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A. BEDNAREK*, M. ZALEWSKI*,**

POTENTIAL EFFECTS OF ENHANCING DENITRIFICATION RATES IN SEDIMENTS OF THE SULEJÓW RESERVOIR

Denitrification is quantitatively the most important process of removing nitrates from freshwater ecosystems, thus contributing to the reduction of eutrophication. Littoral denitrification rates in a research period from 1998–2001 ranged from 0 to 833 μ mol N₂ m⁻² h⁻¹ and was mainly determined by organic carbon availability in the sediments (r = 0.6). It was calculated that 18.5% of the external total nitrogen load incoming to the reservoir was removed from the bottom sediments via denitrification. This value can be increased by enhancing sedimentation of organic matter, thus increasing the organic carbon content in littoral zones of the upper section of the reservoir. Enhanced denitrification lowers the N/P ratio and inhibits phytoplankton growth, especially during spring period. During summer, water temperature increases and cyanobacteria dominate, lowering the N/P ratio, which may provide an advantage in competition for nutrients over other phytoplankton groups.

1. INTRODUCTION

Denitrification is the most important process of nitrogen removal from aquatic systems. In this process, facultative anaerobic bacteria transform nitrate or nitrite into nitrogen gas, which is released to the atmosphere [15]. In freshwater ecosystems, denitrification primarily occurs in the sediments, but its rate is highly variable both in different systems [23] as well as over time within one system [17], [5]. Denitrifying bacterial activity is stimulated by an increase in water temperature [22], [28], low redox potential [22] and anaerobic conditions [13], [28]. However, nitrate and organic matter availability are the main factors limiting denitrification rates [30], [25], [14]. The main goal of ecohydrology is to increase the ecosystem's resistance to human activity [31]. Enhancement of denitrifiers by controlling hydrological parameters, i.e., by reducing high levels of ambient nitrate – an efficient and low-cost tool for preventing eutrophication – is critical, especially in the areas where nitrogen loads from the catchment increase due to human activi-

^{*} University of Łódź, Department of Applied Ecology, ul. Banacha 12/16, 90-237 Łódź, Poland; agnik@biol.uni.lodz.pl

^{**} International Center for Ecology, Polish Academy of Sciences, ul. Tylna 3, 90-364 Łódź, Poland.

ties [31], [19].

The aims of the study were as follows: to assess the denitrification role in nitrogen balance of the Sulejów Reservoir, to determine the main environmental factors influencing this process in sediments and to understand potential effects of this enhancement.

2. STUDY AREA

The study was conducted on the Sulejów Reservoir, a 22 km² lowland reservoir located in central Poland. It is a shallow (mean depth of 3.2 m) polymictic reservoir, with a maximum storage capacity of 75×10^6 m³ and a mean retention time of about 30 days [1]. About 64% of the catchment area is used as arable land, and about 30% is covered with forest. This is a eutrophic ecosystem, where during periods of mean water temperature exceeding 18 °C intensive cyanobacterial blooms are observed [27]. The occurrence of toxic algal blooms are highly dangerous and may restrict the reservoir's use as a recreational area for up to 60000 people and actually alternative source of drinking water to the city of Łódź.



Fig. 1. Location of sampling stations on the rivers for the evaluation of nitrogen balance in Sulejów Reservoir and stations for measurement of denitrification rate in bottom sediments (1–12)

There are two main tributaries supplying the reservoir, i.e., the Pilica and Luciąża Rivers (figure 1), with agriculturally used catchments (64%). High ratio of an agricultural area within the catchment to the reservoir surface results in temporarily high loads of nutrients discharged into the reservoir, mainly via tributaries. Non-point pollution sources make an important contribution to eutrophication of both rivers and consequently the reservoir.

3. METHODS

Sampling stations for the evaluation of nitrogen load transported to the reservoir were situated on the Pilica and Luciąża Rivers and six small direct tributaries (figure 1). Water samples were taken usually two to four times per month in the hydrological years 1998–2001. Water for chemical analysis was filtered directly after sampling through Whatman GF/F filter and analysed for total nitrogen (TN) using a Hach test N'Tube (0–25 mg/dm³) (No. 10071), nitrate nitrogen (N–NO₃) using a Hach test NitraVer 5 and ammonia nitrogen (N–NH₄) concentration according to GOLTERMAN et al. [9]. Precipitation data were obtained from the Institute of Meteorology and Water Management in Warsaw.

The measurements of denitrification rates in the sediments were conducted in the littoral zone of the reservoir (figure 1), at 12 littoral sites, using an *in situ* chamber method for direct measurements of gaseous reaction products [28], [29]. The *in situ* denitrification rate was calculated from the total N₂ flux out of the sediment. Sediment cores were collected and organic carbon content was analysed. Fresh samples of sediment were dried and subjected to chemical analysis after grinding. Organic matter (OM) was determined as a mass loss on ignition at 550 °C; organic carbon was determined by the Thiurin method [21], and total nitrogen by the Kjeldahl method. The results were calculated as percentage of dry weight [12]. The Pearson correlations (*r*) were calculated using Statistica 6.0 for Windows.

4. RESULTS AND DISCUSION

During the research period, the nitrogen load transported by the major tributaries – the Pilica and Luciąża Rivers – contributed to more than 90% of the reservoir total supply (table 1). This results from the agricultural use of the catchments and probably improper application of mineral and natural fertilizers (leaching from manure storage in farms).

Spatial variation of the *in situ* denitrification rate was mainly determined by the availability of organic carbon in the sediment structure [3], [4], [29] (table 2). The *in situ* denitrification rate ranged from 0 to 833 μ mol N₂ m⁻² h⁻¹ and was characteristic of

eutrophic reservoirs. A significant relationship between the denitrification rate (µmol $N_2 \text{ m}^{-2} \text{ h}^{-1}$) and the percentage of organic carbon in sediments (% of dry weight) (r = 0.6039, p = 0.038, N = 12) was established. It has been estimated that the bottom sediments with organic matter content of nearly 20% and organic carbon of about 10% occupy about 26% of the bottom area (Timchenko's unpublished data). Assuming that the mean denitrification rate in this zone is 483 µmol $N_2 \text{ m}^{-2} \text{ h}^{-1}$, about 11.6% of the annual nitrogen can be removed from this part of the reservoir via denitrification. About 74% of the bottom area is covered with sediments containing less than 5% of organic matter and organic carbon content. The mean denitrification rate in this zone is 102 µmol $N_2 \text{ m}^{-2} \text{ h}^{-1}$ (table 2). In order to calculate the amount of total nitrogen removed from the reservoir via denitrification, the period of late spring, summer and early autumn (180 days in total) was considered; denitirification rates are not limited by low temperatures during this period. Literature studies show that maximum rates of denitrification in sediments occur most often during late spring and summer and vary mainly with temperature [22], [3], [29], [23].

Table 1

Earm of	Average annual nitrogen load t y $^{-1}$ (%)								
nitrogen	Direct catchment (direct tributaries)		Indirect catchment (Pilica & Luciąża)		Precipitation		Total nitrogen load		
	t y ⁻¹	(%)	ty ⁻¹	(%)	t y ⁻¹	(%)	t y ⁻¹	(%)	
NO ₃ –N	17.1	(1.3)	1313.3	(98.1)	8.3	(0.6)	1339.0	(100)	
NH ₄ -N	2.5	(2.3)	100.6	(90.3)	8.7	(7.5)	111.5	(100)	
TN	30.8	(1.0)	2794.3	(98.2)	22.4	(0.8)	2846.2	(100)	
TON	11.2	(0.8)	1380.0	(98.8)	5.4	(0.4)	1397.0	(100)	

Data of nitrogen supply to the reservoir in 1998-2001

Following the above assumptions, there are 331.8 tons of nitrogen removed by denitrification from the area of 26% (5.72 mln m²) of the reservoir. The remaining area (74%, i.e., 16.28 mln m²) is mostly covered with a sandy bottom and releases 195.4 tons of nitrogen by denitrification. Both of these values amount to a total nitrogen removal of 527.2 tons per year.

Table 2

Chemical composition of the bottom sediments and average denitrification rate

<u>Quality of a</u>	Composition o (% dry mass o	Denitrification rate (μ mol N ₂ m ⁻² h ⁻¹)		
Stations	Average organic matter	Average organic carbon	Average value	
4,5,6,8,9,10,12	16.5 (9.9–21.8)	7.9 (5.2–10.3)	483.1 (130-833)	
1,2,3,7,11	1.8 (0.4-4.2)	1.2 (0.5-2.5)	102.2 (0–278)	

According to data of nitrogen supply to the reservoir in the period 1998–2001 (table 1), 18.5% of the external total nitrogen load (2846.2 t) is removed from the reservoir by denitrification in bottom sediments.

Littoral sediments are more heterogeneous and are characterised by higher metabolic and denitrification rates, compared to the pelagic zone sediments [6], [22]. Many researchers reported that denitrification rates were significantly higher in sediments overgrown with plants [5], [22], [17]. The presence of macrophytes in a littoral zone stimulates sedimentation of organic matter and provides a direct source of organic carbon. Plant roots release oxygen into sediment, thereby increasing the sediment redox potential, creating more favourable conditions for nitrate production via nitrification, and subsequently denitrification [18].

The redox potential influences denitrification rates, which increase in more reduced medium [22]. Sediments rich in organic matter usually are characterized by lower redox potentials. An accumulation of organic matter or long-lasting anaerobic conditions in littoral/riparian zones, e.g., during flooding, can influence denitrification rates [32]. It was calculated that if littoral zone management increases by 10%, the bottom area containing about 10% of dry weight of organic carbon, the nitrogen removal via denitrification will increase by about 4.5% (126 tons) of total incoming nitrogen load [2].

The highest proportion of denitrifiers (26%) was found at station 4, where the content of organic carbon was also the highest (6425.3 µg C-org. g^{-1} d.w.) [2], [3]. These results also suggest that management of littoral zones, which increases nitrate availability, organic matter and organic carbon availability, stimulates growth of naturally occurring denitrifying microflora [23], [8], [30]. In addition, bacterial activity is stimulated by water temperature as observed in warmer littoral zones [16], [22], [10].

The denitrification process may contribute to a decrease in nitrogen levels; the phytoplankton biomass in the reservoir is likely to be essential to this process. Lowering the total phytoplankton biomass may also result in temporal growth stimulation of those species that possess heterocysts and are able to fix nitrogen from the atmosphere under nitrogen-limiting conditions. Especially in the periods of high temperatures, the lowering of the N:P ratio may particularly stimulate cyanobacterial growth [20], [24]. In the Sulejów Reservoir, cyanobacteria dominate when the temperature increases above 18 °C and the N:P ratio stays below 32 [11].

Water retention time (WRT) is another factor that may modify denitrification rates. Increasing WRT enhances sedimentation in the littoral zones of the reservoir and may contribute to intensification of denitrification rates by increasing the OM content in sediments. Enhanced denitrification lowers the N/P ratio and inhibits phytoplankton growth. This is especially evident during the spring period, when water temperature is low and diatoms, which are not able to fix nitrogen from the atmosphere, dominate in phytoplankton communities. During summer, water tem-

perature increases and cyanobacteria dominate, lowering the N:P ratio, possibly providing an advantage in competition for nutrients over other phytoplankton groups [27] (figure 2).



Fig. 2. Schematic diagram of effect of enhancing denitrification rate in sediments of the Sulejów Reservoir

Lowering WRT may decrease cyanobacterial blooms, not only by destabilizing the water table, but also by restricting sedimentation rates, and therefore decreasing denitrification [30]. Additionally, this may cause a physical flushing of phytoplankton from the reservoir [26].

Optimization of the denitrification process by WRT control requires considering its effect on zooplanktivorous fish recruitment. Control of WRT in spring should be adjusted to temperature in order avoid adverse effects on water quality due to a "topdown" effect. Maintaining long WRT during recruitment of zooplanktivorous fish may result in an increase of their pressure down to the trophic pyramid in summer and stimulation of cyanobacterial blooms [33], [7].

5. CONCLUSIONS

1. According to data of nitrogen supply to the reservoir in the period 1998–2001 it has been estimated that 18.5% of the external total nitrogen load (2846.2 t) are removed from the reservoir by denitrification.

2. This process is mainly determined by organic carbon availability.

3. Regulation of hydrological processes by increasing WRT and inundating properly managed littoral zones (through supporting macrophytes) can contribute to the removal of nitrogen via denitrification and hence decreases eutrophication.

4. Control of WRT in spring should be adjusted to temperature in order to avoid adverse effects on water quality due to "top-down" effect.

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POTENCJALNE SKUTKI INTENSYFIKACJI PROCESU DENITRYFIKACJI W OSADACH ZBIORNIKA SULEJOWSKIEGO

Denitryfikacja jest pod względem ilościowym najistotniejszym procesem usuwania azotu z ekosystemów wodnych i przyczynia się do redukcji symptomów eutrofizacji. Tempo procesu denitryfikacji w strefie litoralnej w okresie badawczym 1998–2001 mieściło się w przedziale od 0 do 833 µmol $N_2 m^{-2} h^{-1}$ i było głównie determinowane zawartością węgla organicznego w osadach (r = 0,6). Oszacowano, że rocznie 18,5% zewnętrznego ładunku azotu jest usuwane w procesie denitryfikacji w osadach dennych. Wartość ta może zostać zwiększona dzięki intensyfikacji procesów sedymentacji materii organicznej i tym samym węgla organicznego, zwłaszcza w strefie litoralnej górnej części zbiornika. Wzrost tempa denitryfikacji obniży stosunek N:P, co szczególnie w okresie wiosennym może ograniczyć wzrost fitoplanktonu. Jednak w okresie lata, kiedy temperatura wody wzrasta i zaczynają dominować sinice, dalsze obniżanie stosunku N:P może być dodatkowym czynnikiem dającym tej grupie przewagę w konkurencji o pierwiastki biogenne.