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# PRELIMINARY STUDIES ON THE EXCHANGE OF AMMONIUM AND PHOSPHATES IN BOTTOM DEPOSITS OF DAM RESERVOIRS AND RIVERS

Bottom sediments in reservoirs (in Rożnów and Goczałkowice) and in Rudawa river have been formed by sedimentation of mineral suspended matter. These sediments are capable of adsorbing phosphates and are saturated with ammonium ions. Physico-chemical processes of sorption and desorption depend on degree of humification of organic matter, chemical composition of sediments and concentrations of components in solution.

## 1. INTRODUCTION

A very important role in enrichment of water bodies with nutrients is to be ascribed to the process of sorption and desorption in bottom deposits. Process of sedimentation in rivers and reservoirs is different than that in lakes. Because of soil erosion in a catchment area, large number of soil particles get into water and reservoirs and form there bottom deposits due to sedimentation under conditions of slackening or cessation of gravitational currents. These sediments are called allochtonic.

In lakes bottom sediments are formed from autochtonic matter, especially organic matter. Therefore, organic matter content is a major criterion in classification of bottom sediments. In the case of reservoirs, content of organic matter in bottom sediments (allochtonic material) is lower than 5% [6, 15], while in bottom sediments of lakes (autochtonic material) it exceeds 20% [9], [13]. This distinct difference in chemical composition of bottom sediments in lakes and reservoirs affects considerably exchange of nutrients between sediments and water [4], [7], [8], [14]. Sorption or/and desorption of nutrients in bottom sediments decide whether their content in reservoir water is low or high.

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Bottom sediments consisting mainly of clay minerals washed down from soils in a catchement area are negatively charged and they usually adsorb cations [3]. Such anions as phosphates are adsorbed, while easily leached nitrates [11] are not adsorbed.

The purpose of these studies is an attempt to explain how bottom sediments of rivers and reservoirs affect content of ammonium nitrogen and phosphate in water (under laboratory conditions).

## 2. MATERIAL AND METHODS

Bottom sediment samples have been collected from central parts of dam reservoirs in Goczałkowice and Rożnów as well as from Rudawa river at its mouth to Vistula river. Grain size and chemical composition of the bottom sediments have been determined. Grain size has been estimated according to aerometric method after PRÓSZYŃSKI [5]. Chemical analyses of bottom sediments have been carried out according to standard methods [5]. Humus compounds in bottom sediments were identified in 0.1n NaOH extract at high temperature [1]. Contents of ammonium and phosphates have been determined using 2.5% extract of sodium chloride in 0.1n hydrochloric acid. Ammonium content has been determined according to Nessler method, while phosphates have been determined colorimetrically according to molibdene method [2].

Sorption and desorption were investigated as follows: 1 g of bottom sediment (air dry) has been treated with 100 $cm^3$ of solution of known concentrations of phosphates and mixed in a mixer at the rate of 30 revolutions/minute. Sorption of the ions studied has been calculated from a difference in the initial concentration of phosphates and after the following time intervals: 1/2h, 1h, 3h and 24h. Sorption and desorption of ammonium nitrogen were estimated similarly. Differences in exchange of ions have been determined using distilled and river water as solvents of ion extract. Chemical composition of water used for experiments has been determined according to standard procedures [2].

## 3. RESULTS AND DISCUSSION

Grain sizes and chemical composition of bottom sediments are different in the Rożnów and Goczałkowice reservoirs and in Rudawa river (figure 1, table 1).

Material collected from the Rożnów reservoir is composed of heavy clay without sand fraction. Samples taken from the Goczałkowice reservoir consist of medium loams with admixture of sand fraction. Bottom sediments in Rudawa river are composed of the same amounts of silt and clay. Grain size composition of sediments indicates large sorption capacity of the deposits in question.

pH values of bottom sediments vary in the range from 5.8 to 7.6 and deposits in the Goczałkowice reservoir are slightly acid.

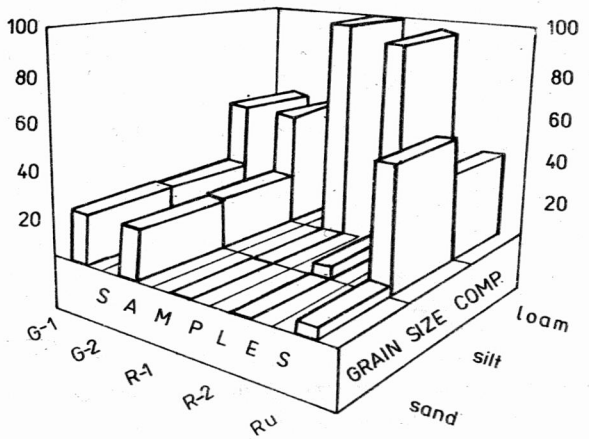


Fig. 1. Grain size composition of bottom sediments

G-1, G-2 – sediments in Goczałkowice reservoir, $R_1$, $R_2$ – sediments in Rożnów reservoir, Ru – sediments in Rudawa river

Table 1

Chemical composition of bottom sediments

| Parameter | | Goczałkowice | | Rożnów | | Rudawa river |
|---|---|---|---|---|---|---|
| | | G-1 | G-2 | R-1 | R-2 | Ru |
| pH value | | 5.8 | 6.0 | 7.6 | 7.6 | 7.0 |
| Organic carbon | [%] | 2.77 | 2.90 | 2.52 | 2.49 | 2.37 |
| Nitrogen | [%] | 0.26 | 0.27 | 0.20 | 0.22 | 0.27 |
| Ammonium nitrogen | [mg N/g] | 1.60 | 1.54 | 1.67 | 1.57 | 0.34 |
| C/N ratio | | 10.65 | 10.62 | 12.60 | 11.33 | 8.8 |
| Humification degree | [%] | 44.48 | 45.52 | 33.80 | 39.80 | 64.50 |
| Phosphates | [mg P/g] | 0.49 | 0.45 | 0.54 | 0.52 | 0.09 |
| Magnesium | [mg Mg/g] | 0.44 | 0.45 | 0.65 | 0.64 | 0.30 |
| Calcium | [mg Ca/g] | 0.13 | 0.12 | 0.22 | 0.20 | 0.17 |
| Iron | [mg Fe/g] | 3.8 | 3.7 | 4.1 | 3.9 | 2.2 |
| Manganese | [ppm Mn] | 553 | 564 | 1312 | 1200 | 414 |

Contens of organic matter were very low and slightly differentiated. Thus, the sediments can be classified as mineral. Contents of total nitrogen were slightly differentiated and varied from 0.20 to 0.27%. Per cent of exchangeable ammonium ions amounted 67.8% and 12.6% (of the total nitrogen) in reservoir sediments and in river sediments, respectively. Large portion of ammonium ions in the total nitrogen in the reservoir bottom sediments was cased by saturation of their sorption complex with these ions originating as a result of organic matter decomposition (mineralization).

Reservoir bottom sediments, in contrast to river bottom sediments, were also rich in exchangeable phosphorus (0.50 mg/g at average). In river sediment, phosphoric

ions constitute only 18% of phosphates. The interesting thing is that contents of phosphates are larger in samples of higher concentrations of iron. Hydrogen oxide of iron is the major sorbent of phosphates.

Table 2

Chemical composition of water tested

| Parameter | | Value |
|---|---|---|
| pH value | | 8.0 |
| Akalinity | [meq] | 4.3 |
| Total hardness | [G.d.] | 16.0 |
| Calcium | [mg $Ca/dm^3$] | 94.0 |
| Magnesium | [mg $Mg/dm^3$] | 13.0 |
| Potassium | [mg $K/dm^3$] | 2.5 |
| Sodium | [mg $Na/dm^3$] | 9.8 |
| Iron | [mg $Fe/dm^3$] | 0.24 |
| Chloride | [mg $Cl/dm^3$] | 16.5 |
| Ammonia | [mg $N–NH/dm^3$] | 0.50 |
| Phosphates | [mg $P/dm^3$] | 0.50 |
| Oxidability | [mg $O/dm^3$] | 6.8 |
| Turbidity | [mg $SiO/dm^3$] | 13.4 |

A narrow range of C/N ratio (8.8–12.60) may result from the presence of nondegraded admixtures of plankton for which the ratio of C/N is 6 according to STANGENBERG [10].

Degree of organic matter humification was differentiated and on average reached 40.9% and 64.5% in reservoirs sediments and in river deposits, respectively. Considerable degree of humification of river sediments results probably from the fact that the river drainage area is of agricultural character and during heavy downpours strongly eroded soils together with humus form bottom sediments.

The ratio of calcium to magnesium indicates that magnesium dominates.

Large amounts of iron have been recorded (table 1). Content of iron in the reservoir bottom deposits was two times higher than in river sediments.

Concentrations of manganese were the highest in the Rożnów deposits (1256 ppm on average), and the smallest in Rudawa river sediments (414 ppm).

Results of the experiments carried out prove that in each case desorption of ammonium ions and strong sorption of phosphate ions occur (table 3, figures 2, 3, 4).

Desorption of ammonium from sediments in both distilled and river water at its concentration of 0.5 mg $N–NH_4$ took place. Desorption of ammonium in distilled water was more efficient than in river water and reached 23.6% and 41.2% of exchangeable ammonium ion in the case of reservoir sediments and bottom sediments, respectively. Desorption of ammonium ions occurs because of the saturation of sorption complex with these ions and due to physico-chemical character of that proces which makes

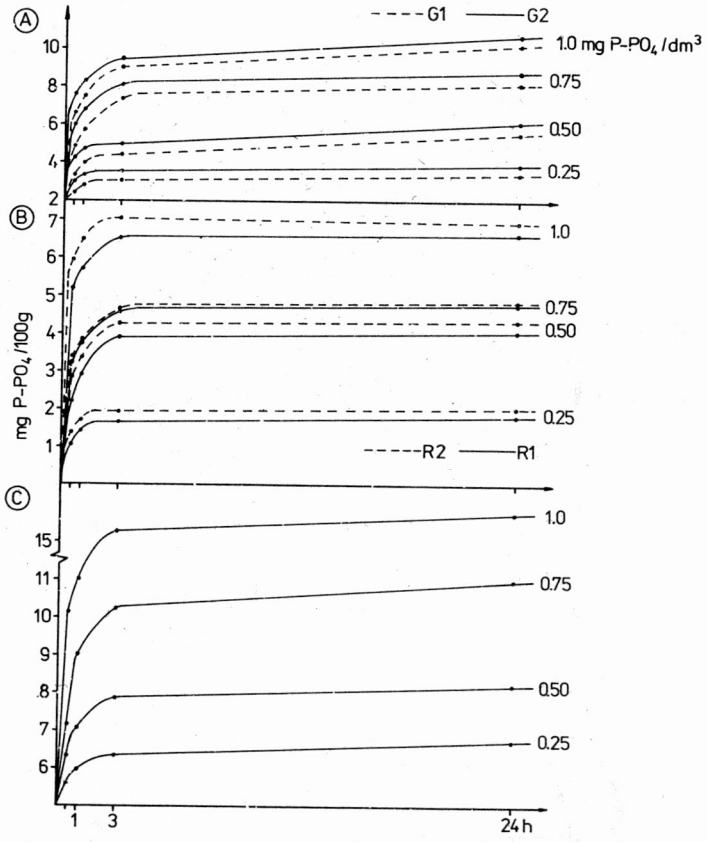


Fig. 2. Sorption of phosphates in sediments in solutions of concentrations of 1.00, 0.75, 0.50, and 0.25 mg P/dm$^3$

A – Goczałkowice reservoir, B – Rożnów reservoir, C – Rudawa river

migration of this ion easy. The interesting thing is that the river bottom sediment containing the smallest amounts of exchangeable ammonium released most of that ion (table 3). Chemical composition of the bottom sediment of Rudawa river can explain this phenomenon.

All sediments are highly capable of adsorbing phosphates. Efficiency of adsorption was correlated with concentration of phosphates in solution (figure 2). It has been stated that for a given concentration of phosphates in solutions, sorption is inversely proportional to the content of exchangeable phosphorus and directly proportional to the degree of humification of organic matter (table 1). Sorption of phosphates in river water is similar to sorption in solution of the same concentration of phosphates (figure 3). It proves that sorption of phosphates depends first of all on chemical composition of sediments and concentration of phosphates in water.

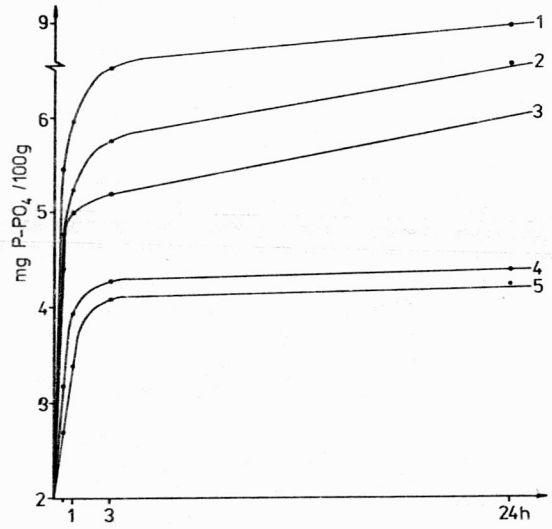


Fig. 3. Sorption of phosphates from water of known chemical composition by sediments from 1 — Rudawa river, 2 — Goczałkowice reservoir G1, 3 — Goczałkowice reservoir G2, 4 — Rożnów reservoir R2, 5 — Rożnów reservoir R1

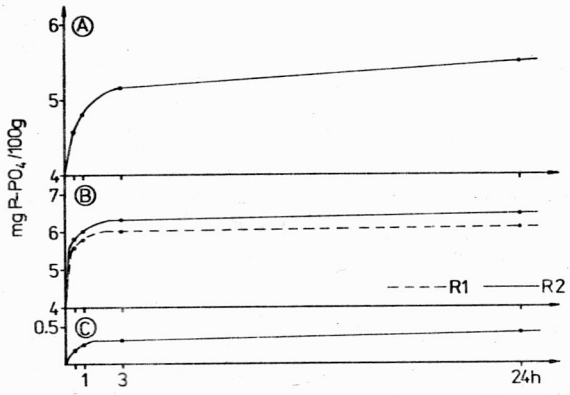


Fig. 4. Desorption of phosphates to distilled water from sediments
A — Goczałkowice reservoir, B — Rożnów reservoir, C — Rudawa river

Desorption of phosphates in distilled water was smaller in the case of river sediments and reached only 0.37 mg P/100 g of sediment, while in reservoir sediments it was about 6 mg P/100 g of sediment.

A low efficiency of phosphate desorption in river sediment resulted probably from a small content of exchangeable phosphorus in the sediment. Amount of phosphates which were desorbed from reservoir bottom sediments to water was also limited by iron content in sediments (table 1). Similar relation was reported

Table 3

Desorption of ammonium ions from bottom sediments

| | Goczałkowice | | Rożnów | | Rudawa river |
|---|---|---|---|---|---|
| | G-1 | G-2 | R-1 | R-2 | Ru |
| Desorption to distilled water [mg N/g sed.] | 0.396 | 0.352 | 0.401 | 0.361 | 0.140 |
| Nitrogen release from bottom sediments [%] | 24.75 | 22.86 | 24.01 | 22.99 | 41.18 |
| Desorption to the river water [mg N/g sed.] | 0.193 | 0.189 | 0.220 | 0.182 | 0.120 |
| Nitrogen release from bottom sediments [%] | 12.06 | 12.26 | 13.17 | 11.59 | 35.29 |

by TROJANOWSKI [12] who proved that in the lake sediments the amount of exchangeable phosphorus depended on iron and aluminium contents in the deposits.

In all the cases, the equilibrium between water and deposits has been quicky achieved (ca. 3h).

## 4. CONCLUSIONS

1. Bottom sediments in reservoirs and river are composed of heavy loams and clays. Therefore their sorption capacities are great.

2. Contents of organic matter in bottom sediments in reservoirs and rivers are small, which supports the statement that due to sedimentation of mineral suspended matter the bottom deposits are formed.

3. Sediments in reservoirs and river adsorb phosphates in all cases and release ammonium nitrogen when saturated with ammonium ions.

4. Sediment capacity for sorbing and desorbing ammonium and phosphate ions indicates that the sediments can be considered a factor controlling concentrations of fundamental nutrients in reservoirs.

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## WSTĘPNE BADANIA NAD WYMIANĄ JONÓW AMONOWYCH I FOSFORANOWYCH PRZEZ OSADY DENNE ZBIORNIKÓW ZAPOROWYCH I RZEK

Osady denne badanych zbiorników zaporowych (w Rożnowie i Goczałkowicach) i rzeki Rudawy powstałe podczas sedymentacji zawiesiny mineralnej sorbowały fosforany, były wysycone natomiast jonami amonowymi. Obserwowano też zależność fizykochemicznych procesów sorpcji i desorpcji od stopnia humifikacji materii organicznej, składu chemicznego osadów oraz stężenia badanych składników w roztworze.

## ПРЕДВАРИТЕЛЬНЫЕ ИССЛЕДОВАНИЯ ОБМЕНА АММОНИЕВЫМИ И ФОСФАТНЫМИ ИОНАМИ ДАННЫМИ ОТЛОЖЕНИЯМИ ПЛОТИННЫХ ВОДОЕМОВ И РЕК

Данные отложения исследуемых плотинных водоемов (в Рожнуве и Гочалковицах) и реки Рудавы, образующиеся во время седиментации минеральной суспензии, сорбировали фосфаты, зато они были насыщены аммониевыми ионами. Наблюдалась также зависимость физико-химических процессов сорбции и десорбции от степени гумификации органического материала, химического состава, а также концентрации исследуемых составных элементов в растворе.