was obtained for the Blanický mlýn (BLM) site including standard water quality indicators (pH, EC – electrical conductivity, dissolved O_2 (DO), chemical oxygen demand – COD_{Cr}, total organic carbon – TOC, total nitrogen – TN, $N\text{-}NH_4$, $N\text{-}NO_2$, $N\text{-}NO_3$, total phosphorus – TP, $P\text{-}PO_4$) at monthly steps for the 2003–2019 period (193 observations), while TOC and TN were measured only during the 2007–2019 period (150 observations). Daily discharge data was provided by the Czech Hydrometeorological Institute (http://chmi.cz).

For the Spálenecký brook site (SPA), which is a small right tributary of the Blanice River in the central part of the catchment, the Czech Geological Survey (CGS 2016) provided monthly data (discharge, pH, EC, Al, Ca, Fe, K, Mg, Na, Cl, F, $N\text{-}NO_3$, SO_4, TOC) for the 1994–2006 period (154 observations). The SPA site was one of the forested catchments from GEOMON network till 2006 (Oulehle et al. 2017).

The last data source was obtained from the field monitoring and water sampling. For a detailed evaluation of the recent water quality state in the whole catchment, surface water sampling was done at 9 sites (Fig. 1, Table 3) in 2018–2019 with focus on different seasons and runoff conditions. Overall, 8 measurements and water sampling were done on the same date (except MEL site – only 3 sampling, parameter Ca – 6 sampling). Parameters analysed in the laboratory were Al, Ca, Fe, K, Mg, Na, TP, Si, N-NH_4, Cl, F, N-NO_3, SO_4, Zn, COD_{Mn} and DOC at selected sites (ARN, TET, SPA, BLM). At the time of sampling, electrical conductivity (EC), dissolved oxygen (DO), pH and water temperature were measured using the Hach-Lange HQ40-D Multimeter. The discharge was measured using the Flow Tracker (SONTEK) device. Water samples were collected and transported in the cool (< 10 °C) and dark box for further analysis. Cations and anions were measured in the laboratories of the Geological Institutes and Laboratory of Environmental Chemistry and Soil Analysis within 24 hours after collection. Cations were measured by the ICP-OES method with Agilent 5110 and anions were measured with the Dionex ICS-2000 HPLC ion chromatography system. The degree of pollution based on COD_{Mn} was determined in the Charles University's Institute for Environmental Studies by the so-called Kubel method based on the oxidation of organic substances by potassium permanganate in an acidic environment. Samples for dissolved organic carbon (DOC) analyses were filtered by a 0.45 μm membrane filter and measured by the differential method using the Formacs TOC/TN analyser (Skalar).

Additional 10-minutes rainfall, water levels and EC data measured by an automatic water quality and rain gauge station of the Department of Physical Geography and Geoecology, Charles University was used (CUNI 2020).

The land cover data was obtained from the Consolidated Layer of Ecosystems (NCA CR 2013; Hönigová, Chobot 2014). This dataset contains a detailed land cover information divided into 41 classes. For our study purposes, some classes were merged into generalized classes according to similar characteristics of the vegetation cover (more in Table 3). Forest clear cutting areas were identified by 2015 orthophoto image (CUZK 2021).

Hydromorphic soils data was obtained from the Czech Geological Survey (CGS 2019), subsurface drainage data originated from the Research Institute for Soil and Water Conservation (VUMOP 2019) and landscape protection data was from the State Administration of Land Surveying and Cadastre (CUZK 2020). Number of livestock were obtained from The Ministry of Agriculture of the Czech Republic (eAgri 2021).

2.3. Data analyses

Significant trends in long term monthly and annual data series (2003–2019) for the BLM site were identified using the Mann-Kendall (MK) trend test (Mann 1945, Kendall 1975). Significance of the trend was tested at the level alpha = 0.05. Additional analyses of continual (10-minutes data) EC changes during WWTP construction in Zbytiny (before and after) was done for sites above and under WWTP. The outlet load (the amount of certain substances in mg.l^{-1}) was calculated, same as for livestock in the catchments. A comparison of mean, median and relative standard deviation values was conducted at site SPA for two periods (1994–2006 and 2018–2019).

For 9 sites, a short-term monitoring period (2018–2019) was evaluated. Sampling was done on the same date during stable hydrometeorological conditions for further analyses and comparison. As many water biogeochemical variables are correlated and could reflect different sampling site characteristics, propriate multidimensional statistical method was applied. Principal component analysis (PCA), which explains the relationships on different spatial planes and explicably shows these planes by means of the axes (Davis 1973) was used for median values of the 20 selected parameters (pH, EC, DO, temperature, Al, Ca, Fe, K, Mg, Mg:Ca ratio, Na, TP, Si, N-NH_4, F, Cl, N-NO_3, SO_4, Zn, COD_{Mn}) for 9 sites. Second analysis comprises also land use, subsurface drainage system, main anthropogenic activities and state of the land protection in the catchment. Before analyses, the data were standardized to a unit scale by subtracting the site mean for the whole time series and dividing by the site standard deviation. PCA were performed with the XLSTAT 2019 software.

Because surface water quality has been frequently identified as critical stressor for freshwater pearl mussel, results from two-year (2018–2019) monitoring were compared with freshwater pearl mussel water quality limits for temperature, EC, pH, Ca, TP, Cl, N-NO_3 and Mg:Ca ratio according to limits in Absolon, Hruška (1999).

The specific discharge [$l.s^{-1}.km^{-2}$] was calculated for 19 subcatchments during two different hydro-meteorological situations in spring 2017 and 2018. Hydrometeorological preconditions were evaluated by the precipitation amount 30, 14, 7 and 1 day before the measurements from an automatic meteorological station in Zbytiny (CUNI 2020).

3. Results

3.1. Long-term changes of water quality in the catchment (outlet profile)

The most pronounced resuts of MK-trend analyses are shown in Table 4. A significant decreasing trend was observed for N-NO_3 during seven months (November, January, February, March, June, July and October) and also in the annual data series. Mean annual N-NO_3 concentration decreased from 1,175 $\mu g.l^{-1}$ in 2004 to 587 $\mu g.l^{-1}$ in 2018. The other nitrogen compounds also showed some significant trends. N-NO2 decreased in July and in annual series. TN decreased in February and July (Table 4). On the contrary, N-NH_4 increased in spring (April, May), however about half of the measured N-NH_4 concentrations were below the detection limit (0.02 $mg.l^{-1}$). Even if TP didn't reveal any trend, P-PO_4 decreased during the year. The last trend was observed for dissolved O_2, which decreased in October.

Table 4 – Mann-Kendall trend test results for the Blanický mlýn (BLM) site (outlet profile at upper Blanice River)

	$N\text{-}NO_3$		TN		$P\text{-}PO_4$		$N\text{-}NH_4$		DO	
Month	MK-Stat	p-value	MK-Stat	p-value	MK-Stat	p-value	MK-Stat	p-value	MK-Stat	p-value
11	**-3.026**	0.002	0.139	0.89	-0.365	0.715	0.522	0.602	-1.397	0.162
12	-1.085	0.278	-1.548	0.122	-1.548	0.122	1.945	0.052	0.632	0.528
1	**-2.128**	0.033	-0.994	0.32	-0.545	0.585	0.825	0.409	0.362	0.718
2	**-3.026**	0.002	**-2.656**	0.008	0.643	0.52	-0.553	0.58	-0.181	0.856
3	**-2.266**	0.023	-1.37	0.171	-0.591	0.554	1.915	0.055	-0.587	0.557
4	-1.451	0.147	1.245	0.213	0	1	**2.005**	0.045	-1.263	0.207
5	-0.863	0.388	0.436	0.663	-0.091	0.928	**2.482**	0.013	1.083	0.279
6	**-2.142**	0.032	-0.615	0.539	0.375	0.708	0.042	0.966	0.619	0.536
7	**-1.981**	0.048	**-2.433**	0.015	0	1	0	1	0.907	0.365
8	-1.534	0.125	-1.321	0.187	-0.543	0.587	-0.14	0.889	0.997	0.319
9	-1.848	0.065	-0.63	0.529	-0.858	0.391	1.175	0.24	0.632	0.528
10	**-2.762**	0.006	1.049	0.294	-0.363	0.717	-0.925	0.355	**-2.803**	0.005
Year	**-4.119**	0	-0.43	0.667	**-1.977**	0.048	-0.041	0.967	1.071	0.284

Note: 2003–2019 period (193 observations), TN was measured only during the 2007–2019 period (150 observations). Medium grey refers to p-value < 0.05, dark grey background with white bold letters refers to negative trend and light grey background with black bold letters refers to positive trend. Source: Povodí Vltavy, State Enterprise.

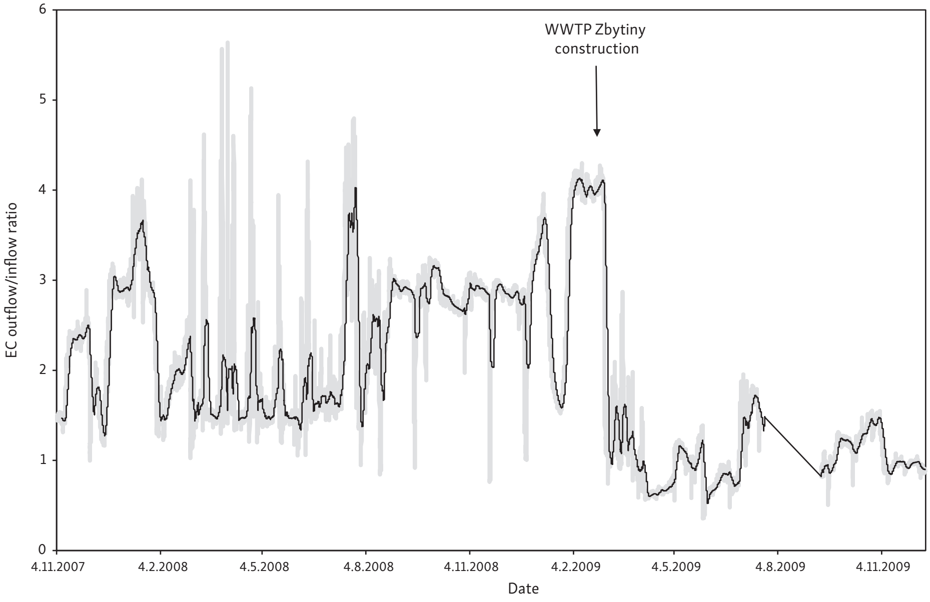

Fig. 3 – EC outflow/inflow ratio for Zbytinský brook in Zbytiny village between 11/2007–11/2009. WWTP Zbytiny was built in the end of 2008. Hourly EC outflow/inflow ratio is represented as grey line and ten hours moving average as black line. Data source: CUNI (2020).

Table 5 – Biogeochemical changes at SPA site. Expressed as mean, median and standard deviation of each period, 1994–2006 and 2018–2019.

Parameter	Units	Mean			Median			Relative standard deviation		
		1994–2006	2018–2019		1994–2006	2018–2019		1994–2006	2018–2019	
Q	l.s^{-1}	5.1	1	↓	3.6	0.3	↓	100.4	129.9	↑
pH		6.4	6.8	↑	6.5	6.9	↑	6.4	5	↓
EC	μS.cm^{-1}	50.5	52.4	↑	49.8	53.6	↑	18.7	8.9	↓
Al	μg.l^{-1}	241.8	223	↓	230	149	↓	53.8	94.8	↑
Ca	mg.l^{-1}	3.5	3.8	↑	3.5	3.9	↑	20.9	13.6	↓
Fe	μg.l^{-1}	588.8	411.3	↓	430	412	↓	88.8	39.9	↓
K	mg.l^{-1}	0.6	0.6	↑	0.6	0.7	↑	31.7	16.8	↓
Mg	mg.l^{-1}	1.2	1.5	↑	1.2	1.5	↑	20.9	12.7	↓
Na	mg.l^{-1}	4	3.7	↓	4.1	3.8	↓	16.2	8.4	↓
Cl	mg.l^{-1}	1.6	1.1	↓	1.6	1.1	↓	21.8	9.2	↓
F	mg.l^{-1}	0.1	0.1	↑	0.1	0.1	↑	70.2	53.1	↓
$N\text{-}NO_3$	μg.l^{-1}	95.1	167.6	↑	33.9	105.3	↑	122	120.4	↓
SO_4	mg.l^{-1}	10.5	8.7	↓	10.5	8.7	↓	26.3	12	↓
TOC	mg.l^{-1}	9.1	10	↑	7.6	8.3	↑	35	61	↑
∑BC*	mg.l^{-1}	9.4	9.7	↑	9.3	10.1	↑	17	11.2	↓

Note: 1994–2006 (monthly data, 154 samples), 2018–2019 (seasonal data, 8 samples), dark grey background with white bold letters = decrease, light grey background with black bold letters = increase. *∑BC = sum of base cations. Source: CGS (2016), own monitoring.

Other biogeochemical parameters show predominance of insignificant trends (p-value > 0.05) for the BLM site (main catchment).

Analyses of EC changes during WWTP Zbytiny construction in 2008 shows strong decrease of mean EC under the WWTP (Fig. 3). While above Zbytiny village was EC values before and after WWTP construction almost the same (around 70 μS.cm^{-1}), under the Zbytiny village and also under WWTP EC values have changed from 175 μS.cm^{-1} before WWTP construction to 71 μS.cm^{-1} after WWTP construction.

For the SPA site, it is possible to summarize the main changes (see Table 5). Values of pH increased, which corresponds with the overall trend and recovery from acidification in Central Europe. Together with this change, decreases in SO_4, Na, Al and Fe concentrations were detected. However, some of the base cation (Ca, Mg, K) and $N\text{-}NO_3$ concentrations increased.

3.2. Current state of water quality

Principal component analysis was carried out to group sites with similar natural conditions and to determine the most important biogeochemical parameters affecting the water quality. The two main components explained 64.7% of the data

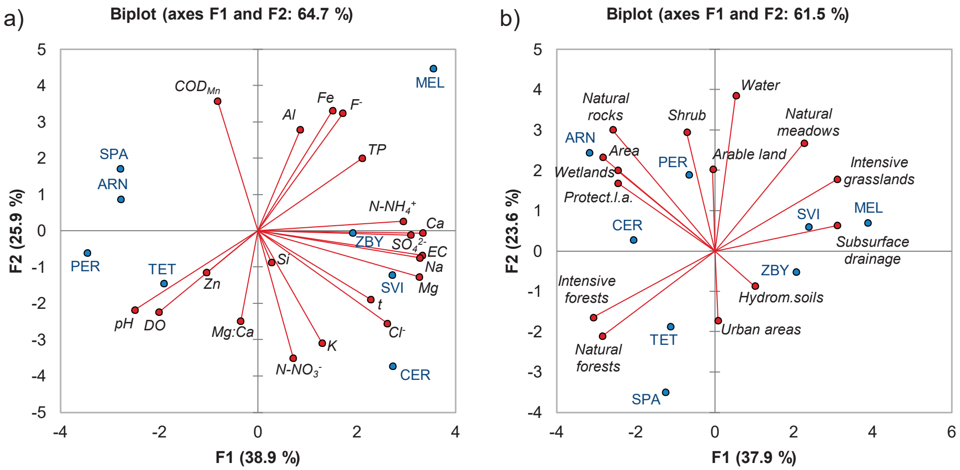

Fig. 4 – Principal component analysis of selected biogeochemical parameters and their median concentration level at the studied sites (left) and catchment characteristics (right). Sites are represented as filled blue circles and the variables as filled red circles with lines. 2018–2019 seasonal data (8 measurements).

set variability (Fig. 4a). Analysis of factor loadings showed that EC, COD_{Mn}, Ca, Mg, Na, SO4, and N-NH_4 were the major factors affecting the water quality (factor loading value > 0.8). The sites could be divided into 3 subgroups: (A) with less anthropogenic influence, near the spring area and with the highest degree and proportion of the protection area (ARN, SPA, PER, TET), characterized by higher concentrations of diss. O_2, pH, Mg:Ca ratio; (B) sites with greater anthropogenic influence, partially drained (ZBY, SVI, CER), with higher concentrations of base cations (Ca, Mg, Na, K), higher concentrations of nitrates and sulphates, higher Cl values, especially at the CER site, and higher EC. (C) subsurface drainage to the Zbytinský brook (MEL), characterized by higher values of N-NH_4, TP, Fe, F, Al.

Water quality could be considered as unpolluted or slightly polluted in the catchment, main biogeochemical characteristics could be found in Table 6. However, COD_{Mn} and TOC concentrations were considerably higher, demonstrating the organic pollution, which may be caused by the occurrence of peatlands in the upper parts of the river catchment where the highest concentrations also occurred (site 1: COD_{Mn} 15.7 mg.l^{-1}, TOC 17.2 mg.l^{-1}). The subsurface drainage to the Zbytinský brook (MEL) had a great influence on the increased rate of matter flow, where the values of EC, COD_{Mn}, Fe, TP and dissolved O_2 were considerably higher. Besides the MEL site, SVI and ZBY sites are the most affected by the subsurface drainage (30%, resp. 20% of the catchment area is drained). In comparison to other sites, at SVI and ZBY sites were higher concentrations of SO_4, N-NO_3, TP and EC. Specifically, different conditions were visible at the CER site. This site is influenced

Table 6 – Main biogeochemical characteristics

Profile		EC μS.cm^{-1}	DO mg.l^{-1}	Al μg.l^{-1}	Fe μg.l^{-1}	Zn μg.l^{-1}	TP μg.l^{-1}	Cl mg.l^{-1}	F mg.l^{-1}	N-NO$_3$ μg.l^{-1}	SO$_4$ mg.l^{-1}	DOC mg.l^{-1}	COD$_{Mn}$ mg.l^{-1}
1	ARN	66.1	8.9	232	404	6	60	1.1	0.1	86	10.4	17.2	15.7
2	PER	56.8	9.0	169	342	15	24	1.6	0.1	472	7.6	NM	8.6
3	TET	80.8	9.0	198	364	10	25	2.8	0.3	1 106	11.4	13.4	12.2
4	SPA	56.3	7.9	296	524	8	32	1.2	0.3	183	9.9	13.0	12.5
5	MEL	138.3	4.7	200	4 510	7	101	2.5	0.1	23	14.4	NM	14.7
6	ZBY	114.8	8.4	294	732	7	49	5.1	0.3	623	20.3	NM	11.4
7	SVI	145.7	8.3	417	699	10	42	3.5	0.1	1 656	16.9	NM	7.8
8	CER	172.3	8.3	280	360	7	100	24.0	0.2	1 127	13.8	NM	5.8
9	BLM	94.7	9.1	260	486	6	60	4.5	0.2	616	11.6	14.4	12.4

Note: EC – electrical conductivity, TP – total phosphorus, DOC – dissolved organic carbon, COD$_{Mn}$ – chemical oxygen demand. Mean values for 2018–2019 (8 seasonal samples).

by the municipal solid waste landfill Libínské sedlo in the upper part of the catchment. Apparently, there were the highest concentrations of Cl (24.0 mg.l^{-1}), higher concentrations of EC (172 μS.cm^{-1}), base cations and N-NO$_3$. Regarding the upper part of the investigated catchment with no subsurface drainage and low anthropogenic influence, the TET site showed some dissimilarities from the others. There were slightly higher concentrations of N-NO$_3$, Ca, Na, Si, and EC.

3.3. Water Chemistry and catchment characteristics

Firstly, PCA with different catchment characteristics was done at 9 sites (Fig. 4b) to illustrate main differences between catchments. First two components, which had eigenvalue greater than 1, explain 61.5% of the data set variability. PCA showed that subcatchments in the upper part of the catchment (ARN, PER) were characterized by larger area with wetlands and protected landscape area. MEL, SVI and ZBY sites were significantly influenced by subsurface drainage and were characterized by great area of intensive grassland. Remaining SPA, TET and CER sites are characterized by great area of forest cover.

Secondly, the values of 20 selected parameters and 15 catchment characteristics (Area, Hydromorphic soils, Subsurface drainage system, Land protection, Urban areas, Green urban areas, Arable land, Intensive grasslands, Natural meadows, Intensive forests, Natural forests, Shrub, Wetlands, Water, Natural rocks) were analysed using PCA together. The first two principal components explained 54.6% of the data set variability. Focusing on catchment characteristics, the most influencing factor was subsurface drainage (factor loading value > 0.92) followed by intensive grasslands (factor loading value = 0.83). Results of water chemistry

Table 7 – Approximate number of livestock and nutrient input in the catchments

	Nr. of cattle	nr. of sheep	N [kg.day^{-1}]	P [kg.day^{-1}]	K [kg.day^{-1}]
ARN	23	6	5.1	2.0	6.4
PER	25	7	5.4	2.1	6.8
TET	7	2	1.6	0.6	2.1
SPA	0	0	0.0	0.0	0.0
MEL	4	1	0.8	0.3	1.1
ZBY	13	4	2.8	1.1	3.6
SVI	22	6	4.9	1.9	6.2
CER	26	7	5.8	2.3	7.3
BLM	361	98	79.2	31.3	100.5

Note: Calculation of nutrients according to Act No. 399/2004 page 7879.
Source: eAgri (2021).

showed that in the upper parts of the catchment there was a higher diss. O_2 concentration. Conversely, the lower concentrations of Si, SO_4, Mg, Na, Ca, and lower temperature were detected. As in the previous chapter (3.2), there were higher concentrations of N-NH_4, TP, Fe, F and Al in catchments with subsurface drainage and with larger area of intensive grassland. Urban areas were mostly correlated with higher concentration of N-NO_3, TP, Cl, Mg, Ca, EC and higher temperature.

Important source of water pollution could be cattle and sheep grazing in the catchment. Intensive grasslands cover almost 20% of the whole catchment, while there are significant differences between river catchments (from 0% to 72%, more in Table 3). Since 2004, number of cattle fluctuated between 0.2–0.3 cows.ha^{-1} and number of sheep fluctuated between 0.05–0.1 per ha according to eAgri (2021). In 2018–2019 there was 0.22 cows.ha^{-1} of intensive grasslands and 0.06 sheep.ha^{-1} of intensive grasslands (Table 7), which is under the limit according to Act No. 399/2004, where the limit for permanent grassland is 0.5–1.25 cows per ha. Nutrient input for intensive grasslands in the catchments is about 48.3 g N.day^{-1}.ha^{-1}, 19.1 g P.day^{-1}.ha^{-1} and 61.3 g K.day^{-1}.ha^{-1}, which is mostly consumed by plants, but during rainfall-runoff events can be flushed into the river water.

3.4. Freshwater pearl mussel

The most important water biogeochemical parameters (pH, Ca, TP, Cl, N-NO_3 and Mg:Ca ratio) limiting the natural reproduction and life of highly endangered freshwater pearl mussel (*Margaritifera margaritifera*) were compared with freshwater pearl mussel threshold limits according to Absolon, Hruška (1999) and are mentioned in Table 8. It is obvious that river water in upper parts of the catchment (above the Zbytiny village) had more suitable conditions for freshwater pearl mussel. Although there was higher TP concentration near the spring area, which corresponds with higher peatland cover in upper parts of the catchment. The Tetřívčí River (TET) tributary had elevated concentration of $N\text{-}NO_3$ (upper limit 564.5 $\mu g.l^{-1}$ was exceeded in every sample) and EC. River water under the Zbytiny village and water from drainage exceeded upper limits of EC, Ca and Mg:Ca ratio for almost all samples. TP concentration exceeded the upper limit ($< 35\ \mu g.l^{-1}$) in half of the cases in the river water under the Zbytiny village.

3.5. Extreme rainfall-runoff conditions

With regard to runoff conditions, there was an obvious increase in Al, COD_{Mn}, DOC and TP at all studied sites during a rainfall-runoff event (Table 9). The largest increases were registered for Al concentrations, where the Al concentrations were more than three times higher during the rainfall-runoff event than under normal conditions at all sites. At 4 sites the Al concentrations were more than five times higher and at two sites (TET and CER) were ten times higher than under normal conditions. The concentrations of Al reached almost 1,000 $\mu g.l^{-1}$ during the increased discharge in these two catchments. Apart from CER, the concentrations of COD_{Mn} were more than three times higher at all sites (Table 9). Higher concentrations were also observed for DOC, but this parameter was measured only at 4 sites. A significant increase in TP concentrations was also registered. The highest increase was detected at the TET site (more than five times higher), followed by CER, ZBY, SPA and BLM sites (more than three times higher).

3.6. Specific discharge

Two hydrometeorological situations were evaluated in detail for the whole catchment during spring 2017 and 2018 (Fig. 5). The situation in 2017 was characterized by wetter conditions than in 2018. The precipitation amount 30 days before field measurement was 41.8 mm in 2017 and 14.4 mm in 2018 (more in Table 10). In 2017 the field measurement day was rainy day, while in 2018 there was no rain during field measurement. Specific discharge and EC values in each part of the catchment are displayed in Figure 5. When comparing these hydrometeorological situations, the water quality was influenced negatively by the highest water temperature and lowest discharge in 2018. Mean concentration of dissolved oxygen was the lowest (mean 8.8 $mg.l^{-1}$) and mean value of EC was the highest (mean 87.9 $\mu S.cm^{-1}$). Focusing on different parts of the catchment, there are visible influences of the subsurface drainage systems, which, even during relatively low flows, drain water

Table 8 – Exceeding the freshwater pearl mussel limits at 9 sites in 2018–2019 period

Profile		Temp.	EC	pH	Ca	TP	Cl	NO$_3$	Mg:Ca		Limit exceeding [%]
	limit	0–20 °C	< 70 μS.cm^{-1}	6.0–7.1	< 8 mg.l^{-1}	< 35 μg.l^{-1}	< 10 mg.l^{-1}	< 2.5 mg.l^{-1}	1:2.8–1:3.2		
1	ARN	0/8	0/8	1/8	0/6	6/8	0/8	0/8	6/6		0.0
2	PER	0/8	0/8	2/8	0/6	0/8	0/8	0/8	5/6	▨	12.5
3	TET	0/8	6/8	1/8	0/6	1/8	0/8	8/8	6/6	▨	25.0
4	SPA	0/8	0/8	2/8	0/6	1/8	0/8	1/8	6/6	▨	37.5
5	MEL	0/3	3/3	0/3	3/3	3/3	0/3	0/3	3/3	▨	50.0
6	ZBY	0/8	8/8	2/8	6/6	4/8	0/8	2/8	4/6	▨	62.5
7	SVI	0/8	8/8	1/8	6/6	4/8	0/8	8/8	6/6	▨	75.0
8	CER	0/8	8/8	2/8	6/6	3/8	8/8	8/8	6/6	▨	87.5
9	BLM	1/8	7/8	4/8	0/6	4/8	0/8	2/8	6/6	▨	100.0

Note: Before slash – number of samples exceeding the limit, after slash – number of samples, EC – electrical conductivity, Temp. – water temperature, TP – total phosphorus. According to limits in Absolon, Hruška (1999).

Table 9 – Increased concentrations of selected water quality parameters during rainfall-runoff event (13. 6. 2018)

Profile		Al [μg.l^{-1}]		COD$_{Mn}$ [mg.l^{-1}]		DOC [mg.l^{-1}]		TP [μg.l^{-1}]	
		Median	Event	Median	Event	Median	Event	Median	Event
1	ARN	191.0	940.0	12.2	38.1	14.3	25.2	40.0	90.0
2	PER	85.0	440.0	5.4	25.0	NM	NM	15.0	30.0
3	TET	82.5	940.0	6.9	31.2	7.5	26.1	15.0	80.0
4	SPA	149.0	750.0	7.2	32.6	8.3	23.2	15.0	50.0
6	ZBY	127.0	950.0	6.2	27.2	NM	NM	33.0	130.0
7	SVI	250.0	840.0	4.2	17.0	NM	NM	33.5	80.0
8	CER	82.0	900.0	4.9	12.3	NM	NM	25.0	100.0
9	BLM	139.0	1 130.0	8.2	35.8	9.7	27.5	35.5	110.0

Note: Increased values are highlighted by three shades of grey according to their increased levels (no colour for 0–3 times higher; light for > 3 times higher; medium for > 5 times higher; dark for > 10 times higher), NM – Not measured.

Table 10 – Precipitation amounts before spring measurements during spring 2017 and 2018

Days before measurement	Period	Precipitation amount [mm]
30 days	5. 3.–3. 4.	41.8
14 days	21. 3.–3. 4.	12.8
7 days	28. 3.–3. 4.	8
measurement day	4. 4. 2017	2.6
30 days	2. 4.–1. 5.	14.4
14 days	18. 4.–1. 5.	4.4
7 days	25. 4.–1. 5.	0.1
measurement day	2. 5. 2018	0

Source: CUNI (2020)

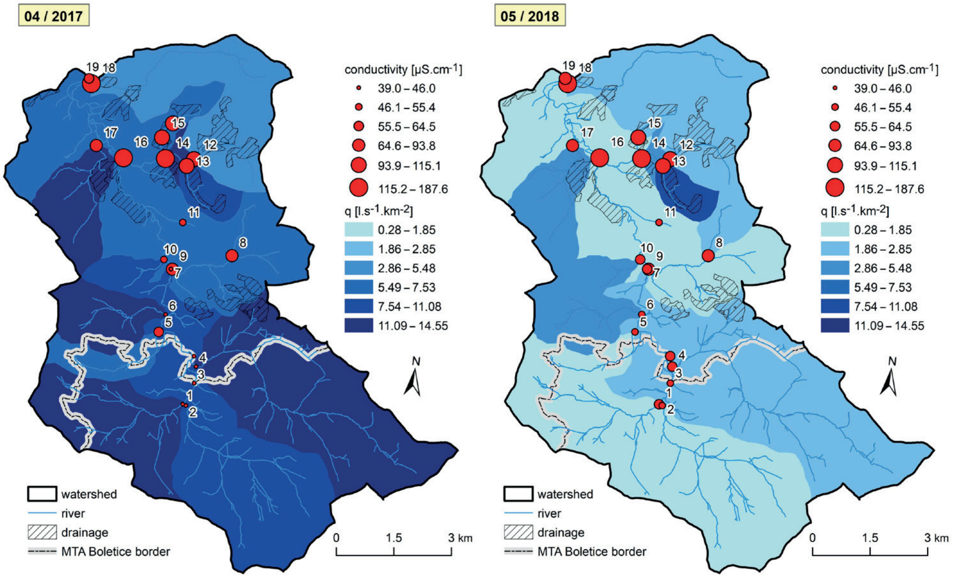

Fig. 5 – Specific discharge and basic biogeochemical parameters during two hydrometeorological situations in 2017 (wet conditions, left) and 2018 (dry conditions, right). Background source: VUV (2019).

from the catchment quickly (site 13 [ZBY] and 17 [Magdalénský brook]). Site 15 (SVI), which is also largely drained (20%) showed a higher specific discharge during wetter conditions in 2017 only.

4. Discussion

4.1. Trends in water quality

Long-term (2003–2019) N-NO_3 concentrations decreased significantly (from 1,175 μg.l^{-1} in 2004 to 587 μg.l^{-1} in 2018) at the outlet (BLM site). Bílý and Simon (2007) registered the concentration of nitrates reduction by approximately 50% over the 15 years between 1990–2005 at 3 sites of the Blanice River catchment previously and explained it by the elimination of intensive agriculture because of the protective conditions of the national park reserve and by an overall reduction in the intensity of operations of mountain farms. Our findings have different explanation, as land use in the catchment have been relatively stable since 2003. N-NO_3 concentration reduction since 2003 could be caused mainly by the construction of WWTP Zbytiny in 2009 and WWTP Křišťanov in 2016. Additional analyses of EC changes during the construction time of WWTP confirmed effectiveness of the water treatment. EC values of river water under the village decreased near the values as were measured above the village (around 70 $\mu S.cm^{-1}$, the EC outflow/inflow ratio decreased near 1). Wanner, Simon, Kladivová (2012) observed treatment efficiency > 90% for organic pollution and only 60% removal efficiency for total nitrogen (TN) and total phosphorus (TP) in the WWTP effluent between November 2008 and November 2010. Though, the two stabilisation ponds located behind the wastewater treatment plant greatly improved the total treatment efficiency up to 77% (TN) and 96% (TP). However, when comparing the 1994–2006 and 2018–2019 periods at the SPA site, $N\text{-}NO_3$ mean concentrations have increased from mean values 95 $\mu g.l^{-1}$ in 1994–2006 to 168 $\mu g.l^{-1}$ in 2018–2019 (median values: 34 $\mu g.l^{-1}$ (1994–2006), 105 $\mu g.l^{-1}$ (2018–2019). The $N\text{-}NO_3$ increase at the SPA site, which is a catchment with no agriculture area and settlement, could be a result of forestry activities (Reynolds, Edwards 1995; Hughes, Quinn 2019) as more than 60% of the catchment is covered by intensive forest and forest clear-cutting was registered near spring area in the immediate vicinity of the brook channel between 2008 and 2011 according to orthophoto images (CUZK 2021). Climate change is considered as another factor that may cause more $N\text{-}NO_3$ leakage because of hydrological events (runoff after heavy rain) and increased decomposition and mineralisation of organic matter (Kaste, Austnes, De Wit 2020) or relatively high N deposition in upland forests, which might still exceed long-term sustainable levels (Hůnová, Maznová, Kurfürst 2014). However, this result could be also influenced by the number and frequency of observations. Values of $P\text{-}PO_4$ registered an annual decrease at the BLM site. Together with a decrease in $N\text{-}NO_3$, it could be a result of water quality improving measures in the Blanice River catchment such as construction of WWTPs. A significant decreasing trend (MK-Stat – 2.8, $p < 0.05$, $n = 16$) of dissolved O_2 has been detected at the BLM outlet profile in October, which could reflect increasing air and water temperature or more NOM in water (Oulehle, Hruška 2009). Moreover, this could have a negative effect on biota in the river.

Values of pH increased and SO_4 concentrations decreased at SPA site, which is in correspondence with the overall trend and recovery from acidification in Central Europe (Oulehle, Hruška 2009; Oulehle et al. 2013, 2017; Kaste, Austnes, De Wit 2020). Some of the base cations concentrations increased as well (Ca, Mg, K). Although higher concentrations of base cations are mainly associated with higher SO_4 buffering the effect of SO_4 on pH (Mattsson 2010). The increased values at this site could be associated also with other factors. One of them is forest clear-cutting which was registered in the upper parts of this catchment. Changes in forest cover considerably alter the flow of base cations through forest ecosystem because forests also take up base cations (Skeffington, Cosby, Whitehead 2016). Forest clear cutting, which was registered at SPA site between 2008 and 2011 could be the main driver for increased values of base cations in river water.

4.2. Land cover and anthropogenic impact

While the presence of land and water protection should improve water quality (Helin et al. 2013), protected areas cannot assure the water quality improvement in streams automatically (Mancini et al. 2005, Pešić et al. 2020). In our study, analyses of water chemistry characteristics in small catchments revealed that the degree and area of land protection are supposed to have a positive impact on water quality. Small catchments with less than 50% of the total area belonging to Protected Landscape Area and Bird Area had similar water quality parameters. Nevertheless, there are still higher concentrations of COD_{Mn} in the upper parts of the catchment caused by peat bogs. The influence of peatland on water quality was assessed as negative, while the intensity of the effect is related to the area and volume in the catchment (Kocum et al. 2016). Although the runoff from peat bogs decreases during dry periods and the river water quality improved (Ferda et al.1971; Hruška, Johnson, Krám 1996; Hruška, Kohler, Bishop 1999; Oulehle, Janský 2003), during some summer rainfall periods and spring snowmelt, there is a decline in water quality, which is primarily related to greater mineralization when groundwater levels drop and the subsequent washing out of these materials after rain or snowmelt (Kocum et al. 2016).

Cattle and sheep grazing is present by 0–72% (Table 3). Catchments with concentrated livestock populations have been shown to discharge as much as 5 to 10 times more nutrients (especially N and P) than catchments in cropland or forestry (Hubbard et al. 2004). Although, there is only 0.2–0.3 cows per ha and 0.05–0.1 sheep per ha, catchment with 72% of grazing area had the highest mean concentration of $N\text{-}NO_3$ (1,656 $\mu g.l^{-1}$), which is 9–19 times higher than in catchments with < 6% of intensive grassland. Not only area of grazing land but also the unrestricted access of livestock to water sources could be most probably cause of the surface water deteriorating, which was already pointed out by Fučík, Novák, Žížala (2014). On the contrary, mean TP concentration was below the whole catchment mean values (only 42 $\mu g.l^{-1}$, mean TP concentration for whole catchment is 55 $\mu g.l^{-1}$). However, lower TP concentration in river water in catchments dominated by grasslands could be caused by the application of compounds rich in P-sorptive Al, Fe, and, to a lesser extent, Ca (McDowell, Norris 2014) which are used on agricultural land to increase soil P retention. These compounds are higher in catchments with grazing, especially Al (417 $\mu g.l^{-1}$, mean Al concentration for whole catchment is 261 $\mu g.l^{-1}$).

Another important factor related to stream water quality is subsurface drainage and forest ditching. Higher specific discharge and higher concentrations of SO_4, $N\text{-}NO_3$, base cations, Fe, TP, and EC were measured in the catchments with subsurface drainage. This is connected to increased aeration of soil profile and then subsequently mineralization of organic matter and reduced denitrification in previously waterlogged soils (Kulhavý, Fučík 2015). Even if the concentrations of COD_{Mn} were higher at most of the sites in the catchment, the restored brook SVI had lower concentrations (7.8 $mg.l^{-1}$). In contrary to earlier study (Kliment et al. 2008), the water quality at this site indicated an improvement. Phosphorus loss along agricultural drainage ditches represents one of the biggest risks for river water quality (Moloney, Fenton, Daly 2020). Švanyga et al. (2013) presented the total phosphorus (TP) concentration in the upper Blanice River together with eutrophication as a significant problem. Our results indicated that higher TP concentrations came from the drainage system and represent a problem mainly during precipitation events. The subsurface drainage and ditching in the forested catchment TET could be considered as one of the reasons causing water quality degradation. Despite more than 70% forest cover in TET catchment, there are slightly higher concentrations of $N\text{-}NO_3$, Ca, Na, Si, and EC, which could be connected with ditching (ditching density is 7.4 $km.km^{-2}$ there, Kalkus 2012) as Åström, Aaltonen, Koivusaari (2001) registered similar increase of the concentrations of Mn, Ca, Mg, suspended material and alkalinity in a boreal forested catchment with ditching in Finland.

As a positive effect could be considered significantly higher runoff during a dry period in drained catchments as previously observed Královec, Kliment, Matoušková (2016) in TET catchment. This result is in accordance with earlier studies worldwide indicating that ditching has an overall levelling effect on discharge such that peak runoffs commonly are slightly reduced, while during low-flow periods the discharge increased (Seuna 1982; Prevost, Plamondon, Belleau 1999; Åström, Aaltonen, Koivusaari 2001).

4.3. Freshwater pearl mussel thresholds

Even as a freshwater pearl mussel (*M. margaritifera*) locality (Absolon, Hruška 1999; Simon et al. 2015), it should be considered that only some of the study localities are suitable as their habitat in terms of water quality. The most frequently exceeded limits were for EC, Ca, TP, $N\text{-}NO_3$ and Mg:Ca ratio in the lower parts of the upper Blanice catchment. Concentrations of TP, as well as concentrations of $N\text{-}NO_3$ and EC exceeded the critical upper limits for the survival of *M. margaritifera* at more than half of the sites (according to limits in Absolon, Hruška 1999). Most suitable site for freshwater pearl mussel (*Margaritifera margaritifera*) according to water chemistry was site near the freshwater pearl mussel breeding program (PER), and in the smallest forest subcatchment (SPA). Water biogeochemical parameters are however only a part of ecological requirements of freshwater pearl mussel. Other factors not included in this study were especially substratum quality, hydromorphological characteristics, content of fine sediment, host fish abundance or presence of predators (Stoeckl, Denic, Geist 2020).

4.4. Rainfall-runoff event

Climate changes (Soulsby et al. 2001; Evans, Monteith, Cooper 2005; Bates et al. 2008; Oulehle, Hruška 2009) and changes in rainfall-runoff regime (Blahušiaková et al. 2020) affect surface water quality significantly. Moreover, heavy precipitation events are one of the risky situations in drinking water quality degradation (Delpla et al. 2009). Although total aluminium concentrations decreased significantly after 1990s (Oulehle et al. 2013, 2017), results of our study show that heavy precipitation event cause higher release of Al compounds into the river water – up to more than 1,000 $\mu g.l^{-1}$ and up to more than 10 times higher than median values, which could affect freshwater pearl mussel population negatively (Taskinen et al. 2011). During the rainfall-runoff event, increased concentrations of COD_{Mn}, DOC and TP were also registered. TP concentrations were higher one to almost four times than the freshwater pearl mussel limit (35 $\mu g.l^{-1}$, except profile PER with 30 $\mu g.l^{-1}$). Higher concentration of organic matter threatens organisms, among other things (e.g. increased oxygen demand, water eutrophication), by increased bioavailability of contaminants (Thorsen, Cope, Shea 2007).

5. Conclusions

The upper Blanice catchment is an important, partly specially protected area due to its high biological diversity and protection of freshwater pearl mussel (*Margaritifera margaritifera*) population, which is on the IUCN Red List.

Results showed that in long-term perspective there was registered an improvement in water quality in decreasing trends of N and P compounds in the main stream during 2003–2019 period, which could be explained by the higher efficiency of water treatment in WWTPs. Nevertheless, most water pollution in the Blanice catchment is currently directly linked to anthropogenic activities like subsurface drainage (higher TP, Fe, EC), municipal solid waste landfill (higher Cl, base cations, $N\text{-}NH_4$) and grazing cattle and sheep (higher $N\text{-}NO_3$). As natural sources of water pollution are considered peatlands in the upper parts of the catchment (higher concentrations of COD_{Mn}, TP, lower pH together with higher concentrations of Al and Fe). Water quality in terms of freshwater pearl mussel requirements was at most of the sites still insufficient. The most frequently exceeded limits were for EC, Ca, TP, $N\text{-}NO_3$ and Mg:Ca ratio. Heavy precipitation event caused higher releases of Al, COD_{Mn}, DOC and TP, which could also affect freshwater pearl mussel population negatively.

Overall, the results of this study emphasize, that even in near-natural catchment with a significant area of landscape protection, previous and current interventions are reflected very sensitively through water quality changes. Thus, future studies focused on changes in water quality parameters during different rainfall-runoff events and with connection to various landscape characteristics and anthropogenic activities are needed to comprehend the main sources of the compounds and to develop appropriate strategies to protect water quality in this vulnerable ecosystem.

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