www.czasopisma.pan.pl www.journals.pan.pl

Archives of Environmental Protection
Vol. 48 no. 1 pp. 31–40

PL ISSN 2083-4772
DOI 10.24425/aep.2022.140543

© 2022. The Author(s). This is an open-access article distributed under the terms of the Creative Commons Attribution-ShareAlike 4.0 International Public License (CC BY SA 4.0, https://creativecommons.org/licenses/by-sa/4.0/legalcode), which permits use, distribution, and reproduction in any medium, provided that the article is properly cited.

Impact of flow and damming on water quality of the mountain Raba River (southern Poland) – long-term studies

Ewa Szarek-Gwiazda*, Robert Gwiazda

Institute of Nature Conservation, Polish Academy of Sciences, Krakow, Poland

*Corresponding author's e-mail: szarek@iop.krakow.pl

Keywords: flow, physicochemical parameters, Carpathian river, impact of dam

Abstract: Climate change, manifested by long term periods of drought to heavy rainfall, may remarkably modify river flow regimes. We hypothesize that flow prevailing in a given year determines water chemistry of the Carpathian Raba River above and below Dobczyce Reservoir (southern Poland), used for drinking purposes. Based on the mean annual river flow for years 1991–2017, hydrologically dry (HD), hydrologically average (HA) and hydrologically wet (HW) years were distinguished. We found significant differences in the values of most studied physicochemical parameters of river water above and below the reservoir between studied hydrological years (for a period of April–November). In HD years, the water above the dam had significantly higher temperature and values of conductivity (point pollution source, groundwater inflow), while lower ones of nutrients NO_3^- and P-tot (diffuse pollution) compared to those in HA and/or HW years. The best GLM models for mean monthly flows above and below the dam include 3–5 factors among which conductivity and NO_3^- concentration were always present. The reservoir in different ways influences the water chemistry below the dam in HD, HA and HW years. The impact of flow on the water quality in hydrologically varied years is discussed. The obtained results are important for appropriate management in catchment basins of mountain rivers and the protection of dam reservoirs against the eutrophication processes in changing climate and flow regime.

Introduction

It was predicted that in the European scale, climate change remarkably modifies flow regimes. In the temperate continental climate zone high impacts are expected around the Carpathians and the Balkan mountains (Schneider et al. 2013). In the mountain areas of central Europe and Poland a decreasing trend of precipitation related to the increasing air temperature and a decreasing one of snowfall fraction is observed (Blahušiaková et al. 2020, Wilk-Woźniak et al. 2021). In the Carpathian region the changes in precipitation are irregular after 2000 and causing periods of drought to heavy rainfall (Wilk-Woźniak et al. 2021). The impact of flow on river water quality has been discussed in numerous scientific publications. In this aspect much attention was paid to the temperature and nutrients (Nilsson and Renöfält 2008, Szarek-Gwiazda 2013, Bowes et al. 2015) that are crucial components of eutrophication processes of rivers and water bodies (Genkai-Kato and Carpenter 2005, Wilk-Woźniak 2009, Yamamoto and Nakahara 2005, Bouraï et al. 2020, Mazierski and Kostecki 2021). We hypothesize that hydrological regime prevailing in a given year may determine the physicochemical composition of mountain river water. Such knowledge is important for the appropriate management in the catchment basins and the protection of reservoir built on the river against the eutrophication process.

In Poland, there are 69 large dams (with the dam height of 15 m and more) located mostly in the valleys of the Carpathian and Sudeten rivers and streams, which is favoured by appropriate geological and hydrological conditions (Kasza 2009). Dam reservoirs are important from the economic and recreational point of view, but also can significantly alter the river continuity as well as hydrological, chemical, biological and physical properties of rivers (Kasza 2009, Winton et al. 2019, Wiatkowski and Wiatkowska 2019). The impact of the dam on river chemistry depends on many factors, such as reservoir morphometry, function, age, rate of water exchange, reservoir stratification, biogeochemical processes and the level of water release from the reservoir (Wang et al. 2018, Winton et al. 2019). As high river flow or flow events may disturb thermal stratification and biogeochemical processes taking place in the reservoir (Geraldes and Boavida 2005, Szarek-Gwiazda et al. 2009) we hypothesize that the reservoir in a different way may effect the downstream water chemistry in hydrologically various years. The impact of reservoirs on river water quality in this aspect remains poorly understood.

This study aimed to assess the differences in the values of physicochemical parameters in water of the Carpathian river in southern Poland between various hydrological years – dry (HD), average (HA) and wet (HW) ones. Moreover, the influence of the dam reservoir on the river water chemistry in various hydrological years as a side aspect was investigated. Additionally, we estimated physicochemical parameters related to mean water flow in HD, HA and HW years.

Material and methods

Study area

The Raba River, a length of 137.4 km, is a right-side tributary of the Vistula River in southern Poland and the main tributary (88.6% of the total inflow) of the dimictic Dobczyce Reservoir (49"52'N, 20"02'E, alt. 269.9 m a.s.l.) (Mazurkiewicz-Boroń 2002). The river is characterized by a large amplitude of runoff, with the spring–summer flow regime and by a clear dominance of summer high flows (70% of annual maxima) (Punzet 1969). It is mainly contaminated by municipal sewage from three small towns (less than 18 000 inhabitants), by wastewater from villages and agriculture. In the river catchment of the above reservoir (area of 784 km^2) the structure of agricultural use showed too much arable land and too little permanent grassland (Mazurkiewicz-Boroń 2002). The mountain and piedmont part of the catchment area is afforested in the range of 36–41%, arable land covers 60–73% in the total area of agricultural land, the remaining part is grassland. However, during the years 1990–2018 the changes in the land use (increase of forest from 45 to 50% and decrease of agricultural land from 53 to 43%) and the modernization and introduction of new technologies in sewage treatment plants were observed (Wilk-Woźniak et al. 2021). Dobczyce Reservoir has a capacity of 99.2×10^6 m^3, an area of ~ 985 ha, a length of 10 km, and a mean depth of 11 m (maximum ~ 27 m), water exchange of 3.6 times a year (Mazurkiewicz-Boroń 2002). It is a meso-eutrophic reservoir of a submontane type (Wilk-Woźniak et al. 2009) and a drinking water reservoir for the Krakow agglomeration.

Methods

The data of mean daily flow of the Raba River for the period 1994–2017 were obtained from Regional Water Management Board in Krakow, Poland. Daily flow of the river upstream the reservoir was obtained from gauging station at Stróża village (78.07 km of river course), while downstream the reservoir it was calculated for the dam cross-section (59.70 km). Based on the daily flow, the mean annual Raba River flow for the period 1994–2017 was calculated and used to determine hydrologically dry, average and wet years. We considered years with the mean annual flow (1) lower than the multiannual mean flow as hydrologically dry, (2) close to the multiannual mean flow as hydrologically average, and (3) higher than the multiannual mean flow as hydrologically wet. The mean annual flow for years 1994–2017 was 11.0 m^3 s^{-1}, and without taking into account 2010, it was 10.4 m^3 s^{-1}. The year 2010 was hydrologically extremely wet with four floods and the mean annual flow of 23.6 m^3 s^{-1}. For the statistical analysis including flow and water chemistry we distinguished five HD, five HA, and five HW years each from the period 1994–2017. We distinguished the years 2003, 2008, 2011, 2012 and 2015 with the mean annual flows of 6.0–7.7 m^3 s^{-1} as hydrologically dry. The years 2000, 2005, 2006, 2009 and 2016 with the mean annual flows of 10.0–11.4 m^3 s^{-1} were distinguished as hydrologically average, and the years 1997, 1998, 2001, 2007 with the mean annual flows of 12.3–14.1 m^3 s^{-1} and 2010 (23.6 m^3 s^{-1}) as hydrologically wet.

The present analyses are possible thanks to long-term studies on the water chemistry of the Raba River carried out by the Karol Starmach Institute of Freshwater Biology, presently Department of the Institute of Nature Conservation, Polish Academy of Sciences. The sampling sites were located above the Dobczyce Reservoir, near the inlet (site 1) and below the reservoir, near the outlet (site 2) (Fig. 1). We analysed the changes of physicochemical parameters (water temperature, conductivity, pH, dissolved oxygen (DO), oxygen saturation, and nutrients – NO_3^-, NH_4^+, total phosphorous (P-tot), and

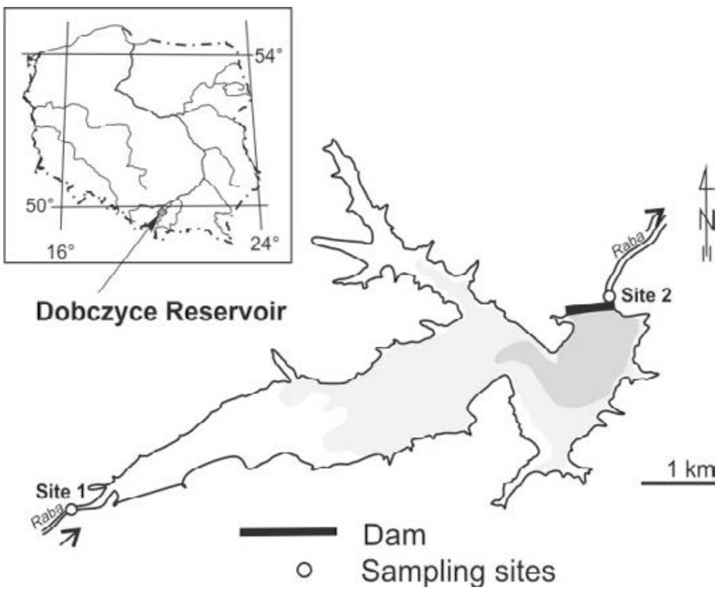

Fig. 1. Locations of the sampling sites in the Raba River

biochemical oxygen demand (BOD5)) of surface water collected monthly from April to November (with the exception of August 2005 and November 2016) in the above distinguished HD, HA and HW years. BOD5 was not analysed in the years 1997, 1998, 2000, 2001, while P-tot in 1997, 2000, 2003, 2015, and 2016.

Water temperature, conductivity and pH were measured *in situ*. The pH and conductivity were measured with an Orion pH meter (Expandable ion Analyser EA 940) till 2005, and using a WTW apparatus from 2005. Dissolved oxygen and BOD5 were determined according to the Winkler method (APHA 1992). Nitrates (till 2005) were analysed by the hydrazine reduction method, ammonia (till 2008) by the nesslerization method, and P-tot (after mineralization) by the molybdenum blue method (APHA 1992). Nitrate from 2005 and ammonia from 2009 were analysed by ion chromatography (DIONEX ICS 1000 and IC DX 320, Dionex Corporation, Sunnyvale, USA). Before analysis water samples were filtered through pore-sized syringe filters (Ministart RC 25, Sartorius Stedim Biotech GmbH, Germany) into polyethylene sample tubes.

Statistics

The differences in the values of physicochemical parameters in the Raba River water above and below the reservoir in HD, HA and HW years were calculated using the Wilcoxon test, while between the studied hydrological years (HD, HA and HW) using the Mann-Whitney test. The comparative studies carried out for two different methods used for NO_3^- and NH_4^+ analysis (described above) showed negligible differences for NO_3^- and considerable ones for NH_4^+. Therefore for NH_4^+ ion the data obtained from ion chromatography method were used only for the calculation of Mann-Whitney test, while all the data were used for Wilcoxon test. As a few data for the NH_4^+ concentration were below the detection limit, we put the value 0.001 in the place of these data for statistical calculations. Spearman correlation coefficients were calculated to determine the relationship between the values of the studied parameters in the river water.

Principal Component Analysis (PCA) was used to study collinearity among the studied factors (Freckleton 2011). Generalized Linear Model (GLM) with the Poisson error distribution and logit-link function distribution was used to determine the relationship between physicochemical parameters (temperature, pH, DO, conductivity, NO_3^-, P-tot, BOD5) and the mean river flow in HD, HA and HW years. Akaike's information criterion (AIC) was used for model selection. The model with the lowest AIC score and the highest weight (*w*) is the most parsimonious. To determine the significance of particular variables, Akaike weights (AIC *w*) for models containing given variables were used (Burnham and Anderson 2004). The predictor with the highest AIC *w* was considered to be the most important. We used STATISTICA version 10 for the statistical analyses (Statsoft 2014).

Results

Flow and water chemistry in the river above the reservoir

In the Raba River above Dobczyce Reservoir the flow on the sampling day ranged from 0.5 to 179 $m^3 s^{-1}$ and the mean monthly flow was 0.8–86.3 $m^3 s^{-1}$ (Fig. 2). A significantly higher flow on the sampling day was found in HA and HW years than in HD years. The mean monthly flow showed significant differences between HD, HA and HW years (Table 1).

Water temperature above the reservoir ranged from 3.0 to 24.7°C, pH 6.9–9.2, DO content 6.9–16.6 mg dm^{-3}, conductivity 192–478 µS cm^{-1}, BOD5 0.5–5.6 mg dm^{-3}, and nutrients (in mg dm^{-3}) – NO_3^- 0.7–11.2, NH_4^+ (not detected) -0.208 (analysed by chromatography method), P-tot 0.004–0.743 (Fig. 2). The median of water temperature was higher by 3.1°C in HD than HW years (15.4 and 12.3°C, respectively), the difference between HD and HW years was statistically significant (Table 1). The median of nutrient (NO_3^-, P-tot, NH_4^+) concentrations increased from HD to HW years (1.6, 3.8 and 6 times, respectively). The differences in NO_3^- concentrations between HD, HA and HW years, while P-tot concentrations between HD years as well as HA and HW years were significant (Table 1). There were no differences in pH, DO content, oxygen saturation, values of conductivity and BOD5, and NH_4^+ concentration between the studied hydrological years. The maximum values of conductivity occurred in HD years (Fig. 2).

Flow and water chemistry in the river below the reservoir

In the river below the reservoir the flow on the sampling day ranged from 1.8 to 175 $m^3 s^{-1}$ and the mean monthly flow 1.8–81.2 $m^3 s^{-1}$ (Fig. 2). The flow on the sampling day was significantly higher in HA and HW years in comparison to HD years, while the mean monthly flow was significantly higher in HW years than in HD and HA years (Table 1).

The water temperature ranged from 3.7 to 19.4°C, pH 7.0–8.8, DO content 3.8–13.6 mg O_2 dm^{-3}, oxygen saturation 38.5–126.9%, conductivity 215–406 µS cm^{-1}, BOD5 0.3–4.5 mg dm^{-3}, and nutrients (in mg dm^{-3}) – NO_3^- 1.0–9.4, NH_4^+ nd (not detected) –0.604, P-tot 0.001–1.916 (Fig. 2). There were no significant differences in water temperature, DO content, oxygen saturation, and BOD5 values in water among the studied hydrological years. The pH values were significantly higher in HW as compared to HA years (Table 1). The highest median value of conductivity was found in HD years, while nutrient concentrations in HA (NO_3^-, NH_4^+) or HW years (P-tot) (Fig. 2, Table 1). The concentrations of NO_3^- and P-tot were significantly higher in HA and HW years than HD years, while NH_4^+ in HA years than in HD and HW years (Table 1).

Differences in flow and water chemistry between the river above and below the reservoir

The water temperature (with the exception of HW years), pH, DO content, and oxygen saturation in the studied hydrological years were significantly higher in the river water above than below the dam (Table 2). The decreases in the medians of these parameters from upstream to downstream of the dam in HD, HA and HW years were respectively the temperature 3.0 and 2.1 and 1.3°C, pH 0.5, 0.5 and 0.3, DO 1.3, 1.4 and 0.3 mg O_2 dm^{-3} and oxygen saturation 16.6, 18.6 and 8.5%. This indicates a lower decrease in the medians of these parameters in HW years than in HD and HA years. Similarly, the values of conductivity (in each year) were significantly higher in the river water above than below the dam (Table 2).

The distribution pattern of nutrient was varied from upstream to downstream of the dam. An increase in the concentrations of NO_3^- (with the exception of HW years) and NH_4^+ in HD years, and inversely, a decrease in the concentration of NH_4^+ in HW years were found (Table 2). The P-tot concentration and BOD5 values in the river water above and below the dam were similar.

Generalized linear model (GLM)

GLMs showed that the most parsimonious models included 3–5 factors in the studied hydrological years (Table 3). The best model describing the mean river flow above the dam in HD years included temperature, conductivity, NO_3^- and P-tot (AIC=97.62, w=0.15), in HA years conductivity, DO, NO_3^- and P-tot (AIC=84.89, w=0.19), while in HW years temperature,

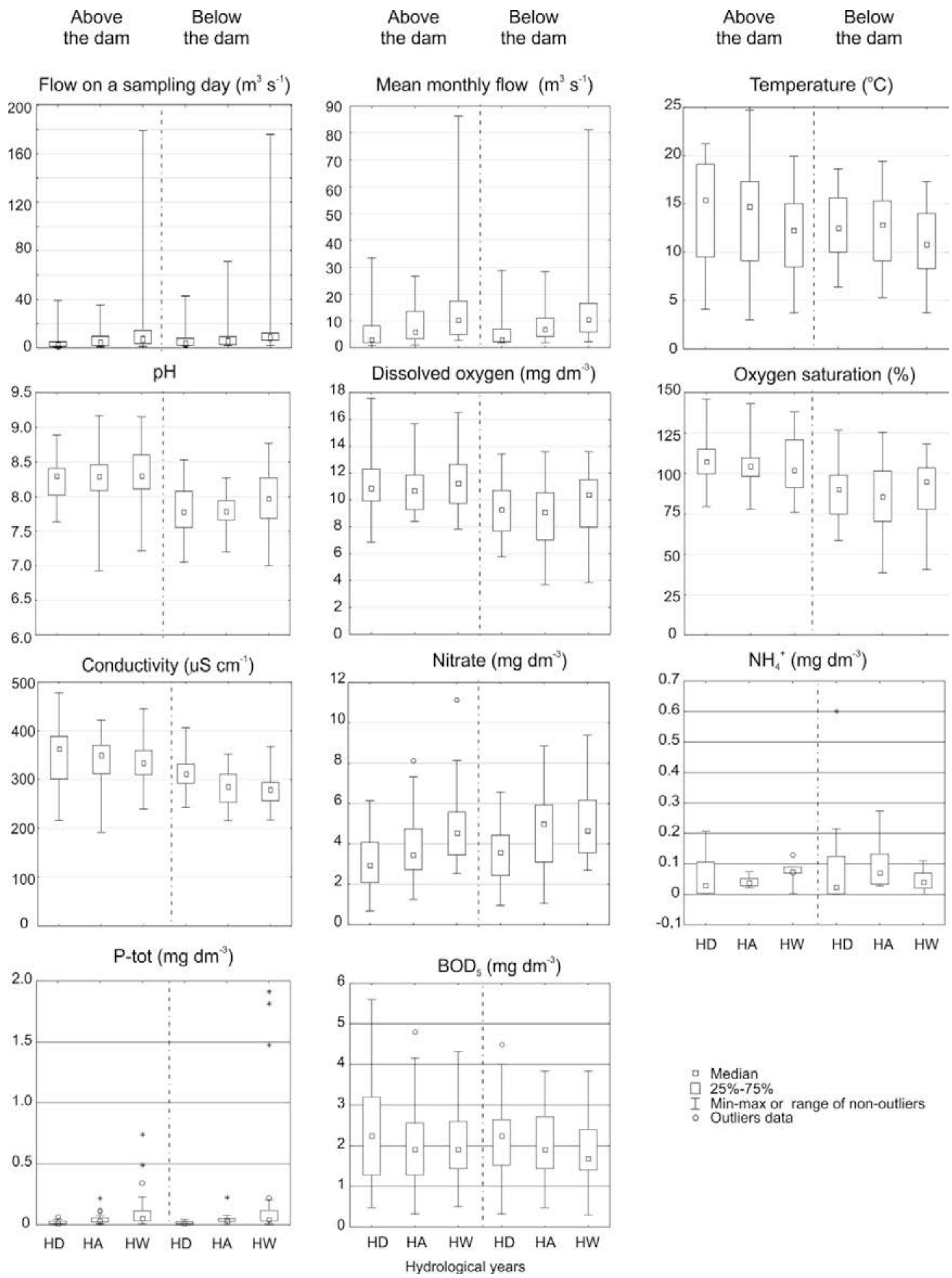

Fig. 2. Flow and water chemistry of the Raba River water above and below the Dobczyce Reservoir in the hydrologically dry (HD), average (HA) and wet (HW) years

www.czasopisma.pan.pl PAN www.journals.pan.pl

conductivity, BOD5, NO_3^- and P-tot (AIC=158.90, *w*=0.52). The best model describing the mean river flow below the dam in HD years included conductivity, NO_3^- and P-tot (AIC=128.59, *w*=0.11), in HA years temperature, conductivity, pH, DO and NO_3^- (AIC=73.83, *w*=0.19) and in HW years conductivity, pH, DO, NO_3^- and P-tot (AIC=86.69, *w*=0.24) (Table 3).

In the river water above the reservoir the most important factors for the mean flow in HD, HA, and HW years were conductivity (∑ AIC *w*= 1.00, 1.00, 0.99, respectively) and NO_3^- concentration (∑ AIC *w*= 0.85, 0.99, 1.00, respectively). Other parameters important for the mean flow in some studied hydrological years were the temperature in HD years (∑ AIC *w*=0.88), DO content in HA years (∑ AIC *w*=0.82), while BOD5 (∑ AIC *w*=1.00) and P-tot (∑ AIC *w*=0.98) in HW years. In the river water below the reservoir the most important factor for the mean flow in all studied hydrological years was only conductivity (∑ AIC *w*=0.88, 1.00, 1.00, respectively). The ion NO_3^- was important in HD and HW years (∑ AIC *w*=0.77 and 1.00, respectively), P-tot in HD years (∑ AIC *w*=0.93), the temperature (∑ AIC *w*=0.94) in HA years, while in HA and HW years DO content (∑ AIC *w*=1.00 and 1.00, respectively) and pH (∑ AIC *w*=0.96 and 1.00, respectively).

Table 1. Significance differences in the flow and values of physicochemical parameters in the Raba River water above (site 1) and below (site 2) the dam between in the hydrologically dry (HD), average (HA) and wet (HW) years (Mann-Whitney test). Only significant differences are given

Parameter	Site	Hydrological years						
		N	HD-HA		HD-HW		HA-HW	
		HD, HA, HW	Z	p	Z	p	Z	p
Flow on the day	1	40, 38, 40	-2.43	0.015	-4.53	0.000		ns
	2	40, 38, 40	-2.37	0.018	-3.86	0.000		ns
Mean monthly flow	1	40, 38, 40	-2.39	0.017	-4.27	0.000	-2.10	0.035
	2	40, 38, 40	-2.79	0.005	-4.34	0.000	-2.26	0.024
Temperature	1	39, 35, 39		ns	2.03	0.042		ns
	2	39, 35, 39		ns		ns		ns
pH	1	39, 37, 39		ns		ns		ns
	2	39, 37, 39		ns		ns	-2.30	0.022
Conductivity	1	40, 37, 40		ns		ns		ns
	2	40, 37, 40	2.89	0.004	3.47	0.001		ns
NO_3^-	1	39, 37, 40	-2.28	0.023	-4.65	0.000	-2.41	0.016
	2	40, 37, 40	-2.53	0.011	-2.92	0.003		ns
NH_4^+	1	23, 12, 8		ns		ns		ns
	2	23, 12, 8	-2.07	0.039		ns	1.97	0.049
P-tot	1	24, 21, 32	-4.15	0.000	-4.91	0.000		ns
	2	24, 23, 32	-4.75	0.000	-5.35	0.000		ns

Flow on the day – flow on the sampling, day N – number of samples

Table 2. Significance differences in the flow and values of physicochemical between the river water above and below the dam in the hydrologically dry, average and wet years (Wilcoxon test). Only significant differences are given

Parameter	N			Hydrological years					
				Dry		Average		Wet	
	HD	HA	HW	Z	p	Z	p	Z	p
Flow on the day	40	38	37	2.93	0.003	–	ns	–	ns
Temperature	38	35	39	2.26	0.024	2.08	0.038	–	ns
Conductivity	38	37	40	3.31	0.001	4.41	0.000	4.48	0.000
pH	38	37	39	4.95	0.000	4.71	0.000	4.40	0.000
Dissolved oxygen	36	34	39	4.28	0.000	3.16	0.002	4.03	0.000
Oxygen saturation	38	34	39	4.63	0.000	3.34	0.001	4.04	0.000
NO_3^-	39	37	40	2.50	0.012	2.56	0.011	–	ns
NH_4^+	32	31	34	2.03	0.042	–	ns	3.14	0.002

Flow on the day – Flow on the sampling, day, N – number of samples

Table 3. Sets of GLM analysis (the best 3 models) describing the mean flow of the Raba River above and below the Dobczyce Reservoir in the studied hydrological years

Hydrological years	No	Models	k	AIC	Delta	w
River above the dam						
Dry	1	Temp+Cond+NO_3^-+P-tot	4	97.62	0.00	0.150
	2	Temp+Cond+pH+NO_3^-+P-tot	5	98.13	0.51	0.116
	3	Temp+Cond+pH+NO_3^-	4	98.30	0.68	0.107
		Intercept		100.95	3.33	0.028
Average	1	Cond+DO+NO_3^-+P-tot	4	84.89	0.00	0.193
	2	Cond+DO+ BOD5+NO_3^-+P-tot	5	86.52	1.63	0.086
	3	Cond+ pH+Oxy+NO_3^-+P-tot	5	86.55	1.66	0.084
		Intercept		88.89	4.00	0.026
Wet	1	Temp+Cond+BOD5+NO_3^-+P-tot	5	158.90	0.00	0.517
	2	Temp+Cond+DO+BOD5+NO_3^-+P-tot	6	160.86	1.96	0.194
	3	Temp+Cond+pH+BOD5+NO_3^-+P-tot	6	160.89	1.99	0.191
		Intercept		168.23	9.33	0.005
River below the dam						
Dry	1	Cond+NO_3^-+P-tot	3	128.59	0.00	0.111
	2	Temp+Cond+DO+NO_3^-+P-tot	5	128.64	0.05	0.108
	3	Cond+Oxy+NO_3^-+P-tot	4	129.65	1.06	0.065
		Intercept		130.70	2.11	0.039
Average	1	Temp+Cond+ pH+DO+NO_3^-	5	73.83	0.00	0.258
	2	Temp+Cond+ pH+DO	4	74.40	0.57	0.194
	3	Temp+Cond+ pH+DO+NO_3^-+P-tot	6	75.52	1.69	0.111
		Intercept		79.08	5.25	0.019
Wet	1	P-tot+NO_3^-+DO+ pH+Cond	5	86.69	0.00	0.242
	2	NO_3^-+ DO+pH+Cond	4	87.05	0.36	0.202
	3	P-tot +NO_3^-+BOD5+DO + pH +Cond	6	87.49	0.80	0.163
		Intercept		96.02	9.33	0.009

Temp – Temperature, Cond – conductivity, DO – Dissolved oxygen

Spearman correlations

In the river above the dam, the water flow (on the sampling day or/and mean monthly) showed a negative correlation with conductivity (HD, HA and HW years), pH, DO content and oxygen saturation (HA and HW years), and a positive one with the concentrations of nutrients such as NO_3^- (HD, HA and HW years), P-tot (HD and HA years), and NH_4^+ (HA years) (Table 4). The concentrations of NO_3^- in HD ($r= -0.50$, $p<0.05$) and HA ($r= -0.35$, $p<0.05$) years as well as P-tot in the HA ($r= -0.54$, $p<0.05$) and HW ($r= -0.37$, $p<0.05$) years showed negative correlations with the conductivity. Moreover, the BOD5 values in HD ($r= 0.40$, $p<0.05$) years were positively correlated with water temperature.

In the river below the dam, the water flow (on the sampling day or/and mean monthly) showed a negative correlation with conductivity values (HA and HW years), temperature (HA years), and a positive one with the concentrations of NO_3^- (HD, HA, HW years) and DO (HA years) as well as oxygen saturation (HD and HA years) (Table 4). Conductivity values were negatively correlated with the P-tot concentration in the HA ($r= -0.44$, $p<0.05$) and HW years ($r= -0.57$, $p<0.05$).

Discussion

The river above the reservoir

We found a negative impact of the flow on water temperature (GLM, high value $\sum$ AIC w in HD years, negative correlation in HA years) in a medium-sized Carpathian Raba River. It was expressed in a significantly higher water temperature (median 3.1°C) in HD years than HW years that may be important for eutrophication processes in the reservoir. The temperature is a crucial factor controlling the growth of algae and cyanobacteria (Yamamoto and Nakahara 2005, Wilk--Woźniak 2009) and influencing digenesis processes in the water-sediment system and phosphate release from sediments (Genkai-Kato and Carpenter 2005). Increasing river water temperature is one of the factors causing an increase in water temperature of dam reservoirs. Indeed, this phenomenon was observed in Dobczyce Reservoir (Wilk-Woźniak et al. 2021). The change in water temperature in deep reservoirs affects the mixing patterns, the onset and duration of thermal stratification, which was also found in Dobczyce Reservoir (Wilk-Woźniak et al. 2021). This phenomenon means longer stabilization of water column, longer summer changes in nutrients dominance and, as a consequence, the possibility of more often and/or longer cyanobacterial abundance if other factors such as availability of nutrients are fulfilled. Climate warming and drying in the Carpathians show a north-to-south trend with sub-regions with remarkably high climate exposure (hot spots) located mainly in the lowland to foothill areas. An increase in the mean annual air temperature of 3.2–3.8°C by the end of the century in the Carpathians, and in some locations up to 5.1°C is predicted (Hlásny et al. 2016). The warming magnitude of the Polish Carpathians region is seasonally and elevation dependent. In the foothills more intense temperature increase occur in summer, whereas the winters have warmed more at the summits (Wypych et al. 2018). It seems that predicted future increase in the air temperature may potentially result in an increase in water temperatures of the Raba River, especially during long periods without rainfall (HD years).

The Raba River water was well oxygenated and pH was from neutral to alkaline, like other Carpathian river waters in Poland (Szalińska and Dominik 2006, Szarek-Gwiazda et al. 2018). Higher pH values and DO contents in waters are usually associated with primary production processes taking place in rivers (Mazurkiewicz-Boroń 2002, Wetzel 2001). In HA and HW years an increase in the flow disturbed the primary production processes, which resulted in a decrease in pH values and DO contents in water (negative correlations). It is known that storm water is usually colder, has a lower pH value and DO content and carries greater loads of suspended matter leached from the catchment (Nilsson and Renöfält 2008).

The flow determined the concentrations of mineral salts (expressed as conductivity) (GLM, high value ∑ AIC *w*) in the Raba River water in all hydrological years. The dominant sources of major ions in the Carpathian river waters are sewage from small towns and nearby villages located in the catchment area as well as groundwater inflow (Szarek-Gwiazda 2013, Szarek-Gwiazda et al. 2018). Therefore, the highest conductivity values occurred in water at low flows, and lower ones at higher flows when wastewaters were diluted by spring thaw and long–lasting summer rain. The low conductivity value of water during a flood event in Dobczyce Reservoir (Szarek-Gwiazda et al. 2009) or Lake Dalrymple in Australia (Faithful and Griffiths 2000) confirmed this phenomenon.

The flow governed also NO_3^- and P-tot concentrations in the Raba River water (GLM, positive correlation) in all hydrological years. It caused significant differences in NO_3^- concentration in water among HD, HA and HW years and a significantly higher P-tot concentration in HA and HW years than in HD years (median 3.8 times higher in HW than HD years). Fertilization and soil erosion are recognised as main nitrate source, while municipal sewage as main P-tot and NH_4^+ source in Carpathian river waters in Poland (Mazurkiewicz-Boroń 2002, Szarek-Gwiazda 2013) and in rivers in rural areas where diffuse sources of nitrate dominate (Bouraoui and Grizzetti 2011). Therefore, the highest nitrate concentration occurred in the Raba River water in HW years when soil erosion in the catchment was the strongest. A high portion of agricultural land (presently ~ 43%, Wilk-Woźniak et al. 2021) in the river catchment area favoured this process. Bouraoui and Grizzetti (2011) suggested that nitrate concentrations in rivers contaminated by diffuse sources should be lower in dryer years and higher in wet years. Our studies confirmed their suggestions. We found that the diffuse sources prevailed over the point sources of pollution with P-tot of the river water in HA and HW years when heavy rainfall events induced intensive soil erosion and leaching of P from agricultural areas. An increase in the NO_3^- and P-tot concentrations in the water of Dobczyce Reservoir during the flood event (Szarek-Gwiazda et al. 2009) confirms the phenomena described above. The point source of emission was recognized as the main pollution source of P for many rivers discharging into the European seas (Bouraoui and Grizzetti 2011). In EU countries, where the point–source P inputs were markedly reduced by wastewater treatment, the agricultural ones constitute a higher proportion ~ 50% (range 25–75%) of the total annual P loads input/charge to waters (EEA 2005, Withers and Haygarth 2007). We found also a greater importance of diffuse contamination

Table 4. The Spearman correlation coefficients between the flow and physicochemical parameters of the Raba River water above and below the dam in the hydrologically dry, average and wet years (significant at p<0.05).

Parameter	River above the dam						River below the dam					
	Hydrological years											
	dry		average		wet		dry		average		wet	
	DF	MF	DF	MF	DF	MF	DF	MF	DF	MF	DF	MF
Mean monhly flow	0.82	1.00	0.68	1.00	0.60	1.00	0.94	1.00	0.80	1.00	0.70	–
Temperature	–	–	-0.28	-0.23	–	–	–		-0.30	-0.29	–	–
pH	–	–	-0.31	–	-0.57	-0.38	–	–	–	–	–	–
DO	–	–	-0.28	–	-0.47	–	–	–	0.32	0.27	–	–
Oxyg. sat.	–	–	-0.47	–	-0.48	–	–	0.33	0.27	0.27	–	–
Cond.	-0.56	-0.43	-0.72	-0.46	-0.61	-0.32	–	–	-0.34	-0.23	-0.32	–
NO_3^-	0.76	0.62	0.62	0.45	0.53	–	0.62	0.65	0.37	0.37	–	–
NH_4^+	–	–	0.44	–	–	–	–	–	–	–	–	–
P-tot	–	0.47	0.30	–	–	–	–	–	–	–	–	–
BOD5	–	–	–	–	–	–	–	–	–	–	–	–

DF – flow on the sampling day, MF – mean monthly flow in NH_4^+ concentration in water in HA (positive correlation with the flow) and HW years (median ~ 6 times higher than in HD years). Higher load (5.3 times) of NH_4^+ in the Raba River water in hydrologically wet (I–X.2005) as compared to dry (V–XII 2003) year (Pawełek and Spytek 2006) confirmed our results. The long-term predictions of the climate change (temperature and precipitation) show the future substantial increase in the total sediment production in the Wolnica River, a direct tributary for Dobczyce Reservoir, dependent on land use types and season (Szalińska et al. 2021). Therefore, it can be assumed that climate change may also influence the future loads of suspended solids and nutrients delivered from diffuse sources to the Raba River.

The organic matter contents (expressed as BOD5) in the waters of Carpathian rivers in Poland are not very high (Mazurkiewicz-Boroń 2002) which our study confirms. In HD years positive correlations between BOD5 values and DO content indicated its association with the primary production processes in the Raba River. In turn, in HW years its higher content in water was associated with the river flow indicating its higher leaching from the catchment that is a known phenomenon (Nilsson and Renöfält 2008). However, it was not reflected in differences in the BOD5 values (like pH values and DO content) between the studied hydrological years.

Differences in water quality above and below the reservoir

Our results indicate a significant effect of the dam reservoir on the values of most physicochemical parameters (temperature, pH, DO content, oxygen saturation, conductivity, nutrients NO_3^-, NH_4^+) in the studied mountain river, however, the intensity of this phenomenon is related to the climate and river hydrology. The best models (GLM) describing the mean river flow in the river below the dam (like in the river above the dam) included temperature, conductivity, NO_3^-, P-tot, DO and additionally pH.

We found a significant decrease in temperature, pH, DO contents and oxygen saturation in the Raba River water from upstream to downstream of the dam (for a period of April–November), that was also usually found in other river – reservoir – river systems, which use bottom release of water from the dam (Kasza 2009, Soja and Wiejaczka 2014, Kędra and Wiejaczka 2018), although changes in water pH were much smaller compared to temperature (Soja and Wiejaczka 2014). A decrease in the pH values, DO contents and oxygen saturation in water was associated with their low values (DO even below 4 mg dm^{-3}, oxygen saturation even below 20%) in the reservoir hypolimnion during summer stratification due to the processes of organic matter decomposition taking place in the sediment (Szarek-Gwiazda 2013). The highest decrease in the parameter values in water occurred in HD years, when the reservoir stratification was the least disturbed by the higher river flow, and the lowest one in HW years when thermal stratification was strongly disturbed (temperature 3.0°C and lack of changes, pH 0.5 and 0.3, DO contents 1.3 and 0.3 mg dm^{-3}, oxygen saturation 16.6 and 8.5% in HD and HW years, respectively). As it was seen in 2007, the stratification in Dobczyce Reservoir may be completely disrupted during flood events (water was exchanged within a few days) resulting in pH equalization in the water column and the improvement oxygenation of the hypolimnetic water (Szarek-Gwiazda et al. 2009). A similar phenomenon was also found in other dam reservoirs (Geraldes and Boavida 2005). The length of the river in which the temperature change caused by damming is revealed can reach from 20 to 100 km in Carpathian rivers (Kędra and Wiejaczka 2018). Unlike the temperature, the oxygen conditions improve usually several meters below the dam (Berkamp et al. 2000).

Dobczyce Reservoir caused a significant decrease in the conductivity values in the downstream water in all hydrological years. Such a decrease was usually related to storing waters with low conductivity originating from spring thaws and summer risings in reservoirs and then gradual releasing of water from the reservoir during the year (Soja and Wiejaczka 2014) and was found in other river waters below the dams elsewhere (Soja and Wiejaczka 2014, Wiatkowski and Wiatkowska 2019).

We found an increase in the NO_3^- concentrations in the Raba River water from upstream to downstream of the dam in HD and HA years like in the waters of other Carpathians rivers below the reservoirs in summer season (Kijowska--Strugała et al. 2016). Such phenomenon is explained by an increase in the intensity of nitrification process taking place in the reservoir (Woyciechowska and Dojlido 1982). A lack of such a phenomenon in the Raba River water in HW years was associated with more dynamic water movement through the reservoir. The impact of the reservoir on ion NH_4^+ concentration in the river water was more complex in hydrologically varied years. The enrichment of water with NH_4^+ ions in HD years was mainly associated with the organic matter decomposition in the reservoir bottom resulting in its increase in the near–bottom water (Szarek-Gwiazda 2013). A decrease in NH_4^+ concentration in water below the dam in HW years, when the Raba River above the dam transported NH_4^+ ions in high concentrations (median ~ 6 times higher as compared to HD years) shows its deposition in the reservoir bottom. Our research showed no effect of the reservoir on P-tot concentration and BOD5 values in the river below the dam. The reservoirs are usually considered a good phosphorus trap (Maavara et al. 2015) due to its precipitation or uptake by organisms (Kasza 2009). The content of easily degradable organic matter usually does not change or decreases below the dam, that is associated with its accumulation or the processes of biochemical decomposition proceeded in the reservoirs (Kasza 2009).

The dominant impact of flow on the differentiation of the conductivity values and NO_3^- and P-tot concentrations between studied hydrological years in the Raba River water below the dam was well visible. Significantly higher conductivity values associated mainly with the point sources of contamination were found in HD years, while NO_3^- and P-tot concentrations associated mostly with diffuse contamination sources in HA and HW years (like in the river abow the dam). The flow was also important for the differentiation of NH_4^+ concentrations (higher in HA than in HD or/and HW years) and pH values (higher in the HW than HA years) in the river water, but not for water temperature, DO content, oxygen saturation, and BOD5 values.

Conclusions

Global warming due to increasing both long lasting droughts as well as high rainfall and more frequent flood events causes differences in annual river flow regime. We found that hydrological condition prevailing in a given year determines the temperature and the nutrient concentrations in a medium-sized mountain river in southern Poland. The river water had the highest temperature in HD years, while the higher nutrient (NO_3^-, P-tot) contents related to the diffuse contamination in HA and HD years which is important for eutrophication processes taking place in the reservoir. The water quality above the dam was dependent on flow in terms of the conductivity values as well as NO_3^- and P-tot concentrations. Such knowledge is necessary for appropriate management in the catchment basins and the protection of dam reservoirs (especially of the drinking water ones) against the eutrophication process. We found a significant impact of the mountain reservoir on the values of most physicochemical parameters (temperature, pH, DO content, oxygen saturation, conductivity, nutrients NO_3^-, NH_4^+) in the river water, however the intensity of this phenomenon was related to the climate and hydrology. The lowest impact or its lack was found in HW years when the water exchange in the reservoir was most dynamic. Our results provide further knowledge in the discussion regarding the effect of a dam reservoir on the river water quality, also in the aspect of climate change.

Acknowledgement

The study was financed by the Institute of Nature Conservation, Polish Academy of Sciences, Krakow, Poland. We sincerely thank all employees of the Institute of Freshwater Biology PAS who took part in the sampling and laboratory analyses.

References

APHA. (1992). *Standard methods for the examination of water and wastewater* (18th ed), American Public Health Association, Washington 1992

Berkamp, G., McCartney, M., Dugan, P., McNeely, J. & Acreman, M. (2000). Dams, ecosystem functions and environmental restoration thematic review II.1 prepared as an input to the World Commission on Dams, Cape Town 2000 (http: www.dams org (28.05.2021)).

Blahušiaková, A., Matoušková, M., Jenicek, M., Ledvinka, O., Kliment, Z., Podolinská, J. & Snopková, Z. (2020). Snow and climate trends and their impact on seasonal runoff and hydrological drought types in selected mountain catchments in Central Europe, *Hydrol Sci J*, 65, pp. 1–14. DOI: 10.1080/02626667.2020.1784900

Bouraoui, F. & Grizzetti, B. (2011). Long term change of nutrient concentrations of rivers discharging in European seas, *Sci Total Environ*, 409, pp. 4899–4916. DOI: 10.3390/w12030779.

Bouraï, L., Logez, M., Laplace-Treyture, Ch. & Argillier, Ch. (2020). How do eutrophication and temperature interact to shape the community structures of phytoplankton and fish in lakes?, *Water,* 12*,* 3, pp. 779. DOI: 10.3390/w12030779

Bowes, M.J., Jarvie, H.P., Halliday, S.J., Skeffington, R.A., Wade, A.J., Lowenthal, M., Gozzard, E., Newman, J.R. & Palmer-Felgate, E.J. (2015). Characterising phosphorus and nitrate inputs to a rural river using high frequency concentration-flow relationships, *Sci Total Environ*, 511, pp. 608–620. DOI: 10.1016/j.scitotenv.2014.12.086

Burnham, K.P. & Anderson, D.R. (2004). Multimodel inference. Understanding AIC and BIC in model selection, *Sociol Method Res*, 33, pp. 261–304. DOI: 10.1177/0049124104268644

EEA. (2005). *Source apportionment of nitrogen and phosphorus inputsinto the aquatic environment*. EEA Report No. 7⁄2005. European Environment Agency, Copenhagen 2005.

Faithful, J.W. & Griffiths, D.J. (2000). Turbid flow through a tropical reservoir (Lake Dalrymple, Queensland, Australia): Responses to a summer storm event, *Lakes Reserv Res Manag*, 5, pp. 231–247.

Freckleton, R.P. (2011). Dealing with collinearity in behavioural and ecological data: model averaging and the problems of measurement error, *Behav Ecol Sociobiol*, 65, pp. 91–101. DOI: 10.1007/s00265-010-1045-6

Genkai-Kato, M. & Carpenter, S.R. (2005). Eutrophication due to phosphorus recycling in relation to lake morphometry, temperature, and macrophytes, *Ecology*, 86, 1, pp. 210–219, DOI: 10.1890/03-0545.

Geraldes, A.M. & Boavida, M.-J. (2005). Seasonal water level fluctuations: Implications for reservoir limnology and management, *Lakes Reserv Res Manag*, 10, pp. 59–69, DOI: 10.1111/j.1440-1770.2005.00257.x.

Hlásny, T., Trombik, J., Dobor, L., Barcza Z. & Barka I. (2016). Future climate of the Carpathians: climate change hot-spots and implications for ecosystems, *Reg Environ Change* 16, pp. 1495–1506. DOI: 10.1007/s10113-015-0890-2

Kasza, H. (2009). [*Dam reservoirs. Importance – eutrophication – protection*], Wydawnictwa Akademii Techniczno-Humanistycznej, Bielsko-Biała 2009. (in Polish)

Kędra, M. & Wiejaczka, Ł. (2018). Climatic and dam-induced impacts on river water temperature: Assessment and management implications, *Sci Total Environ*, 626, pp. 1474–1483. DOI: 10.1016/j.scitotenv.2017.10.044

Kijowska-Strugała, M., Wiejaczka, Ł. & Kozłowski, R. (2016). Influence of reservoirs on the concentration of nutrients in the water of mountain rivers, *Ecol Chem Eng S*, 23, 3, pp. 413–424, DOI: 10.1515/eces-2016-0029.

Mazurkiewicz-Boroń, G. 2002. Factors of eutrophication processes in sub-mountain dam reservoirs, *Supplementa ad Acta Hydrobiol*, 2, pp. 1–68. (in Polish with English summary).

Maavara, T., Parsons, C.T., Ridenour, C., Stojanovic, S., Dürr, H.H., Powley, H.R. & Van, C.P. (2015). Global phosphorus retention by river damming, *P Natl Acad Sci USA*, 112, pp. 15603–15608. DOI: 10.1073/pnas.1511797112

Mazierski, J. & Kostecki, M. 2021. Impact of the heated water discharge on the water quality in a shallow lowland dam reservoir. *Arch Environ Prot*, 47, 2, pp. 29–46, 10.24425/aep.2021.137276

Nilsson, C. & Renöfält, B.M. (2008). Linking flow regime and water quality in rivers: A challenge to adaptive catchment management, *Ecol Soc*, 13, 2, 18. (http://www.ecologyandsociety.org/vol13/iss2/art18/(28.05.2021))

Pawełek, J. & Spytek, M. (2006). Biogenic loads carried by the Raba River into the Dobczyce Reservoir in 2002–2005, *Infrastruktura i Ekologia Terenów Wiejskich*, 3, pp. 107–116. (in Polish with English summary)

Punzet, J. (1969). Hydrological characteristics of the river Raba, *Acta Hydrobiol,* 11, pp. 423–477. (in Polish with English summary)

Schneider, C., Laizé, C.L.R., Acreman, M. & Flörke, M. (2013). How will climate change modify river flow regimes in Europe?, *Hydrol Earth Sys Sci*, 17, 1, pp. 325–339. DOI: 10.5194/hess-17-325-2013

Soja, R. & Wiejaczka, Ł. (2014). The impact of a reservoir on the physicochemical properties of water in a mountain river, *Water Environ J*, 28, pp. 473–482. DOI: 10.1111/wej.12059

Szalińska, E. & Dominik, J. (2006). Water quality changes in the Upper Dunajec Watershed, Southern Poland, *Pol J Environ Stud*, 15, pp. 327–224.

StatSoft 2014. STATISTICA (data analysis software system), v. 12. http://www.statsoft.pl Accessed 7 Jan 2016.

Szalińska, E., Zemełka, G., Kryłów M., Orlińska-Woźniak P., Jakusik E. & Wilk, P. (2021). Climate change impacts on contaminant loads delivered with sediment yields from different land use types in a Carpathian basin. *Sci Total Environ*, 755, pp. 142898. DOI: 10.1016/j.scitotenv.2020.142898

Szarek-Gwiazda, E., Mazurkiewicz-Boroń, G., Gwiazda, R. & Urban, J. (2018). Chemical variability of water and sediment over time and along a mountain river subjected to natural and human impact, *Knowl Manag Aquat Ecosyst*, 419, 5. DOI: 10.1051/kmae/2017056

Szarek-Gwiazda, E., Mazurkiewicz-Boroń, G. & Wilk-Woźniak, E. (2009). Changes of physicochemical parameters and phytoplankton in water of a submountain dam reservoir – effect of late summer stormflow, *Arch Environ Prot*, 35, 4, pp. 79–91.

Szarek-Gwiazda, E. (2013). Factors influencing the concentrations of heavy metals in the Raba River and selected Carpathian dam reservoirs, *Studia Naturae,* 60, pp. 1–146. (in Polish with English summary)

Wang, F., Maberly, S.C., Wang, B. & Liang, X. (2018). Effects of dams on riverine biogeochemical cycling and ecology, *Inland Waters*, 8, 2, pp. 130–140. DOI: 10.1016/j.chemgeo.2018.04.006

Wetzel, R.G. (2001). *Limnology, lake and reservoir ecosystem* (3rd Edition), Academic Press, Elsevier Science, San Diego, San Francisco, New York, Boston, London, Sydney, Tokyo, 2001.

Wiatkowski, M. & Wiatkowska, B. (2019). Changes in the flow and quality of water in the dam reservoir of the Mała Panew catchment (South Poland) characterized by multidimensional data analysis, *Arch Environ Prot*, 45, 1, pp. 26–41, DOI: 10.24425/aep.2019.126339.

Wilk-Woźniak, E. (2009). [Population changes in the communities of planktonic algae and their life strategies under the conditions of artificially altered aquatic ecosystems]. *Studia Nature*, 55, pp. 1–132. (in Polish with English summary)

Wilk-Woźniak, E., Krztoń, W. & Górnik, M. (2021). Synergistic impact of socio-economic and climatic changes on the ecosystem of a deep dam reservoir: case study of the Dobczyce dam reservoir based on a 30-year monitoring study, *Sci Total Environ*, 756 (144055). DOI: 10.1016/j.scitotenv.2020.144055

Woyciechowska, J. & Dojlido, J. (1982). Changes in the quality surface waters under the influence of the hydrotechnical constructions, *Gosp Wod*, 5, pp. 47–50. (in Polish)

Yamamoto, Y. & Nakahara, H. (2005). The formation and degradation of cyanobacterium *Aphanizomenon flos-aquae* blooms: the importance of pH, water temperature, and day length, *Limnology* 6, 1, pp. 1–6. DOI: 10.1007/s10201-004-0138-1.

Winton, R.S., Calamita, E. & Wehrli, B. (2019). Reviews and syntheses: Dams, water quality and tropical reservoir stratification, *Biogeosciences*, 16, pp. 1657–1671. DOI: 10.5194/bg-16-1657-2019

Withers, P.J.A. & Haygarth, P.M. (2007). Agriculture, phosphorus and eutrophication: a European perspective. *Soil Use Manage*, 23(Suppl. 1), pp. 1–4. DOI: 10.1111/j.1475-2743.2007.00116.x

Wypych, A., Ustrnul, Z. & Schmatz, D.R. (2018). Long-term variability of air temperature and precipitation conditions in the Polish Carpathians. *J Mt Sci,* 15, pp. 237–253. DOI: 10.1007/s11629-017-4374-3

Wpływ przepływu i piętrzenia na jakość wody górskiej rzeki Raby (południowa Polska) – badania wieloletnie

Streszczenie: Zmiany klimatu, przejawiające się długotrwałymi okresami suszy lub obfitych opadów, mogą znacząco zmienić roczny reżim przepływów. Stawiamy hipotezę, że przepływ dominujący w danym roku determinuje chemizm wody rzeki górskiej. Celem pracy było określenie (1) różnic w chemizmie wody górskiej rzeki pomiędzy latami hydrologicznie suchymi (HD), przeciętnymi (HA) i mokrymi (HW), (2) wpływu zbiornika zaporowego na chemię wody odpływającej rzeki w różnych latach hydrologicznych, (3) parametrów fizyczno-chemicznych związanych ze średnim miesięcznym przepływem wody w latach HD, HA i HW. Badania prowadzono w karpackiej rzece Rabie powyżej i poniżej Zbiornika Dobczyckiego w południowej Polsce. W oparciu o średni roczny przepływ rzeki z wielolecia 1991–2017 wyróżniono lata HD, HA i HW. Przeanalizowano zmiany parametrów fizyczno-chemicznych wody (temperatura, przewodność elektrolityczna, pH, tlen rozpuszczony, nasycenie tlenem, BZT5, biogeny: NO_3^-, NH_4^+, P-tot) pobieranych co miesiąc w okresie kwiecień–listopad. Stwierdziliśmy istotne różnice w chemizmie wody rzeki między badanymi latami hydrologicznymi. W latach HD wody powyżej zbiornika miały istotnie wyższą temperaturę i wartości przewodności elektrolitycznej, natomiast niższe wartości biogenów NO_3^- i P-tot (zanieczyszczenie obszarowe) w porównaniu do lat HA i/lub HW. Zbiornik w różny sposób kształtował skład chemiczny wody rzeki poniżej zapory w latach HD, HA i HW. Najlepsze modele GLM dla średnich miesięcznych przepływów obejmowały 3–5 czynników, wśród których zawsze występowały przewodność elektrolityczna i stężenia NO_3^-. Uzyskane wyniki mają istotne znaczenie dla właściwego gospodarowania w zlewniach rzek górskich i ochrony zbiorników zaporowych przed procesami eutrofizacji.