Journal of Ecological Engineering
Volume 18, Issue 4, July 2017, pages 178–184
DOI: 10.12911/22998993/74277

Research Article

CHARACTERISTICS OF SPATIAL DISTRIBUTION OF PHOSPHORUS AND NITROGEN IN THE BOTTOM SEDIMENTS OF THE WATER RESERVOIR PORAJ

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Received: 2017.04.10
Accepted: 2017.05.31
Published: 2017.07.01

ABSTRACT

The aim of this study was to determine the content of phosphorus and nitrogen in the bottom sediments of the Poraj Reservoir located on the Warta River, along with defining their spatial distribution and the relationship between these elements and organic matter, aluminum and iron. Samples of bottom sediments were collected on the basis of regular measurement grid of 46 points located in the area of the water reservoir Poraj. The collected samples were analyzed in terms of content of following elements, which values are in range: total phosphorus (TP) 0.06 – 5.06 g/kg, total nitrogen (TN) 0.17 – 9.66 g/kg, organic matter (OM) 0.49 – 28.41% of solid content, aluminum (Al) 2.44 – 145.15 g/kg and iron (Fe) 0.28 – 16.50 g/kg. By using of GIS system, spatial distribution of obtained results of laboratory analyzes were interpolated (Inverse Distance Weighted method was used). On basis of spatial distribution it was noted that in northern part of water reservoir bottom sediments have greater values of TP, TN and OM than in southern part. The study also included calculation of correlation between: OM and TN (n=46, R^2 = 0.9335), TN and Fe (n=46, R^2 = 0.8782), TN and Al (n=46, R^2 = 0.8629), OM and Fe (n=46, R^2 = 0.8243), OM and Al (n=46, R^2 = 0.7981), TP and Fe (n=46, R^2 = 0.7456), TP and Al (n=46, R^2 = 0.6209). The presented pilot studies show that the potential content of phosphorus, nitrogen and organic matter in the sediments of the water reservoir Poraj can reach a significant level. The need to plan and carry out further research allowing the evaluation of the properties of the analyzed elements and examining their potential impact on water quality in the tested water reservoir was stated.

Keywords: bottom sediments, spatial distribution, eutrophication

INTRODUCTION

Eutrophication is a very common phenomenon occurring in inland water ecosystems. This process occurs in surface waters, but primarily refers to standing waters and reservoirs characterized by properties matter accumulation [Kasza 2009]. The increase in the fertility of reservoirs is part of a natural process, which is sometimes referred to as “water aging” and is a manifestation of the natural evolution of all water reservoirs. Sometimes, however, it happens that the accelerated eutrophication of many reservoirs is the result of broader human activity [Siemieniuk et al. 2016].

The main biogenic elements, which largely contribute to increasing the fertility of the reservoirs and rapid progress of eutrophication are nitrogen and phosphorus. These biogenic substances are the basis for proper existence of flora and fauna, but their excessive amount in the aquatic environment can also cause damage in the form of a significant growth of algae and aquatic plants. Nitrogen and phosphorus transfer into surface water mainly from point sources (e.g. domestic and industrial sewage discharge) and area sources (e.g. surface run-off from fertilized fields, precipitation) [Gałczyński 2008, Bartoszek et al. 2014]. In Poland, an overwhelming amount of nitrogen and phosphorus compounds migrating to surface and ground water originates from agriculture. It is estimated that approximately 50–60% of nitrogen and phosphorus flowing to the Baltic Sea come from agricultural area sources [Kiryluk et al. 2011].

Biogenic substances (nitrogen, phosphorus) after entering into water are accumulated in sediments and water column. Sediments have high storage capacity of nutrients getting into the tank from the water catchment area, as well as those that are already in the water. Only in a 10-cm layer of sediment, there can be over 90% of the phosphorus contained in the tank. In most of the cases, under favorable conditions, nutrients can again be released into the water column, acting as a potential source of danger for the whole ecosystem [Dąbrowska et al. 2012, Karwacka et al. 2015, Rozpondek et al. 2016].

Organic and inorganic forms of phosphorus in bottom sediments are converted into orthophosphate, and nitrogen compounds into ammonium, nitrite or nitrate. Their replacement with water from the tank can occur through chemical or microbiological means. In the sediments, there is a thin layer (from a few millimeters to a few centimeters), which is dominated by processes involving anaerobic bacteria. The decomposition of organic matter by bacteria is usually the basic mechanism of supplying the internal tank with nutrients. After exceeding a nutrient load acceptable for a given reservoir, a so-called supplying or internal import process is started based on releasing nutrients, especially phosphate accumulated in bottom sediments [O'Sullivan et al. 2004, Dąbrowska et al. 2012]. The transformation of phosphorus in the aquatic environment depends on many factors, including those such as water quality (pH, reduction potential, the content of Fe, Al, Ca) [Small et al. 2013]. The most important processes in the retention of phosphorus in bottom sediments are sorption and binding of this element by iron hydroxides, joining by the calcium carbonate and autogenous mineral formation. Supplying water with biogenic compounds contained in bottom sediments plays the most important role during summer stagnation, mainly due to bacteria and release under anaerobic conditions for the combinations of solutions like Fe-P and Al-P [Kubiak et al. 2005].

Differentiation of accumulation for biogenic substances in bottom sediments depends on the environmental conditions, the morphology and hydrology of the tank (flow fluctuations and constant water level). However, the greatest amount of nutrients is accumulated in bottom sediments in the deepest parts of the water tanks, in stagnant water areas adjacent to agricultural land and places where fine-grained fractions predominate in the composition of the deposited material [Small et al. 2013].

The aim of the study was to determine the content of phosphorus and nitrogen in the sediments of the Poraj Reservoir located on the Warta River, along with defining their spatial distribution and the relationship between these elements and organic matter, aluminum and iron.

STUDY AREA AND METHODOLOGY

Sampling of bottom sediments from the Poraj Reservoir was conducted in August 2016. On the basis of 46 measuring points total of 92 samples of bottom sediments (two from each point) were collected. The analyzed reservoir is located in the Poraj and Koziegłowy municipality in the Myszków County, in the northern part of the Śląskie Voivodeship. It has an area of 550 hectares, making it the leading Polish dam reservoir. It was created in 1978 in order to create a reservoir of water for Huta Czestochowa. Currently, it is the subject of interest to local residents because of the possibility of the development of water sports and tourism, as well as recreation in the region.

The Warta River is the main tributary directly supplying the Poraj water tank. For this reason, it substantially affects the quality of the water and bottom sediment of the reservoir. The waters of the river are polluted inter alia by sewage, which are supplied mainly from the area of Zawiercie and Myszków. They come mainly from rural areas, without a sewerage system. Domestic wastewater is directly introduced into the surface waters, which are located in the catchment area of the reservoir. In the immediate vicinity of the lake, there are numerous resorts because of its recreational character. They constitute point sources of pollution, which directly participate in shaping the quality of water and sediment tank [Jaguś et al. 2000, Jachniak et al. 2013].

Samples of bottom sediments were collected at 46 measuring points with depths ranging from 0.4 m to 7.4 m below the water table. The research material was collected using a specialized hook of bottom sediments of Van Veen's KC Denmark type. To develop an arrangement grid for sampling, the ArcGIS software was used, as well as an orthophotomap shared within the WMS service (Web Map Service) by the Geoportal portal. For the location of sampling points which were previously scheduled, the GPS system was used [Rozpondek et al. 2017].

Sampled bottom sediments were dried under air-dry conditions, and then weeded out through a sieve with aperture of 2 mm. They were subsequently dried in an oven at 105°C to constant weight and ground in a vibrating mill to a sediment fraction with a particle size <0.2 mm. From each measuring point, 3 samples were prepared for analysis. Samples of bottom sediments have been tested to define the content of total phosphorus (TP). The spectrophotometric method with ammonium molybdate was used for this purpose in accordance with EN ISO 6878: 2004. The content of total nitrogen (TN) was designated by distillation according to the Polish Standard PN-ISO11261: 2002. To measure the content of organic matter (OM) the weight method was used according to the standard ISO 11465: 1999. In bottom sediments, the total content of iron (Fe) and aluminum (Al) were designated. For their extraction, aqua regia was used (a mixture of concentrated hydrochloric acid and nitric acid in a volume ratio of 3:1). Mineralization was carried out at the temperature of 180°C for 30 minutes with the use of a high-pressure microwave mineralizer of the Berghof company. The content of Al and Fe was determined on an ICP-OES Thermo IRIS plasma spectrometer [Rozpondek et al. 2016].

In the Statistica program, a statistical analysis of the results was carried out. It included basic statistical characteristics (Tab. 1) – arithmetic mean, range of variation (minimum, maximum), kurtosis and asymmetry factor. Using the ArcGIS program, the coefficient of determination (R^2) was designated between the designated content of individual elements in bottom sediments.

Maps showing spatial distribution of TP, TN, OM, Al and Fe (Fig. 2, Fig. 3) and the depth map (Fig. 3) was interpolated using the inverse distance weighting method [Uygur et al. 2010 Xu, et. al. 2001]. Analyses were performed in the ArcGIS program. The analyses were based on the ArcGIS program. The Geographical Information System (GIS) is becoming one of the most important tools to assess the state of the environment. This system allows for effective conducting of spatial analyzes on large volumes of data and their subsequent visualization. GIS also allows the classification of the results obtained and their prediction on the basis of additional information [Zang et al. 1998].

RESULTS AND DISCUSSION

The results of the selected sample designations of bottom sediments are presented on Figure 2 and 3, which shows the average values for each test.

Bottom sediments of the tested reservoir were characterized by a relatively high content of total phosphorus (TP). It ranged in the scope of 0.06 g/kg in point 9 to 5.06 g/kg in point 45. The histogram of TP content (or the assumed intervals) shows that its content in most samples (n=36) was in the lowest range value (0.06- 0.89 g/kg). The remaining samples (n=10) were in the range of 0.89 to 5.06 g / kg (Fig. 1). It clearly shows a very strong right-hand asymmetry with an asymmetry

Table 1. Statistics of total phosphorus (TP), total nitrogen (TN), Al, Fe and OM contents in sediments of the Poraj Reservoir

Statistic	TP [g/kg]	TN [g/kg]	Al [g/kg]	Fe [g/kg]	OM [%]
Mean	0.82	2.47	4.84	12.17	6.63
Minimum	0.06	0.17	0.83	2.21	0.49
Maxiumum	5.06	9.66	2.21	47.67	6.31
Median	0.54	1.05	3.11	6.31	2.36
Kurtosis	8.42	0.67	-0.14	1.16	0.42
Skewness	2.78	1.46	4.03	11.84	1.34

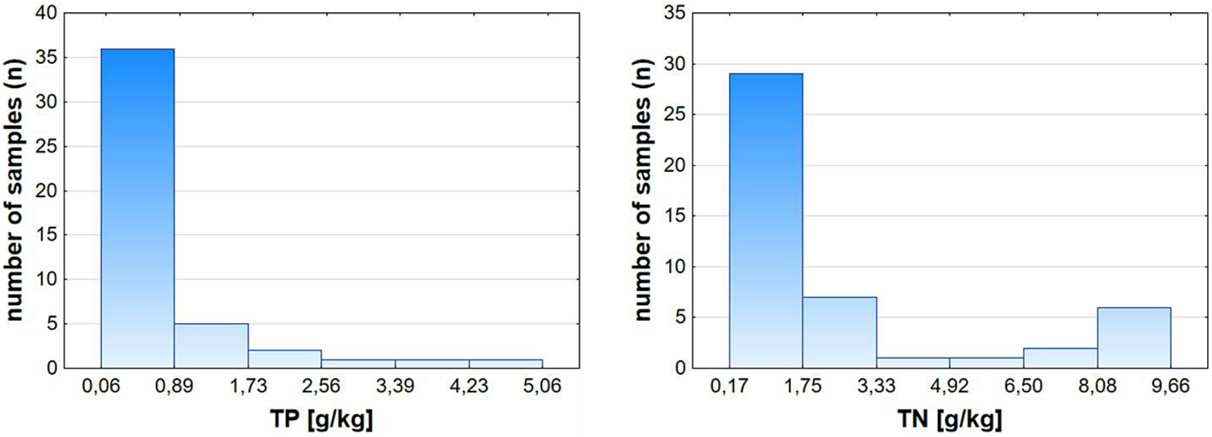

Figure 1. Histogram of TP and TN distribution in bottom sediments of Poraj Reservoir

index (As) equal to 2.78 (Tab. 1). The average content of TP (0.82 g/kg) in the bottom sediments of the Poraj Reservoir was at a slightly higher level in abducting to other reservoirs, for example the Chańcza Reservoir [Tarnawski et al. 2012] or Zembrzycki Reservoir [Small et al. 2013]. The minimum and maximum total value of phosphorus in bottom sediments of exemplary water tanks (the Chańcza Reservoir 0.25–1.93 g/kg, the Zembrzycki Reservoir 0.23–0.62 g / kg) differs from the obtained value range of the Poraj Reservoir. This fact testifies of the high content of phosphorus in bottom sediments of the tested tank.

Depending on the sampling locations, the total values of nitrogen content (TN) in bottom sediments of the Poraj Reservoir were different. The range of values differed from 0.17 g/kg at point 41 to 9.66 g/kg at point 17 (Tab. 1). Analyzing the histogram, it has been found that the majority of samples (n = 29) shows the contents of TN in the range of 0.17–1.75 g/kg (Fig. 1). As a result, it was found that the distribution of the total nitrogen content in the sediments of the Poraj Reservoir is characterized by a right-sided asymmetry (a = 1.46) (Tab. 1). The carried out statistical analysis confirms that the data obtained as a result of environmental research is usually the most numerous in the lowest range of values, and it is characterized by right-sided asymmetry [Yang et al. 2011, Small et al. 2013]. The interval of minimum and maximum content of TN in bottom sediments of the Poraj Reservoir in comparison to another water reservoir (Chańcza Reservoir 0.45 – 4.93 g/kg [Tarnawski et al. 2012]) was characterized by a greater variation of values.

There was determined a linear relationship between studied elements by Ordinary Least Squares (OLS) linear regression. Regression is used to evaluate relationships between two or more elements. Ordinary Least Squares (OLS) is one of the most popular regression techniques. [Mitchell 2005] Coefficient of determination were calculated between research parameter of bottom sediments (TP, TN, OM, Al, Fe) (Tab. 2). Analysis showed high R^2 values between various parameters of the studied sediments. The results confirmed a strong linear relationship between phosphorus, organic matter, aluminum and iron also described by other authors [House et al. 2002, Smal H. et al. 2013].

The Al content in bottom sediments of the Poraj Reservoir was between 0.83–13.51 g/kg, and the Fe content in the range 2.21–47.67 g/kg (Table 1). On the basis of Figure 3 it was noted that the spatial distributions of Al and Fe are similar, this is also confirmed by R^2 value (0.9191) (Table 2). The highest concentrations occurs mainly in the northern part of reservoir, which is also the deepest one. Al and Fe can affect incorporation and liberation of P from sediments, which

Table 2. Correlation coefficient between the TP, TN, OM, Al and Fe content in surface sediments of Poraj Reservoir

Correlation	Coefficient of determination (R^2)*
TP/OM	0.6560
TP/Al	0.6209
TP/Fe	0.7456
TN/OM	0.9335
TN/Al	0.8629
TN/Fe	0.8782
TP/TN	0.6030
OM/Al	0.7981
OM/Fe	0.8243
Al/Fe	0.9191

*numer of samples = 46

is related to phosphorus retention in sediment and its realease into the water column [Trojanowska and Jezierski 2011]. It is the main reason why Al and Fe should be monitored along with the content of phosphorus.

The lowest concentration of organic matter (OM) was observed in the sediments in point 41 (0.49%) and the highest at point 17 (28.41%) (Table 1). In terms of organic substance content, the studied sediments were divided into 3 groups: mineral sediments (<5% organic matter), organic and mineral sediments (5–20% organic matter) and organic sediments (> 20% organic matter) [Dąbkowski et al. 2003]. In 30 points, they were mineral sediments, 9 – organo-mineral and 7 – organic. This shows that in the Poraj Reservoir bottom sediments, there is a significant, but not excessive amount of organic matter. Based on Figure 2 and Figure 3, it is concluded that the content of OM takes the highest values in the deepest places of sampling [Trojanowski et al. 1982]. An increased content of OM in shallower sampling places was also observed. The probable cause of this phenomenon is the uneven distribution of water plants, which when dying supplies organic matter to the bottom sediments [Trojanowski et al. 2005].

TP distribution was also dependent on the spatial distribution of Al and Fe (Fig. 3), or metals which have the ability to bind phosphorus. Confirmation of this statement is high statistical correlation between these elements (Table 2). A similar pattern was also observed for total nitrogen, where the coefficient of determination (R^2) for TN and Al was 0.8629, while for TP and Fe it was 0.8782 (Table 2). On the basis of Table 2 and Figure 2, it was noted that the concentration of TP and TN in bottom sediments of the Poraj Reservoir depends strongly on the concentration of OM.

Analyzing spatial distribution of TP and TN (Fig. 2), it was observed that the lowest concentration of these elements is characterized by the south-eastern part of the studied area. The highest concentration of nutrients exists in the north-

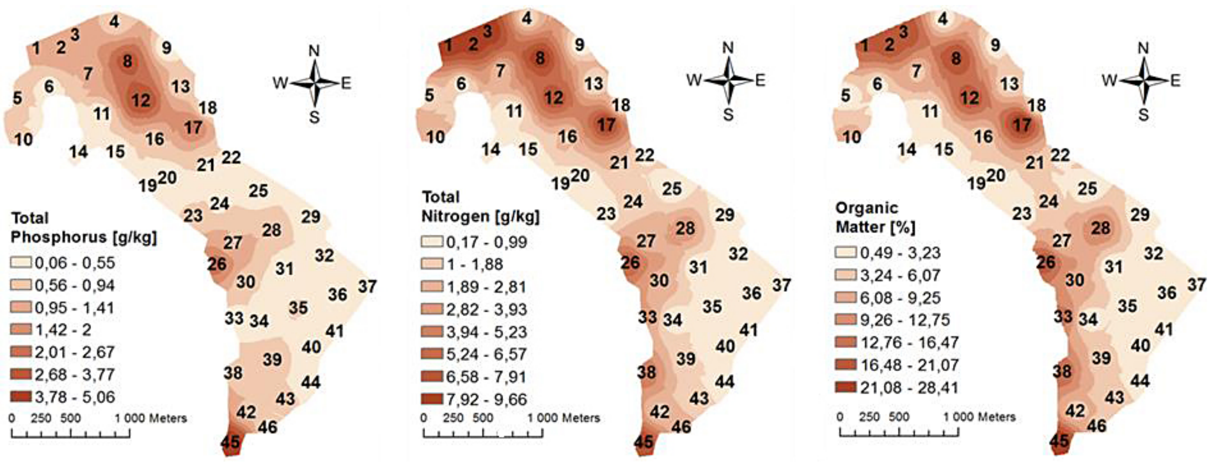

Figure 2. Spatial distribution of TP, TN and OM in bottom sediments of Poraj Reservoir

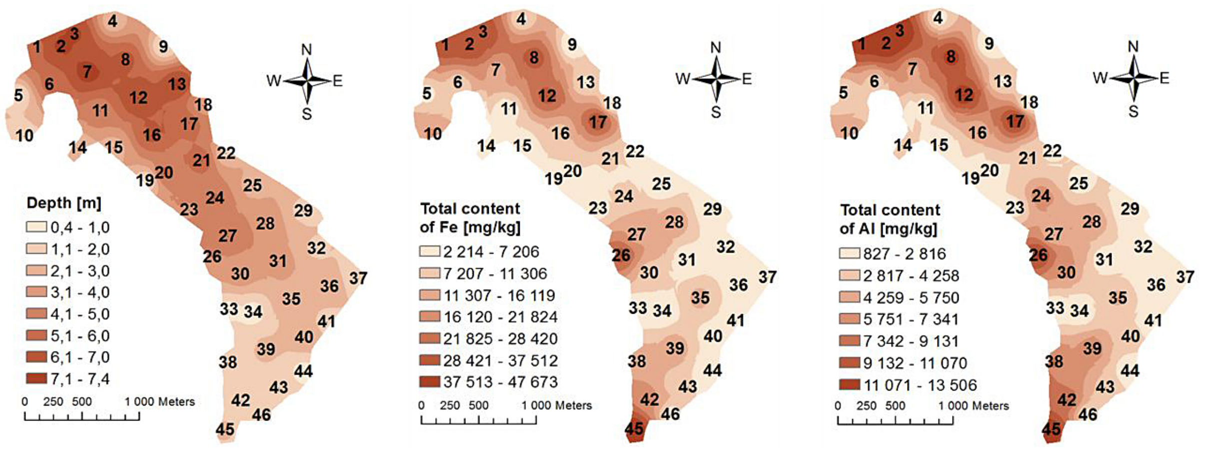

Figure 3. Spatial distribution of depth, Fe and Al in bottom sediments of Poraj Reservoir

ern part (near dam) of the Poraj Reservoir and in point 26 and 45. With the increasing of sediment sampling distance from the dam the concentrations of total nutrient mainly decreases. Additionally the northern part is the deepest part of the reservoir – concentrations of studied nutrients rise with increasing of the sampling depth. This fact probably corresponds to higher fertilizer application in the high ’80s and low ’90s. The same results are also described by other authors [Junakova et al. 2013, Small et al. 2013, Szarek-Gwiazda and Sadowska 2010, Kovalikova and Balintova 2007]. Near the north-western part of the reservoir, there is a well-developed tourist infrastructure, which can provide an additional source of pollution especially in the summer months. Due to the fact that the increased content of TP and TN also has a local character, systematic monitoring of the selected sites must be carried out. Additionally the studies should be broadened by heavy metals content and toxicity analysis.

The increased content of general phosphorus (TP) and general nitrogen (TN) in bottom sediments of the Poraj Reservoir may indicate that the tested reservoir and its catchment area is under the influence of harmful anthropogenic activities. Most likely, this state is associated with supplying domestic and industrial sewage to the catchment tank adjacent to the urban agglomerations (Myszków, Zawiercie). Additionally, the increased content of biogenic substances in the tested object can also be related to the surface runoff, which introduces pollution from agricultural areas (fertilizers, pesticides) as well as sewage sludge, with which fields are fertilized [Gruca-Rokosz et al. 2011 Jachniak et al. 2013,]. The Poraj Reservoir is exposed to supply of a significant amount of pollution and biogenic compounds. This object has, inter alia, a recreational function, and therefore should be constantly monitored due to the health and vitality of the people resting there.

CONCLUSIONS

The obtained results and their analysis made it possible to present the following conclusions:

1. The concentration of phosphorus and nitrogen in the bottom sediments of the Poraj Reservoir is characterized by a similar spatial distribution. The highest concentration of biogenic substances can be found in the northern part of the Poraj Reservoir and in section 26 and 45, and the smallest concentration in the south-eastern part of the studied area.
2. The high content of organic matter, aluminum and iron favors the accumulation of biogenic substances in the bottom sediments of the tested reservoir. This is evidenced by the high values of determination coefficients for individual elements.
3. The spatial distribution of nitrogen and phosphorus obtained using the GIS system is the basis for a comprehensive understanding of the current level of concentration of biogenic substances in bottom sediments of the Poraj Reservoir providing knowledge about the places that should be subject to constant monitoring.

The increased content of TP and TN in the tested object can also be related to the surface runoff, which introduces pollution from agricultural areas (fertilizers, pesticides) as well as sewage sludge, with which fields are fertilized. The presented pilot studies are the basis for identifying malicious human action and defining the directions of their prevention and establishing appropriate rules of water management.

Acknowledgment

The study was supported by an internal grant in the Czestochowa University of Technology BS/MN-401–302/16.

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