

Nitrification in the Surface Water of the Włocławek Dam Reservoir. The Process Contribution to Biochemical Oxygen Demand (N-BOD)

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Abstract

Nitrifying activity in the surface water of the Włocławek Dam Reservoir (WDR) was determined by use of a nitrification selective inhibitor (ATU). The highest values of nitrification were observed in the stations nearer the dam, with lower flow velocity, where the activity amounted to up to 120 $\mu\text{g N/dm}^3/\text{day}$. Nitrification process [%] involvement in biochemical oxygen demand increased with passing from lotic to lenitic conditions and reached maximum values up to 70% or even 100% BOD₅. Chemoautotrophic nitrifiers participation increase in oxygen consumption in the reservoir was probably caused by sedimentation of allochthonous, easily decomposable organic matter and a significant reduction in carbonaceous oxygen demand (C-BOD). Ammonium ion release from sediments was the decisive factor of shallow flooding nitrification.

Keywords: nitrification, potential nitrification activity, allythiourea, biochemical oxygen demand, river water, dam reservoir

Introduction

Nitrification is a process of ammonium ions (NH_4^+) biochemical oxidation to nitrates (NO_3^-), mediated by chemoautotrophic bacteria of the genus *Nitrosomonas* $\text{NH}_4^+ \rightarrow \text{NO}_2^-$ (the first stage) and *Nitrobacter* $\text{NO}_2^- \rightarrow \text{NO}_3^-$ (the second step).

This process is very significant for water quality of fluvial ecosystems (mainly polluted ones) and the organisms occupying them, because it is an integral part of the biological mechanism of river self-purification and takes part in the nitrogen cycle. Due to the influence of this process on ammonia concentration reduction and dissolved oxygen absorption, nitrification is often included in water quality modelling.

Nitrifying activity is determined by physico-chemical factors such as temperature and oxygen concentration,

and is proportional to the substrate concentration (NH_4^+) and to microorganisms biomass [1]. Biochemical oxygen depletion for nitrification (N-BOD) and the inhibitors influence upon the nitrifying activity have been earlier studied as possible parameters for assessment of the sewage treatment system functioning [2, 3].

Environmental studies concern, among others, the influence of sewage discharge on nitrification dynamics in the receiving river [4], the assessment of nitrifying activity in the water column and sedimenting lake trypton [5, 6, 7], fluvial systems [8, 9, 10, 11] and riverine-lacustrine ones [12]. The majority of environmental studies concern polluted ecosystems, mainly with ammonia. So far nitrification has often been treated as the first order kinetic reaction. Nitrification amount was calculated on the basis of ammonium nitrogen concentration in water depths [7, 11]. Other authors determined nitrifying bacteria activity in laboratory experiments, using specific inhibitors [5, 9, 10]. Nitrifying bacteria develop when suspended in water depths, on the surface of or-

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ganic seston and in bottom sediments. It has been shown that suspended particle matter stimulates nitrification processes. Kholdebarin & Oertli [13] suggested that such an effect of suspended particles on the nitrification rate in the surface water might be due to physical support for the proliferation of the nitrifying bacteria rather than to the adsorption of ammonium of the suspended particles.

Yoshioka et al. [5] found, however, that inactive nitrifiers can be connected with sedimenting seston, due to photoinhibition or their location within particle, implying unfavourable physico-chemical properties for their activity. Considering that the number of nitrifying bacteria in deposit surface layer is some orders of magnitude higher than in water depths, many researchers say that nitrification is usually located in deposits, and its importance in water depths is marginal [8, 12, 14].

In shallow rivers and streams, where relatively large water volume is in touch with bottom sediments, nitrification can be much higher than in big and deep rivers, in which the effect of deposits on water can be less significant [15]. That is why it is thought that nitrification of water depths (pelagic) can occur under properly long retention time only, e.g. in slowly flowing rivers. It is caused by a slow development of plankton nitrifiers and their high dispersion in water depths. A small population of nitrifiers can often be a limiting factor of effective process of ammonia purification in the river. It is proved that sewage bacteria biomass inflow can be a significant source of active nitrifiers and continuous improvement of sewage purification can paradoxically lead to a decrease in river self-purification ability by means of nitrification [4, 16].

The results presented below concern reconnaissance studies of nitrifying potential activity and measurement of this process oxygen demand (N-BOD) in the surface water of the Vistula section of the Włocławek Dam Reservoir (WDR). The studies of this river section conducted from the 80s [17, 18] showed a significant influence of river water lifting and flow rate lowering on nitrogen compound dynamics. In the water outflowing the reservoir a significant increase in nitrogen mineral forms concentration (DIN) was observed – especially ammonium form, relative to the inflowing concentrations. The ratio of mineral nitrogen to total nitrogen (TN) also increased – from 1:3 at the reservoir inflow to 1:2 at the outflow. The authors [17, 18] suggested that the differences observed pointed to intensive mineralization processes occurring in the water and bottom sediments of the WDR. Ammonium nitrogen (nitrification process substrate) concentration increase, retention time extension and increased influence of sediments accumulated in the dam reservoir on water volume flowing above them, seem to form favourable conditions for planktonic nitrifiers development and active nitrification in the WDR water. On the other hand, a decrease in the flow rate leads to a significant reduction of suspension concentration in this river section. The limitation of turbulent flow maintaining suspension particles and attached bacteria in water depths can be a factor limiting pelagic nitrification [4].

The above circumstances have inspired studies whose results are presented in this paper.

Table 1. Morphometric and hydrological parameters of the Włocławek Dam Reservoir (WDR).

total area	about 70 km ²
reservoir initial volume (1970)	408x10 ⁶ m ³
length (measured along the former river course)	55-58 km (backwater range)
width	500-2500 m (mean value 1210 m)
mean depth	5.5 m
maximum depth (by the dam)	15 m
water level fluctuations	0.8 m
retention time (by mean flow of about 900 m ³ x s ⁻¹)	4.5-5 days

The aim of the study was a recognition of the river Vistula lifting influence on nitrogen compounds conversion occurring in water depths, and particularly on nitrification processes and their significance for ecosystem oxygen regime. In the studies the zones of various hydrological conditions (current and flooding) were taken into account to observe differences in nitrification process dynamics. The studies also enabled a determination of a river regulation influence on its self-purification ability.

The Study Area

General Characteristics

With regard to its basin size and average annual flow (mean Q at the outflow – 1050 m³/s) the Vistula river is the second river in the Baltic Sea catchment area. The basin area within Poland boundaries amounts to 168 thousand km², that is 55% of the country area. The lower section of the Vistula is usually assumed to be a section of about 390 km river from the Narew river mouth to the Vistula river mouth to the Baltic Sea. The Włocławek Dam Reservoir (WDR), in use since 1970, has a significant influence on hydrology, chemistry and biotic elements of the lower Vistula. The WDR is the largest reservoir in Poland. Some important morphometric and hydrological properties of the WDR, described earlier [19, 20, 21, 22], are presented in Tab. 1.

The WDR is characterized by a significant length and a relatively small width, which determines its fluvial, channel character. Shallow floodings make only 14% of its area and are localized at the left, low bank, on the former flooding terraces. The former river channel goes mainly along the right bank, elevated up to 30-40 m morainal plateau [20]. According to the hydrological features, Grześ [23] divides the reservoir into the following parts: a) upper – rheolimnic – with a flow rate of about 1m/s in the current and of true fluvial character, b) lower – more limnic – with flow velocity of 0.1 – 0.4 m/s, including the section between the dam and 640 – 645 km (Fig. 1). The Vistula river carries in over 98% of water

inflowing the reservoir, so the inflow is equivalent to the flow [20]. Glazik [24] emphasizes that the WDR is characterized by small capability of flood water retention and river flow regulation. Water exchange takes place every 5 days on average. However, at flood it flows above 4800 m³/s, the water exchange period drops below one day. It testifies to the reservoir flowing character, and limited ability to soften overbank flows below the drop. Giziński [25] qualified the WDR among “super-rheolimnic” reservoirs due to exceptionally short retention time (complete water exchange happens about 70 times a year). From hydrological and morphological points of view the WDR remains rather a dammed river with a slow flow rate than a typical dam reservoir. That is why Giziński [25] proposed that this reservoir should not be called a dam reservoir, but a run-of-river reservoir. In spite of its flow character, the reservoir keeps every year about 2 mln m³ of sediments. The slow flow rate is responsible for retention of all dragging debris [26] and 32-65% of suspended matter load [17].

Research Stations Description

Three research stations of sampling were determined in the river section examined. Their localization was as follows:

Station 1 “Płock”. – The research station situated at the level of the road bridge in Płock (632 km of the river course), about 12-14 km down from the upper border of backwater. It is the top part of the reservoir. The reservoir is here of decidedly fluvial character (Fig. 1), which is testified by: a high flow rate close to that of a freely flowing river (0.7-1 m/s) and the small width of the river bed. This research station can be treated as the reservoir “entrance”. The samples were collected from the river current part.

Station 2 “Dobiegniewo”. – The research station situated in the lower part of the reservoir, at 660 km of the river course. The reservoir is here of more lenitic character than in the upper part. Its width increases to about 1800 m. The former river bed and main current of about 7 m in depth run along the right bank, cutting morainal plateau at the base. The flow rate in the cur-

rent zone oscillates in the range of 0.1-0.4 m/s. Beyond the current zone, there is a dominant flooding zone, extending over the flat area of a former flooding terrace. The depth of this zone oscillates between 1 m and 4 m. Lenitic conditions dominate in flood waters. However, the dynamics of water mass changes significantly with time and is determined by the strength and direction of wind mainly. During the period of wind blowing along the reservoir axis, i.e. from the west direction, the height of waves can reach 1 m and is often a cause of resuspension and redeposition of bottom sediments [20]. The formation of typical reservoir sediments distinguishes this part of the reservoir from a freely flowing river [18]. The samples were taken in a shallow flooding zone (depth of about 2.5 m) in 100 m distance from the left bank of the river.

Station 3 “Włocławek”. – The station is situated before the dam, at the 674 km of the river course. The depth in the former current reaches here about 13 m. This part of the reservoir is of the most limnic nature. In a small distance from the dam a significant influence of hydroelectric power plant cycling work on water mass dynamics can occur [20]. Giziński [25] suggests that during the hydroelectric power plant work the WDR is of more lotic character. However, during the reservoir filling – lenitic conditions dominate. Station 3 can be treated as the reservoir “outlet”. Samples were collected in the current part of the river.

Methods

The research was conducted at one month intervals (excluding June) from April to November 2002. The surface water samples were collected by use of a Patalas sampler of 5 dm³ capacity, then transported to the laboratory for direct analysis. Prior to the chemical analyses the samples were stored at 5°C.

BOD₅ and N-BOD₅ Determination

BOD₅ and N-BOD₅ determination was performed by a manometric method, using electronic pressure measurement (OxiTop System WTW Company). The water

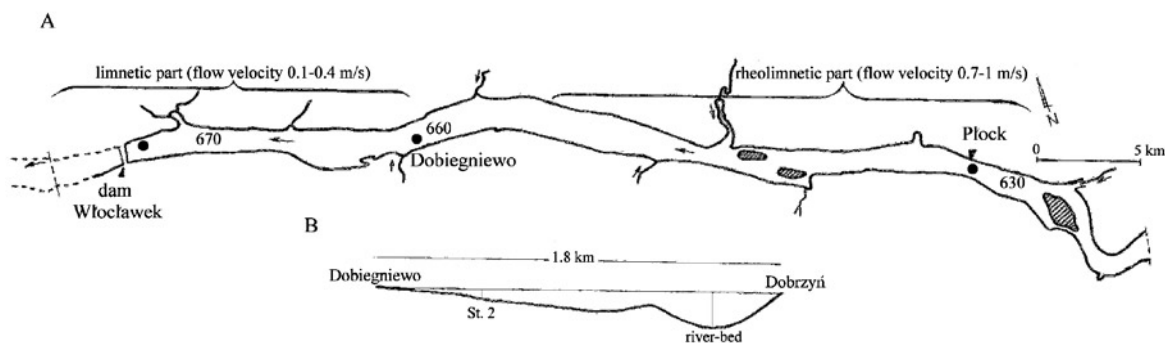


Fig. 1. The Włocławek Dam Reservoir section of the Vistula River. A. – location of regular stations, B. – location of the flooding zone and Station 2 in the Dobiegniewo – Dobrzyń cross-section (by Zytkowicz et al. [20] – modified).

samples of 432 ml volume were incubated for 5 days at a constant temperature of 20°C ($\pm 1^\circ\text{C}$). Incubation proceeded in brown glass bottles equipped with a magnetic stirrer. BOD measurement reflects the processes of organic matter decomposition in water. It involves two stages: carbonaceous, during which oxygen consumption for microbiological decomposition of carbon compounds occur (C-BOD) and nitric, during which mineral nitrogen compounds are oxidated (N-BOD) [1, 3]. In order to assess the amount of oxygen consumed during nitrification, an allylthiourea inhibitor (ATU) was used. ATU is a commonly used selective inhibitor of nitrification first stage [2, 3, 5, 9, 27, 28]. The inhibitor was added in the amount giving the final concentration of about 5 mg/l ATU in the sample. This concentration efficiently inhibits bacteria of the genus *Nitrosomonas* activity [29] and secures a complete blockage of the first stage of nitrification during the incubation period. Oxygen consumption determination was made in three replicates, in the samples with and without inhibitor, respectively. The difference in measurements between these samples allowed N-BOD₅ calculation.

Seston Quantitative and Qualitative Analyses

The water samples were filtered through glass fibre filters Whatmann GF/C, stopping particles above 0.45 μm . Filtration was performed in three replicates, 1 dm³ each, due to suspension determination before BOD₅ measurement, and most frequently in 6 replicates, 0.4 dm³ each, after incubation ending. The filters were dried in 105°C, weighed and burnt at 550°C in order to determine organic matter content.

Chemical Analyses

The contents of ammonium, nitrite and nitrate ions were determined in the water samples before and after BOD₅ measurements, according to standard methods [30]:

- nitrate nitrogen was determined by colorimetric method with phenoldisulphonic acid;
- nitrite nitrogen was determined by the reaction with sulphanilic acid and α - naphthylamine;
- ammonium nitrogen was determined by a direct nesslerization method.

Potential Nitrifying Activity Measurements

Nitrifying activity measurements were made on the basis of chemical analyses conducted immediately after BOD₅ measurements. The water was filtered through GF/C filters and the concentrations of nitrate, nitrite and ammonium ions were determined. Nitrifying activity was calculated by the difference between the sum of nitrite and nitrate ions in the samples incubated without and with ATU inhibitor, respectively:

$$NA (\mu\text{g N/dm}^3/\text{day}) = ([\text{NO}_2^- + \text{NO}_3^-] - [\text{NO}_2^- + \text{NO}_3^-]_i)/t;$$

where:

NA – nitrifying activity;

[...]; [...]_i – the sum of nitrite and nitrate ions expressed in $\mu\text{g N/dm}^3$, in the sample without and with ATU inhibitor, respectively;

t – experiment duration.

Such a mode of calculations is determined by ATU selectivity in relation to the first stage of nitrification. The inhibitor enables NH_4^+ ion oxidation to nitrites but does not exclude the growth of bacteria oxidating nitrite ions [5].

The calculations based exclusively on concentration differences of nitrates (the nitrification final product) did not give reproducible results (data not shown).

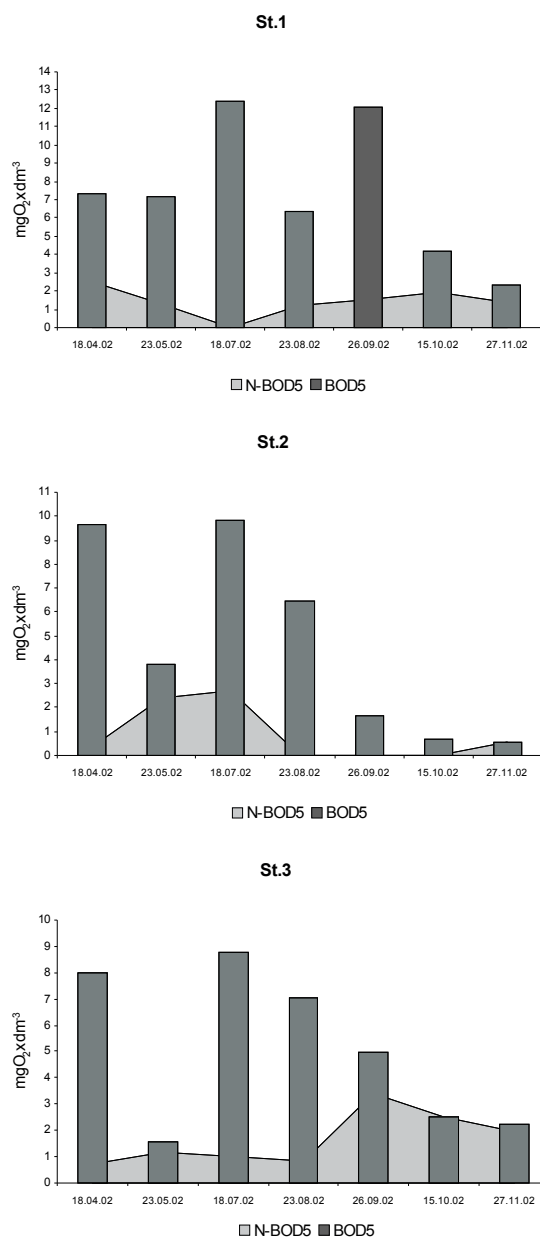


Fig. 2. Seasonal dynamics of total BOD₅ and oxygen consumption during nitrification. (N-BOD₅) measured in the WDR water from April to November 2002.

Table 2. Mean values of potential nitrifying activity NA ($\mu\text{g N}/\text{dm}^3/\text{day}$), biochemical oxygen demand: total BOD_5 , carbonaceous C-BOD_5 and nitric N-BOD_5 ($\text{mg O}_2/\text{dm}^3$). Contribution [%] of nitric oxygen demand in BOD total and concentrations of nitrates, nitrites, ammonium ions ($\text{mg N}/\text{dm}^3$), seston and particulate organic matter ($\text{mg s.m.}/\text{dm}^3$) in the WDR water, measured from April to November 2002.

	St.1		St.2		St.3	
	mean value	range	mean value	range	mean value	range
NA	42.0	1.3-76.6	45.1	6.8-121.3	53.5	26.3-107.7
BOD_5	7.4	2.3-12.4	4.7	0.6-9.9	5.0	1.6-8.8
C-BOD_5	6.0	1.0-12.4	3.8	0.0-9.3	3.4	0.0-7.8
N-BOD_5	1.4	0.0-2.5	0.9	0.0-2.7	1.6	0.7-3.4
N-BOD/BOD	27%	0-59	27.7%	0-100	51.7%	9-100
N-NO_3	0.74	0.1-2.2	0.44	0.1-1.2	0.37	0.1-0.8
N-NO_2	0.02	0.01-0.04	0.04	0.02-0.09	0.03	0.01-0.04
N-NH_4	0.26	0.1-0.4	0.55	0.2-1.1	0.69	0.3-1.3
seston	29.7	12-67	11.2	4-29	10.5	4-19
POM	12.8	8.2-18.1	5.1	1.3-9.0	6.0	1.5-7.7

Results

BOD_5 and N-BOD_5

Mean BOD_5 values observed during the studies were the highest at the reservoir "entry", that is, at Station 1 and clearly decreased toward the dam – Station 3 (Tab. 2).

BOD_5 reduction in relation to the values observed in the inflow amounted on average to 37% at the shallow flooding of Station 2 and 32% at the reservoir "exit." The highest BOD_5 value was noted in July at St. 1 – 12.4 $\text{mg O}_2/\text{dm}^3$, and the lowest one, 0.6 $\text{mg O}_2/\text{dm}^3$ in November at St. 2. Large differences in the nitrification process intensity were found during the whole period of study. N-BOD_5 measurements oscillated from values near zero at St. 1 and 2 to maximum value 3.4 $\text{mg O}_2/\text{dm}^3$ measured in September at St. 3 (Fig. 2). Mean N-BOD_5 values were the highest at the station near the dam (St. 3), while the lowest were in the Dobięgniewo shallow flooding (St. 2), where from August to October a lack of oxygen absorption in nitrification process was observed.

As approaching the dam, the nitrification process participation [%] in BOD_5 total increased almost twice with simultaneous significant, about 57%, reduction in C-BOD_5 (Tab. 2). N-BOD_5 values measured at St. 1 and 3 pointed to a high, statistically significant negative correlation with C-BOD_5 (Fig. 6). A significant relationship between N-BOD_5 and ammonia nitrogen concentration was indicated at St.2 (correlation coefficient 0.94; $p < 0.05$).

Potential Nitrifying Activity

Nitrifying activity differentiation was high during the studies. Nitrifying activity values changed from those near detection limit, with the methods used – 1.3 $\mu\text{g N}/$

dm^3/day , to above 120 $\mu\text{g N}/\text{dm}^3/\text{day}$. The mean activity was the highest at St. 3 and the lowest in water inflowing the reservoir – St. 1 (Tab. 2). However, the differences were not statistically significant (Fig. 3). Potential nitrifying activity showed a different seasonal course at all the three stations (Fig. 4). At the Plock Station, the maximum activity (77 $\mu\text{g N}/\text{dm}^3/\text{day}$) was observed in May. It was the highest value noted during this month in the reservoir. In July the activity at St. 1 dropped to the lowest value measured in the reservoir and, in relation to the method error, it can be recognized as being near zero. From August the activity increased gradually, reaching the second peak in October (66 $\mu\text{g N}/\text{dm}^3/\text{day}$). In the Dobięgniewo flooding (St. 2) the activity increased from April to July, when its highest value in the reservoir was measured – 121 $\mu\text{g N}/\text{dm}^3/\text{day}$. A decrease to 30 $\mu\text{g N}/\text{dm}^3/\text{day}$ was noted in August. Then the activity stabilization occurred at the level 30 – 50 $\mu\text{g N}/\text{dm}^3/\text{day}$ until the end of November. During the nitrification course at Station 3 in Włocławek, two activity peaks were observed: in July (71

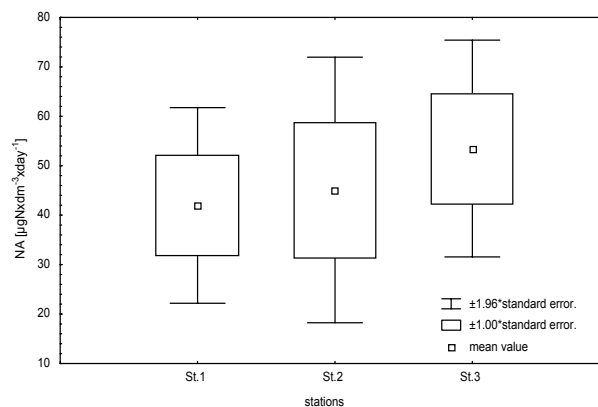


Fig. 3. Nitrifying activity (NA) variability in the WDR water.

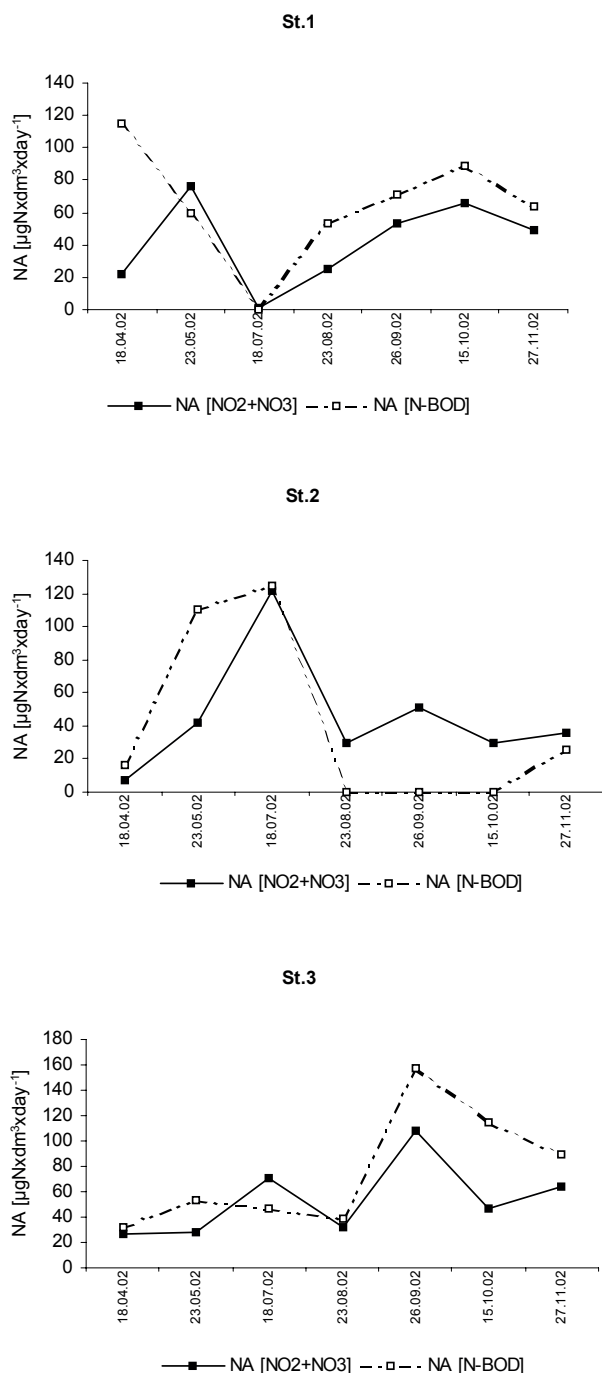


Fig. 4. Seasonal dynamics of potential nitrifying activity, measured in the WDR water during April–November 2002 period. The activity was measured by use of two methods – on the basis of oxygen consumption (N–BOD) and nitrification products ($\text{NO}_2^- + \text{NO}_3^-$) in the presence of selective inhibitor ATU.

$\mu\text{g N/dm}^3/\text{day}$) and in September ($108 \mu\text{g N/dm}^3/\text{day}$). It is worth emphasizing that the activity peaks usually overlapped at more limnic stations and were opposed to the trends observed at St. 1. Such a trend discrepancy was particularly seen during the July maximum.

A positive correlation was shown between potential nitrifying activity (assessed on the basis of nitrification products concentration) and oxygen consumption in this process (N–BOD). The correlation coefficient showed rather

strong relations between the above parameters, mainly at the stations of more limnic character – St. 2 (c.c. 0.7) and St. 3 (c.c. 0.8; $p < 0.05$). Assuming that in total nitrification process 4.34 mg of oxygen are used for each 1 mg of nitrogen oxidated to nitrates [31], it was possible to assess nitrifying activity on the basis of oxygen consumption in nitrification processes. The mean values of nitrification calculated in this way were close to those obtained by measurements of the process products, especially at St. 2 (about $40 \mu\text{g N/dm}^3/\text{day}$). At St. 1 and 3 nitrifying activity calculated on the basis of oxygen consumption was a little higher (about $20 \mu\text{g N/dm}^3/\text{day}$) and amounted to 65 and $76 \mu\text{g N/dm}^3/\text{day}$, respectively (Fig. 4). A high correlation between nitrifying activity calculated by using the methods – on the basis of oxygen consumption (N–BOD) and nitrification products concentration in the water samples inhibited by ATU – points to the correctness of the obtained results. The studies showed rather a strong relationship between suspension quantity and nitrification at St. 1 only (c.c. – 0.7). Moreover, in the Dobięgniewo flooding, a strong negative correlation was observed between dissolved oxygen concentration and nitrifying activity (c.c. – 0.7; $p = 0.07$) and a positive, statistically significant correlation between ammonium nitrogen concentration and nitrification (c.c. 0.8; $p < 0.05$). No significant correlation between the parameters studied and nitrifying activity was observed at the remaining stations.

Discussion

The maximum potential nitrifying activity measured in the Vistula river water ($120 \mu\text{g N/dm}^3/\text{day}$) was clearly lower than that observed in the river Seine [4] and above two orders of magnitude higher than the activity noted for the surface water of Lake Kizaki [5]. The nitrification magnitude observed in the WDR reached the values which are the most similar to the values observed in the Danube river – about $100 \mu\text{g N/dm}^3/\text{day}$ [10] and in the eutrophic Lake Okaro [6], where nitrifying activity of $98 \mu\text{g N/dm}^3/\text{day}$ was noted in the surface water (Tab.3).

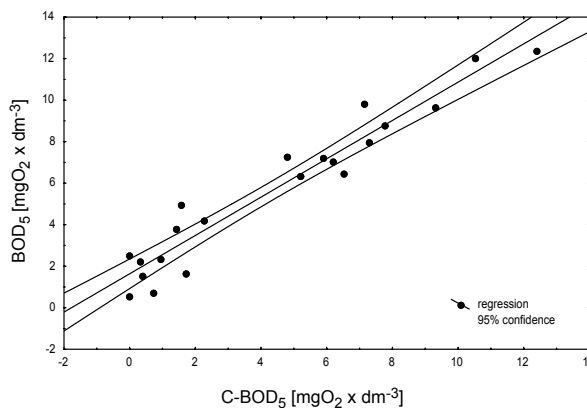


Fig. 5. Relationship between carbonaceous (C–BOD) and general biochemical oxygen demand (BOD) in the WDR water (c.c. 0.96; $n = 21$; $p < 0.01$).

Table 3. A list of nitrifying activity maximum values presented by different authors.

Research area	Water intake	Nitrifying Activity [$\mu\text{g N/dm}^3/\text{day}$]	Authors
Lake Kizaki	surface	0.65	Yoshioka et al. (1985)
Lake Okaro	surface	67-98	Downes (1991)
	above the bottom	134	
Rhone river	surface	28	Feliatra and Bianchi (1993)
Danube river	surface	100	Müller and Kirchesch (1983)
Vistula river (WDR)	surface	120	in the present work
Seine river	surface	340-514	Brion and Billen (2000)
Mosel river	surface	400	Müller and Kirchesch (1983)
Schelde estuary	surface	1120	de Bie et al. (2002)

The results of the studies conducted from April to November 2002 showed a significant influence of the WDR on nitrification process dynamics and its importance to the river oxygen regime. Significant reduction of BOD_5 observed in the reservoir was caused mainly by C- BOD_5 reduction (c.c. > 0.9 at all stations; $p < 0.01$) (Fig. 5). C- BOD_5 reduction was probably connected with suspension intensive sedimentation in the reservoir. Mieszczankin and Ślebioda [32] observed earlier that in the WDR there occurred a significant reduction of C- BOD_5 (about 50%), which was connected, in their opinion, with about 60% sedimentation of the largest allochthonous fraction of suspension, >25 μm in diameter.

A similar reduction of C- BOD_5 was observed in the present study. It was accompanied by nitrification contribution increase to total BOD_5 , and an increase in potential nitrifying activity from the reservoir "entrance" toward the dam. It was probably conditioned by two factors: suspension significant sedimentation and ammonium ions (NH_4^+) larger availability for the nitrifiers at the stations of more lenitic character. A higher contribution of nitrification to oxygen absorption in the water

at St. 3, where the concentration of the largest fraction of suspended particles was significantly reduced, suggested that the nitrifying activity was connected with its smaller fraction. Yoshioka et al. [5] reported that nonactive nitrifiers could be associated with the quickly sinking, largest trypton particles. Oxygen absorption increase for nitrification process was quantitatively insignificant in the water outflowing the reservoir (the differences were not significant statistically). However, during the season, the periods could occur, when this process made 70-100% of BOD_5 total. Such a situation was observed at St. 3 from September to November. The highest N- BOD_5 values and the highest nitrifying activity were noted during this period. The magnitude of oxygen absorption in the nitrification process and N- BOD_5 share in total BOD_5 are comparable with medium and poorly polluted rivers. Muller and Kirchesch [10] observed in the polluted Mosel river N- BOD_5 values amounting to above 11 $\text{mg O}_2/\text{dm}^3$ and several times exceeding C- BOD_5 . In the Danube River the same authors noted N- BOD_7 value at 2-3.3 $\text{mg O}_2/\text{dm}^3$ level and nitrification contribution at the level 20-40% to total BOD_7 .

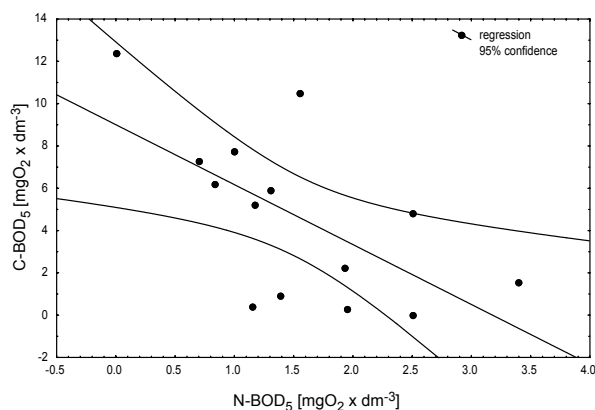


Fig. 6. Carbonaceous and nitric oxygen demand relationship in the WDR water at the river current stations (c.c. - 0.62; $n = 14$; $p = 0.017$).

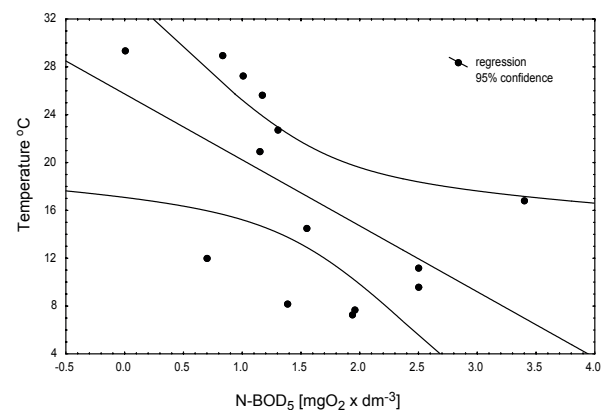


Fig. 7. The relationship between nitric oxygen demand and water temperature in the WDR water at the river current stations (c.c. - 0.58; $n = 14$; $p = 0.032$).

Table 4. Net changes in concentration of ammonium, nitrite and nitrate ions, and mineral nitrogen sum (expressed in $\mu\text{g N}/\text{dm}^3$) in the WDR water after five-day incubation.

parameters	St. 1	St. 2	St. 3
N-NH ₄	+52	-230	-291
N-NO ₂	+94	+67	+36
N-NO ₃	*-122	+111	+231
DIN	+14	-52	-24

*except for the data from November, it equals $+34\mu\text{gN}/\text{dm}^3$

Nitrification process rate is determined by many factors, such as temperature, oxygen concentration, bacteria biomass or NH₄⁺ substratum concentration. That is why it is difficult to assess which of the above-mentioned parameters decided about the described seasonal course of this process in the WDR. It seems that nitrification in the reservoir depths was not limited by dissolved oxygen concentration. The lowest oxygen concentration in the surface water (about $2\text{ mg}/\text{dm}^3$) was observed at Station 3. in May. However, the most frequent oxygen concentration was higher than $4.8\text{ mg}/\text{dm}^3$ (excluding three cases). Such oxygen availability rather should not limit nitrification, as the process could go on even at very low oxygen concentrations. Hao and Martinez [33] stated nitrification at oxygen concentration of $0.2\text{--}0.6\text{ mg}/\text{dm}^3$, and Downes [6] even below $0.12\text{ mg}/\text{dm}^3$. Under such conditions the main nitrification products are nitrites and simultaneous nitrate reduction to gaseous nitrogen as a result of denitrifying bacteria respiration, is also probable. In the surface water where the samples were collected, such situations were not observed. However, reduction conditions existed in the water above sediments. Oxygen concentration limiting influence on nitrifiers activity was probable only in the case of heterotrophic bacteria high activity.

It was noticed that nitrifying activity peaks at the river current stations were connected with temperature and

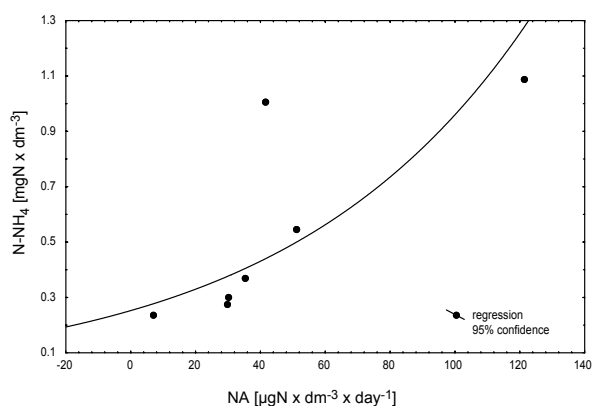


Fig. 8. Nitrifying activity and ammonium nitrogen concentration relationship observed in the Dobiegniewo flooding water (c.c. = 0.79; n = 7; p = 0.037).

C-BOD₅. Such a relationship is confirmed by high and statistically significant negative correlations between C-BOD₅ and water temperature, and N-BOD₅ at these stations (Figs. 6, 7). However, a close relationship between water temperature and potential nitrifying activity was not found; it is noticeable that activity collapse at St. 1 in July and at St. 2 and 3 in August was observed in the period when the temperature at these stations reached maximum values during the season and in every case was near or exceeded 29°C . These results are contradictory to other authors' studies. Dojlido [34] stated nitrifying activity increase also at the temperature above 30°C . Grunditz and Dalhammar [28] determined optimum temperature for bacteria of *Nitrosomonas* genus as 35°C and 38°C for the genus *Nitrobacter*. The cause for such different results can be the fact that during the determination of nitrifiers optimum temperature, pure bacterial cultures were used, avoiding interaction between microorganisms. Such interactions do exist in water with natural bacterial microflora. Together with water temperature increase, heterotrophic bacteria activity increase was also probable, which could repress plankton nitrifiers activity. Such an effect is possible when heterotrophic biomass increases, forming on the organic matter particles surface a layer absorbing dissolved oxygen and limiting its availability to nitrifiers. Such interactions were observed during the studies concerning microorganisms composing biofilm [35]. A similar explanation was suggested by Yoshioka et al. [5] for their results of trypton-connected nitrifying activity studies. It is also known that an inflow of potentially easy available carbon compounds can cause microorganism activity shift toward heterotrophy [33, 37]. Therefore during summer period, at high C-BOD₅ values, competition for oxygen and autotrophs activity limitation could occur.

Microbiological studies conducted parallel to nitrifying activity measurements (Wilk 2002, unpublished results) showed a high reduction of heterotroph abundance in the reservoir depths, compared with earlier investigations [36]. A negative correlation found between the total number of heterotrophic bacteria and suspended matter concentration, and potential nitrifying activity at the station of fluvial character in Płock (c.c. - 0.7) can confirm the superiority of heterotrophs "involved" in seston organic matter mineralization over planktonic nitrifiers activity. Similar conclusions can be drawn when observing net changes of nitrogen mineral forms concentration in water after a 5-day-incubation period (Tab. 4). The dissimilarity of processes taking place in water at more lenitic stations (St. 2 and St. 3) and at the station of firmly lotic character, can be clearly seen. The processes of nitrite release and ammonium ions release dominated at St. 1, which testifies to organic seston mineralization. At the lenitic stations (St. 2 and St. 3), reduction of ammonium ions concentration and nitrates concentration increase were observed most frequently. This may confirm the increase in autotrophic nitrification contribution to nitrogen conversions in the WDR water.

The relationships between nitrifying activity and environmental factors at the shallow flooding in Dobięnowo were of less complex character. Cross-determined high correlations for activity, oxygen concentration and ammonia form of nitrogen concentration point to close relationships between these parameters. Probably, in the flooding, the main factor deciding about the appearance and the magnitude of nitrification is substrate (NH_4^+) releasing from bottom sediments. At the river current stations no close relationship between the concentration of ammonium form of nitrogen and nitrification was observed. In the flooding, water temperature increases were accompanied by oxygen concentration decrease, ammonium nitrogen concentration increase and related increase in activity and oxygen consumption during nitrification processes (Fig. 8). It seems that at the flooding station "sediment metabolism" has a higher influence on nitrification processes than at the current stations, which can be a result of longer retention time of water being in touch with sediments. Nitrification process seasonal course in flooding can be disturbed by sediment resuspension, probably on windy days. In the river about 80% of nitrifying bacteria can occur in about 1 cm thick sediment surface layer [8, 9]. That is why sediment resuspension can be a significant source of nitrifiers and an important factor determining nitrifying activity in the WDR shallow zones. A higher nitrifying activity in water being in touch with sediments was observed, among others, by Downes [6], Pauer and Auer [12].

The superiority of ammonium nitrogen release from sediments over nitrification process was confirmed during the WDR studies. Despite nitrification activity reaching up to $120 \mu\text{g N/dm}^3/\text{day}$ during the research season, nitrate concentration significant reduction was observed in the reservoir at more lenitic stations, which pointed to phytoplankton assimilation and denitrification processes in bottom sediments. It should be stressed, however, that the accurate determination of factors influencing nitrifying activity in the WDR water was not possible due to relation complexity and the small number of measurements. Nitrifying activity values measured should be treated as potential ones. De Bie et al. [16] observed that potential nitrifying activity values measured under laboratory conditions could be higher in relation to in situ measurements, particularly in autumn, when the temperature could be a factor limiting nitrification in a natural environment. Considering environmental factors variability it is difficult to shift experimental results into situations in the ecosystem. In the future, nitrification measurement studies should be connected with determination of nitrifier biomass or, at least, their abundance.

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References

1. DOJLIDO J. R. Chemistry of water and water pollution. Wydawnictwo Ekonomia i Środowisko 1995 (in Polish).
2. SURMACZ-GORSKA J., GERNAEY K., DEMUYNCK C., VANROLLEGHEM P., VERSTRAETE W. Nitrification monitoring in activated sludge by oxygen uptake rate (OUR) measurements. *Wat. Res.* **30** (5), 1228, 1996.
3. KÖNIG A., BACHMANN T. T., METZGER J. W., SCHMID R. D. Disposable sensor for measuring the biochemical oxygen demand for nitrification and inhibition of nitrification in wastewater. Springer-Verlag, Appl. Microbiol. Biotechnol. **51**, 112, 1999.
4. BRION N., BILLEN G., 2000. Wastewater as a source of nitrifying bacteria in river systems: the case of the river Seine downstream from Paris. *Wat. Res.* **34** (12), 3213, 2000.
5. YOSHIOKA T., TAKAHASHI M., SAIJO Y. Active nitrification in the hypolimnion of Lake Kizaki in early summer. 1. Nitrifying activity of rapidly sinking particles. *Arch. Hydrobiol.* **104** (4), 557, 1985.
6. DOWNES M. T. The production and consumption of nitrate in an eutrophic lake during early stratification. *Arch. Hydrobiol.* **122** (3), 257, 1991.
7. GELDA R. K., BROOKS C. M., EFFLER S. W., AUER M. T. Interannual variations in nitrification in a hypereutrophic urban lake: occurrences and implications. *Wat. Res.* **34** (4), 1107, 2000.
8. CURTIS E. J. C., DURRANT K., HARMAN M. M. I. Nitrification in rivers in the Trent basin. *Wat. Res.* **9**, 255, 1975.
9. GARLAND J. H. N. Benthic nitrification in rivers. [w] Interactions between sediments and fresh water. Proceedings of an international symposium held at Amsterdam, the Netherlands, 1976. Dr W. Junk B. V. Publishers, 1977.
10. MÜLLER V. D., KIRCHESCH V. On nitrification in the rivers Moselle and Danube. *Arch. Hydrobiol. Suppl.* **68**, 63, 1983.
11. SCOTT J. A., ABUMOGHLI I. Modelling nitrification in the river Zarka of Jordan. *Wat. Res.* **29** (4), 1121, 1995.
12. PAUER J. J., AUER M. T. Nitrification in the water column and sediment of a hypereutrophic lake and adjoining river system. *Wat. Res.* **34** (4), 1247, 2000.
13. KHOLDEBARIN B., OERTLI J. J. Effect of suspended particles and their size on nitrification in surface water. *J. Wat. Pollut. Control. Fed.* **49**, 1693, 1977.
14. HUTCHINSON G. E. A treatise on limnology. Vol. 1. Geography, physics, and chemistry. John Wiley & Sons, Inc. New York, 1957.
15. CIRELLO J., RAPAPORT R. A., STROM P. F., MATULEWICH V. A., MORRIS M. L., GOETZ S., FINSTEIN M. S. The question of nitrification in the Passaic River, New Jersey: analysis of historical data and experimental investigation. *Wat. Res.* **13**, 525, 1979.
16. DE BIE M. J. M., STARINK M., BOSCHKER H. T. S., PEENE J. J., LAANBROEK H. J. Nitrification in the Schelde estuary: methodological aspects and factors influencing its activity. *FEMS Microb. Ecol.* **42**, 99, 2002.
17. KENTZER A., GIZIŃSKI A., MIESZCZANKIN T. Hydrochemistry of the Lower Vistula River in the section Płock – Toruń during the period 1986-1995: The influence of the Włocławek Dam Reservoir on water quality. *AUNC Limnological Papers*, **20**, 13, 1999.
18. KENTZER A. Hydrobiology of the Vistula River between Wyszogród and Toruń. An assessment of the influence of the Włocławek dam on the structure and functions of the river ecosystem. Part IV: Hydrochemistry of the Vistula be-

- tween Płock and Toruń. AUNC Limnological Papers, **21**, 33, **2000**.
19. GRZEŚ M. Problems of the „Włocławek” fall and its reservoir. *Czasopismo Geograficzne* **54**, 439, **1983** (in Polish).
 20. ŻYTKOWICZ R., L.A. BŁEDZKI, A. GIZIŃSKI, A. KENTZER, R. WIŚNIEWSKI, ŻBIKOWSKI J. WDR. Ecological characteristics of the only dam reservoir of the planned cascade on the Lower Vistula River. In: The functioning of rivers and reservoirs. SGGW – AR, **1990** (in Polish).
 21. BABIŃSKI Z. The present-day fluvial processes of the Lower Vistula River. *Prace Geograficzne* 157, IGIPIZ PAN, Warszawa **1992** (in Polish).
 22. GŁOGOWSKA B. Hydrobiology of the Vistula River between Wyszogród and Toruń. An assessment of the influence of the Włocławek dam on the structure and functions of the river ecosystem. Part II: A geographical and hydrological profile of the study area. AUNC Limnological Papers, **21**, 11, **2000**.
 23. GRZEŚ M. Ice jams and floods on the Lower Vistula River. Mechanisms and processes. IGIPIZ PAN, **1991** (in Polish).
 24. GLAZIK R. Hydrological and geomorphological problems of the Włocławek Reservoir. Ponding of the Vistula River, morphometry and hydrology of the reservoir. 44 Zjazd Polskiego Towarzystwa Geograficznego, Toruń **1995** (in Polish).
 25. GIZIŃSKI A. Hydrobiology of the Vistula River between Wyszogród and Toruń. An assessment of the influence of the Włocławek dam on the structure and functions of the river ecosystem. Part I: General introduction – topics and preliminary effects of the research programme. AUNC Limnological Papers, **21**, 3, **2000**.
 26. BANACH M. Hydrological and geomorphological problems of the Włocławek Reservoir. Accumulation of sediments and ice in the reservoir. 44 Zjazd Polskiego Towarzystwa Geograficznego, Toruń **1995** (in Polish).
 27. FELIATRA F., BIANCHI M. Rates of nitrification and carbon uptake in the Rhone River plume (Northwestern Mediterranean Sea). *Microb. Ecol.* **26**, 21, **1993**.
 28. GRUNDITZ C., DALHAMMAR G. Development of nitrification inhibition assays using pure cultures of *Nitrosomonas* and *Nitrobacter*. *Wat. Res.* **35** (2), 433, **2001**.
 29. WOOD L. B., HURLEY B. J., MATTHEWS P. J. Some observations on the biochemistry and inhibition of nitrification. *Wat. Res.* **15**, 543, **1981**.
 30. HERMANOWICZ W., DOŻAŃSKA W., DOJLIDO J., KOZIOROWSKI J. Physico-chemical analyses of water and sewage. Wydawnictwo Arkady. Warszawa **1976** (in Polish).
 31. WEZERNAK C. T., GANNON J. J. Oxygen-nitrogen relationships in autotrophic nitrification. *Appl. Microbiol.* **15**, 1211, **1967**.
 32. MIESZCZANKIN T., ŚLEBIODA K. Biochemical oxygen demand of suspended matter in the Vistula river. [in print]
 33. HAO X., MARTINEZ J. Removing nitrate and ammonium from drainage water by simulation of natural biological processes. *Wat. Res.* **32** (3), 936, **1998**.
 34. DOJLIDO J. Influence of temperature increase on biochemical processes occurring in surface waters. *Mater. Bad. IMiGW nr 7*, 116, **1976** (in Polish).
 35. NOGUEIRA R., MELO L. F., PURKHOLD U., WUERTZ S., WAGNER M. Nitrifying and heterotrophic population dynamics in biofilm reactors: effects of hydraulic retention time and the presence of organic carbon. *Wat. Res.* **36**, 469, **2002**.
 36. DONDESKI W., WILK I. Bacteriological studies of water and bottom sediments of the Vistula river between Wyszogród and Toruń. *Pol. J. Environ. Stud.* **11** (1), 33, **2002**.
 37. BUTTURINI A., BATTIN T. J., SABATER F. Nitrification in stream sediment biofilms: the role of ammonium concentration and DOC quality. *Wat. Res.* **34** (2), 629, **2000**.