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Author: Roman Celiński, Marek Ruman

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Roman CIEŚLIŃSKI[1*] and Marek RUMAN[2]

TEMPORAL VARIABILITY IN CONCENTRATION OF SELECTED PHYSICAL AND CHEMICAL PARAMETERS WITH RESPECT TO DISCHARGE IN A RIVER IN THE PUCK BAY BASIN

CZASOWA ZMIENNOŚĆ STĘŻEŃ WYBRANYCH WSKAŹNIKÓW FIZYCZNO-CHEMICZNYCH NA TLE NATĘŻENIA PRZEPŁYWU WÓD JEDNEJ Z RZEKI ZLEWISKA ZATOKI PUCKIEJ

Abstract: The goal of this work is to determine the concentration variability and the values of selected physical and chemical parameters, including the discharge values for the Plutnica River, as well as the causes for changes in these values. When it comes to physical and chemical water quality, the downstream waters of the Plutnica are freshwaters with elevated chloride concentrations. This is due to the fact that the Baltic Sea acts on shallow groundwater along this part of the coast as well as to periodically occurring saltwater intrusions into inland surface waters. The concentrations of the remaining common ions were fairly stable during the course of the year and their annual variability levels were similar.

Keywords: water quality, discharge, temporal variability, physical and chemical parameters

The degradation of man's natural environment is one of the most important, if not the most important, problem of the modern world. Worsening water quality leads to limiting of its use, and it becomes a problem in many areas [1]. It is especially noticeable on a local basis. Although globally, the processes and natural phenomena adversely affecting water quality are still dominant with respect to anthropogenic processes and phenomena [2], locally it is just the opposite. The degradation of water quality, and related to it water deficits, including river discharge magnitude decreases, are always noticeable on the local scale first. Natural characteristics of river flow and initial quality of water are more and more often just an abstraction. At present, human beings significantly influence the natural environment causing the initiation, acceleration or slowdown of certain physical, geographic, and biochemical processes [3]. The Plutnica River is an example of a river on

[1] Department of Hydrology, University of Gdansk, ul. R. Bażyńskiego 4, 80-952 Gdańsk, Poland, tel. +48 58 523 65 30
[2] Department of Physical Geography, Faculty of Earth Sciences, University of Silesia, ul. Będzińska 60, 41-200 Sosnowiec, Poland, tel. +48 32 368 94 37, email: marek.ruman@us.edu.pl
[*] Corresponding author: georc@univ.gda.pl

the Polish coast of the southern Baltic Sea, where many coexisting factors are observed, both natural and anthropogenic (Fig. 1).

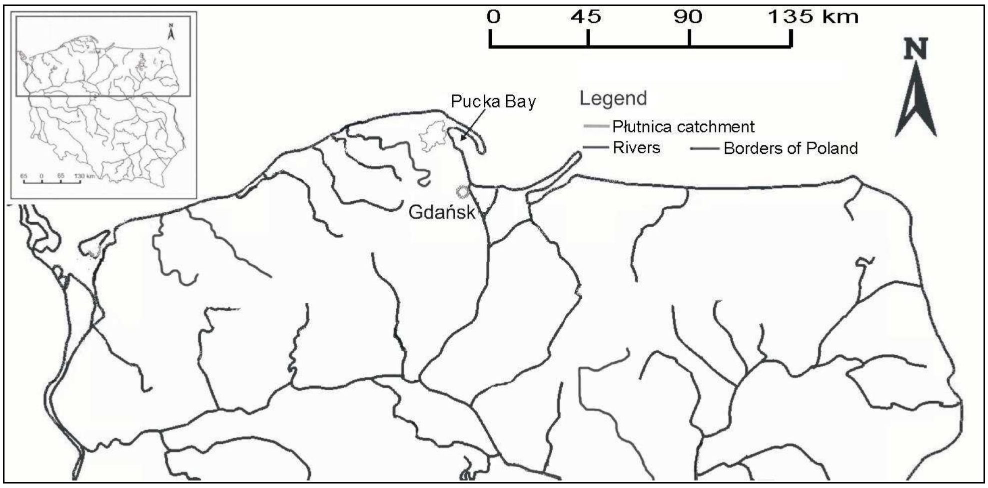

Fig. 1. Location of the research area in northern Poland

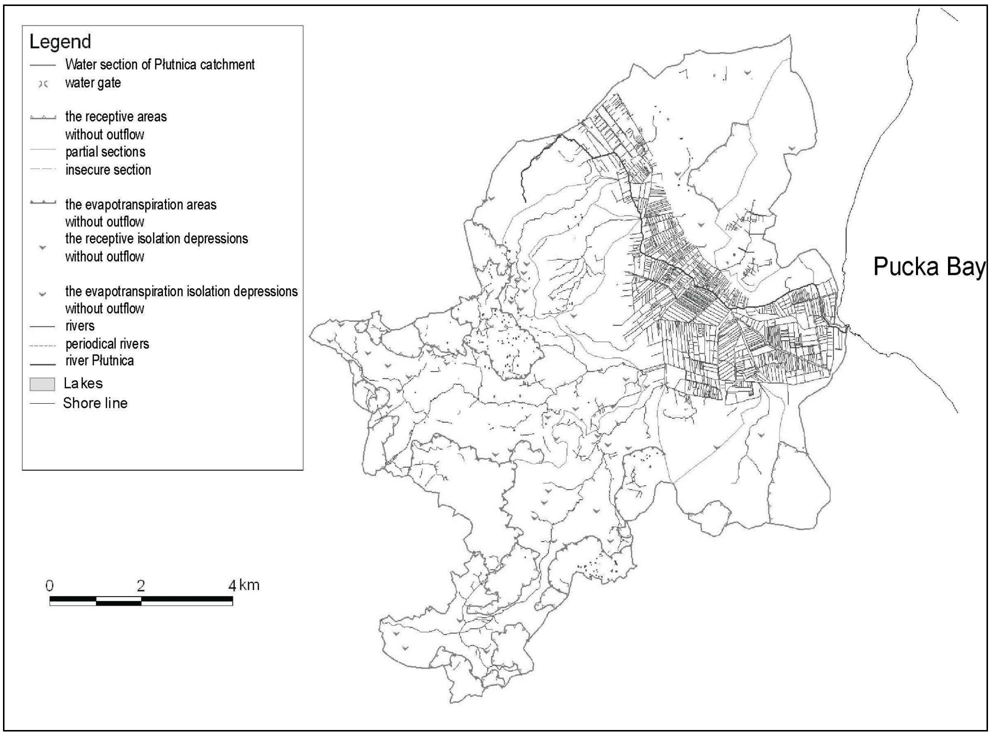

Fig. 2. Hydrographic map of the Plutnica River basin

Today, it is a hydrographic entity, whose surrounding environment has been modified by man to a lesser or greater degree. One should not forget that, once naturally formed, the environment still plays a fundamental role in the shaping of water relationships in this basin. The Plutnica River, in its downstream section, has been entirely reengineered by man, creating a polder system with forced water circulation (Fig. 2). Its headwaters and middle section have been significantly reengineered but water circulation remains gravity-based. The most natural conditions exist in the upland part of the basin, where the hydrological conditions are controlled primarily by natural processes.

The goal of this work is to determine the concentration variability and the values of selected physical and chemical parameters, the discharge values for the Plutnica River, as well as the causes for changes in these values.

Hydrological characteristics of the Plutnica River basin

The Plutnica is a small coastal river flowing across a lowland. It empties into the Bay of Puck (Fig. 1). The river originates in the Puck Hills in the vicinity of the town of Starzynski Dwor. It is 11.2 km in length and the area of its basin is 85.2 km^2. The Plutnica flows in a proglacial valley and drains the southern part of the Swarzew Hills as well as the northeastern part of the Puck Hills. The river drains the area's autochthonous waters. The water level in the river influences the drainage of the basin. In the downstream section, the drainage of the basin depends on the water level in Puck Bay. With a heightened water level in the Bay, the outflow comes to a halt, and during storms, seawater intrusions into the river channel do occur. In its downstream section, the river flows through wetlands, called Puck Swamps. They cover an area of 1,600 hectares. A polder was created in the swamp area and is maintained by a pumping station that serves irrigation and drainage purposes. The station is located on the Pump Canal at its outlet to the Plutnica River. In this area, there are several operational locks and a weir that are used to control the drainage and irrigation system. There are no lakes in this basin, if a lake is defined as a reservoir whose area is greater than 1 hectare. In the Puck Upland, it is typical for numerous ponds and kettle lakes to be found (over 200), quite often functioning as fisheries. Several reservoirs were built in the river valley in the 1960s. Since 1992, seven new small reservoirs have been built on streams flowing down from the Puck Hills. The reservoirs' area totals 0.14 km^2, which produces a low lake area to overall land area ratio, which equals 0.0016%.

Methods

Fieldwork was performed during the 2006 hydrological year. Water samples were collected monthly in the Plutnica River at a point located 400 m upstream from its mouth. The point was chosen because it lies downstream from all the tributaries and the influence of Puck Bay waters on river water quality can be detected here. The water samples were tested at the Hydrochemical Laboratory of the University of Gdansk Department of Hydrology in order to determine the basic ion content (chloride, sodium, potassium, calcium, magnesium, sulfate, bicarbonate, as well as BOD_5 and COD-Cr) in the waters of the Plutnica River. The methods used to perform applicable measurements are described in Table 1. The fieldwork for this project involved performing the following measurements:

- dissolved oxygen (DO) via the electrometric method using an oxygen electrode CellOx 325 made by WTW,

- water pH via the electrometric method using an SenTix 41-3 gel electrode made by WTW,
- electrical conductivity and water temperature via the TetraCon 325 conductometric probe made by WTW.

Table 1

Methods used to determine basic ion content of water, BOD_5 and COD

Parameter Being Determined	**Method**	**Standard Procedure Equivalent**
Chloride	Titration	PN-ISO 9297:1994
Sulfate	Colorimetry	None
Calcium	Titration	PN-ISO 6058:1999
Magnesium	Titration	PN-ISO 6059:1999
Sodium	Flame photometry	PN-ISO 9964-3/AK:1997
Potassium	Flame photometry	PN-ISO 9964-3/AK:1997
Bicarbonate	Titration	None
BOD_5	Electrochemistry	PN-EN 1899-2:2002
COD-Cr	Colorimetry	ISO 6060-1989

Concurrently to the collection of water samples, measurements of the discharge rate were conducted using a StreamPro Acoustic Doppler Current Profiler (ADCP). Measurements using this device are done as follows: ADCP emits acoustic waves and receives them after they are reflected off particles suspended in the water and in the river bed. The time needed for a wave to reflect and come back determines the distance from the suspended particle, while the frequency change of the reflected waves determines the direction of movement. Waves reflected by the river bed carry information about its shape. Waves reflected off suspended particles are used to measure discharge. The device does not measure discharge in the subsurface layer or close to the river bed; instead, it takes an average of it based on calculated flow velocity in adjacent layers. Today, this is the most accurate of discharge measurement methods.

The discharge irregularity coefficient **α** was also used in this work, where α is the ratio of maximum discharge to minimum discharge [4]:

$$\alpha = \frac{Q_{max}}{Q_{min}}$$

Based on the instantaneous discharge values measured during fieldwork, average monthly discharge values were calculated as follows: a graph was drawn on technical paper, where 1 mm corresponds to 1 day in a year. Then, the end of each month was marked with a vertical line and points were marked that represented the instantaneous discharge value for the particular day. The next step was to connect the points and read off the values for discharge at the points of intersection of the curve and the vertical lines marking the end of each month. Finally, an average of three numbers was taken: the discharge value read at the beginning of a particular month, the instantaneous discharge value, and the discharge value at the end of a particular month. In this manner, the monthly average discharge values were obtained.

Results and discussion

The direct cause that influences discharge variability in rivers is weather conditions, especially the amount of rainfall and its timing. These factors are further affected by the geographic characteristics of the natural environment of a basin [5]. Highly variable discharge is typical of basins with poorly permeable surfaces, a significant slope of land, and a scarce amount of forest. In basins with highly permeable surfaces, a small slope of land, large forested areas, and a significant presence of lakes, the rate of discharge is stable throughout the year [6].

The basin of the Plutnica River is dominated by low permeability surfaces (58%) and variable permeability surfaces (17%). Moreover, the lake to overall land ratio is low and equals 0.0016%, and the slope of land is rather steep. These factors lead to an irregular regime in the basin, as evidenced by a high coefficient of discharge irregularity ($\boldsymbol{\alpha} = 11.4$).

Table 2

Instantaneous discharge during the 2006 hydrological year

Date	Instantaneous discharge [$m^3 \cdot s^{-1}$]
30.11.05	0.617
15.12.05	0.993
30.01.06	0.128
23.02.06	0.56
30.03.06	1.1
13.04.06	1.12
27.04.06	1.08
17.05.06	0.197
22.06.06	0.782
20.07.06	0.098
30.08.06	0.959
27.09.06	0.865
25.10.06	1.1

Table 3

Average specific runoff during the 2006 hydrological year

Months	Average specific runoff [$dm^3 \cdot s^{-1} \cdot km^{-2}$]
XI	7.27
XII	9.08
I	4.03
II	5.55
III	11.05
IV	12.27
V	6.05
VI	6.94
VII	3.75
VIII	8.86
IX	10.75
X	11.88
Average	8.12

The instantaneous discharge rate (Table 2) for the Plutnica River during the 2006 hydrological year ranged from 0.098 $m^3 \cdot s^{-1}$ to 1.12 $m^3 \cdot s^{-1}$, and its specific runoff (Table 3) ranged from 1.165 $dm^3 \cdot s^{-1} \cdot km^{-2}$ to 13.317 $dm^3 \cdot s^{-1} \cdot km^{-2}$. The average discharge in the 2006 hydrological year was 0.68 $m^3\ s^{-1}$. Compared with 1988, it was lower by 0.23 $m^3 \cdot s^{-1}$, and compared with the year 2000, it was higher by 0.21 $m^3 \cdot s^{-1}$. The average specific runoff for the Plutnica River was 8.12 $dm^3 \cdot s^{-1} \cdot km^{-2}$. This value is close to the average specific runoff values for rivers such as the Reda (a.s.r. = 9.2 $dm^3 \cdot s^{-1} \cdot km^{-2}$) and the Radunia, whose average specific runoff is 7.9 $dm^3 \cdot s^{-1} \cdot km^{-2}$ [7].

Maximum discharge values, over 1.0 $m^3 \cdot s^{-1}$, occurred in mid-April, in March, and in October (Table 2). The lowest discharge rates were recorded in the Plutnica River in July and January (Fig. 3).

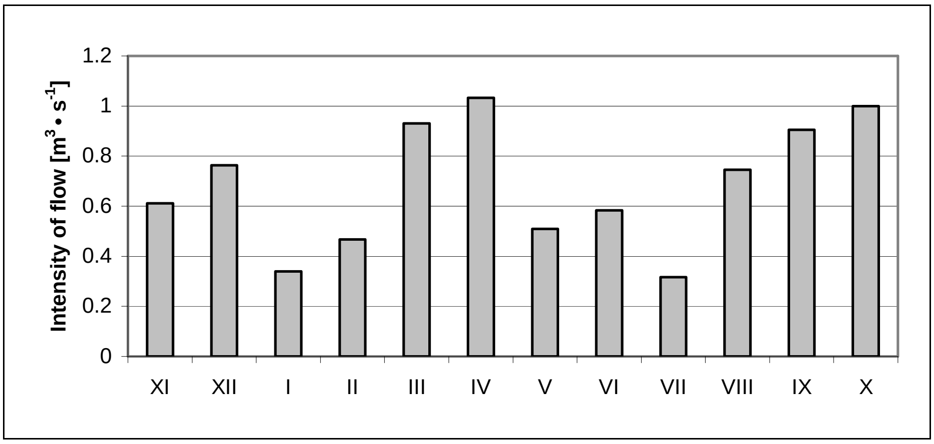

Fig. 3. Average discharge rate for the Plutnica River during the 2006 hydrological year

Comparing the winter half of the year (Nov.-Apr.) with the summer half of the year (May-Oct.), it can be concluded that the average discharge rate in the winter half of the year was greater and equaled 0.7 $m^3 \cdot s^{-1}$, and in the summer half of the year, it was slightly lower and equaled 0.68 $m^3 \cdot s^{-1}$.

The monthly discharge coefficient, which is a ratio of the average monthly discharge to the average yearly discharge, and is expressed as a percentage, shows an existence of two flood events that took place during the 2006 hydrological year - a spring flood event and an autumn flood event (Fig. 4). In the case of the Plutnica River, one can infer the existence of a spring and an autumn regime.

It should be mentioned, that the discharge rate in the Plutnica River depends on the operation of a pumping station, which is located at the outlet of the Pump Canal to the Plutnica River. In early spring and in autumn, the downstream part of the basin is drained, therefore the discharge values are higher. In late spring and summer, when high temperatures increase evaporation and a water deficit occurs, the irrigation system is turned on, which decreases the amount of water flowing out.

In order to determine the quality of the water in question, the water's hydrochemical type has to be determined first. Water type is based on the content of the following ions:

calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{+}), bicarbonate (HCO_3^-), sulfate (SO_4^{2-}), chloride (Cl^-), and the ratios between them, expressed in the form of equivalents [8, 9].

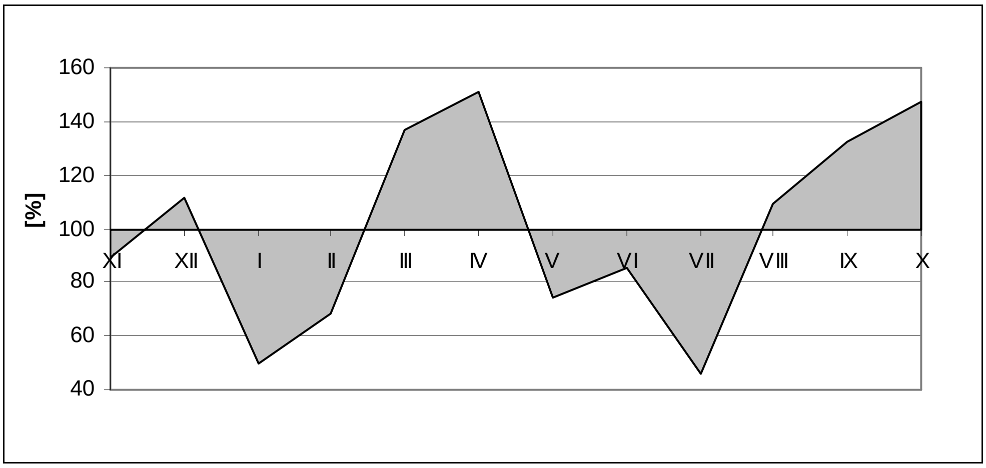

Fig. 4. Monthly discharge coefficient for the Plutnica River during the 2006 hydrological year

According to Alekin's classification system [10], water is divided into the following types: bicarbonate-, sulfate-, and chloride-type water, depending on the dominant anion. Plutnica River water is classified as bicarbonate water (Fig. 5). Groundwater belongs to this group and so does lake water and river water poor in mineral content [11]. Next, waters were divided into three groups, depending on the dominant cation: calcium, magnesium, and sodium. As shown in Figure 6, the dominant cation here is calcium (Ca^{2+}). The groups are then divided into three water types, which are determined by the ion concentration ratio. For the waters of the Plutnica River, the concentration ratio is as follows:

$$[HCO_3^-] < [Ca^{2+}] + [Mg^{2+}] < [HCO_3^-] + [SO_4^{2-}]$$

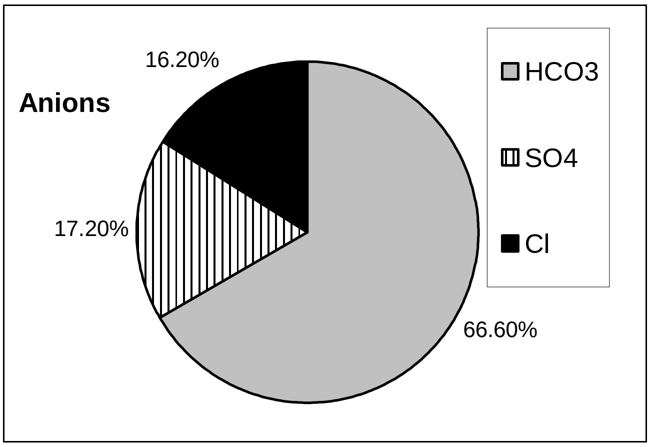

Fig. 5. Circle graph of common anions in Plutnica River waters during the 2006 hydrological year

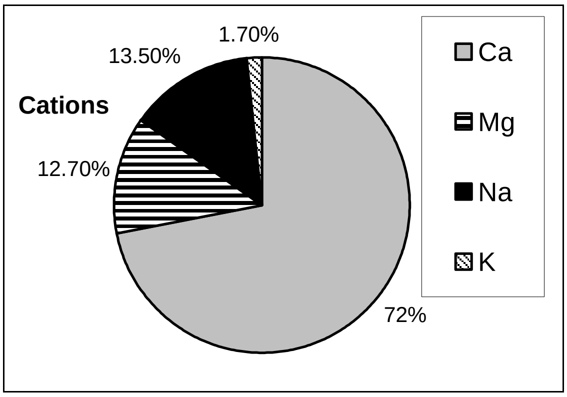

Fig. 6. Circle graph of common cations in Plutnica River waters during the 2006 hydrological year

The third ion, dominant for most of the year, is the sulfate ion (SO_4^{2-}). Only in autumn, this ion is replaced by the chloride ion (Cl^-), which may be related to storms taking place in that period of time, which in turn, cause saltwater intrusions [12]. Seasonal variability of sodium and magnesium with respect to one another may also be observed. Magnesium concentration reaches higher values in the winter and the spring, while sodium concentration does so in the summer and the autumn (Fig. 7).

Considering the results obtained for the selected chemical parameters, on a monthly basis, it can be observed that the lowest concentrations of most of the parameters occurred in March, and the highest in November (Fig. 8). Potassium reached one of its higher concentrations of the year in March only, and in November, one of its lowest. Usually, the potassium to sodium concentration ratio is about 1:4, but in this case, it was almost 1:2.

The concentrations of all the parameters considered during the research period are shown in Table 4.

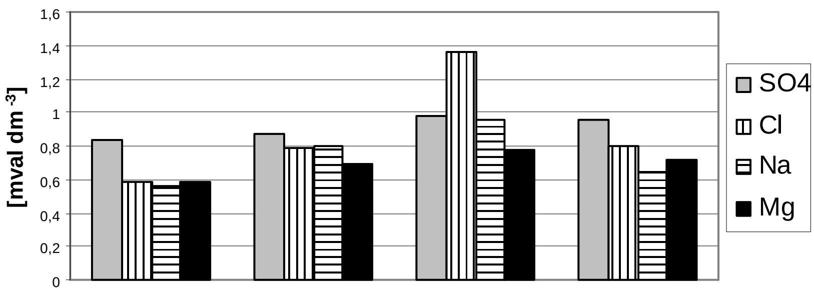

Fig. 7. Seasonal variability of sulfate, chloride, sodium, and magnesium concentrations during the 2006 hydrological year

The temperature variability of the Plutnica River water during the 2006 hydrological year corresponded to variability in air temperature. One unusual increase in water temperature was noted: from 2.5°C in November to 4.9°C in December. The average temperature of the river water was 9.9°C (Table. 4).

In the course of the year, pH ranged from 7.0 to 7.6, which is a range that falls within what is considered to be a neutral range for water (6.5÷8.5) (Table 4). Similarly, the average value of pH of the river water (7.3) was approaching neutral.

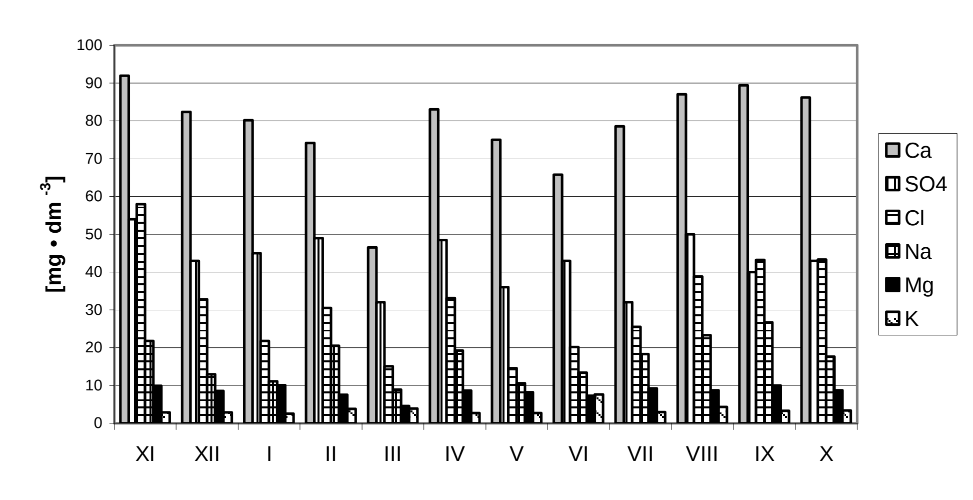

Fig. 8. Variability in the concentrations of common ions during the 2006 hydrological year

Table 4

Variability of selected physical, chemical, and biological parameters during the 2006 hydrological year

Months	Temperature [°C]	pH	Conductivity [µS · cm^{-1}]	Dissolved oxygen [$mgO_2 \cdot dm^{-3}$ / %]	BOD_5 [$mgO_2 \cdot dm^{-3}$]	COD [$mgO_2 \cdot dm^{-3}$]
XI	2.5	7.4	641.0	6.8 / 50.0	0.97	80.0
XII	4.9	7.6	478.0	9.4 / 73.5	1.82	-
I	1.0	7.2	461.0	-	-	-
II	2.6	7.4	470.0	-	-	-
III	5.5	7.4	284.0	11.1 / 88.0	3.65	34.3
VI	8.8	7.2	491.0	8.5 / 73.3	1.68	22.8
V	11.2	7.2	403.0	13.6 / 122.7	13.59	26.2
VI	18.9	7.2	405.0	3.3 / 35.6	2.72	46.9
VII	20.1	7.5	449.0	3.8 / 41.7	1.10	15.2
VIII	20.1	7.4	450.0	3.4 / 37.3	0.70	24.9
IX	11.8	7.4	547.0	3.9 / 35.7	0.98	16.4
X	11,0	7.1	484.0	3.5 / 31.9	0.37	18.8
Average	**9.9**	**7.3**	**463.6**	**6.7 / 59.5**	**2.76**	**31.7**

The conductivity of the waters of the Plutnica during the 2006 hydrological year ranged from 284 to 641 µS · cm^{-1}. In clean surface waters, conductivity is in the 50÷1000 µS · cm^{-1} range [13]. Higher values usually indicate the presence of wastewater pollution in analyzed water samples. Seawater intrusions are another potential reason for elevated values. The conductivity values calculated for the Plutnica River water indicate that it is clean.

Dissolved oxygen content in clean water usually corresponds to 100% saturation. The lower the value, the more polluted the water. Reduction of dissolved oxygen content below 40% may be dangerous to equilibrium in natural habitats [14]. Plutnica River water is characterized by unfavorable living conditions, given that the average oxygen saturation during the 2006 hydrological year was 59.5%. The cleanliness of the river's water was unsatisfactory from June until October, with dissolved oxygen content below 42%. The best oxygen saturation was detected in the spring, when dissolved oxygen content was 94.7%, on average, as well as in May, when full oxygen saturation was noted.

In the case of BOD_5, its lowest values were recorded in the autumn, when the average value was 0.8 $mgO_2 \cdot dm^{-3}$ (Fig. 9), with a minimum of 0.37 $mgO_2 \cdot dm^{-3}$ in October (Table 4). The highest values of BOD_5 were recorded in the spring (the average value of 6.3 $mgO_2 \cdot dm^{-3}$), with a maximum of 13.59 $mgO_2 \cdot dm^{-3}$ recorded in May (Table 4).

The average value of COD during the 2006 hydrological year was 31.7 $mgO_2 \cdot dm^{-3}$. In the case of COD, it is difficult to speak of seasonal variability, because low and high values occur regardless of the season. However, the highest average values of COD were recorded in the autumn (38.4 $mgO_2 \cdot dm^{-3}$); specifically, 80 $mgO_2 \cdot dm^{-3}$ was recorded in November (Table 4).

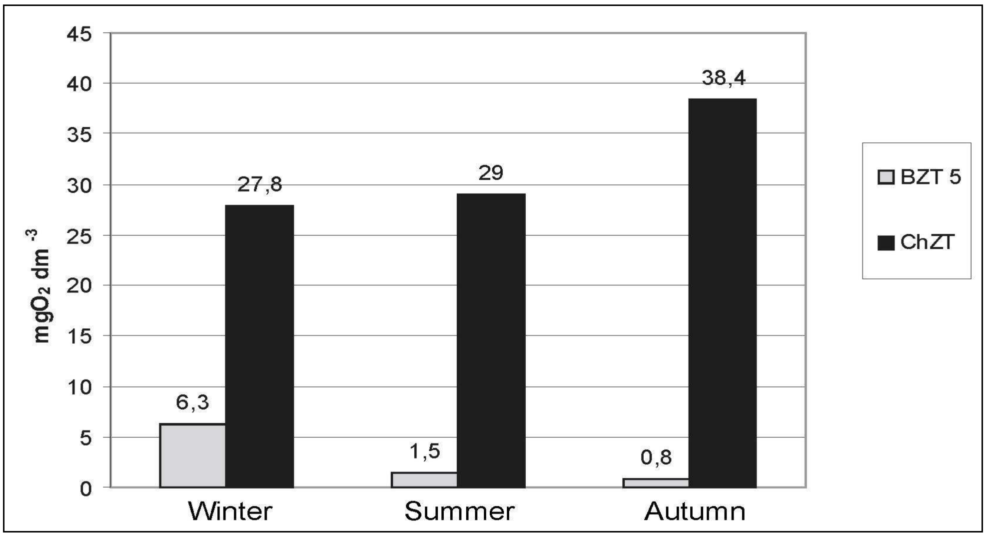

Fig. 9. Seasonal variability in BOD_5 and COD [$mgO_2 \cdot dm^{-3}$] in Plutnica River water

The average concentration of chloride in the Plutnica River was 31.5 $mgCl^- \cdot dm^{-3}$ and chloride concentration ranged from 14.5 to 58 $mgCl^- \cdot dm^{-3}$. Measured values of chloride concentration in Plutnica River water did not confirm a significant influence of Puck Bay on the water in the Plutnica River (no evidence of seawater intrusions). A chloride concentration above 100 $mgCl^- \cdot dm^{-3}$ was not observed at any time. However, there are periods of time during which values occur that exceed 30÷40 $mgCl^- \cdot dm^{-3}$ (Fig. 10). This is at least double the concentration values observed in inland waters [15].

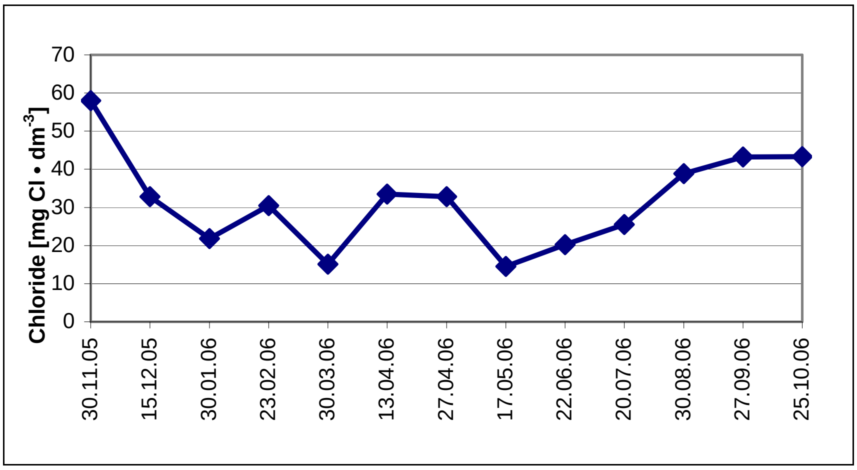

Fig. 10. Temporal variability of chloride concentration in Plutnica River water during the 2006 hydrological year

Conclusions

Human activity, concentrated primarily in the Plutnica Valley, is the reason why it is difficult to compare this river to any other river in the Pomerania coastal region. This applies not only to hydrographic or hydrological characteristics but to qualitative characteristics as well. The reengineered mouth of the Plutnica River may be compared with the mouth of the Reda River. The Reda, however, has been substantially reengineered only in its downstream stretch, while the Plutnica has been reengineered along its entire length.

When it comes to physical and chemical water quality, the downstream waters of the Plutnica are freshwaters with elevated chloride concentrations. This is due to the fact that the Baltic Sea acts on shallow groundwater along this part of the coast [16] as well as to periodically occurring saltwater intrusions into inland surface waters [12]. The concentrations of the remaining common ions were fairly stable during the course of the year and their annual variability levels were similar. For all common ions, except potassium, the lowest concentration values were noted in March, which can be linked to the spring snowmelt season. On the other hand, the highest values were detected in November, and this increase was due to storm weather conditions. An increase in the concentrations of chemical parameters commonly known as *maritime* normally takes place in November.

Water quality in the Plutnica River, as indicated by chemical parameters, is not the best. Human impact on the river's basin is significant, and the results of tests show that its water quality is bad. The cleanliness of Plutnica River water was unsatisfactory from June until October, with dissolved oxygen content below 42%. BOD_5 values for the autumn, with the minimum being in October, confirm the bad condition of the river water as far as its level of cleanliness is concerned. This is primarily due to wastewater pollution. The low COD values, determined during the entire research period, also confirm that the river's water quality is not as good as it could be.

In the 20th century, especially during its second half, the Plutnica River basin became more agricultural in nature, crop areas increased in size, and the amount of artificial fertilizers and pesticides being used increased. At present, arable land occupies 57% of the basin area. Due to the agricultural land use, primarily the use of fertilizer, a seasonal increase in potassium concentration is observed, regardless of discharge rate. This occurred in March, when potassium concentration reached one of the high values for the year, regardless of the high rate of discharge. This was due to the washing out of potassium fertilizer applied to crop fields in the autumn. The highest potassium concentration was recorded in June, which was related to fertilizer use on meadows following the first hay harvest of the year.

The monthly discharge coefficient values for the Plutnica River are different than those for other coastal rivers in Poland. For the Reda and Leba rivers, coefficient values were higher than 100% (which means that discharge was higher than average annual discharge) from November until April, but they were lower from May until October [17]. In the Lupawa River, discharge values that were higher than average annual discharge were noted from October until April. In the case of the Plutnica River, values of the monthly discharge coefficient that were higher than 100% occurred during different months of the year: in May, April, from August until October, and in December. Values lower than 100% were noted in January, February, from May until July, and in November. According to Bogdanowicz [17], coastal rivers are characterized by "negligible discharge variability and a high degree of discharge steadiness". Research on discharge rate variability during the 2006 hydrological year indicates that the above conclusion does not apply to the Plutnica River, where discharge is not steady.

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CZASOWA ZMIENNOŚĆ STĘŻEŃ WYBRANYCH WSKAŹNIKÓW FIZYCZNO-CHEMICZNYCH NA TLE NATĘŻENIA PRZEPŁYWU WÓD JEDNEJ Z RZEK ZLEWISKA ZATOKI PUCKIEJ

[1] Katedra Hydrologii, Uniwersytet Gdański
[2] Katedra Geografii Fizycznej, Zakład Hydrologii i Gospodarki Wodnej Obszarów Urbanizowanych
Uniwersytet Śląski

Abstrakt: Celem niniejszej pracy było ustalenie zmienności stężeń i wartości wybranych wskaźników fizyczno-chemicznych oraz przepływów na rzece Płutnicy, a także określenie przyczyn tych zmian. Pod względem jakości fizyczno-chemicznej wody rzeki Płutnicy w jej dolnym biegu są wodami słodkimi o podwyższonych wartościach stężeń chlorków. Wpływa na to niewątpliwie sąsiedztwo morza, które oddziałuje na płytkie wody podziemne w tej części wybrzeża, a także okresowo występujące zjawisko intruzji wód słonawych drogą powierzchniową. Stężenia pozostałych głównych jonów w ciągu roku charakteryzowały się dużą stabilnością i podobną zmiennością roczną uzyskanych wyników.

Słowa kluczowe: jakość wody, natężenie przepływu, czasowa zmienność, wskaźniki fizyczno-chemiczne