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# CONDITION OF THE POST-RECLAMATION PRZYKONA RESERVOIR (TUREK, POLAND): WATER AND SEDIMENT CHEMISTRY

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**Abstract.** The work discusses the water and sediment geochemistry of the post-reclamation Przykona water reservoir. The analysis mainly focuses on the reservoir's through-flow nature, given that its post-mining history has not resulted in any important contamination of its waters. In the water, cations ($Na^+$, $NH_4^+$, $K^+$, $Ca^{2+}$ and $Mg^{2+}$) and anions ($Cl^–$, $NO_3^–$, $NO_2^–$ and $SO_4^{2–}$) were examined using ion chromatography (IC). Metals (Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) in the water and sediment were analysed using inductively coupled plasma mass spectrometry (ICP-QQQ). Extractions with 3 mol/L HCl were used to prepare sediment samples. It was shown that the Teleszyna River waters on the side of its inflow have significantly higher contents of all elements than do the reservoir waters. In addition, CA chemometric analysis allowed the samples to be divided into two groups. The first included samples from the Teleszyna River inflow and those closest to it, while the second included samples from the river outflow and those close to it. A comparison of elemental concentrations in the reservoir's waters and the river inflow and outflow indicate that the river's waters undergo purification as they flow through the reservoir. This is confirmed by analysis of metals in bottom sediments at the Teleszyna River inflow, where sedimentation of metals transported by the river takes place. In addition, calculations of the $I_{geo}$, CF and PLI indices clearly confirmed the lack of toxicity of the deposited metals.

**Key words:** water chemistry, bottom sediments, post-mining area, lignite coal mines, Przykona reservoir, pit lake

## Introduction

Global environmental changes are forcing more and more countries to move away from lignite mining (Madhavi, Nuttall 2019). Each of them, especially Poland, Germany, Australia and China, are carrying out tasks to reclaim post-mining areas (Amirshenava, Osanloo 2022; Rahmonov *et al.* 2022; Gerwin *et al.* 2023). In addition, Poland, being one of the largest lignite producers in the world, has committed itself to strict regulations and standards for reclamation (Pietrzykowski, Krzaklewski 2018; Kaźmierczak, Strzałkowski 2019). This has resulted in the creation of numerous reclaimed areas in Poland (Kasztelewicz

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*et al.* 2010; Kasztelewicz 2014; Placek-Lapaj *et al.* 2019; Przybyszewski, Kruszyńska 2019), and among the directions of reclamation, the focus on water is becoming increasingly popular (Stachowski *et al.* 2018a). This is leading to the creation of an increasing number of artificial pit lakes (Szczepiński *et al.* 2010a, b; Marszelewski *et al.* 2017; Stachowski *et al.* 2018b; Marszelewski 2023).

The resulting pit lakes can improve the local microclimate and aesthetic qualities and find uses in recreation, fishing and water supply or as habitat areas (Doupé, Lymbery 2005; Stachowski *et al.* 2018a). Their usefulness for these purposes varies depending on topography, climate, safety (risk of rockfall, landslide susceptibility, etc.), and hydrological characteristics (Gammons *et al.* 2009; Al Heib *et al.* 2023).

One way to fill open pits with water is to divert the course of a river into the pit. This solution has been used many times (Schulze *et al.* 2010; McCullough, Schultze 2018; Sakellari *et al.* 2021). This allows, on the one hand, the hydrographic system to be enclosed when the exploitation of the mine stops, and, on the other hand, to quickly and efficiently fill the mine with water (Fagiewicz 2013a; Stachowski *et al.* 2018a). In this way, flow-through lakes are formed whose geochemistry is determined by various factors (e.g., groundwater connectivity, presence of acid mine drainage, reservoir size, etc.) (Golder Associates 2017; McCullough, Schultze 2018; Gąsiorowski *et al.* 2021). Klapper and Schultze (1995) pointed to saprobization and excessive eutrophication, which can increase heavy-metal sedimentation, as some of the problems of this type of lake resulting from surface water inflow. Additionally, Friedland *et al.* (2021) emphasise that lignite mining affects the geochemical composition of sediment and water resources of areas directly and indirectly affected by the mine. Consequently, many lakes in areas reclaimed from former lignite mines contain higher concentrations of heavy metals and/or metalloids (Soni *et al.* 2014; Umbría-Salinas *et al.* 2021).

In analysing particularly successful reclamation cases such as Przykona in Poland, it is possible to focus primarily on their flow-through nature, due to the low impact of mining history (Marszelewski *et al.* 2017; Goździejewska *et al.* 2019, 2021). One of the important aspects of flow-through reservoirs is considered to be their ability to hold pollutants and suspended sediment in the course of a river, so they are often described as "water treatment stations" (Sojka *et al.* 2018). Especially important is the holding back of metals that sediment out into the lake bottom sediments (Klemm *et al.* 2005; Kuriata-Potasznik *et al.* 2016). Depending on the concentration of inflowing pollutants and a range of hydrological and morphogenic characteristics of a lake, this can affect the quality of its waters to varying degrees (McCullough, Schultze 2018; Sojka *et al.* 2018, 2019a, 2022). Therefore, regular monitoring of lake ecosystem hydrogeochemistry by examining the concentration of metals in bottom sediments is highly recommended, as this allows assessment of the state of aquatic pollution (Doupé, Lymbery 2005; Sojka *et al.* 2013).

The designed objectives of this study are: (1) to study the spatial variability of the water and bottom sediment chemistry of the Przykona reservoir, (2) to study the water chemistry of the Teleszyna River at the inflow and outflow from the reservoir, (3) to identify whether the pollution of the Teleszyna River is reduced by the flow of the river through the reservoir and (4) to assess the degree of contamination of bottom sediments using a contamination factor (CF), a geoaccumulation index ($I_{geo}$) and a pollution load index (PLI).

## Materials and methods

### Research area

The Przykona reservoir is located in eastern Greater Poland (Fig. 1), in the Kolska Basin physico-geographical mesoregion (Solon *et al.* 2018). Based on documented lignite deposits, the area is one of eight lignite coal mining regions in Poland (Kasztelewicz 2008). The reservoir was created between 1996 and 2004 as a result of the reclamation of post-mining areas of the Adamów opencast (Orlikowski, Szwed 2009; Fagiewicz 2013b). It is one of the reservoirs that have been created on the internal spoil tips as a result of the floating of pit mines (Stachowski *et al.* 2018b).

The sediments building the reservoir bed are mainly glacial till and a small amount of sand, additionally sealed by clay sediments (Polak, Klich 2009). This prevents direct contact of the reservoir waters with Quaternary sediments and water outflow towards the Adamów mine (Widera 2022). In the past, the reservoir was periodically fed with clean waters from the dewatering of the nearby Adamów open pit, which were used to fill it (Różkowski *et al.* 2010). Currently

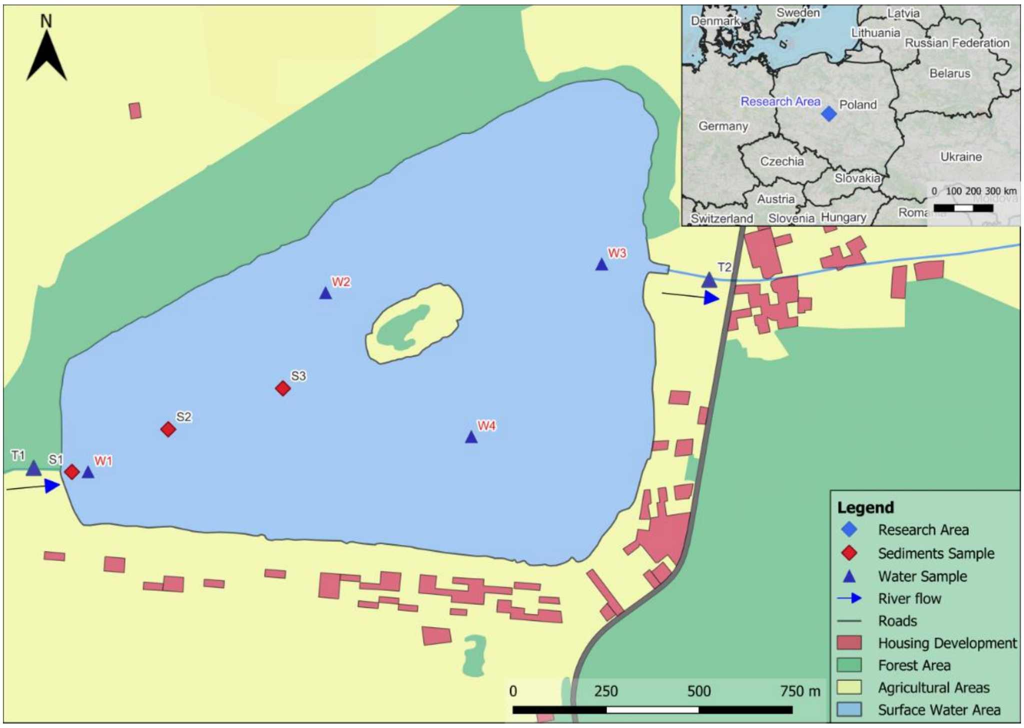

Fig. 1. Location of the Przykona reservoir and the sampling sites for water (W1, W2, W3, W4) and sediment (S1, S2, S3)

the reservoir is mainly fed by waters from its own catchment and the Teleszyna River (Orlikowski, Szwed 2009). The outflow is regulated by the adjustment of a floodgate and is variable over time. Studies conducted by Polak and Klich (2009) have shown that the infiltration coefficient of bottom-building sediments is about $4\cdot10^{-8}$ m/s. This results in a water loss on the Teleszyna River flow through the infiltration of water caused by the depression cone of the Adamów mine. The study by Marszelewski *et al.* (2017) show that the total outflow of reservoir water (surface and underground) was 0.087 $m^3/s$. Their proposed water exchange rate for the lake was $0.45\cdot year^{-1}$, so the reservoir has a low water exchange rate.

The maximum depth of the reservoir is 7.6 m, its area is 142.4 ha, and its capacity is 6.5 mln $m^3$ (Marszelewski *et al.* 2017). This polymictic reservoir has high water mixing dynamics at an average depth of 4.3 m and trophic development (Goździejewska *et al.* 2019, 2021). It has a flat bottom and gently shaped slopes, allowing the introduction of aquatic vegetation and beach access (Stachowski *et al.* 2018a). A buffer zone has not been designated around the reservoir, so there is recreational infrastructure and allotment gardens immediately around it (Fagiewicz 2013b). This green infrastructure performs a number of ecosystem services in the reclaimed area.

## Sample collection and preparation

The sites for water sampling were selected on the basis of a bathymetric map drawn by Marszelewski *et al.* (2017). Samples were taken at four locations in the lake (Fig. 1) every 1 m depth in each profile. A 1.7-litre Niskin-Type Plastic Water Sampler (Hydro-Bios, Altenholz) was used. In addition, water was surface sampled from the Teleszyna River, from both the west and east sides of the lake (inflow and outflow). Water samples were taken on 03.08.2022, and 26 samples were collected. Precipitation in the study area the month before collection was 94.9 mm, while the mean monthly precipitation for the six months was 45.6 mm (Turek station, Institute of Meteorology and Water Management National Research Institute data). The basic physical parameters of pH, temperature, dissolved oxygen (DO), electrical conductivity (EC), total dissolved solids (TDS) and oxidation reduction potential (ORP) were determined *in situ* during sampling using a YSI Professional Plus probe (Ohio, USA). Water samples of 500 mL were collected to polyethylene bottles (HDPE) by Nalgene®. Samples used for chemical analyses were fixed *in situ*. The samples for nitrogen compound analyses were treated with chloroform and, for metals testing, were treated with $HNO_3$ (Merck, Darmstadt, Germany). After collection, the samples were taken to a chemical laboratory in a mobile refrigerator at a temperature of 4±2.5°C. Adequate precautions were applied to avoid water contamination during sample collection, transport and handling.

The sediment collection took place on 01.08.2023. The purpose of sediment collection was to determine the inflow of contaminants from the river Teleszyna and their deposition on the bottom of the reservoir. The sampling locations were determined from the bathymetric map drawn by Marszelewski *et al.* (2017), preliminary results of water analyses and field vision. It was decided to take samples directly at the river inflow and according to the direction of flow towards the island, at equal distances. Sediments were taken from three points (Fig. 1), up to 4 cm depth from the top. The sediments were then sectioned at 1-cm-thick intervals, resulting in a total of 12 samples for analysis. A Limnos sediment sampler (Limnos, Komorów, Poland) was used for this purpose.

## Chemical analysis

Surface water samples were also analysed for their cations ($Na^+$, $NH_4^+$, $K^+$, $Ca^{2+}$ and $Mg^{2+}$) and anions ($Cl^-$, $NO_3^-$, $NO_2^-$ and $SO_4^{2-}$) using a Metrohm ion chromatograph (IC), model 881Compact IC Pro (Metrohm, Switzerland) (Walna, Siepak 2012; Siepak *et al.* 2023). Concentrations of Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn in surface water and bottom sediments were determined by inductively coupled plasma mass spectrometry (ICP--QQQ 8800 Triple Quad, Agilent Technologies, Tokyo, Japan) (Siepak, Sojka 2017; Sojka *et al.* 2020, 2021). Alkalinity was measured by *in situ* titration with HCl (0.1 N) using methyl orange as an indicator. As a quality control measure, the ionic error balance was calculated. The calculated error did not exceed ±3%. Dry bottom sediment samples were mineralised with 3 mol/L HCl by Merck (Merck, Darmstadt, Germany) (Frankowski *et al.* 2008; Sojka *et al.* 2018). The samples were extracted using the MARS 5 Xpress (CEM, Matthews, NC, USA) microwave digestion system.

## Reagents

The reagents used were analytically pure, and the water was purified to the resistivity of 18.2 MΩ.cm (at 25°C) in a Direct-Q UV3 Ultrapure Water Systems apparatus (Millipore, France). During ion chromatography (IC) assays, standard solutions from Merck (Merck, Darmstadt, Germany) and CPAchem (C.P.A. Ltd., Stara Zagora, Bulgaria) were used. The mobile phase for cations and anions was made from Fluka reagents (Sigma-Aldrich, Steinheim, Switzerland). Assays using the ICP-QQQ technique were performed using calibration curves obtained from the diluted stock multi-element standard at 100 µg/mL (VHG Labs, Manchester, NH, USA). Analytical quality control was verified by the analysis of certified reference materials, viz. SRM 1643f (National Institute of Standards and Technology, Gaithersburg, USA), and the Certified Reference Material CRM no. LGC 6187 used for river sediments (Manchester, England).

## Statistical analysis

Statistical analysis was performed using STATISTICA 13.3 (TIBCO Software Inc., Palo Alto, CA, USA) to determine the spatial variability of the chemical composition of 24 water samples from the reservoir. Basic measures of location (mean, median), scatter (maximum and minimum value, lower and upper quartile, standard deviation) and shape of distribution (skewness) were calculated for macroelements (ME) and trace metals (TE) (Tab. 1). Moreover, for ease in comparing the results, the coefficient of variability and the interquartile range (IQR) were calculated based on the mentioned parameters.

In addition, a multivariate statistical analysis of CA was performed for 26 samples – 24 from the reservoir and two from the Teleszyna River. Cluster analysis (CA) was performed to illustrate similarities and differences between water points (Sojka *et al.* 2013). Metals (Al, As, Cd, Cr, Cu, Fe, Mn, Ni, Pb, Zn) were considered in this analysis. Before performing the analysis, the conformity of the distribution of the metals studied to the normal distribution was checked at the $p_\alpha = 0.05$ level using the W test (Shapiro-Wilk). The test showed that the metals in the water of the studied reservoir and river do not have a normal distribution. Trying to transform the data using simple formulas (Mazerski 2009; Przybyła *et al.* 2015) did not produce a normal distribution, so the Box-Cox transformation was used (Box, Cox 1964; Chuchro 2011). Box-Cox transformation was performed using PQStat Software (Poznań, Poland). Then the data were standardised. Data prepared in this way were submitted to hierarchical agglomerative CA using the squared Euclidean distance with Ward's method (Siepak, Sojka 2017).

For sediment samples, an additional assessment of contamination by selected metals was carried out. $I_{geo}$ (Müller 1981) and CF (Martin, Meybeck 1979) indexes were calculated to determine the contamination of each selected element (As, Cd, Cu, Cr, Mn, Ni, Pb, Zn). The PLI index (Tomilson *et al.* 1980) was then calculated to describe the cumulative impact of the metals. Details of the methodology used to calculate $I_{geo}$, CF and PLI are described in Sojka *et al.* (2019b). The geochemical background for As, Cd, Cr, Cu, Ni, Pb, Zn was determined based on the work of Bojakowska and Sokołowska (1998) and amounted to: Cd – 0.5 mg/kg, Cu – 6 mg/kg, Cr – 5 mg/kg, Ni – 5 mg/kg, Pb – 10 mg/kg and Zn – 48 mg/kg. The geochemical background for Mn determined based on Pasieczna (2012) and amounted to 73 mg/kg. The background value for Fe was assumed to be 10,000 mg/kg (Sojka *et al.* 2019a). It was decided to exclude Al from the analyses due to a major problem with the availability of representative geochemical background data, as well as the low toxicity of the element.

Table 1

Selected statistical parameters of water of Przykona reservoir based on 24 samples

| | Parameters | Units | Mean | Median | Min. | Max. | Lower Quartile | Upper Quartile | Standard Deviation | Skewness | Coefficient of variation |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Physical | Temperature | °C | 21.5 | 21.4 | 19.9 | 23.8 | 20.7 | 22.4 | 1.0 | 0.33 | 5% |
| | pH | - | 7.86 | 7.85 | 7.60 | 8.21 | 7.82 | 7.96 | 0.13 | 0.79 | 2% |
| | Conductivity | µS/cm | 434.0 | 433.2 | 427.1 | 461.6 | 432.3 | 434.1 | 6.2 | 4.17 | 1% |
| Macro elements | Alkalinity | [mval/L] | 2.4 | 2.5 | 2.2 | 2.6 | 2.4 | 2.5 | 0.1 | -1.10 | 4% |
| | $HCO_3^-$ | [mg/L] | 149.2 | 152.5 | 134.2 | 158.6 | 146.4 | 152.5 | 5.4 | -1.10 | 4% |
| | $CaCO_3$ | | 187.4 | 188.5 | 178.2 | 191.4 | 185.9 | 190.3 | 3.8 | -1.24 | 2% |
| | $Cl^-$ | | 24.1 | 24.0 | 23.9 | 25.0 | 23.9 | 24.1 | 0.3 | 2.46 | 1% |
| | $NO_2^-$ | | 0.005 | 0.005 | 0.002 | 0.011 | 0.003 | 0.007 | 0.002 | 0.76 | 45% |
| | $NO_3^-$ | | 0.090 | 0.089 | 0.015 | 0.160 | 0.062 | 0.106 | 0.040 | 0.19 | 45% |
| | $SO_4^{2-}$ | | 56.5 | 56.5 | 56.0 | 57.1 | 56.3 | 56.8 | 0.3 | 0.05 | 0,5% |
| | $Na^+$ | | 11.3 | 11.3 | 10.5 | 12.2 | 11.2 | 11.4 | 0.3 | 0.40 | 3% |
| | $NH_4^+$ | | 0.124 | 0.113 | 0.011 | 0.343 | 0.047 | 0.192 | 0.089 | 0.80 | 72% |
| | $K^+$ | | 3.06 | 3.05 | 2.99 | 3.14 | 3.04 | 3.08 | 0.03 | 0.56 | 1% |
| | $Ca^{2+}$ | | 60.4 | 60.9 | 56.9 | 61.5 | 60.2 | 61.2 | 1.4 | -1.66 | 2% |
| | $Mg^{2+}$ | | 8.93 | 8.96 | 8.20 | 9.50 | 8.73 | 9.14 | 0.34 | -0.29 | 4% |
| | Fe | [µg/L] | 3.48 | 3.17 | 2.13 | 6.30 | 2.98 | 3.82 | 0.99 | 1.43 | 29% |
| | Mn | | 19.9 | 17.4 | 11.8 | 41.9 | 14.9 | 22.1 | 7.5 | 1.68 | 38% |
| Trace elements | Al | | 7.89 | 7.86 | 3.58 | 12.56 | 6.61 | 9.13 | 2.08 | 0.08 | 26% |
| | As | | 1.14 | 1.13 | 1.03 | 1.30 | 1.08 | 1.21 | 0.09 | 0.38 | 8% |
| | Cd | | 0.011 | 0.009 | 0.001 | 0.024 | 0.005 | 0.019 | 0.008 | 0.43 | 73% |
| | Cr | | 0.55 | 0.73 | 0.10 | 0.95 | 0.20 | 0.78 | 0.30 | -0.40 | 54% |
| | Cu | | 3.81 | 2.53 | 1.13 | 11.2 | 1.84 | 4.65 | 2.91 | 1.39 | 77% |
| | Ni | | 1.29 | 1.06 | 0.46 | 2.96 | 0.72 | 1.73 | 0.76 | 1.04 | 59% |
| | Pb | | 0.89 | 0.78 | 0.21 | 2.32 | 0.55 | 1.14 | 0.51 | 0.98 | 57% |
| | Zn | | 5.47 | 5.40 | 1.71 | 9.45 | 3.84 | 7.43 | 2.23 | -0.17 | 41% |

# Results

## Physico-chemical water parameters

The physical parameters measured *in situ* for the reservoir water were within the ranges: pH from 7.60 to 8.21; temperature from 19.9°C to 23.8°C; DO from 39.6% to 94.8%. In general, the values of all of them decreased with depth. A marked decrease in oxygenation occurred from 3 m towards the bottom. At point W1, at the inflow of the river, pH reached the lowest values, while DO reached the highest. On the basis of the pH range, the reservoir waters should be classified as poorly alkaline. The temperature value was not affected by the location of the point. EC values ranging from 427.1 µS/cm to 461.6 µS/cm and TDS values ranging from 278.2 mg/L to 300.3 mg/L generally increased with depth and the results were similar throughout the re-

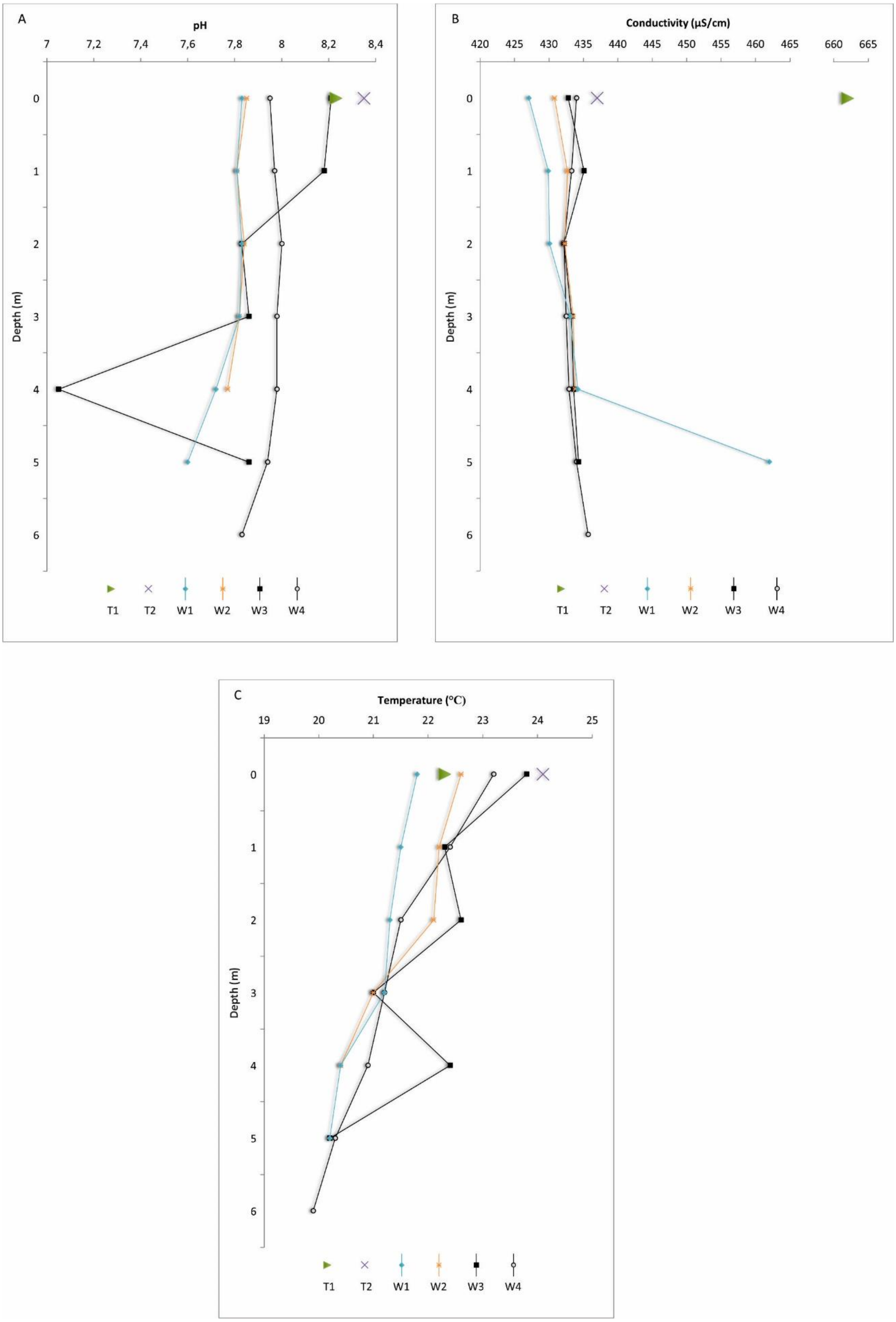

Fig. 2. Changes in pH (A), conductivity (B) and temperature (C) for samples taken from the reservoir (W1, W2, W3, W4) and the river inflow (T1) and outflow (T2)

servoir. ORP values ranging from 74.7 mV to 142 mV showed spatial variation. The ORPs were highest at points W1 and W2 and decidedly lowest at point W3. Samples taken from the river show slightly higher pH values than in the reservoir, respectively: 8.23 for point T1 and 8.35 for point T2 (Fig. 2A). The conductivity of the inflow side of the river (T1) was significantly higher than that in the reservoir, with a value of 662 μS/cm (Fig. 2B). The conductivity for the river outflow (T2) did not differ from the value in the reservoir and amounted to 437 μS/cm. The highest temperature measured was in the river outflow (Fig. 2C).

The reservoir waters were characterised by spatial variability in water chemistry. $NH_4^+$ at all points except W4 increased with depth and reached its maximum value at point W3 at 5 m depth. $NO_2^-$ and $NO_3^-$ concentrations generally decreased with depth. Both reached their lowest concentrations at point W1 near the surface, and the lowest at point W4 near the bottom. $SO_4^{2-}$ concentrations showed little variation throughout the reservoir and showed no significant differences between points. $Cl^-$ and $K^+$ showed little variation, and their spatial distribution and in the vertical profile did not show a concentration-depth relationship and ranged respectively: 23.9–25 mg/L and 2.99–3.14 mg/L. $Ca^{2+}$ did not show much variability, but the W2 point stands out for having by far the lowest concentrations. Related to this is a similar distribution of $CaCO_3$ water hardness, which also had the lowest values at this point and showed no significant differences or concentration-depth relationships at other points. $Na^+$ concentration had the lowest concentration at a depth of 3 m at point W2, and the highest concentration near the bottom at point W1. $Na^+$ obtained similar results in most samples. $Mg^{2+}$ generally had the lowest concentrations at point W2 and the highest at W4. Thus, it should be noted that point W2 for many components has the lowest concentrations. Compared to the reservoir waters, the waters of the Teleszyna River from the inflow (T1) were characterised by higher concentrations of all constituents except $Mg^{2+}$ (Fig. 3). On the outflow (T2), the chemistry of Teleszyna's waters is closer to the chemistry of the reservoir compared to the inflow (T1).

The highest concentrations of the studied metals were located at various sampling points. Cd and Zn have their highest concentrations at point W1, and their concentrations within the reservoir generally decreased with depth. As also had the highest values at point W1 but did not show a concentration–depth relationship. The only element that had the lowest concentrations at river inflow (W1) was Cr, which was equal to a maximum of 0.24 μg/L. Cr had the highest concentration at point W2 and was equal to a maximum of 0.95 μg/L. Ni and Cu also had the highest concentrations at this point, except that Ni showed no concentration–depth relationship, and Cu increased with depth. Pb and Al were the only highest concentrations shown at point W3. Additionally, within the reservoir, Pb concentrations increased with depth, but Al concentrations increased with depth only at points W1 and W2. Mn and Fe concentrations showed elevated value at points near the river inflow (W1) and river outflow (W3) and did not show a concentration-depth relationship. Conclusions on the spatial distribution of metals within the reservoir correspond with their increased concentrations in the Teleszyna River (Tab. 2).

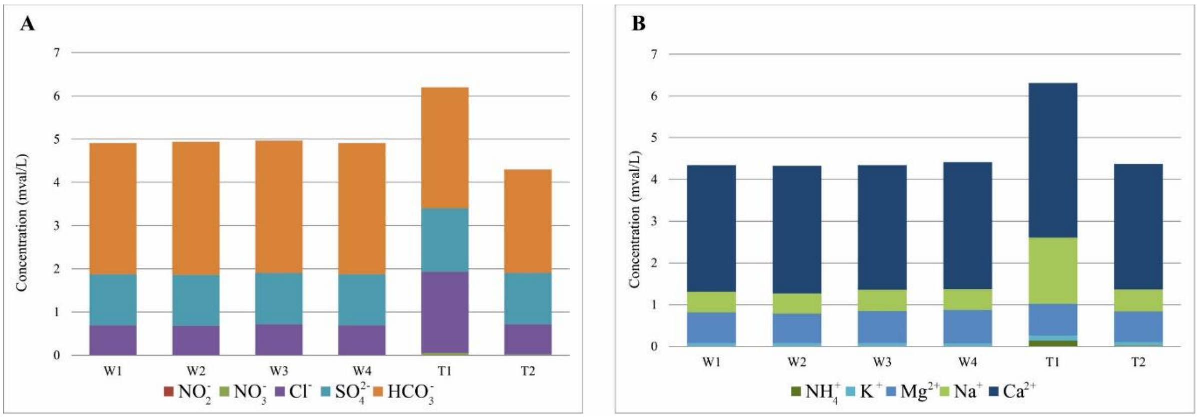

Fig. 3. Proportion of anions (A) and cations (B) in samples from the surface reservoir (W1, W2, W3, W4) and river inflow (T1) and outflow (T2)

Table 2

Comparison of the average content of elements in the reservoir and the Teleszyna River

| | Units | Parameters | Reservoir (mean) | Teleszyna (inflow) | Teleszyna (outflow) |
|---|---|---|---|---|---|
| Physical | °C | Temperature | 21.5 | 22.3 | 24.1 |
| | - | pH | 7.86 | 8.23 | 8.35 |
| | µS/cm | Conductivity | 434.0 | 662.0 | 437.0 |
| Macro elements | mval/L | Alkalinity | 2.4 | 2.8 | 2.4 |
| | mg/L | $HCO_3^-$ | 149.2 | 170.8 | 146.4 |
| | | $CaCO_3$ | 187.4 | 222.1 | 186.2 |
| | | $Cl^-$ | 24.1 | 65.8 | 24.4 |
| | | $NO_2^-$ | 0.005 | 0.025 | 0.019 |
| | | $NO_3^-$ | 0.090 | 3.08 | 1.03 |
| | | $SO_4^{2-}$ | 56.5 | 70.5 | 57.0 |
| | | $Na^+$ | 11.3 | 36.5 | 12.1 |
| | | $NH_4^+$ | 0.124 | 2.38 | 0.40 |
| | | $K^+$ | 3.06 | 5.18 | 3.15 |
| | | $Ca^{2+}$ | 60.4 | 74.1 | 60.1 |
| | | $Mg^{2+}$ | 8.93 | 9.05 | 8.81 |
| | µg/L | Fe | 3.48 | 1072.5 | 3.8 |
| | | Mn | 19.9 | 1670.8 | 14.4 |
| Trace elements | | Al | 7.89 | 91.3 | 12.1 |
| | | As | 1.14 | 2.94 | 0.94 |
| | | Cd | 0.011 | 0.061 | 0.003 |
| | | Cr | 0.55 | 14.1 | 0.54 |
| | | Cu | 3.81 | 28.3 | 1.26 |
| | | Ni | 1.29 | 5.03 | 0.69 |
| | | Pb | 0.89 | 2.52 | 0.62 |
| | | Zn | 5.47 | 3132.6 | 3.56 |

## Statistical water analysis

A statistical analysis of the 24 water samples taken within the reservoir (Tab. 1) showed that both pH and conductivity had insignificant variability and their coefficient of variability was, respectively: 2% and 1%. For temperature it was slightly higher at 5%. However, it should be noted that the distribution of conductivity is strongly right-skewed. Alkalinity, hardness and carbonate content show strong left-skewedness, but the coefficient of variability of these parameters is small at 4%, 4% and 2%, respectively. The concentrations of $NO_2^-$ and $NO_3^-$ are low and fall within the ranges of 0.002–0.011 mg/L for $NO_2^-$ and 0.015–0.16 mg/L for $NO_3^-$, resulting in a high coefficient of variation for both of them of 45%. By far the lowest coefficients of variation were obtained by ME: $Cl^-$ – 1%, $Na^+$ – 3%, $K^+$ – 1%, $Ca^{2+}$– – 2%, $Mg^{2+}$– 4%. Of these, $Ca^{2+}$ has a strongly left-skewed distribution, while $Cl^-$ has a strongly right-skewed distribution. $NH_4^+$ concentrations range from 0.011 to 0.343 mg/L, which gave a coefficient of variation of 72%. The high coefficient of variation for $NH_4^+$ is due to the low concentrations of this element in the water. The lowest coefficient of variation was found for $SO_4^{2-}$ at 0.5% with a skewness of 0.05, indicating virtually no variability in concentration within the reservoir.

The mean TE concentrations in the reservoir water can be arranged in decreasing order as follows Al>Zn>Cu>Ni>As>Cr>Pb>Cd. The mean concentrations of these elements ranged from 0.011 to 7.89 µg/L. In addition, Cr and Zn have a left-skewed distribution, while Pb and Cd have a right-skewed distribution. A strongly right-skewed distribution characterised Ni and Cu. Al has a skewness of 0.08. The variability of the studied elements was examined by calculating the IQR median ratio and coefficient of variation, whose values ranged from 32% (for Al) to 160% (for Cd) and from 8% (for As) to 77% (for Cu).

The calculated mean concentrations for ME and TE in the reservoir (Tab.1) were compared with values from the river inflow (T1) and outflow (T2) (Tab. 2). The comparison clearly shows that the content of most elements is by far the highest in the Teleszyna inflow. The greatest differences in ME levels are shown by Fe and Mn, whose concentrations are about 308 and 84 times higher than in the reservoir. For most MEs, concentrations in the Teleszyna outflow are lower than or comparable to those in the reservoir. Only $NO_2^-$, $NO_3$ and $NH_4^+$ have significantly higher concentrations than in the reservoir. The comparison also showed that Zn and Cr show the greatest differences in TE between the river outflow and the reservoir. Their concentrations in the river are 573 and 26 times higher than in the reservoir. Higher concentrations of only one element were found in the river outflow than in the reservoir, and that is Al.

The CA analysis conducted made it possible to separate two main groups of water sampling points (Fig. 4A). The P1 group includes two sub-groups. The first, group P1-1, includes sampling points W1 and W2 at all depths studied. Group P1-2 includes only the sample from river influence T1, which was significantly differentiated by higher elemental concentrations. Group P2 includes points W3, W4, T2 and allows us to conclude the similarity between these points.

CA analysis for metals based on 26 water samples allowed us to identify two groups and two subgroups (Fig. 4B). The M1 group consists of two subgroups, M1-1 and M1-2. The first of which contains two elements: Al and Mn. The second contains four elements: Cr, Pb, Fe and Cu. The M2 group contains the metals Ni, Cd, Zn and As and exhibits a high correlation in their occurrence.

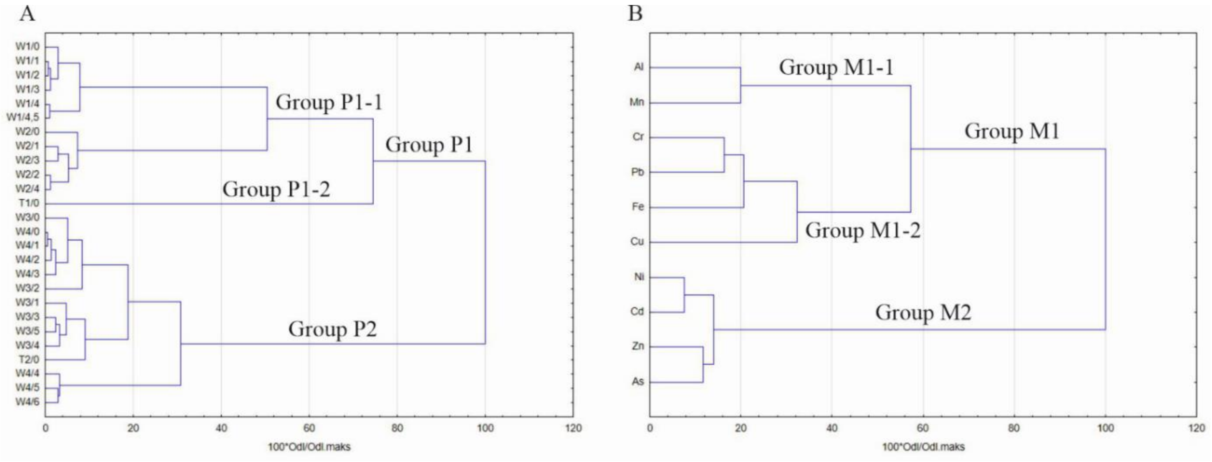

Fig. 4. Dendrogram showing clustering of (A) reservoir and river water sampling points (name of sample/depth) and (B) metals

## Sediment samples

Analysis of metals in sediment was performed for three points. At each of them, four samples from the first 4 cm of the core were examined (Tab. 3). It was found that all elements reached the highest concentration in the 1st centimetre from the top and the lowest in the 4th deepest centimetre. In order to better visualise the data, means were calculated based on four samples for each point (Fig. 5). This helped to conclude that the concentrations of Mn, Fe, Ni, Cu, As, and Pb increase from the river inflow to the centre of the reservoir. The concentration of Cr in the sediment had the highest value at point S2, while Al had the lowest value at this point. Only Zn had the highest concentration in sediment taken directly at the river's inflow, which should be related to the very high Zn concentrations in the river. The concentration of Cd at all points was the same and showed no spatial variation. However, the described trends in sediment metal concentrations are not the same for all centimetres in depth (Tab. 3).

The calculated $I_{geo}$ index ranged from -0.78 (for Mn) to -0.13 (for As) and indicates the absence of metal contamination of bottom sediments (Tab. 4). The same result is presented by CF, whose values range from 0.01 (for As) to 0.61 (for Mn). The result is that the PLI index indicating total metal pollution also showed no pollution (PLI values<1).

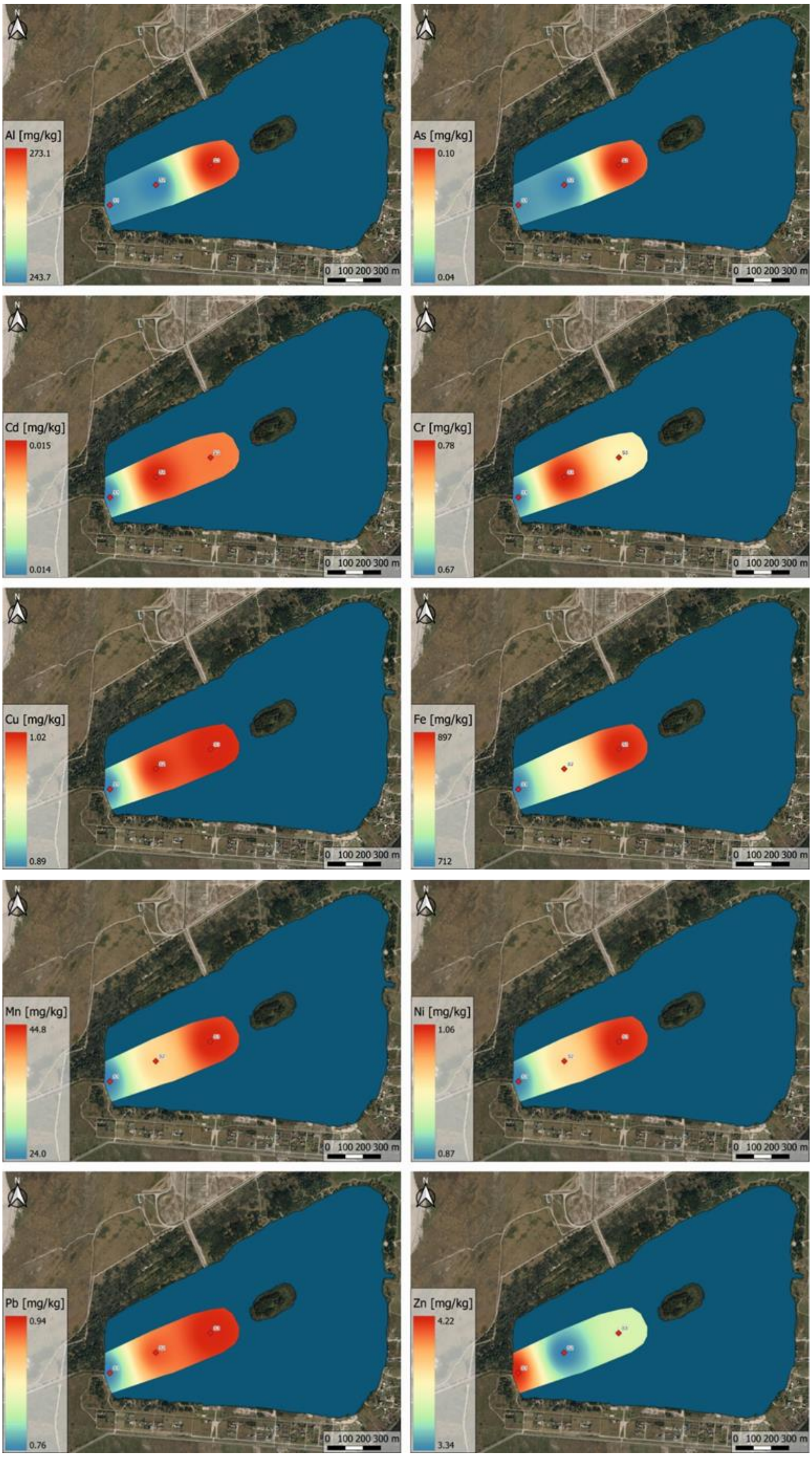

Fig. 5. Mean metal concentrations in the sediment samples (S1, S2, S3) of the Przykona reservoir

Table 3

Results of metal determinations in sediment

| Sample number | Depth | Metals [mg/kg ] | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Al | Cr | Mn | Fe | Ni | Cu | Zn | As | Cd | Pb |
| 1 | 1 | 290.4 | 0.77 | 27.6 | 780 | 0.93 | 1.07 | 4.97 | 0.05 | 0.015 | 0.83 |
| 1 | 2 | 239.7 | 0.67 | 22.5 | 736 | 0.85 | 0.86 | 4.01 | 0.05 | 0.014 | 0.77 |
| 1 | 3 | 238.7 | 0.70 | 23.9 | 719 | 0.87 | 0.90 | 4.06 | 0.05 | 0.015 | 0.78 |
| 1 | 4 | 209.2 | 0.55 | 22.1 | 612 | 0.84 | 0.76 | 3.85 | 0.01 | 0.014 | 0.68 |
| 2 | 1 | 256.9 | 0.79 | 42.0 | 880 | 1.01 | 1.08 | 3.50 | 0.06 | 0.015 | 0.99 |
| 2 | 2 | 248.1 | 0.77 | 37.4 | 843 | 0.98 | 1.03 | 3.46 | 0.05 | 0.015 | 0.97 |
| 2 | 3 | 241.7 | 0.78 | 35.0 | 843 | 0.99 | 1.09 | 3.26 | 0.04 | 0.016 | 0.92 |
| 2 | 4 | 228.3 | 0.75 | 34.9 | 663 | 0.97 | 0.85 | 3.14 | 0.01 | 0.016 | 0.80 |
| 3 | 1 | 297.0 | 0.82 | 56.0 | 1116 | 1.15 | 1.17 | 3.99 | 0.21 | 0.016 | 1.06 |
| 3 | 2 | 277.2 | 0.84 | 47.4 | 1022 | 1.12 | 1.15 | 3.87 | 0.13 | 0.017 | 1.09 |
| 3 | 3 | 263.0 | 0.80 | 40.1 | 961 | 1.07 | 1.11 | 3.67 | 0.07 | 0.016 | 0.96 |
| 3 | 4 | 255.4 | 0.44 | 35.9 | 489 | 0.90 | 0.63 | 3.02 | 0.01 | 0.012 | 0.65 |

Table 4

Analytical results for sediment contamination based on the mean concentration at a point

| Sample | $I_{geo}$ | | | | | | | | | CF | | | | | | | | | PLI |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Cr | Mn | Fe | Ni | Cu | Zn | As | Cd | Pb | Cr | Mn | Fe | Ni | Cu | Zn | As | Cd | Pb | |
| 1 | -0.29 | -0.46 | -0.23 | -0.32 | -0.30 | -0.24 | -0.13 | -0.18 | -0.23 | 0.13 | 0.33 | 0.07 | 0.17 | 0.15 | 0.09 | 0.01 | 0.03 | 0.08 | 0.08 |
| 2 | -0.31 | -0.64 | -0.24 | -0.34 | -0.32 | -0.23 | -0.13 | -0.18 | -0.25 | 0.16 | 0.51 | 0.08 | 0.20 | 0.17 | 0.07 | 0.01 | 0.03 | 0.09 | 0.09 |
| 3 | -0.30 | -0.78 | -0.25 | -0.35 | -0.32 | -0.23 | -0.16 | -0.18 | -0.25 | 0.15 | 0.61 | 0.09 | 0.21 | 0.17 | 0.08 | 0.02 | 0.03 | 0.09 | 0.10 |

# Discussion

The literature on the course of reclamation and its progress of the Konin lignite mines is very abundant (e.g., Polak, Klich 2009; Kasztelewicz *et al.* 2010; Szczepiński *et al.* 2010a, b; Fagiewicz 2013a, b; Kasztelewicz 2014; Stachowski *et al.* 2018a; Marszelewski 2023). The information on Przykona clearly shows that dewatering waters from the Adamów pit were fed into it in the past. However, this is not currently being done. Therefore, the only direct impact of the mine is increased infiltration of lake water caused by the pit depression cone. In 2021, lignite mining at the Adamów mine was stopped and water reclamation activities were begun (Marszelewski 2023). With the progress of a nearby open-pit reclamation, the infiltration problem should be solved. This allowed the analysis to focus on the reservoir's through-flow nature.

Kuriata-Potasznik *et al.* (2016) showed that the complex elements that make up a reservoir-river aquatic ecosystem can counteract pressure by temporarily removing pollutants. Water analyses have shown that the flow of the Teleszyna River through the reservoir leads to an improvement in the quality of river water in terms of all elements examined (Tab. 2). In particular, concentrations of Mn, Fe and Zn are significantly higher at the river inflow than at the other points. These conclusions are confirmed by the CA analysis performed, which clearly indicated that point T1 shows a significant outlier in chemical composition. However, it is closest to the points that are directly influenced by the water coming from the river (W1, W2). The formation of water chemistry at these points is possibly due both to the direction of water flow and to the catchment development character of the reservoir's northern side, which differs significantly from the southern side (Fig. 1). However, measured water temperatures suggest that water exchange is higher in the northern part of the reservoir, which may also be due to its depth in this part. The river outflow and points W3, W4 formed the second group. This indicates the probable impact of the island in shaping its geochemistry by determining the direction of water flow. Additionally, the CA analysis showed that depth of sampling is far less important than location within the reservoir, and this is related to the high wind exposure resulting in the intense mixing of the waters. Purification from dissolved components in water, including pollutants, is well illustrated by the decrease in conductivity from the river's inflow to the reservoir's outflow. The concentrations obtained in comparison with Marszelewski *et al.* (2017) shows that, with the passage of time, TE concentrations in the waters of the reservoir have significantly decreased. This may reflect that the quality of Przykona's waters has improved over the years. ME obtained mostly similar results to Marszelewski *et al.* (2017).

Bottom sediment analysis has made it possible to describe the purification of surface water at the river's inflow, through the processes of dissolved metal forms sorption and sedimentation of suspended material (Rabajczyk 2007; Kuriata-Potasznik *et al.* 2016, 2020). Measured ORP and pH values indicate that the metals in the case studied should exist primarily in the forms of insoluble oxides, hydroxides or carbonates (Takeno 2005). Moreover, due to the high concentrations of manganese and iron, it should be noted that their oxides have a high ability to sorb other metals (Aleksander-Kwaterczak, Kostka 2015; Linnik *et al.* 2023). It should therefore be assumed that the dominant metal transport process in the Teleszyna River is suspension. However, it should be emphasised that the process of metal transport in natural waters is complex, and these conclusions should only be regarded as preliminary and in need of further research.

The variability of the sedimentation process is particular to each reservoir and depends on the morphogenic parameters of the reservoir, the time of water exchange, and operating conditions (Sojka *et al.* 2018). In the case of the Przykona reservoir, this is a process that consists of several elements – the variable inflow of the river, the regulation of the outflow by means of a floodgate, and the infiltration process caused by the depression cone of the nearby open pit. However, the lake is generally characterised by a low rate of water exchange (Polak, Klich 2009; Marszelewski *et al.* 2017). The metal content can therefore both obtain the highest concentrations at the river inflow to the reservoir (e.g., Varol 2013) and increase along the reservoir (e.g., Klaver *et al.* 2007). The variability in metal concentrations is often related to grain size, as metal particles sorb differently depending on granularity (Frankowski *et al.* 2008). However, El-Sayed *et al.* (2015) showed that this is not the case for all elements, and thus granularity is not the only factor affecting their spatial variability. It is also important to take into account the existing trophy in the Przykona reservoir (Goździejewska *et al.* 2019, 2021), which, through bioaccumulation processes, can support water purification processes (Kuriata-Potasznik *et al.* 2018). Pb, Cd, Cu and Zn have a particularly high affinity for organic matter (Helios-Rybicka *et al.* 1995). The complexity of this issue is very well reflected in the results obtained at the Przykona reservoir. Most of the elements studied (Mn, Fe, Ni, Cu, As, Pb) showed an increase with distance from the river inflow (Fig. 5). However, this relationship is not the same at every centimetre in depth, but only considering the mean of each point (Tab. 3). Skwierawski and Sidoruk (2014) showed that the highest concentrations of metals are to be expected in the highest parts of the sediment. Such variability may be the result of both variation in concentrations over time and the effect of the influent water on the sediment near the river inflow (grain traction, saltation). Zn showed the opposite trend and obtained the highest concentration at the river's inflow, which should be associated with high Zn concentrations in Teleszyna River waters. Cr and Al did not obtain a regular distribution. Cd showed no spatial variability and very low concentrations. Despite the demonstrated deposition of metals and, therefore, an improvement in the quality of the waters of the Teleszyna River, the deposited metals did not show toxic concentrations. This is confirmed by the geoaccumulation index ($I_{geo}$), the CF index and the PLI index (Tab. 4). Their accumulation therefore does not affect the quality of the reservoir's aquatic environment, thus does not lead to a decline in its ecosystem values. In addition, the studied pH values in this work and in Marszelewski *et al.* (2017) and Goździejewska (2019) show the persistence of a slightly alkaline water reaction. Studies have shown that such a pH reduces the potential for migration and re-release of metals from the sediment into the water (Huang *et al.* 2017; Linnik *et al.* 2023). Probably, the persistence of a slightly alkaline pH of the reservoir waters is a positive effect of the use of Quaternary sediments for its formation (Marszelewski *et al.* 2017). In addition, this solution has allowed the reservoir to form and operate during ongoing mining in the nearby Adamów open pit. This may also protect the reservoir in the future when groundwater levels rebuild after mining in the area, excluding the geogenic hazards typical of lignite pit lakes (Golder Associates 2017; McCullough, Schultze 2018).

This is particularly important because, in an old-glacier landscape devoid of natural lakes, they take on a number of ecosystem functions (Fagiewicz 2013a). Among the most important functions performed by the Przykona reservoir are recreational, fire-fighting, flood control and natural (Fagiewicz 2013a; Marszelewski 2023). Due to the small number of lakes in the Konin area, there has been a rapid expansion of the tourist and recreational base around the reservoir. In addition, as shown in this publication, the water flow of the river Teleszyna through the reservoir leads to an improvement in its chemical condition. Therefore, due to its importance to the local community and the ecosystem, the preservation of the Przykona reservoir in good geochemical condition should be treated as an important task.

## Conclusions

Based on the geochemical study of sediments and waters of the Przykona reservoir, it was concluded that:

1. The waters of the reservoir show spatial variability in chemical composition;
2. CA analysis made it possible to distinguish two groups for water samples: one near the inflow of the Teleszyna River and the other near the outflow;
3. The flow-through nature of the reservoir leads to improvement of the Teleszyna River water quality by dilution and deposition of TE in the reservoir;
4. The analysis of bottom sediments showed that metals carried by the Teleszyna River are deposed in the sediment;
5. In general, except for Zn, metals deposition increases with distance from the Teleszyna River inflow;
6. Calculations of $I_{geo}$, CF and PLI indexes show that the deposited metals are not toxic.

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