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## SEASONAL CHARACTER OF CHANGES IN NITROGEN FORMS IN WATERS OF KORYTÓW AND ŁĄKI KORYTOWSKIE RETENTION RESERVOIRS

The aim of the research was to determine the concentrations of nitrogen forms in the waters of Korytów and Łąki Korytowskie reservoirs located on the Pisia-Gagolina River, which flows through the Żyrardów area. Four analyses of water quality in both reservoirs were performed and their results were compared. After detailed examination, the influence of such factors as seasonal character, characteristics and location of the reservoirs was analyzed. Based on the research results, the quality of the water can be described as satisfactory. The research proved significant variability of certain nitrogen forms over time. The concentrations of ammonium, nitrates, nitrites and total nitrogen were variable, depending on the location of research sites. The analysis of nitrogen forms' concentrations proved some disturbances of a natural nitrogen cycle over time. Increased concentrations of total nitrogen and nitrates(V) indicate that the water in the reservoirs can be prone to agricultural pollution.

### 1. INTRODUCTION

Nitrogen is a biogenic element, appearing in surface waters in a form of organic compounds as well as inorganic complexes, such as  $\text{NH}_4^+$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$  ions. Nitrogen compounds enter bodies of water from natural sources (as a result of organic matter decomposition) and from anthropogenic ones. The greatest contribution to the sources connected with industrial activity is reported from: municipal sewage systems, industrial sewage systems, flows from fields fertilized with nitrogen compounds and deposition of atmospheric pollutants [2].

Nitrogen, as a basic component of proteins, is indispensable to life forms. In aqueous environment, it is subject to various changes. To play its metabolic and structural role, this element has to be taken from aqueous environment and built into cellular structures of organisms. The main sources of nitrogen for water plants are ammonium salts and nitrates. Physicochemical conditions observed in bodies of surface waters

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cause changeable preferences for assimilating nitrates or ammonium form. In the environment displaying acid reaction, nitrates are assimilated faster, while in the basic one – ammonium form [1].

Industrial activity causes an excessive enrichment of surface waters with biogenic complexes (mainly nitrogen and phosphorus). In order to ensure an appropriate quality of water resources, the Nitrates Directive 91/676/EWG has been implemented in Poland. It aims at supporting the implementation of rules of good agricultural practice [5]. According to the Nitrates Directive objectives, certain areas where rivers, lakes, inshore waters and underground waters can be prone to agricultural pollution, shall be outlined. In order to avoid water pollution, some special precautions have to be applied within these areas, including effective usage of chemical fertilizers and proper storage of natural fertilizers. Appropriate planning of these tasks will certainly bring great benefits to the farming industry, without posing threat to the environment. In Poland, 21 areas which are extremely exposed to agricultural nitrates, have been outlined. The total surface of these areas covers 7760 square km, which accounts for 2.48% of the surface of the country [6].

Therefore, an important issue in the protection of water reservoirs against the processes leading to their eutrophication is the control of biogenic elements concentration.

## 2. SUBJECT DESCRIPTION

The Pisia-Gągolina River flows through the Żyrardów area located in the county of Mazovia (Mazowsze). In the upper reaches, the river is a relatively shallow (0.2–0.7 m) natural flow of varied width, meandering in some places. Its catchment area consists mainly of sands and gravels of numerous alluvial cones, which create alluvial plains with well-developed, light and well-permeable soils. Down the river there are artificial weirs accompanied by bodies of water. They are multi-task reservoirs with the surface varying from 0.7 ha to 14 ha and the volume of about 10,000 m<sup>3</sup> to 400,000 m<sup>3</sup>. Their total water surface is about 120 ha, and the total surface of the catchment area calculated in accordance with the Hydrographic Division of Poland (IMGW – the Institute of Meteorology and Water Management) covers 501.4 km<sup>2</sup> [12], [6]. Some of the most important reservoirs are: Radziejowice, Hamernia and Łąki Korytowskie. The main function of these reservoirs are: retention of water in the period of increased flow and river alimentation in the period of low water levels. These reservoirs balance the flow of the river below the town of Żyrardów. The recreation functions are noticeable as well, especially those of Łąki Korytowskie reservoir, which was thoroughly modernized in 1997. All the bodies of water are also used for sports fishing.

### 2.1. KORYTÓW RESERVOIR

Korytów reservoir is located in the village of Korytów, 3.5 km far from the centre of Żyrardów. Its front barrage, with the other at the top, is situated on the 38th km of the course of the Pisia-Gągolina River, and it closes the catchment area covering 73.0 km<sup>2</sup>. The body was created in 1910 by the damming up of the river waters by means of a front earth dam with a weir having abutments made of bricks. It is located in a natural valley, without side dams. The water body has not any other devices to let flood water in, the whole flow goes through the main section of the weir [11], [12]. Due to significant surface (3.4 ha) and natural shape of the shoreline, as well as shallow depth in the backwater area, the body is a natural refuge for animals and plays a role of a bird sanctuary [12].

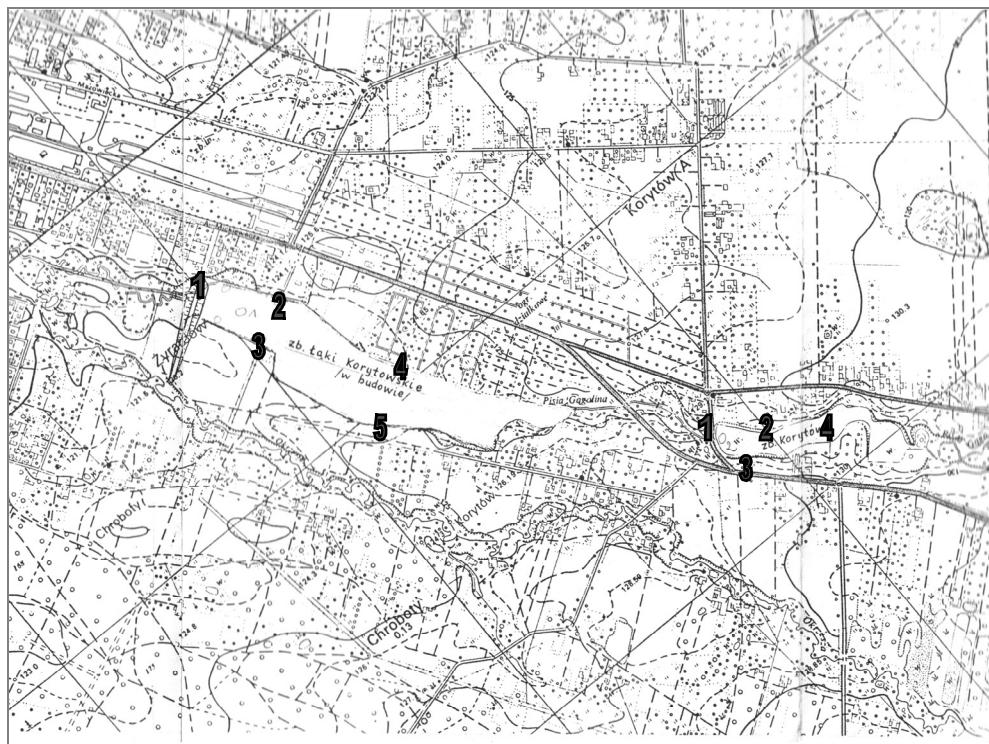


Fig. 1. Map of Korytów and Łąki Korytowskie reservoirs on the Pisia-Gągolina River

### 2.2. ŁĄKI KORYTOWSKIE RESERVOIR

The reservoir is situated on the 36th km of the course of the Pisia-Gągolina River, in the south-eastern part of Żyrardów. It is a lake with the surface of 13.8 ha. In the

natural part of the valley, it is 1160 m long, and its width varies from 110 to 150 m. The maximum water depth by a dam is 4.5 m, while the total volume of the lake is 401,000 m<sup>3</sup>. On its right bottom side, an estate of detached houses is situated, and at the upper part of the lake there are garden plots. The left lower side is covered with meadows, areas of bushes, and little enclaves of forest. The reservoir protects the water, plays bioclimatic and biotic role and modifies a natural landscape. It levels off the flows of water, decreases natural and economic losses during floods and periods of low water level. On the left shore a beach is located, as well as tourist and holiday facilities [12].

### 3. MATERIALS AND METHODS

The research was aimed at two retention reservoirs: Kotyrów (K) and Łąki Korytowskie (ŁK). In the area of the reservoirs, research sites were chosen: four at Kotyrów reservoir and five at Łąki Korytowskie reservoir. The samples of surface water were taken from each measuring point in four research periods: December 2006, February, March and May 2007. The scope of research covered the analysis of the content of total nitrogen and its forms: ammonium, nitrate and nitrite nitrogen. The analysis was carried out in accordance with standard methodology [3].

### 4. RESEARCH

Figures 2–5 present the concentrations of four forms of nitrogen ( $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$  and  $\text{N}_{\text{tot}}$ ) in subsequent research periods at the research sites.

In the period analysed, ammonium nitrogen remained at the average level of 0.63 mg N dm<sup>-3</sup> for Łąki Korytowskie reservoir (ŁK) and 0.4 mg N dm<sup>-3</sup> for Kotyrów reservoir (K). During the whole research period, in the area of ŁK the ammonium nitrogen concentration reached higher levels (0.08–2.71 mg N dm<sup>-3</sup>) compared with the K area (0.12–0.69 mg N dm<sup>-3</sup>). The lowest concentrations of  $\text{NH}_4^+$  for both reservoirs were reported at research sites behind the dam. The concentrations were the highest in the area of retention water, and reached their maximum in the spring period (April). Taking into consideration a high level of water at that time, the air temperature above zero and rainfall, the supposed causes for high concentrations could be as follows: the flow of ammonium compounds from the surrounding meadows and wastewater channelling from the households. An uncontrolled, coincidental emission of pollutants cannot be excluded either.

Among the forms of nitrogen the most widespread ones were nitrate(V) ions ( $\text{N}-\text{NO}_3^-$ ). The main sources of nitrates are municipal wastewater and intensive farming. Fertilization of the farmlands located by the river is responsible for the enhanced concentrations of nitrates, especially during rainfalls [2], [3], [9].

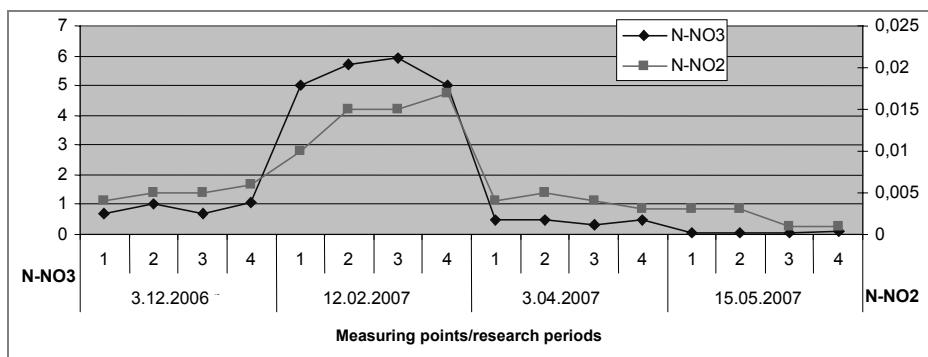


Fig. 2. Seasonal changes of nitrogen forms (N-NO<sub>3</sub> and N-NO<sub>2</sub> [mg N/dm<sup>3</sup>]) in Korytów reservoir

Average nitrate concentrations in the research period reached 1.7 mg N dm<sup>-3</sup> for K and 1.3 mg N dm<sup>-3</sup> for ŁK. The total N-NO<sub>3</sub><sup>-</sup> concentrations varied for both reservoirs, ranging from 0.05 to 5.9 mg N dm<sup>-3</sup> and from 0.09 to 5.0 mg N dm<sup>-3</sup>, respectively. The highest concentrations were measured in February 2007. Lower nitrate concentrations were reported in December, March and May within the scope of temporal changes. They were caused by the contemporary weather conditions as well as the growing season, which in higher temperatures leads to intense assimilation of nitrates and orthophosphates.

Another form of nitrogen analysed was nitrate(III) ions. They are intermediate products in the nitrogen cycle. Their presence in water is caused mainly by oxidation of ammonia in the nitrification process. Nitrate(III) ions are often called nitrite ions, and they are an unstable form of nitrogen. Depending on conditions, they can be either oxidized to nitrates or reduced to ammonium ions [2], [3], [10].

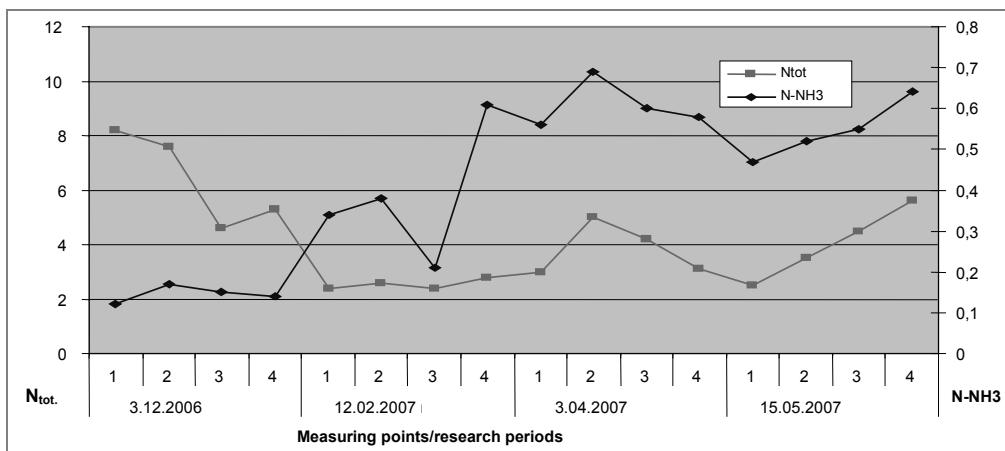


Fig. 3. Seasonal changes of nitrogen forms (N<sub>tot</sub> and N-NH<sub>3</sub> [mg N/dm<sup>3</sup>]) in Korytów reservoir

The average concentration of  $\text{N-NO}_2^-$  ions was  $0.01 \text{ mg N/dm}^3$  for both reservoirs. The concentrations reported here were relatively even, both over time and all over the reservoirs, which is presented in figures 2 and 4, showing fluctuations of  $\text{N-NO}_2^-$  concentrations in particular months. In the period reported, higher concentrations ( $0.01\text{--}0.017 \text{ mg N dm}^{-3}$ ) in Korytów were marked only in February, whereas for ŁK, they were recorded in February and May ( $0.15\text{--}0.020 \text{ mg N dm}^{-3}$ ). In February, higher concentration of nitrates(III) corresponded to higher concentration of nitrates(V) and low concentration of ammonium nitrogen. As it was a winter period, the reservoirs were covered with ice and thermal stagnation occurred in water. The water flowing through reservoirs, after having flown through dams, is rich in oxygen, which explains low concentration of nitrites. Lower level of water table and laminar flow of water in winter periods make nitrates cumulate in retention reservoirs, especially in the areas of deep water (around dams).

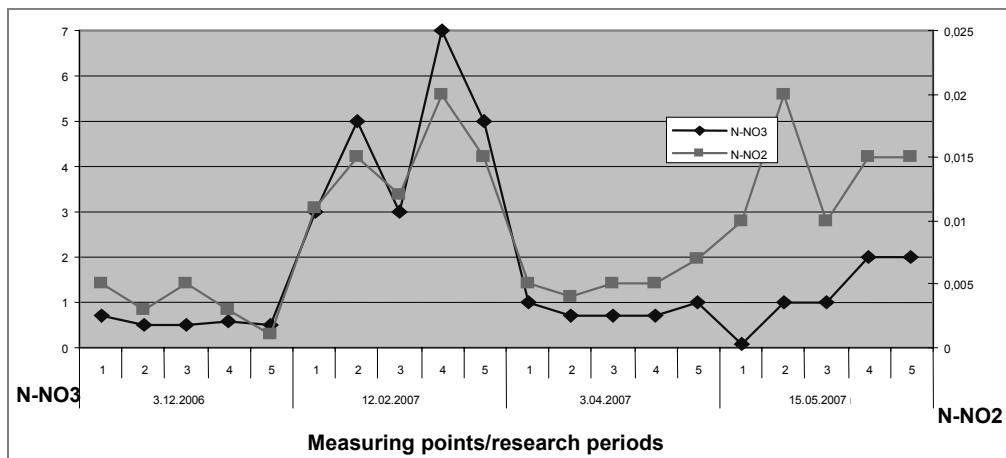


Fig. 4. Seasonal changes of nitrogen forms ( $\text{N-NO}_3$  and  $\text{N-NO}_2$  [ $\text{mg N/dm}^3$ ]) in Łaki Korytowskie reservoir

The analysis of the research results proves that the total nitrogen concentration is inversely proportional to that of ammonium nitrogen. In Korytów reservoir, when the concentration of total nitrogen decreased in winter time, ammonium nitrogen concentration was reported to increase. In April and May, the tendency was opposite for both forms. Since May, the increase of  $\text{NH}_4^+$  in ŁK reservoir was observed along with the decrease of the total nitrogen content. The highest concentration of ammonium form, reaching up to  $2.7 \text{ mg N dm}^{-3}$ , was reported in May along the right shore of the lake, approximately 300 meters far from the dam. The above changes were dependent on the growing season processes, the oxygenation and the level of water table and temperature.

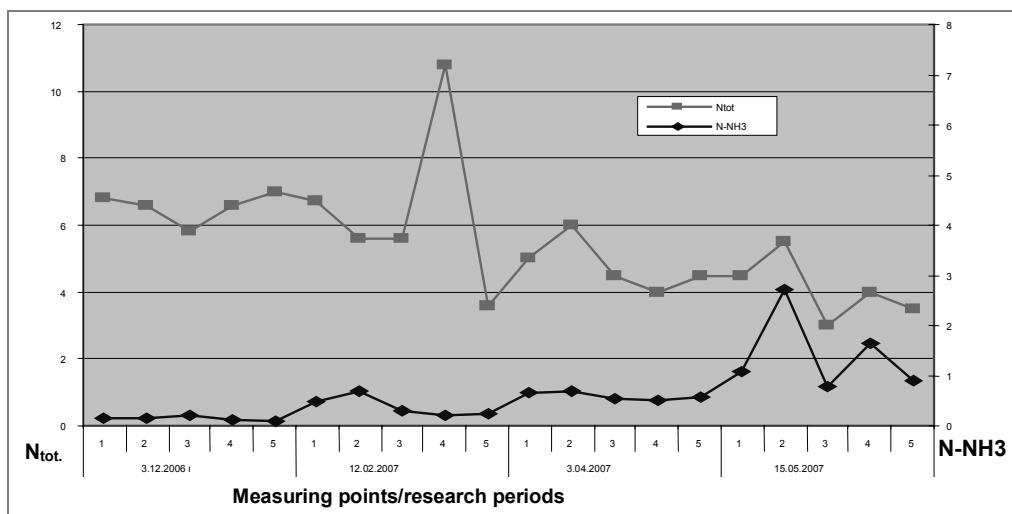


Fig. 5. Seasonal changes of nitrogen forms ( $N_{tot}$ . and  $N\text{-NH}_3$  [ $\text{mg N/dm}^3$ ]) in Łąki Korytowskie reservoir

Statistical analysis showed significant correlations between concentrations of nitrate and nitrite nitrogen in both reservoirs, which can be the basis of functional relation. The correlation coefficients were 0.95 and 0.62 for K and ŁK, respectively. Equations and correlation ceofficients are presented in figures 6 and 7 ( $p < 0.005$ ,  $n = 16$  for K and  $n = 20$  for ŁK).

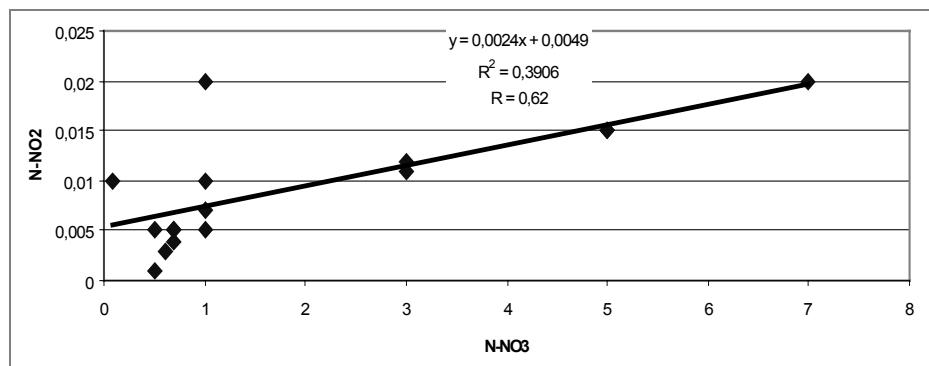


Fig. 6. Relationship between nitrate-nitrogen(III) and (V) in research period of December 2006–May 2007 in Łąki Korytowskie reservoir

The concentrations of other nitrogen forms did not correlate in any significant way.

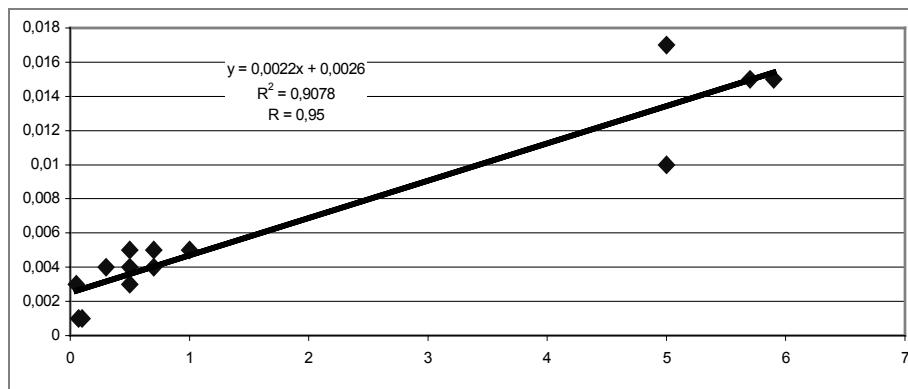


Fig. 7. Relationship between nitrate-nitrogen(III) and (V) in research period of December 2006–May 2007 in Korytów reservoir

## 5. DISCUSSION

The results obtained prove some temporal and spatial variations in the concentrations of indicators analysed in the retention reservoirs in the upper catchment area of the Pisia-Gagolina River. Concentration values corroborate similar spatial variations reported in 2005; however, the concentrations of nitrogen forms measured in the years 2006 and 2007 were higher [11]. The nitrogen concentrations in subsequent years prove that the inflow of biogenic substances from anthropogenic sources and feeding from some internal source have occurred [11]. Having analysed the changes of nitrogen concentrations in both reservoirs, the differences in water quality can be reported, which may be caused by dissimilar morphological characteristics and differences in development of adjoining areas. The research shows that the waters downriver are richer in nitrogen [6], [7], [10]. High concentrations of total nitrogen and periodically high concentrations of ammonium nitrogen indicate the inflow of polluted water from the catchment area. It is agricultural activities and uncontrolled emissions of municipal wastewater from the surrounding towns, whose water and sewage management systems proved to be inefficient, that are primarily responsible for the river pollution.

The waters of the above-mentioned reservoirs meet the criteria for outlining waters prone to nitrogen compound pollution resulting from agricultural activities established by the Directive of Minister for the Environment on December 23, 2002. The concentrations of total nitrogen and nitrates were 5.4 and 1.6 mg N/dm<sup>3</sup>, respectively. These numbers exceed the critical values ( $N_{tot.} > 1.5 \text{ mg N/dm}^3$  for stagnant water and  $N_{tot.} > 5 \text{ mg N/dm}^3$  and  $N-NO_3^- > 2.2 \text{ mg N/dm}^3$  for flowing water) above which eutrophication occurs.

The quality of retention water is proved to be dependent on the sort and quantity of pollutants and their susceptibility to degradation as well as a self-cleaning ability of

rivers and reservoirs [8]. In the case of the Pisia-Gagolina River, the self-cleaning process was accompanied by an increasing level of anthropogenic pollution (especially of nitric compounds) caused by industrial changes in the catchment area of the river, e.g. an increase in the quantity of household waste and appearance of illegal landfill sites, motorization and construction industry development, water supply system development, etc. Retention reservoirs, which reduce the rate of the water flow in rivers, contribute to an increasing water eutrophication.

## 6. CONCLUSIONS

1. In the period of time between 2005 and 2007, an increase in the level of nitric nitrogen in the water collected from both reservoirs has been noted.
2. Pollutants that are discharged into the river are connected with the agricultural production in the adjacent areas.
3. The research indicates that pollution of water with nitric nitrogen in the deeper parts of both reservoirs is caused by the inflow of polluted water and the internal feed of the reservoirs.
4. An increased quantity of biogenes introduced into the rivers accelerates the eutrophication process.

## BIBLIOGRAPHY

- [1] CHEŁMICKI W., *Woda – zasoby, ochrona, degradacja*, Wydawnictwo Naukowe PWN, Warszawa, 2001.
- [2] DAVID A.J., *Ekologia wód płynących*, Wydawnictwo Naukowe PWN, Warszawa, 1998.
- [3] HERMANOWICZ W., DOJLIDO J., DOŻAŃSKA W., KOZIOMSKI B., ZERBE J., *Fizyczno-chemiczne badanie wody i ścieków*, II ed., Arkady, Warszawa, 1999.
- [4] Dyrektywa Rady 91/676/EWG dotycząca ochrony wód przed zanieczyszczeniami powodowanymi przez azotany pochodzenia rolniczego (DzU WE nr L 375, z 31.12.1991 r.)
- [5] Rozporządzenie Ministra Środowiska z dnia 23 grudnia 2002 w sprawie kryteriów wyznaczania wód wrażliwych na zanieczyszczenie związkami azotu ze źródeł rolniczych. Dostępne w Internecie.
- [6] Informacja na temat wyznaczania w Polsce obszarów szczególnie narażonych na azotany pochodzenia rolniczego i niezbędnych działań z tym związanych [online], Warszawa, 2003, Ministerstwo Środowiska, Departament Zasobów Wodnych, [dostęp: listopad 2003]. Dostępny w Internecie: [http://www.mos.gov.pl/2materiały\\_informacyjne/raporty\\_opracowania/obszar\\_azotan.pdf](http://www.mos.gov.pl/2materiały_informacyjne/raporty_opracowania/obszar_azotan.pdf)
- [7] KOSZELNIK P., TOMASZEK J., *Retencja azotu w zbiorniku solińskim*, II Kon. Inż. Środ., 2005, 543–551.
- [8] KOSZELNIK P., *Zmiany stężeń związków azotu i fosforu w wodach zbiorników zaporowych Solina-Myczkowice w latach 1970–2005*, Inż. i Och. Śr., 2007, 10, nr 4, 309–319.
- [9] LAMPERT W., SOMMER U., *Ekologia wód śródlądowych*, Wydawnictwo Naukowe PWN, 2001.
- [10] MIGASZEWSKI Z.M., GALUSZKA A., *Baseline versus background concentration of trace elements in sediments of Lake Wigry, NE Poland*, Limn. Rev., 2003, 3, 165–171.
- [11] WOJTKOWSKA M., *Charakterystyka hydrochemiczna górnej zlewni rzeki Pisi-Gagoliny*, Inf. i Ekol. Ter. Wiejs., 2006, 189–196.

- [12] ZAWADZKI K., *Ocena stanu czystości wód zlewni rzeki Pisi-Gagoliny*, 2002.
- [13] ZAWADZKI K., *Ogólna charakterystyka warunków hydrologiczno-meteorologicznych powiatu żyrardowskiego wraz z charakterystyką wybranych potencjalnych źródeł zagrożeń środowiska przyrodniczego*, Żyrardów, 2003.

#### SEZONOWOŚĆ ZMIAN FORM AZOTOWYCH W WODACH ZBIORNIKÓW RETENCYJNYCH KORYTÓW I ŁĄKI KORYTOWSKIE

Celem badań było określenie stężeń form azotowych w wodach zbiorników Korytów i Łąki Korytowskie zlokalizowanych na rzece Pisi-Gagolinie płynącej przez powiat żyrardowski. Otrzymane stężenia różnych form azotu w dwóch zbiornikach oznaczone w wodzie pobieranej czterokrotnie porównano ze sobą i oceniono, biorąc pod uwagę wpływ sezonu, a także charakter i położenie zbiornika. Na podstawie uzyskanych wyników jakość wody w zbiornikach można określić jako dobrą. Badania wykazały dużą zmienność poszczególnych form azotu, zależną od czasu poboru. Zawartość amoniaku, azotanów, azotynów i azotu ogólnego w analizowanych zbiornikach zmieniała się również w zależności od położenia stanowisk badawczych. Analiza stężeń form amonowych wykazała zaburzenia naturalnego cyklu azotowego w czasie. Podwyższone stężenia azotu ogólnego i azotanów(V) wskazują, że wody badanych zbiorników mogą być podatne na zanieczyszczenia pochodzenia rolniczego.