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Assessment of water quality in the Wiśniówka River considering circulation of organic matter

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Abstract

Variation of hydrochemical conditions, with special reference to adequacy of waters as fish habitats, was traced based on selected hydrochemical parameters obtained during the studies conducted from February 2013 till February 2014 year. The results were compared with earlier studies. The sources of organic pollution were identified, and the effect of biogenic substances on the biomass, as well as the self-purification capability of the river, were assessed. The total suspension exceeded the requirements for waters which are habitats of both salmonid and cyprinid fishes. Compared to the previous years, the load of organic and inorganic matter in the waters of Wiśniówka River increased; this may have resulted from external inflow, neighbourhood of the hatchery but also, to a small extent, from internal supply. The high availability of nitrogen-(N-NH_4^+; N-NO_2^-, N-NO_3^-) and phosphorus-(total phosphorus; P-PO_4^{3-}) based biogenic (substances favoured the biomass production, thus contributing to the increase in organic matter load in the river.

Keywords: Aquatic, Environment, Estuary, Fish, Pollution

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Introduction

As a result of the dynamic development of aquaculture, the demand for water of adequate quality for fish breeding increases, while on the other hand pollution originating during fish production must be treated in order to minimise the negative effect of aquaculture on the environment (Boyd, 2003; Kwei Lin and Yang, 2003; Colt, 2006).

Waters supplying hatcheries often do not meet requirements for fish breeding and keeping, since they are polluted by runoff of fertilizers from agricultural areas, as well as by communal and industrial waste. Salmonids require the highest quality water, and such water should be used to supply hatcheries; during the embryonic development of these sensitive species even small changes in water parameters may cause great losses (Liao and Mayo, 1972; Finn, 2007; Bilotta and Brazier, 2008; Sternecker *et al*., 2013).

Fish production generates water-soluble pollutants which, at high concentration, may pose a serious threat to aquatic organisms. Besides, disregarding the rules of rational fish culture increases the risk of spread of infectious and parasitic diseases (Teodorowicz, 2013).

Post-production waste from fish hatcheries includes mainly nitrogen compounds produced during fry rearing, metabolic products, hatching enzymes and egg envelopes. Periodically, it may contain chemical pollutants arising as a result of applying means of disinfection and maintenance of eggs and fry, and medicinal compounds (Cripps and Kelly, 1996; Boyd, 2003; Coloso *et al*., 2003; Guo and Li, 2003; Teodorowicz, 2013; Saraswathyet *et al*., 2015).

In 2010–2011 the waters of the Wiśniówka River were assessed as less than good (WIOŚ, 2012), and in 2012–2013 as bad (WIOŚ, 2014).

Also earlier studies in 2005-2009 showed that in the section of the Wiśniówka reaching the hatchery the values of such water quality parameters as total suspension, COD_{Mn}, COD_{Cr}, nitrate nitrogen (III), or total phosphorus were increased. For this reason, according to the Decree of the Minister of Environment (DME) of 4.10.2002, they were regarded as out-class waters (Szmukała *et al.,* 2006; Bonisławska *et al.,* 2008, 2011b).

Considering the unsatisfactory water quality in the Wiśniówka River it was decided to re-assess the effect of the hatchery on the water quality, using a wider range of parameters. Considering that the Wiśniówka River flows through rural, urban and agricultural areas, it was decided additionally to check the susceptibility of its waters to eutrophication in the section supplying the hatchery.

Materials and methods

Study area

The Wiśniówka River (53°55’ N, 14°84’E, Poland) is a second-order right-bank tributary to the Ina. It originates in the environs of Rożnów and flows through the Goleniów district in Western Pomeranian voivodeship, to fall into the Ina (Fig. 1). Its length is ca. 14 km, depth 0.2–0.7 m, and its sandygravelly bottom provides ideal substratum for nest building by salmonid fishes, for example trout (Tański *et al.,* 2013).

Figure 1: Wiśniowka River and location of water sampling position A and B during the conducted studies.

The hatchery in Goleniów, supplied by the waters of the Wiśniówka River, has been in operation for more than 50 years (established in 1962). It is part of the Fish Breeding and Stocking Centre, which also holds fry ponds. The object has 16 long-stream apparatus, 94 Weiss jars, 10 fry tanks and two closed circulation systems. The hatchery produces stocking material of both autumn-winter spawning species: salmon (*Salmo salar* L.), sea trout (*S. trutta* L.), river trout (*S. trutta m. fario* L.), European white-fish (*Coregonus albula* (L.)), Baltic white-fish (*C. lavaretus* (L.)), burbot (*Lota lota* (L.)), and spring-summer spawning species: pike (*Esox lucius* L.), asp (*Aspius aspius* (L.), sander (*Sander lucioperca* (L.)), vimba (*Vimba vimba* (L.)), catfish (*Silurus glanis* L.), ide (*Leuciscius idus* (L.)), carp (*Cyprinus carpio* L.), chub (*L. cephalus* (L.)), crucian carp (*Carassius carassius* (L.)), and tench (*Tinca tinca* (L.)). Within the last decade the production of stocking material was extended to include many new species, while earlier it was mainly based on salmonid fishes (Tański and Pender, 2009). The object is supplied by river water at the quantity of 10 L s^{-1} to 20 L s^{-1}, which ensures continuity of production, while the current legislation allows water intake of up to 50 L s^{-1} (Molenda, 2008); the water circulation is open. The water from the river is taken up above the weir into a retention pond, then flows to filter buildings where it is mechanically purified and then it is transferred to the hatchery where it supplies the hatching apparatus. Post-production water flows into the river.

Hydrochemical analyses

The water quality in the Wiśniówka was analysed from February 2013 till February 2014. The water was sampled in two sites: site A was located above the hatchery (above the weir) – the river width there was 2.5 m, the depth 0.6 m (N 53°33'7.61", E 14°50'37.53", Poland). The second site –B– was located below the object – the river width at that point was 1.5 m, depth 0.2 m (N 53°33'8,89", E 14°50'25,49", Poland). The water was sampled once a month (except August, because of conservation-maintenance works at the hatchery).

Chemical analyses were conducted in the laboratory according to the recommendations of the Standards

Methods (APHA, 1999). Temperature (°C), pH and electrolytic conductivity ($\mu S \cdot cm^{-1}$) were measured in the field. The following parameters were determined: total suspension ($mg\ dm^{-3}$), dissolved oxygen ($mg\ O_2\ dm^{-3}$), biochemical oxygen demand after five days – BOD_5 ($mg\ O_2\ dm^{-3}$), chemical oxygen demand – COD_{Cr} ($mg\ O_2 \cdot dm^{-3}$), ammonium nitrogen $N\text{-}NH_4^+$ ($mg\ N\ dm^{-3}$), nitrate nitrogen (III) – nitrites $N\text{-}NO_2^-$ ($mg\ N\ dm^{-3}$), nitrite nitrogen (V) – nitrates $N\text{-}NO_3^-$ ($mg\ N\ dm^{-3}$), total phosphorus TP ($mg\ Pdm^{-3}$), phosphates PO_4^{-3} TRP ($mg\ P\text{-}PO_4^{-3}\ dm^{-3}$), total alkalinity ($mg\ CaCO_3\ dm^{-3}$), hardness ($mg\ CaCO_3\ dm^{-3}$), chlorides Cl^- ($mg \cdot dm^{-3}$) and chlorophyll a–($\mu g\ dm^{-3}$).

The analysed parameters were assessed relative to the reference point provided in two decrees currently in force: DME of 9 November 2011 on the classification of quality of uniform parts of surface waters and the environmental standards for priority substances (Dz. U. 2011 No. 257 item 1545), and DME of 4 October 2002 on the requirements for inland waters which are fish habitats in the wild (Dz. U. No. 176, item 1455) (Table 2).

The susceptibility of the Wiśniówka waters to eutrophication in the section supplying the hatchery was assessed considering the requirements contained in the DME of 23 December 2002 on the criteria of designation of waters susceptible to pollution with nitrogen compounds from agricultural sources (Table 1). The analysis of the effect of the hatchery on the water quality considered the requirements provided by the DME of 24 July 2006 on the conditions which should be met when introducing waste into soil or waters, and on substances which are especially harmful to aquatic environment (Dz. U. No. 137 item 984.) (Table 1).

Statistical analysis using Statistica® 9,0 PL software was performed in order to determine the interdependences between the values of selected parameters over time. It included Pearson's linear correlation; graphic representation of the dependences was based on square polynomial function.

Table 1: Requirements of Decrees of Ministry of Environment (2002; 2011).

Parameters	**DME 04.10.2002**		**DME 09.11.2011r.**		**DME 23.12.2002**
	Salmonids	**Cyprinids**	**Class I**	**Class II**	**Above these values, there eutrophication**
Temperature (°C)	21.5	28	≤22	≤24	–
pH	6-9	6-9	6-8.5	6-9	–
Dissolved oxygen ($mg\ O_2 \cdot dm^{-3}$)	≥7	≥5	≥7	≥5	–
BOD_5 ($mg \cdot dm^{-3}$)	≤3	≤6	≤3	≤6	–
COD_{Cr} ($mg\ O_2 \cdot dm^{-3}$)	–	–	≤25	≤30	–
Electrolytic conductivity ($\mu S \cdot cm^{-1}$)	–	–	≤1000	≤1500	–
Chlorophyll „a" ($\mu g \cdot dm^{-3}$)	–	–	–	–	>25
Nitrite nitrogen $N\text{-}NO_2^-$ ($mg\ N \cdot dm^{-3}$)	≤0.01	≤0.03	–	–	–
Nitrate nitrogen $N\text{-}NO_3^-$ ($mg\ N \cdot dm^{-3}$)	–	–	≤2.2	≤5	>2.2
Ammonium nitrogen $N\text{-}NH_4^+$ ($mg\ N \cdot dm^{-3}$)	≤0.78	≤0.78	≤0.78	≤1.56	–
Total phosphorus ($mg\ P \cdot dm^{-3}$)	≤0.2	≤0.4	≤0.2	≤0,4	>0.25
Phosphates PO_4^{-3} ($mg\ P\text{-}PO_4^{3-} \cdot dm^{-3}$)	–	–	≤0.2	≤0,31	–

Table 1 continued:

Total suspension (mg·dm^{-3})	≤25	≤25	≤25	≤50	–
Total alkalinity (mg $CaCO_3$·dm^{-3})	–	–	≤100	≤150	–
Total hardness (mg $CaCO_3$·dm^{-3})	–	–	≤200	≤500	–
Chlorine (mg Cl^{-}·dm^{-3})	–	–	≤200	≤300	–

Table 2: The values of physical indicators of the lower section of the Wiśniówka; position A and B.

Parameters / Months	Temperature (°C)		pH value		Total suspension (mg·dm^{-3})	
	A	B	A	B	A	B
February	9.7	10.6	7.2	7.4	140	16
March	12.9	12.4	7.3	7.5	40	6
April	15.7	16.9	7.6	7.9	20	14
May	16.9	16.4	7.5	7.6	16	28
June	21.1	18.1	7.6	7.7	36	64
July	18.4	17.7	7.7	7.6	166	52
September	16.4	16.6	7.5	7.5	38	44
October	15.9	15.7	7.3	7.3	54	32
November	8.8	7.7	7.3	7.3	6	30
December	13.5	12.5	7.0	7.0	12	42
January	9.3	7.4	7.7	7.7	4	124
February	17.7	15.2	7.7	7.7	40	26
Mean	14.7	13.9	7.5	7.5	48	40
Evaluation						
DME 04.10.2002	Water appropriate for salmonids		Water appropriate for salmonids		Values increased	
DME 09.11.2011	I	I	I	I	II	II

Results

Seasonal variation of hydrochemical parameters

The analysed physical parameters of water quality included temperature, pH and total suspension.

Water temperature ranged from 8.8°C to 21.1°C in site A and from 7.4°C to 18.1°C in site B. According to the DME of 04.10.2002 and the DME of 09.11.2011, the temperature values were adequate for salmonid fishes (class I of water quality) (Tables 1, 2). The seasonal variation in temperature was typical of temperate climate.

The values of river water pH in sites A and B ranged from 7.0 to 7.9, while the mean annual values in both sites were 7.5 and met the requirements of the DME on the requirements for salmonid fishes and thus were within the range of quality class I (DME of 09.11.2011) (Table 2). The smallest pH (7.0) was recorded in both sites in December 2013, the highest - 7.9 – in site B in April 2014 (Table 2).

During the studies in both sites A and B the mean annual values of total suspension were increased and amounted to 48.0 and 40.0 mg·dm^{-3}, respectively. The parameter disqualified the waters of Wiśniówka for salmonids (DME of 04.10.2002) and placed them in quality class III (DME of 09.11.2011) (Tables 1, 2). In July in site A the value of total suspension exceeded the requirements for water quality class I six times and was as high as 166.0 mg dm^{-3}. In site B the highest value of total suspension was recorded in January 2014 (124.0 mg dm^{-3}) (Tables 1, 2).

The mean annual values of dissolved oxygen in the lower section of Wiśniówka (sites A and B) were high, ensuring favourable conditions for salmonid fishes: class I quality (DME of 04.10.2002 and 09.11.2011) (Tables 1, 3). Only in June the dissolved oxygen in site A (before the hatchery) was relatively low – 2.2 mg O_2 dm^{-3} (Table 3). The oxygen content was the highest in February 2014 – 14.9 mg O_2 dm^{-3} in site A and in March 2013 - 17.7 mgO_2 dm^{-3} in site B (Tables 1, 3).

BOD_5 and COD_{Cr} were adopted as parameters describing the organic matter load in the water. The mean annual values of BOD_5 in both sites: A and B, were below 6.0 mgO_2 dm^3, hence the waters were adequate for cyprinid fishes according to the DME of 4.10.2002, and were within class II of water quality according to the DME of 09.11.2011. The highest values of the parameter were recorded in July in site A: 12.1 mg O_2 dm^{-3} and in Septemeber in site B: 6.2 mg O_2 dm^{-3} (Tables 1, 3).

Table 3: The values of oxygen indicators lower section of the Wiśniówka; position A and B.

Months \ Parameters	Dissolved oxygen (mg O_2 dm^{-3})		BOD_5 (mg O_2 dm^{-3})		COD_{Cr} (mg $O_2 \cdot dm^{-3}$)	
	A	**B**	**A**	**B**	**A**	**B**
February	13.3	15.2	4.4	4.9	37.4	23.8
March	13.3	17.7	2.7	5.3	28.2	10.6
April	10.6	10.8	1.8	2.0	43.1	27.3
May	11.2	8.3	2.3	0.1	11.4	5.3
June	2.2	10.0	1.5	3.3	80.1	38.7
July	12.8	10.4	12.1	3.7	187.8	102.2
September	14.0	12.8	6.7	6.2	10.2	7.8
October	9.3	9.4	2.3	3.6	22.0	37.6
November	11.6	10.9	2.2	2.5	134.7	69.6
December	13.8	13.3	4.4	5.0	33.6	29.6
January	11.1	13.7	2.6	5,1	23.0	33.0
February	14.9	14.6	5.3	4.8	156.4	41.4
Mean	11.5	12.3	4.0	3.9	64.0	35.5
Evaluation						
DME 04.10.2002	Water appropriate for salmonids		Water appropriate for cyprinids		–	–
DME 09.11.2011	I	I	II	II	Above class II	

The mean annual values of COD_{Cr}: 64.0 mg O_2 dm^{-3} and 35.5 mg O_2 dm^{-3} in sites A and B, respectively, were increased (exceeding the threshold value for quality class II - 30.0 mg O_2 dm^{-3}) (Tables 1, 3). The highest values of chemical oxygen demand were recorded in July in both sites A and B (187.8 mgO_2 dm^{-3} and 102.2 mgO_2 dm^{-3}, respectively). The smallest values of the parameter were observed in September in site A – 10.2 mg O_2 dm^{-3} and in May in site B – 5.3 mg O_2 dm^{-3} (Table 3).

Selected inorganic forms of nitrogen and phosphorus were adopted as indices of the content of biogenic substances in the waters of Wiśniówka.

The mean annual content of ammonium nitrogen $N–NH_4$ in the studied sites did not exceed the extreme values for quality class I (DME of 09.11.2011), and thus the waters met the requirements for salmonid fishes (DME of 04.10.2002) (Tables 1, 4). The ammonium nitrogen concentration during the study period in both sites varied from 0.017 to 0.350 mgN-NH_4 dm^{-3}. The highest values of the parameter were recorded in March and April in site A (0.128 mg N-NH_4 dm^{-3} and 0.123 mg N-NH_4 dm^{-3}, respectively), while in site B the highest value was observed in January: 0.350 mgN dm^{-3} (Tables 1, 4).

Table 4: The values of the indicators ammonia nitrogen, nitrite, nitrate lower section of the Wiśniówka; position A and B.

Parameters / Months	Ammonium nitrogen ($mg\ N·dm^{-3}$)		Nitrite nitrogen ($mg\ N·dm^{-3}$)		Nitrate nitrogen $^-$ ($mg\ N·dm^{-3}$)	
	A	**B**	**A**	**B**	**A**	**B**
February	0.071	0.053	0.016	0.018	0.137	0.086
March	0.128	0.052	0.013	0.013	0.086	0.240
April	0.123	0.038	0.030	0.020	0.149	0.322
May	0.088	0.054	0.050	0.051	0.027	0.086
June	0.091	0.051	0.064	0.056	0.012	0.010
July	0.035	0.029	0.031	0.017	0.080	0.174
September	0.021	0.017	0.022	0.022	0.030	0.080
October	0.040	0.038	0.046	0.041	0.043	0.085
November	0.104	0.207	0.021	0.011	0.041	0.049
December	0.018	0.026	0.033	0.027	0.025	0.054
January	0.117	0.350	0.049	0.056	0.086	0.227
February	0.081	0.066	0.021	0.014	0.060	0.137
Mean	0.076	0.082	0.033	0.029	0.065	0.129
Evaluation						
DME 04.10.2002	Water appropriate for salmonids		Water appropriate for cyprinids		–	–
DME 09.11.2011	I	I	–	–	I	I
DME 24.07.2006	–	–	–	–	Values are not indicative of eutrophication	

The highest concentration of nitrates (nitrites) (III) within the 12 months in site A (water supplying the hatchery) was recorded in June and amounted to 0.064 mg N-NO_2 $dm^{–3}$, while in site B it was the highest in June and January when it reached 0.056 mg N-NO_2 $dm^{–3}$ (Table 4). The mean annual value of the parameter was 0.033 mg N-NO_2 $dm^{–3}$ (site A) and according to the DME of 04.10.2002 it only slightly exceeded the acceptable value of 0.030 mgN-NO_2 $dm^{–3}$. In site B the mean annual value was 0.029 mg N-NO_2 $dm^{–3}$ (Tables 1, 4).

The concentration of nitrates (V) varied during the year. In site A in February (2013) and April it was the highest and amounted to 0.137 mgN-NO_3·dm^{-3} and 0.149 mg N-NO_3·dm^3, respectively (Table 4). In May and June the values of N-NO_3 decreased distinctly, and from September till the end of the year they increased slightly (site A). In site B the highest concentration, of 0.322 mg N-NO_3 dm^{-3}, was recorded in April. The mean annual value of the parameter in site A was 0.065 mg N dm^{-3}, while in site B it was twice higher – 0.129 mg N-NO_3 dm^{-3} (Table 4). The values of N-NO_3 were below 2.2 mg N-NO_3·dm^{-3}, and with respect to this parameter the water in the studied river section did not indicate eutrophication as defined in the DME of 23.12.2002 (Tables 1, 4).

The concentration of reactive phosphorus in the water supplying the hatchery ranged from 0.029 to 0.117 mg P-PO_4^{3-} dm^{-3}, and in the water leaving the hatchery it varied from 0.037 to 0.117 mg P-PO_4^{3-} dm^{-3} (Table 5). The highest values of reactive phosphorus were recorded in March in both sites, the smallest in winter months from November till February. The mean annual values of the parameter, of 0.123 mg P-PO_4^{3-} dm^{-3} (site A) and 0.143 mg P-PO_4 dm^{-3} (site B), were within the range for quality class I according to the DME 09.11.2011 (Tables 1, 5).

Table 5: The values of phosphate and total phosphorus in the lower section of the Wiśniówka; position A and B.

Months \ Parameters	Phosphates PO_4^{-3} (mg P-PO_4^{-3}·dm^{-3})		Total phosphorus (mg P·dm^{-3})	
	A	B	A	B
February	0.059	0.037	0.233	0.184
March	0.046	0.046	0.218	0.266
April	0.059	0.038	0.223	0.134
May	0.055	0.048	0.202	0.190
June	0.077	0.086	0.214	0.286
July	0.091	0.089	0.302	0.330
September	0.082	0.068	0.306	0.304
October	0.117	0.117	0.327	0.385
November	0.034	0.038	0.232	0.223
December	0.044	0.077	0.229	0.294
January	0.029	0.042	0.149	0.180
February	0.052	0.043	0.283	0.476
Mean	0.123	0.143	0.251	0.274
Evaluation				
DME 04.10.2002	–	–	Water appropriate for cyprinids	
DME 09.11.2011	I	I	II	II
DME 24.07.2006	–	–	Values indicative of eutrophication	

The mean annual concentration of total phosphorus: in site A–0.251 mg P dm^{-3}, in site B – 0.274 mg P dm^{-3}; according to the DME of 04.10.2002 and 09.11.2011 was adequate for cyprinid fishes (II quality class) (Tables 1, 5). An increased value of the parameter was recorded in site B in February 2014 and was 0.476 mg P dm^{-3} (Table 5). According to the DME of 23.12.2003 the mean values of the parameter only slightly exceeded the threshold value of 0.250 mg P dm^{-3} (Tables 1, 5). The parameters discussed below described the level of mineralization of the studied waters.

Considering the mean values of the electrolytic conductivity, in the light of the current regulations the waters should be qualified as quality class I

(Tables 1, 6). In June the value of the parameter was the smallest in both sites and amounted to 540 µS cm^{-1} and 463 µS cm^{-1}, respectively. The highest conductivity was recorded in November, with 799 µS cm^{-1} in site A and 746 µS cm^{-1} in site B (Tables 1, 6).

In the waters of Wiśniówka supplying the hatchery, the alkalinity in the study period ranged from 205.3 to 274.0 mg $CaCO_3$ dm^{-3} (site A), and from 200.8 to 281.5 mg $CaCO_3$ dm^{-3} in site B. The mean annual value of the parameter in the study period for both sites exceeded the acceptable value required for quality class III (DME of 09.11.2011) (Tables 1, 6).

Table 6: Salinity index values lower part of the Wiśniówka; position A and B.

Parameters / Months	Electrolytic conductivity (µS cm^{-1})		Total alkalinity (mg $CaCO_3$ dm^{-3})		Total hardness (mg $CaCO_3$ dm^{-3})		Chlorine (mg dm^{-3})	
	A	B	A	B	A	B	A	B
February	590	557	206.0	200.8	262.5	260.0	26.6	24.9
March	667	626	205.3	202.8	272.5	275.0	28.4	35.5
April	601	586	229.8	213.3	280.0	252.5	28.4	24.9
May	579	560	251.5	235.5	275.0	262.5	37.3	28.4
June	540	463	252.5	265.5	260.0	272.5	46.2	35.5
July	693	481	274.0	281.5	265.0	267.5	42.6	49.6
September	543	542	214.0	237.0	280.0	282.5	35.5	32.0
October	577	560	221.0	222.0	267.5	272.5	35.5	32.0
November	799	846	240.0	237.5	300.0	300.0	28.4	24.9
December	704	689	245.5	233.0	280.0	280.0	28.9	24.9
January	677	837	235.0	236.0	295.0	290.0	28.4	32.0
February	625	658	228.0	235.0	285.0	295.0	39.1	35.5
Mean	633	617	233.5	232.6	276.9	275.8	33.8	31.7
Evaluation								
DME 04.10.2002	–	–	–	–	–	–	–	–
DME 09.11.2011	I	I	III	III	II	II	I	I
DME 24.07.2006	–	–	–	–	–	–	–	–

Another indicator of mineralization level is the total hardness: the mean annual values of $CaCO_3$ in the water were: for site A – 276.9 mg·dm^{-3} and for site B – 275.8 mg dm^{-3}, and they met the criteria listed in the DME of 09.11.2011 on the classification of surface waters of quality class II (Tables 1, 6). The smallest value of total hardness was recorded in site A in June 2013 (260.0 mg$CaCO_3$ dm^{-3}), and in site B in April (252.5 mg $CaCO_3$ dm^{-3}). The highest value in both sites was observed in November (300.0 mg$CaCO_3$ dm^{-3}) (Table 6).

The content of chloride ions in sites A and B according to the classification of uniform parts of inland waters (DME of 09.11.2011), places the waters supplying and leaving the hatchery as quality class I. The greatest concentration of Cl^- ions was recorded in June in site A and was 46.2 mg Cl dm^{-3}, while in site B the highest value was observed in July 2013, and it was 49.6 mg Cl dm^{-3} (Tables 1, 6).

The chlorophyll concentration was adopted as the indicator of the biomass in the studied waters. It varied according to the season. During the vegetation season it ranged from 0.5 to 21.9 μg dm^{-3}. In site A the value was the highest in July and was 21.9μg dm^{-3}, while in site B the highest value – May - was 11.2 μg dm^{-3} (Table 7).

Table 7: The chlorophyll content of the water the lower section of the Wiśniówka; position A and B.

Months	Chlorophyll (mg·dm^{-3})	
	A	**B**
February	2.7	3.7
March	7.5	8.5
April	5.9	2.1
May	4.3	11.2
June	4.8	5.3
July	21.9	8.5
September	1.1	0.5
October	1.6	3.2
November	3.2	3.8
December	1.1	0.5
January	2.7	1.6
February	2.7	1.6
Mean	4.9	4.2

During the study period the mean annual value of chlorophyll content was at a similar level in the two sites: in site A - 4.9 μg·dm^{-3} and in site B – 4.2 μg·dm^{-3}. The mean values did not exceed the value of 25 mg·dm^{-3} which, for running waters, is the threshold of eutrophication according to the DME of 23.12.2002 (Tables 1, 7).

The results show that, considering the highest acceptable values in waters used for salmonid fish keeping and breeding according to the DME of 24.07.2006 regarding the conditions to be met when introducing waste into water or soil, and regarding substances which are especially harmful to aquatic environment, the content did not exceed the requirements of the above Decree (Table 8).

Table 8: The maximum growth levels in the tested water and the requirements of the DME 24.07.2006.

Parameters	Mean values		The increase in substance (Δ) (B–A)	Requirements (Δ) DME 2006
	A	**B**		
BOD_5 (mg O_2 dm^{-3})	4.1	3.9	–	3.0
COD_{Cr} (mg O_2 dm^{-3})	64.0	35.5	–	7.0
Total suspension (mg dm^{-3})	48	40	–	6.0
Total phosphorus (mg P dm^{-3})	0.245	0.274	0.029	0.1

Temporal changes in selected parameters

It is accepted that among inorganic forms of nitrogen which are important for biomass production in surface waters, ammonium nitrogen and nitrate nitrogen should be considered.

The biomass production in the studied waters took place in the vegetation season from March to

September, and both ammonium and nitrate nitrogen were used in the process (Fig. 2). At the same time it was observed that in the case of nitrate nitrogen in site B, its supply was higher than its utilization for the biomass production. Outside the vegetation period the release of ammonium nitrogen was high in that site. The observed tendencies were statistically insignificant (Table 9).

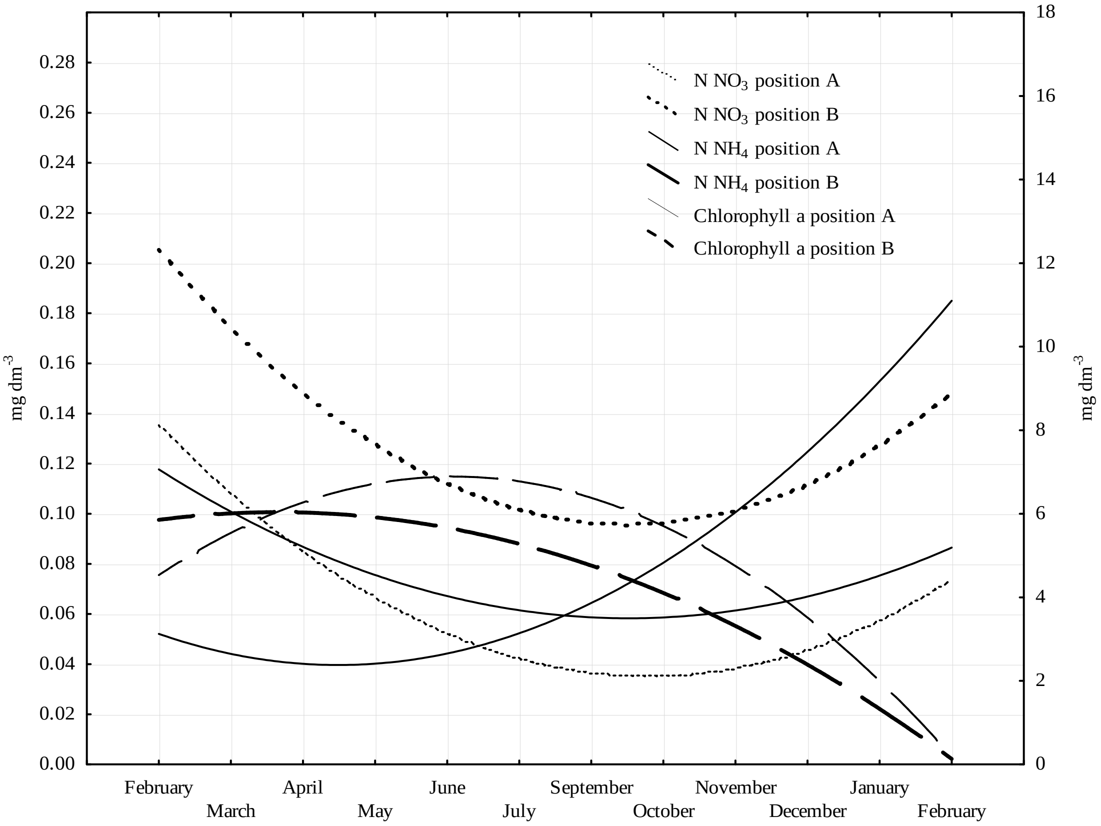

Figure 2: Tendency in relations between concentrations of chosen forms of inorganic nitrogen and chlorophyll a during researched period.

Table 9: The Person's linear correlation coefficients between analyzed factors. The statistical significant factors are bolded.

Index	Dissolved oxygen		Total suspension		Chlorophyll "a"		COD_{Cr}	
	A	B	A	B	A	B	A	B
$N\ NH_4$ A*	-0.24	0.20	-0.36	-0.01	-0.06	0.25	-0.04	-0.17
$N\ NH_4$ B**	-0.05	0.10	-0.37	**0.69**	-0.18	-0.19	0.01	0.14
$N\ NO_2$ A	-0.16	**-0.53**	-0.22	-0.01	-0.04	**0.61**	-0.28	-0.32
$N\ NO_2$ B	**-0.67**	**-0.47**	-0.32	**0.64**	-0.23	0.13	-0.42	-0.25
$N\ NO_3$ A	0.28	0.37	0.37	-0.21	0.23	-0.07	-0.01	0.01
$N\ NO_3$ B	0.26	0.30	-0.01	-0.02	0.33	0.03	-0.05	-0.04
$P\ PO_4$ A	0.11	0.38	-0.04	-0.41	0.17	**0.63**	-0.27	-0.38
$P\ PO_4$ B	0.07	**0.54**	-0.19	0.28	0.07	0.27	-0.32	-0.27
COD_{Cr} A	0.07	-0.10	0.40	-0.02	**0.60**	0.12	-	**0.86**
COD_{Cr} B	-0.06	-0.28	**-0.47**	0.39	**0.68**	0.09	**0.86**	-

* - A means position A

** - B means position B

Dependence between the availability of dissolved oxygen and the concentration of the above mentioned forms of inorganic nitrogen was also analysed (Fig. 3).

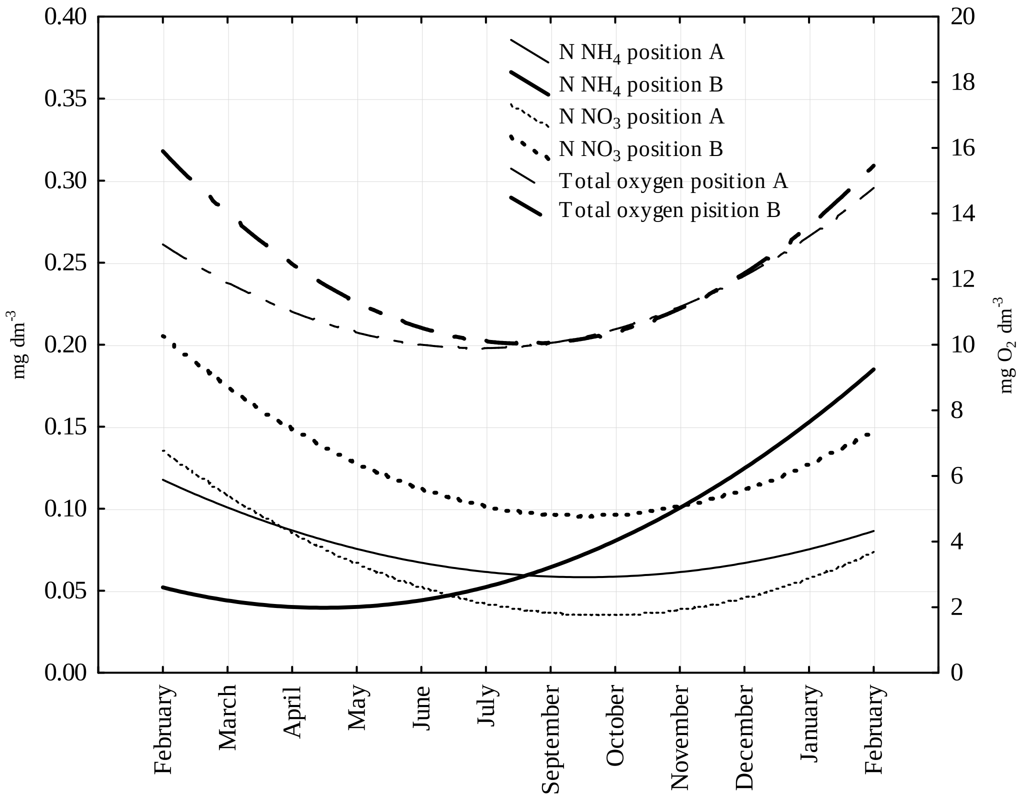

Figure 3: Tendency in relations between concentrations of some forms of inorganic nitrogen and total oxygen during researched period.

During the biomass production, the decrease in the concentration of inorganic forms of nitrogen was accompanied by a decrease tendency in the content of dissolved oxygen (Fig. 3). Most probably, because of the relatively good oxygenation of the river's waters during the study period, the observed tendencies were statistically insignificant (Table 9).

Besides the inorganic forms of nitrogen, also reactive phosphorus may take part in biomass production, but its utilization is as a rule much smaller than that of nitrogen. Despite this we analysed also its variation depending on the concentration of dissolved oxygen (Fig. 4).

It was observed that in both sites, A and B, reactive phosphorus was a biomass-forming factor. The release of reactive phosphorus in site A outside the vegetation season was distinctly slower than that of nitrate nitrogen (Fig. 4). In site B the rate of release of nitrate nitrogen and of reactive phosphorus was similar (Fig. 4).

For reactive phosphorus the dependence between its release and supply of dissolved oxygen was statistically significant (Table 9).

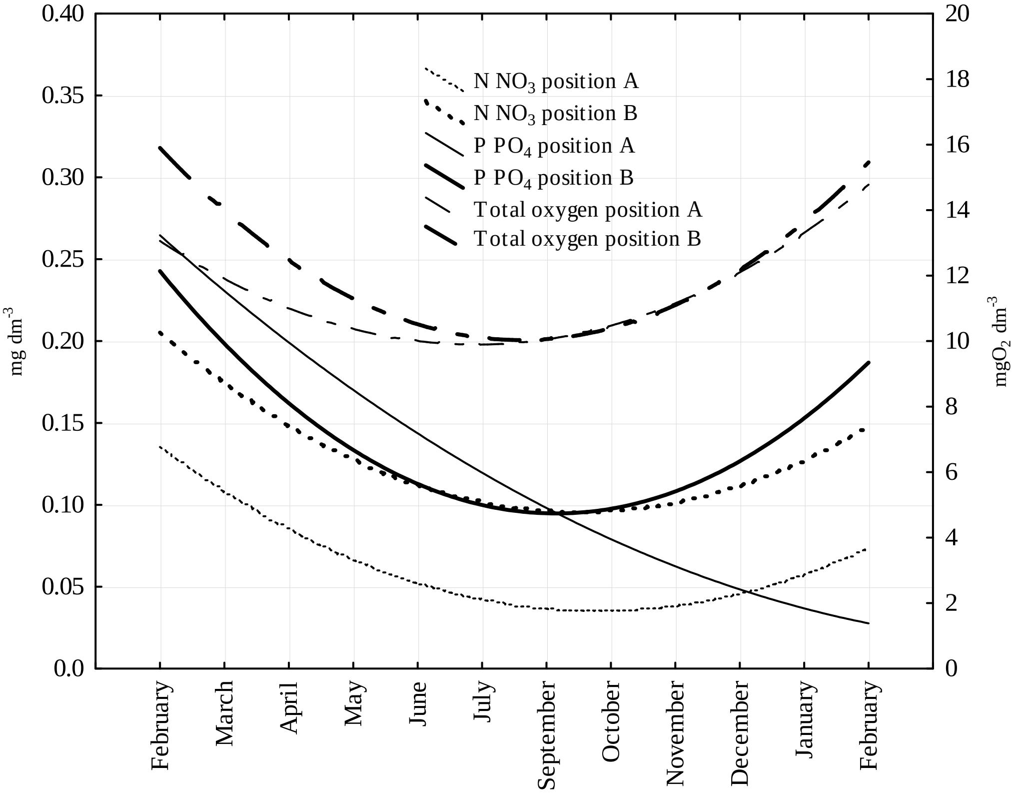

Figure 4: Tendency in relations between concentrations of nitrate nitrogen, reactive phosphorus and total oxygen during researched period.

In order to analyse the intensity of nitrification process in the river waters, and thus the ability of the river to self-purify, we analysed the variation in the concentration of all inorganic forms of nitrogen – ammonium, nitrite and nitrate nitrogen (Fig. 5).

The intensity of nitrification was indicated by the increase in concentration of nitrate nitrogen at a simultaneous decrease in the concentration of ammonium nitrogen. The process was mainly observed in site A, where the decrease in the concentration of nitrite nitrogen (transitional form) was accompanied by an increase in the concentration of nitrate nitrogen (Fig. 5).

In site B the process was slightly inhibited because of the greater release of ammonium nitrogen compared to nitrate nitrogen (Fig. 5).

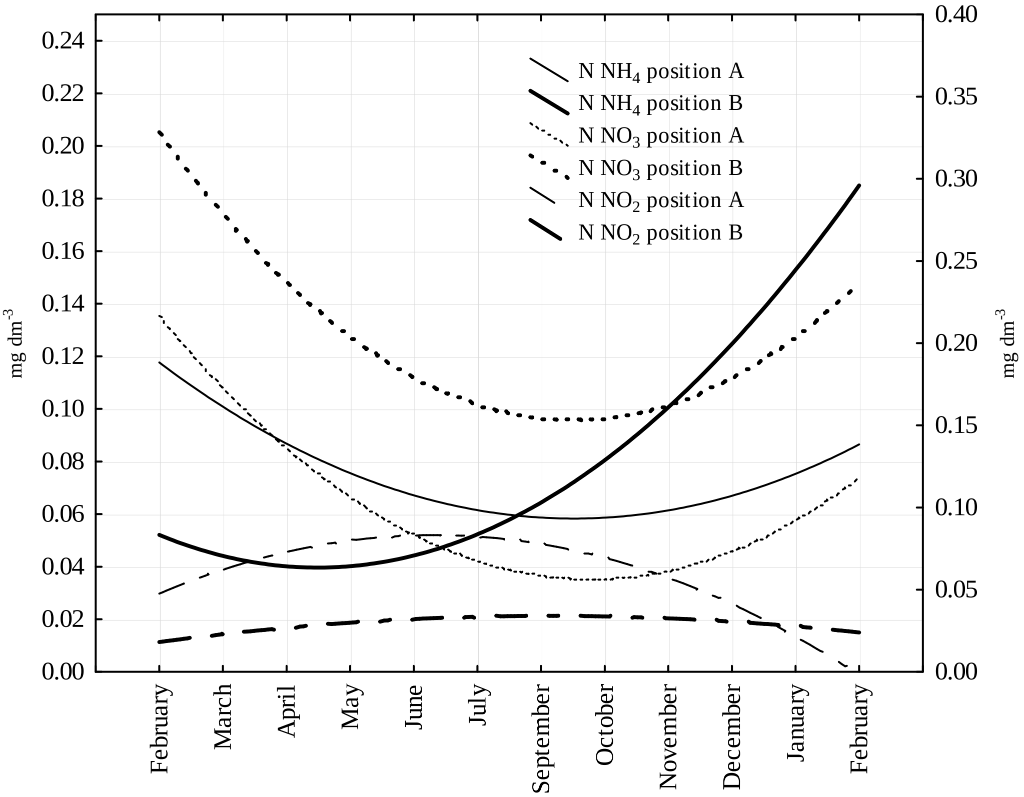

Figure 5: Tendency in relations between concentrations of inorganic forms of nitrogen during researched period.

Besides the biomass production and the effect of biogenic substances on the process, we analysed the effect of selected indices on the load of organic matter in the water. For this purpose we analysed the variation in organic load depending on the total suspension (Fig. 6).

In site A during the study period the organic matter load was in reverse proportion to the total suspension. The dependence was statistically significant (Fig. 6, Table 9). In site B the two parameters were in direct proportion. The correlation coefficient was relatively high, but it was statistically insignificant (Fig. 6, Table 9).

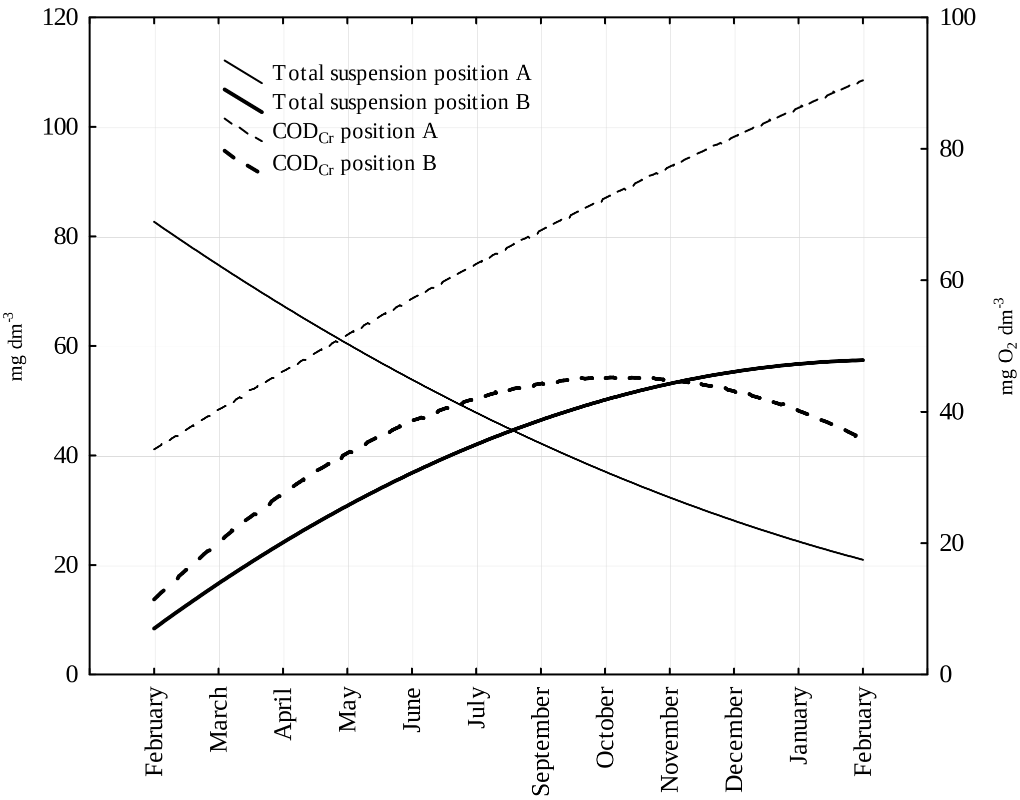

Figure 6: Tendency in relations between concentrations of total suspension and COD_{Cr} during researched period.

The quantity of biomass produced during the study period in the waters of Wiśniówka contributed to its organic matter load (Fig. 7). With decreasing concentration of reactive phosphorus and nitrate nitrogen, the values of COD_{Cr} index increased in both sites. The Pearson coefficient of linear correlation was fairly high in the case of reactive phosphorus, but it was not statistically significant (Table 9).

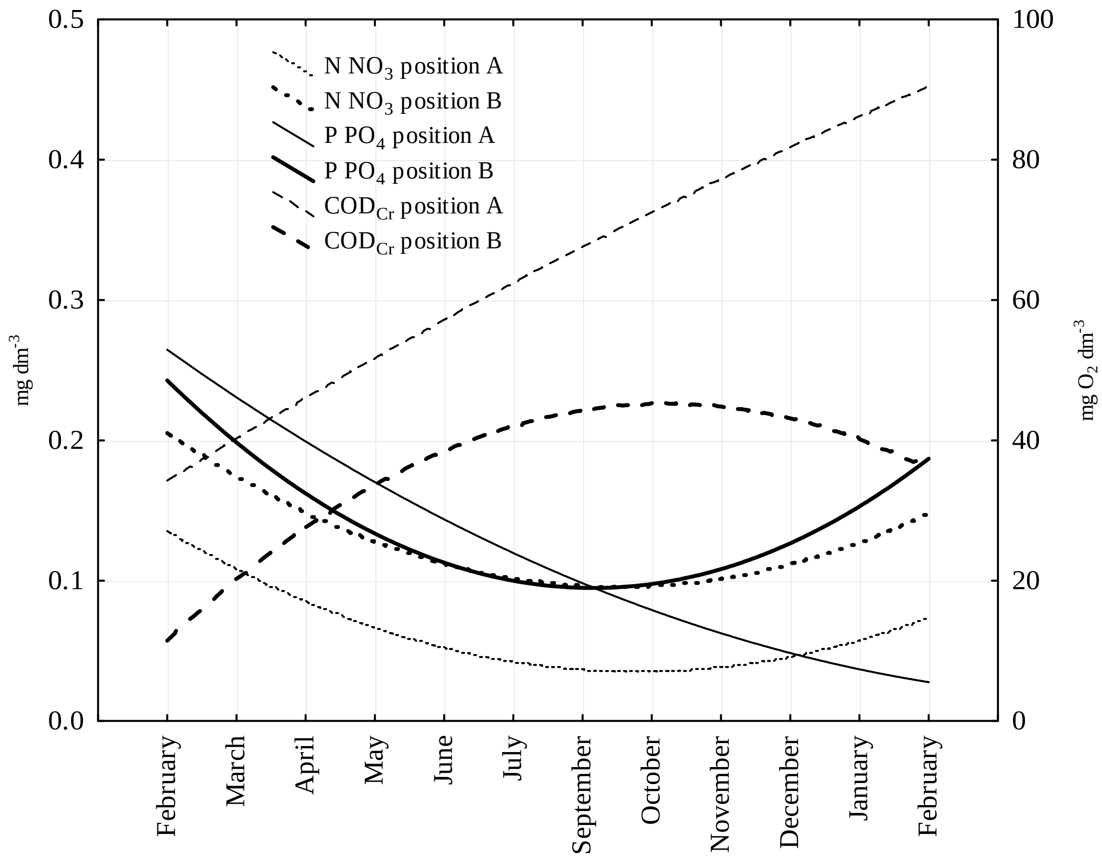

Figure 7: Tendency in relations between concentrations of nitrate nitrogen, reactive phosphorus and COD_{Cr} during researched period.

Discussion

Among the 17 studied parameters of the water quality in the Wiśniówka River, 15 are considered when assessing water quality according to the DME of 09.11.2011. The analysis of the results shows that the mean values of such parameters as temperature, pH, dissolved oxygen, ammonium nitrogen, nitrate nitrogen (V), reactive phosphorus, electrolytic conductivity and chloride ions do not exceed the standards for quality class I. The total suspension, BOD_5, total phosphorus and hardness place the water in class II. The values of two parameters: COD_{Cr} and alkalinity, exceed the acceptable values for class II.

Comparison of the values of eight parameters with the Decree on the requirements regarding inland waters adequate for fishes in natural conditions reveals that 4 of them (temperature, pH, dissolved oxygen and ammonium nitrogen) meet the criteria for waters adequate for salmonid fishes. Such parameters as BOD_5, nitrate nitrogen (nitrite) (III) and total phosphorus correspond to the water quality adequate for cyprinids. Only the total suspension exceeds the acceptable values according to the above Decree.

The studies made it possible to assess the danger of eutrophication of the Wiśniówka by agricultural areas. The mean annual values of concentration of $N\text{-}NO_3$ are smaller than the threshold

values for eutrophication of running surface inland waters (DME of 2002).
The phosphorus concentration during the studies was slightly greater than the threshold values for eutrophication-threatened waters. Also the chlorophyll content did not exceed the requirements of the Decree. According to the respective Decrees (2002, 2006) the waters of the Wiśniówka at present are not threatened with eutrophication of surface running waters, but confirmation of this conclusion would require determining the concentration of total nitrogen to assess the N to P ratio and to ascertain which of the biogenic elements stimulates development of algae.

Based on the studies and compared to the previous results of 2006 (Szmukała *et al.*, 2006) a deterioration was observed in the mean annual values of BOD_5 which, compared to the results of 2006 and 2007 (2.05 mg O_2 dm^{-3}; 2.08 mg O_2 dm^{-3}, respectively), increased twice to reach 4.0 mg O_2 dm^{-3}. Also in the case of COD_{Cr} the mean annual value in 2010-2012 placed the waters in quality class I, while in the study period (2014) the value of COD_{Cr} indicated waters exceeding standards for quality class II. Also the total suspension increased from 44.0 mg dm^{-3} (2011-2012) to 48.0 mg·dm^{-3} in site A (Bonisławska *et al*., 2013) in the study period. All the above parameters indicate an increasing load of organic matter in the water within the last years. The increase in the load of organic matter may result from an array of factors. The relatively high content of total suspension in the spring months may result from thaw and intense rainfall which increase the content of both fast- and slow-settling suspension. Increased content of suspension in the water is deleterious since it contributes to water opacity and thus inhibits penetration of sunlight, which in turn inhibits photosynthesis. The phenomenon causes also impaired vision in aquatic organisms including fishes. Sedimentation of the suspension on the bottom poses a threat for bottom organisms and may disturb development of fish eggs through direct or indirect effect on the oxygen content in the water (Newcombe and Jensen, 1996; Bonisławska *et al.*, 2011a). The increased BOD_5 and COD_{Cr} values, compared to the previous years, indicate an increased load of organic matter in the river. At high temperature and high content of organic matter which is liable to decompose, oxygen consumption is much faster. Such a situation may result from direct inflow from the catchment area (Wetzel, 2001). The increased organic load in the Wiśniówka in recent years may also result from the close vicinity of the hatchery. The view is to some extent supported by the observed dependences between the total suspension and the organic matter load in both sites (Fig. 6). Below the hatchery the content of total suspension was in direct proportion to the organic matter load while above the hatchery the tendency was reversed. Besides, in site B the COD_{Cr} was in reversed proportion to the dissolved oxygen (Table 9), indicating oxygen utilization for decomposition of organic matter.

In waters saturated with calcium and magnesium bicarbonates (it is the typical kind of surface waters in Western Pomerania), during intensive photosynthesis the concentration of reactive phosphorus decreases considerably, not only as a result of its utilization in the process of primary production. It was found that at calcium concentration exceeding 50mg dm^{-3} precipitation of phosphorus in the form of stable $Ca_5(PO_4)_3OH$ increased above 60%. Besides, during precipitation of calcium carbonate reactive phosphorus is absorbed on the surface of carbonates. Thus bivalent metals: Fe, Mg and Ca, contribute to aggregation and sedimentation of phosphorus and exclusion of its part from circulation in appropriate conditions (presence of dissolved oxygen, slightly increased pH during intensive photosynthesis) (Soballe and Kimmel, 1987; Jones, 1990; Noe *et al*., 2001). Thus the inanimate matter forming based on the settling suspension is a very important factor in the circulation of biogenic substances in surface waters. Dissolved forms of phosphorus and nitrogen can be absorbed by fine particles of suspended matter which settles to form bottom deposits. Sediments generally represent both the largest repository and the largest source of phosphorus and nitrogen (Baldwin *et al*., 1996). Therefore, information on sediment phosphorus speciation is important in understanding the aquatic biogeochemistry of the element. The cycling of phosphorus in many aquatic ecosystems is closely associated with the iron cycle (Mitchell and Baldwin, 1998, 2005). Phosphate binds strongly to ferric oxides. Under anaerobic conditions, ferric oxides can be reduced directly by iron-reducing bacteria. Phosphorus associated with the iron surface is released into solution, so the bacterially mediated reductive dissolution of phosphorus is potentially an important process in the biogeochemical cycling of phosphorus. Under oxic conditions, the resultant free phosphate ion irreversibly binds to the mineral surface. However, microbially mediated reductive dissolution of the mineral surface under anaerobic conditions presents a pathway for recycling of the phosphate group. The studies did not include analysis of iron content, but it can be supposed that in good oxygen conditions, which were recorded throughout the study period in the waters of Wiśniówka, inorganic matter may be deposited in the bottom sediments (mainly nitrogen- and phosphorus-derived biogenic substances). Accumulation of bottom deposits may in turn bring about deterioration in oxygen conditions and in consequence “internal supply” of biogenic substances. The process has been especially well studied in lakes (Imboden, 1974; Zdanowski, 1982; Jones, 1990; Tórz and Nędzarek, 2009). The high supply of biogenic (nitrogen and phosphorus) substances contributed to the increase in organic matter content in the river’s waters; the process was especially intensive during the vegetation season (Fig. 7).

Thus the increase in the load of organic and inorganic matter in the waters of Wiśniówka may have been caused by an array of factors – external inflow, neighbourhood of the hatchery, but also to a slight extent by internal supply.

The increase in biomass in surface waters is in direct proportion to the supply of nitrogen and phosphorus which is observed, among others, at an increased supply of elements from the direct or indirect catchment area and from "internal supply" (e.g. Soballe and Kimmel, 1987; Jones, 1990; Noe *et al*., 2001). In the spring-summer season in aquatic ecosystems the uptake of nutrients by phytoplankton increases. Greater availability of light and higher temperature favour and intensify assimilation of nitrogen and phosphorus (Correll, 1998; Wetzel, 2001; Mainstone and Parr, 2002; Jarvie *et al*., 2013). In the waters of Wiśniówka we observed similar tendencies of dependence of chlorophyll a concentration on the concentration of mineral nitrogen and phosphorus (Figs. 2, 4) which coincided with the demand of autotrophic organisms for nitrogen and phosphorus. The observed tendency of decrease in oxygen quantity with increasing biomass (Figs. 2, 3, 4) indicates a considerable accumulation of biomass which, as a result of its vital functions, contributed to the consumption of available oxygen. It can be supposed that in the waters of Wiśniówka the predominant form of matter was organic matter originating from the produced biomass, as indicated by the dependence between the COD_{Cr}, nitrate nitrogen and reactive phosphorus (Fig. 7), and by the effect of these biogenic substances on the size of the biomass production (Figs. 2, 3, 4).

The intensity of self-purification in the Wiśniówka River can be traced based on nitrification. In the winter months, with inhibited vegetation, nitrate and ammonium nitrogen were released from the biomass. On the other hand, in the spring-summer months nitrate and ammonium nitrogen were utilized for the biomass production (Fig. 5). In the same period we recorded an increase in the content of nitrite nitrogen, transitional form in the process of nitrification. Reduction of the produced biomass causes release of ammonium nitrogen which in good oxygen conditions, in the nitrification process, is oxidized first to nitrite and then to nitrate nitrogen. The resulting nitrate nitrogen can be re-used for biomass production. Hence it can be concluded that the self-purification in the waters of Wiśniówka stabilises the environmental conditions in the river.

As has been already mentioned, waters saturated with calcium and magnesium bicarbonates are typical of Western Pomerania. Also the waters of Wiśniówka show this tendency, indicating an appropriate functioning of the carbonate system (Table 6). The stable level of water hardness in the river does not indicate an inflow of pollutants from external sources which would contribute to an increase in total hardness (Hulisz and Skalska, 2005).

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