



Assessment of Agricultural Use of the Bottom Sediments from Eutrophic Rzeszów Reservoir

*Lilianna Bartoszek, Piotr Koszelnik,
Renata Gruca-Rokosz, Małgorzata Kida
Rzeszów University of Technology*

1. Introduction

Natural lakes and artificial reservoirs seem to be ecosystems with very similar structure and similar mechanisms governing their physical, chemical and biochemical changes. However, this is only apparent similarity [21]. Artificial reservoirs in comparison to natural lakes are characterized by a much more frequent water exchange, large fluctuations in water level resulting from the variation of inflow and outflow, which is evident especially in mountainous catchment areas. Reservoirs created in the river valleys by the construction of a dam have also considerably larger catchment area than the lakes. This difference is disadvantageous to the anthropogenic water bodies. A large catchment area delivers to the reservoir greater quantities of pollution produced within its territory causing adverse effects in the ecosystem. A gradual development of undesirable organisms characteristic of stagnant water is observed in the reservoirs, which utilize nutrients causing deterioration in water quality after a few years of exploitation [13].

Degradation of the reservoirs is often irreversible, therefore, the problem of their reclamation and restoration of appropriate parameters is very important [2, 13]. Deposition and settlement of mineral and organic matter proceeds much easier in artificial reservoirs than in natural lakes, also an artificial aging of the reservoirs is faster than lakes by about 10,000 times [8]. Reclamation methods for the reservoirs vary depending

on the severity of the degradation. For the eutrophic water bodies following methods were used: aeration or removal of hypolimnion as well as chemical inactivation of phosphates using Fe, Al, Ca or La salts [2]. If, however, the ecosystem has accumulated debris of various origins in amounts significantly reducing its volume, it is only possible to remove the backlog of bottom sediments through dredging.

The purpose of this paper is the analysis of possible agricultural use of the bottom sediments that were dredged from a planned for reclamation eutrophic reservoir in Rzeszów, SE Poland. The reservoir's degradation strongly limits its agricultural and economic role.

2. Study area

A water reservoir in Rzeszów was built in 1974 by damming the Wislok river in 63+760 km of its course. The reservoir is supplied by two main tributaries: Wislok and Strug. Its main purpose was to allow for the proper operation of the water supply for the city of Rzeszów. Because of its the location on the outskirts of a large city it fulfills a vital role as a sports and recreation lagoon. Morphometric parameters of the reservoir at the time of flooding in 1974 and in 2014 were shown in Table 1. The total volume of the reservoir decreased by 0.7 million m³ of its capacity during last 40 years. Consequently, the reservoir has mostly silted up and gradually transformed into land especially in its upper zone. The attempts to rehabilitate the usability of the reservoir conducted in the years 1986–87 and 1995–1997 consisted of deepening the reservoir next to the dam, and narrowing it by partial backfill on the right part of the bank just by the dam. In both cases, about 250 000–300 000 m³ of sediment was dredged. The objective of both operations was the increase in the flow rate, thereby reducing sedimentation. Unfortunately, restoration has not brought the expected results. Just after seven (7) years, the amount of sedimentation exceeded the amount formerly removed.

The Rzeszów reservoir watershed covers an area of 2,025 km². Its range encompasses a significant acreage of the Subcarpathian Province (Podkarpacie). The difference in water level between the main supply of the Wislok at the source and the mouth of the reservoir is 616 m. The Wislok flows through the foothill areas that are largely agricultural, though, the upper parts are forested, while the middle part is lined with

industrial centers (glassworks, tanneries, refineries). The catchment of a smaller tributary, the Strug, is vastly agricultural in nature which traditionally is comprised of fragmented farmland representing high population density. The reservoir is under strong anthropopressure associated with local agriculture that causes a severe erosion of the land, as a result of depositing the rubble and diffuse pollution [15].

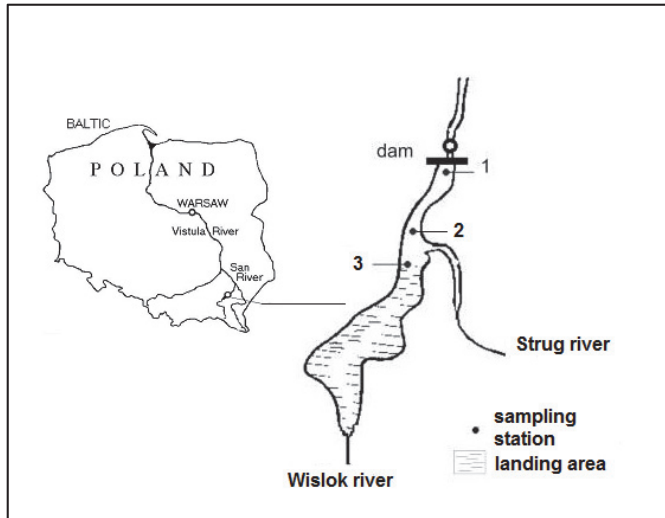


Fig. 1. Location of sampling stations

Rys. 1. Lokalizacja stanowisk badawczych

Table 1. Morphometric parameters of the Rzeszów reservoir

Tabela 1. Parametry morfometryczne zbiornika Rzeszów

Parameter	1974	2014
Surface area; km ²	0.68	0.68
Total volume; 10 ⁶ m ³	1.79	1.10
Depth: max. (mean); m	6.2 (1.5)	4.9 (0.6)
Length; km	6.7	6.7
Hydraulic retention time; day	2	0.8

3. Methods

Sediment samples were taken from the studied reservoir fifteen times (15) in the years 2009–2013, from three points located along the axis of the reservoir (Fig 1). A gravity sediment corer (KC Kajak of Denmark) was used in all cases. Sediment subsamples were dried and further measured for Loss-on-Ignition (LOI) at 550°C for four hours (4h), construed as organic matter content (OM). Another subsample was analyzed for determining total content of organic carbon (TOC) (after the removal of inorganic carbon with 1M HCl) and total nitrogen (TN) using a CN analyzer (CN Flash EA 1112, ThermoQuest). Total phosphorus (TP) was examined spectrophotometrically after microwave mineralization in HNO₃. Some of the heavy metals (Cd, Cr, Cu, Ni, Pb and Zn) were determined with ICP technique (ICP-OES, Quantima GBC) after microwave mineralization. All parameters examined were expressed as % or mg/kg of sediment dry matter. Moreover stable carbon ($\delta^{13}\text{C}$) and nitrogen ($\delta^{15}\text{N}$) isotopic compositions were analyzed using IRMS DEL-TAPlus Finnigan coupled with CN analyzer. The stable isotopic compositions were expressed as “per mil”:

$$\delta R (\text{‰}) = [R_a/R_b(\text{sample})/ R_a/R_b(\text{standard}) - 1] \times 1000,$$

where R_a/R_b are the $^{13}\text{C}/^{12}\text{C}$ or $^{15}\text{N}/^{14}\text{N}$ ratios relative to the isotopic PDB and AIR standards, respectively.

Additionally, for a better interpretation, the paper quotes data from the report of the Regional Water Management Board in Kraków where concentrations of PAHs: benzo[a]anthracene (BaA), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), benzo[ghi]perylene (BghiP), dibenzo[ah]anthracene (DahA), indo[1,2,3-cd]pyrene (IcdP), along with chosen congeners (28, 52, 101, 118, 138, 153 and 180) of PCBs [19] are given.

Obtained concentrations of the heavy metals were compared with most common sediment quality standards: geochemical background [7], threshold effect concentration (TEC) [17] and probable effect concentration (PEC) [17]. The last two data respectively represent the concentrations below which adverse effects are expected to occur rarely (TEC) and the concentration above which adverse effects are expected to occur frequently (PEC). For the organic compounds TEC and PEC values were also used.

4. Results and discussion

4.1. Case specifications and boundary conditions

Table 2 summarizes the content of TN, TP, OM, TOC, and the pH (KCl) in the tested samples. The noted values did not attest to statistically significant differences between stations, therefore all the data were averaged. The analysis of the physical properties of the bottom sediments described in paper [19] indicate that approximately 60% of their dry matter composition constitute of particulate matter fractions (0.002–0.05), 30% of sandy fractions (0.05–2.0) and only 10% of clay fractions (0.001–0.002). The main component is silica deposits 54–70% [19]. Analyzed LOI(OM) ranges from 6.5% to 11.6% and the highest value was noted in the area by the dam. The pH value (KCl) varies within the range of 7.04–7.42 indicating a slightly alkaline environment. The percentage of biogenic elements in bottom sediments of the reservoir is small and ranges between 0.12–0.37% of TN and 0.003–0.067% of TP. The $\delta^{15}\text{N}$ values in the sediments fall within the range -0.53 to 3.16‰, while the $\delta^{13}\text{C}$ values fall between -29.20 and -22.62‰.

The values of TOC to TN ratio (TOC:TN) and of the isotopic composition of the organic carbon and total nitrogen are the main indicators used in an effort of identifying the organic matter origin in the bottom sediments of researched aquatic ecosystems. It is assumed that TOC:TN values in excess of 12:1 are of terrestrial matter in origin. The autochthonous matter is in turn characterized by TOC:TN values below 8 [3,12,18]. The depletion of the ^{12}C isotope from the organic carbon and higher values of the $\delta^{15}\text{N}$ are also characteristic for the autochthonous matter [3,18]. The top layer (0–5 cm) of the studied bottom sediments was characterized by TOC:TN values in the range of 6.6 – 16.1. The average values for this indicator were of about 11–12. Such results indicate that the organic matter deposited in the studied sediments is of mixed origin. The reference values obtained from the literature for planktonic and terrigenous matter indicator, were of 6.8 and 17.1 respectively [14]. The obtained values for the $\delta^{15}\text{N}$ differ, but did not display any clear trends nor did not allow for drawing any definite conclusions. The $\delta^{13}\text{C}$ values suggest that the top surface layer of the sediment was poorer in the ^{12}C , this in turn indicates a greater role of autochthonic organic matter. This conclusion is consistent with the findings for TOC:TN values.

In turn, a higher values of the $\delta^{13}\text{C}$ observed in sediments suggest a greater participation of autochthonous organic matter. This is in line with the research results obtained by Tomaszek et al. [22], for the bottom sediments in Poland's largest dam reservoir. The top- and the lower parts of the sediments profiles were depleted of the ^{12}C isotope in the summer, indicating the influence of phytoplanktonic organic matter [11,18]. A high proportion of an autochthonous OM in sediments can be surprising after comparing it with low content of TOC, TP and TN. However, the reservoir is loaded with significant amount of TP and TN, and the retention of these elements are 7% and 22% of load respectively [16]. This effect is reduced by a significant denitrification and mineralization of the OM sediment regarding emissions of CO_2 and CH_4 into the atmosphere [9, 10]. Moreover, low concentrations of biogenic compounds may result from leaching during high water season (mostly in spring), when the hydraulic retention time in the reservoir is only few hours.

Table 2. Characteristic values of the parameters studied in the sediment.

Abbreviations as in the text

Tabela 2. Wartości charakterystyczne stężeń badanych wskaźników.

Skróty jak w tekście

Parameter	LOI(OM)	TN	TOC	TP	pH(KCl)	$\delta^{13}\text{C}$	$\delta^{15}\text{N}$
	% of dry matter				–	‰	
Mean	8.6	0.21	2.31	0.031	–	-26.56	1.75
Maximum	11.6	0.37	4.39	0.067	7.42	-22.62	3.16
Minimum	6.5	0.12	1.61	0.003	7.04	-29.20	-0.53
Std. dev.	1.2	0.06	0.67	0.002	0.12	1.72	1.07

4.2. Heavy metals in the sediment

An important indicator of reservoirs pollution is concentration of heavy metals in bottom sediments [24]. In water, compounds of those elements remain in a dissolved form for a very short time and quickly precipitate into the sediments. The accumulation of the metals in the deposits is a permanent phenomenon, especially in the case of clay fractions with a high sorption capacity [23]. Table 3 lists the concentrations of metals. On the basis of calculated values of arithmetic means of ob-

served metals concentrations, it can be concluded that the Rzeszów reservoir sediments were contaminated with zinc (Zn) (103.9 mg/kg), copper (Cu) (32.7 mg/kg), lead (Pb) (53.5 mg/kg), nickel (Ni) (35.6 mg/kg), chromium (Cr) (56.3 mg/kg) and cadmium (Cd) (2.5 mg/kg).

Table 3. Concentrations of selected heavy metals in studied sediments.

Abbreviations as in the text

Tabela 3. Stężenia wybranych metali ciężkich w badanych osadach.

Skróty jak w tekście

Concentrations, mg/kg of dry matter	Cd	Cr	Cu	Ni	Pb	Zn
Mean	2.5	56.3	32.7	35.6	53.5	103.9
Maximum	3.1	67.7	38.6	42.9	63.9	133.6
Minimum	2.1	46.9	24.4	28.5	37.8	79.6
Std. dev.	0.2	5.9	4.1	4.2	7.2	15.4
Geochemical background	0.5	6.0	7.0	5.0	15.0	73.0
TEC	0.6	37.3	35.7	18.0	35.0	123
PEC	5.0	111.0	149.0	48.6	128	459

It should be acknowledged that the studied sediments are moderately polluted with the heavy metals. Average concentrations of all metals exceeded the geochemical baseline and the TEC level, moreover only Cu and Zn minimum values were detected below the TEC. The PEC value has not been exceeded in none of the samples analyzed. Despite noted levels of the analyzed metals, there is a risk tied to leaching of the heavy metals into uncontaminated sediments which in turn may pose a threat to the agricultural soils [1].

4.3. Organic compounds

Analysis of the obtained results, in terms of selected compounds content from the PAHs and PCBs group, showed that within PAHs benzo[k]fluoranthene was dominant-reaching an average of 0.1 mg/kg. This value is more than 10-fold higher compared to the dibenzo[a,h]

anthracene for which the lowest concentration was observed in studied sediment (Table 4). However, the greatest impact on the quality of the bottom sediments is connected with the presence of benzo[a]pyrene, mainly due to its high toxicity. In addition, an identifying of BaP in any one element of the environment proves its participation in the overall ecosystem.

Table 4. Characteristic values of the organic compounds studied in the sediment. Data from [19]. Abbreviations as in the text

Tabela 4. Charakterystyczne wartości stężeń zanieczyszczeń organicznych w badanych osadach. Dane opracowane na podstawie [19]. Skrótów jak w tekście

Concentrations mg/kg of dry matter	Mean	Max.	Min.	Std. dev.	TEC	PEC
BaP	0.0894	0.1436	0.0605	0.0256	0.1500	1.5200
BaA	0.0801	0.1382	0.0558	0.0277	–	–
BbF	0.0906	0.1540	0.0573	0.0191	–	–
BkF	0.1000	0.1639	0.0675	0.0275	–	–
BghiP	0.0543	0.0908	0.0348	0.0120	–	–
DahA	0.0097	0.0150	0.0060	0.0022	–	–
IcdP	0.0676	0.1101	0.0424	0.0164	–	–
PCBs	0.0012	0.0028	0.0005	0.0005	0.0590	0.6760

In obtained samples concentrations of BaP were within 0.0605–0.1436 mg/kg and did not exceed the threshold values of PEC (1.52 mg/kg). However, at all studied sites higher amounts of TEC were found with respect to the bottom level of contaminants (0.15 mg/kg). In the same year, an average concentration of the BaP noted for 150 Polish lakes was 3.5-fold higher (0,315 mg/kg) in comparison with sediment cored from the Rzeszów reservoir [6]. A similar range of values was characterized by benzo[b]fluoranthene (0.0573÷0.1540 mg/kg) and benzo[a]anthracene (0.0584÷0.1328 mg/kg). In turn, a slightly lower concentrations were reported for benzo[ghi]perylene at the levels of 0.0348 to 0.0908 mg/kg and indo[1,2,3-c,d]pyrene in the range 0.0424–0.1101 mg/kg.

An important part of the growing problem of the sediments enrichment with organic compounds is an observation of changes within the time context. In 2004 content of BaP in sediments of the Warta river was of ca. 0.02 mg/kg, and in 2005 it already increased to almost 0.4 mg/kg [5]. In the bottom sediment of the Besko reservoir, located in the top section of the Wislok river about 40 km above the Rzeszów reservoir, 0.549 mg/kg of BaP was detected in 2012, which accounted for almost 400 % of the maximum value in the Rzeszów reservoir in 2009 [6]. There is a risk that during high water or flood those deposits will be washed away and transported down the river [4,6]. In addition, conducted correlation analysis has shown that the increase in the concentration of BaP is accompanied by an increase in concentration of other studied PAHs, which confirms the relationship between BaP and other PAHs noted in sediments. The highest correlation coefficient was observed for benzo[a]anthracene ($r = 0.992$), the lowest for benzo[b]fluoranthene ($r = 0.814$, Fig. 2). As reported in the literature, there is a correlation between all 4–6 ring group of PAHs (except for perylene – dominates in the uncontaminated sediments located far from developed areas), which points to a common source of origin, which are combustion processes [5,6]. The degree of contamination of the Rzeszów reservoir bottom sediments with PAHs was relatively low, it does not exceed the values specified by the regulations. The largest was for BaP and accounted for 14% of the allowed amount, whereas all compounds except for dibenzo[a,h]anthracene were characterized by a high variability of concentrations (Table 4).

The studied sediments of the Rzeszów reservoir were also uncontaminated with the PCBs. Their concentration was in the range from 0.0005 mg/kg to 0.0028 mg/kg, which did not exceed the values of TEC (0.059 mg/kg). Despite that, the literature suggests that the content of polychlorinated biphenyls in organisms living in the aquatic ecosystem is much higher than its concentration in sediments [20].

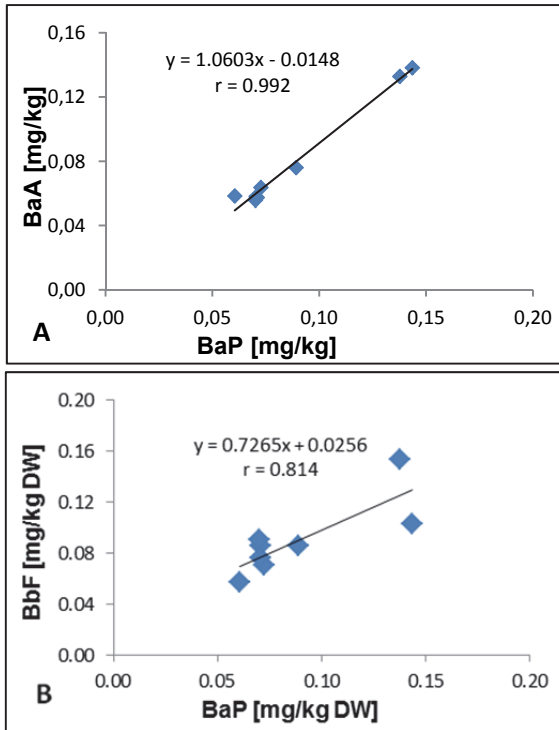


Fig. 2. Relationships between concentrations of benzo[a]pyrene and benzo[a]anthracene (A) and benzo[b]fluoranthene (B)

Rys. 2. Zależność pomiędzy stężeniem benzo[a]pirenu i benzo[a]antracenu (A) oraz benzo[b]fluorantenu (B)

5. Conclusions

The origin of the Rzeszów reservoir bottom sediments is mixed. The unexpectedly high proportion of the autochthonous material is the result of an eutrophic processes. Despite this fact the sediments are relatively poor in nutrients and characterized by slightly elevated concentrations of the heavy metals. Hazardous organic compounds of anthropogenic origin remain in the studied sediments at low concentrations. The characteristics of researched sediments indicate that they are not suitable for agricultural use due to contamination and lack of fertility. However, they can be used for non-agricultural land reclamation. Remediation of the dredged material could possibly result in

the removal of these metals, but due to the significant amounts of dredged materials the process may prove to be an unprofitable operation.

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Ocena możliwości rolniczego wykorzystania osadów dennych z eutroficznego zbiornika zaporowego Rzeszów

Streszczenie

Zbiornik zaporowy Rzeszów na rzece Wisłok w południowo-wschodniej Polsce, został zbudowany w 1973 roku. W trakcie jego eksploatacji, niektóre strefy zbiornika zostały zamulone i załadowione, przez co jego powierzchnia i głębokość istotnie się zmniejszyły. Pomimo kilkukrotnych rekultywacji, zbiornik jest nadal silnie zamulony i jego funkcje użytkowe są mocno ograniczone.

Celem pracy jest analiza zanieczyszczeń i możliwość wykorzystania rolniczego urobku wydobytego ze zbiornika. W pracy dokonano analizy ilościowej zarówno substancji potencjalnie toksycznych jak i biogennych w próbkach osadów pobranych w ciągu ostatnich pięciu lat ze stanowisk zlokalizowanych wzdłuż osi zbiornika. Ponadto, zostało oszacowane pochodzenie materii organicznej zawartej w tych osadach. W tym celu wykorzystano analizy zawartości stabilnych izotopów N i C jak również stosunków elementarnych tych pierwiastków.

Krzemionka była dominującym składnikiem osadu (około 67% suchej masy osadu), zaś materia organiczna (OM) stanowiła około 10% s.m.o. Stężenia związków biogennych: OWO, azotu ogólnego i fosforu ogólnego wynosiły średnio odpowiednio 2,31%, 0,21% i 0,031% s.m.o. Pochodzenie osadów dennych zbiornika Rzeszów jest mieszane. Niespodziewanie wysoki udział materii autochtonicznej może być wynikiem intensywnej eutrofizacji wód zbiornika. Zawartości WWA były stosunkowo niskie. Najwyższe zauważone stężenie wynosiło 0,164 ppm w przypadku benzo(k)fluorantenu. Zawartość benzo(a)pirenu była niższa od 0,14 ppm. Poziomy stężenie wybranych kongenerów PCB mieściły się w przedziale od 0,0006 do 0,003 ppm i były poniżej wartości

normatywnych. Badane osady były umiarkowanie zanieczyszczone metalami ciężkimi (Cu, Cd, Cr, Zn, Ni, Pb). Średnie stężenia wszystkich metali przekraczały sporadycznie tło geochemiczne i poziom TEC, ale wartość PEC nie została przekroczona w żadnej z analizowanych próbek.

Charakter badanych osadów wskazuje, że nie są one odpowiednie do stosowania w rolnictwie ze względu na zanieczyszczenie i brak żyzności. Jednak mogą one być wykorzystywane do rekultywacji gruntów nierolniczych. Istnieją metody umożliwiające usunięcie z wydobytego materiału z tych zanieczyszczeń, głównie metali ciężkich, ale z uwagi na znaczne ilości urobku proces może okazać się nieopłacalny.

Słowa kluczowe:

zbiornik zaporowy, osady denne, stabilne izotopy

Keywords:

reservoirs, bottom sediment, stable isotope