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The influence of the physicochemical properties of sediment on the content and ecotoxicity of trace elements in bottom sediments

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**ABSTRACT**

The sorption mechanisms of the trace elements in bottom sediment are not fully understood. The study aim was to analyse the effect sorption capacity of bottom sediments on the content of trace elements and the bottom sediment ecotoxicity. The study found higher content of trace elements caused higher potential toxicity of bottom sediments. However, the PCA analysis indicated that ecotoxicity to \textit{Heterocypris incongruens} was not related to the trace element content in the sediments. It was found that some of the physicochemical properties of bottom sediments determine the behavior of the test organism. The study revealed a strong relationships between the properties of bottom sediments and trace element sorption, which results from significant differences in the carbonate and organic matter contents. The obtained relationships showed a significant role in trace element sorption of negatively dissociating functional groups (carboxyl, phenolic, alcohol, and carbonyl groups) of Cha, Cha, Cnh and DOC fraction and of clay minerals. Positive correlation between the metal content and the volume of ultramicropores, cryptopores and residual pores suggest that these pore groups contain reactive sites capable of effective element sorption. In contrast, larger pores turned out to be of marginal importance in trace elements sorption, probably participating only in their migration within the bottom sediment structure. An understanding of the above factors will provide comprehensive information on the fate of trace elements in aquatic systems.

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1. Introduction

Contamination of sediments with trace elements has become a growing global problem in recent years especially considering that it is a threat to living organisms in the aquatic environment (Baran et al., 2016; Sirani et al., 2020). Over 90 % of the metal pool in water reservoirs is present in sediments (Zhang et al., 2014), which shows a deterministic importance of solid phase for circulation and ecotoxicity of trace elements. That’s why sorption capacity is an important parameter for sediment quality, since it is essential for limiting migration and bioavailability of trace elements. However, trace elements binding processes can vary considerably depending on the sediment composition, structure and properties. Generally, climate, parent rocks and sediment properties, such as acid-volatile sulphides (AVS), organic matter, texture, pH, redox potential, as well as organism behavior, influence trace element content in bottom sediments (Zhang et al., 2014; Wang et al., 2014; Baran et al., 2019; Lipczynska-Kochany, 2018; Birch et al., 2021; Blecken et al., 2012). In water sediments, trace elements are bound in the structure of minerals present as chemical compounds (sulphides, carbonates, oxides) or in forms absorbed by clay minerals, organic matter, or hydrated iron hydroxides (Wang et al., 2014; Gao et al., 2021). Studies indicate, among other things, the important role of aggregated particles with a size below 0.01 mm (Rzetala et al., 2019). Du Laing et al. (Du Laing, 2009) reported that organic matter of low to medium molecular weight can be a source of dissolved organic compounds for soluble complexes with metals, while macromolecular fraction can reduce mobility of trace elements. Solubility of metals can also be reduced in the presence of acid-volatile sulphides in sediments under anoxic conditions (Burton et al., 2005) and in the higher presence of Fe and Mn oxides under aerobic conditions (Sutherland et al., 2007). The high surface area of components such as Fe and Mn oxides and organic matter can also increase the metal sorption (Zhang et al., 2014). Additionally, the differences in the interaction of metals with sediments also depend on the metal chemical properties (Gao et al., 2021). As stated by Du Laing et al. (Du Laing, 2009), Fe and Mn oxides were a good sorbent of Cd, Zn, and Ni under oxic conditions, while organic matter was the most significant for interactions with Cu. The sorption of trace elements by bottom sediments is a very complicated process which requires extensive research to be fully understood (Zhang et al., 2014; Rzetala et al., 2019; Lin et al., 2013). This problem should be comprehensively examined, especially in terms of the content of different organic carbon and mineral compounds as well as their internal and external physicochemical structure. One of the most interesting analytical alternatives, generating a wide spectrum of information and being a valuable supplement to standard methods, is the use of more specialized methods like mercury porosimetry, nitrogen sorption or potentiometric titration to describe the properties of sediments (Panesar and Francis, 2014; Józefaciuk, 2009; Fenglin, 2018; Skic et al., 2020).

Knowledge of the total trace element content and sorption properties only allows to estimate the potential hazards connected with metals present in bottom sediments. Screening biotests based on crustaceans seem to be a good technique to assess the risk resulting from the presence of trace elements in bottom sediments, their mobility and ecotoxicity using the Heterocypris incongruens biotest. The evaluation of interactions between sorption capacity, trace elements and the response of organisms is useful for a justified ecological risk assessment.

2. Material and methods

2.1. Study area and sediment sampling

Bottom sediments were sampled from two dammed reservoirs: Roźnów (the Dunajec River, Lesser Poland Voivodeship) and Rybnik (the Ruda River, Silesian Voivodeship) located in southern Poland (Fig. 1 SM). The Roźnów reservoir (year of completion 1941) encloses a mountainous catchment basin of an agricultural character, which is subject to intense siltation (Szara et al., 2020). The basic data on the Roźnów reservoir are as follows: catchment area: 4874 km², the main reservoir area: 16 km², flooding surface: 17.76 km², length: 18–22 km, total capacity: 228 million m³, max/mean depth: 4.5/28 m. The Roźnów reservoir serves several important functions: energy, flood control, recreation. The second water body – the Rybnik reservoir (year of completion 1972) – is subject to a strong human impact, as it is a production process of a coal power plant. It encloses a small catchment area which is highly urbanised and strongly influenced by heavy industry (Baran et al., 2019; Baran A et al., 2017; Baran et al., 2020). The reservoir characteristics are as follows: catchment area: 316.78 km², the main reservoir area: 4.44 km², flooding surface: 5.55 km², length: 7 km, total capacity: 24 million m³, max/mean depth 11/5.5 m. The main functions of the reservoir are: supply of water to cool power station, flood-control, and recreation. The sediment samples were collected using an Ekman sampler from 14 set locations (6 from the Roźnów reservoir – Ro and 8 from the Rybnik reservoir – Ry) (Fig. 1 SM). The samples were collected in each sampling point of the bottom sediment upper layer (0–15 cm). The sediments were placed inside polyethylene containers and transported to the laboratory. Next, sediments were air-dried at room temperature, then ground with a mortar and a pestle, and 2 mm sieved (Baran et al., 2019).

2.2. Physicochemical and eco-toxicological analysis

2.2.1. Sorption properties of sediments

The sediment samples were analysed for sediment texture, pHKCl, the contents of carbonate, total organic carbon (TOC), humic acid carbon (Cha), fulvic acid carbon (Cfa), non-hydrolysing carbon (Cnh), and dissolved organic carbon (DOC). The analytical methods used were described in more detail in the previous studies (Baran et al., 2019; Baran A et al., 2017; Baran et al., 2020). FTIR spectra were recorded for dried bottom sediments on Tensor 27 spectrometer (Bruker) in the range of 400–4000 cm⁻¹. For this purpose, 1 mg of each powdered sample was mixed homogeneously with 200 mg of KBr and pelletized. The characteristics were obtained as an average of three measurements with 256 scans at 2 cm⁻¹ resolution each. Distribution functions of apparent dissociation constants of functional groups as well as the surface charge values at different pH were calculated from potentiometric titration curves recorded using Titrino 702 SM instrument (Metrohm). The titration was carried out in 0.3 g sediment suspended in 25 ml of water, at pH 3–9, at ionic strength of 0.1 M (NaCl) and under N₂ atmosphere, using 0.1 M NaOH as a titrant. An Autopore IV 9500 (Micromeritics, USA) mercury porosimeter was used to evaluate pore characteristics, including average pore diameter (Dₘᵢₚ), total pore area (Sₘᵢₚ), and pore volume (Vₘᵢₚ). The cumulative and differential pore size distributions were obtained in the pore diameter range of 0.003 μm–360 μm. The nitrogen gas adsorption data were obtained using 3 Flex surface characterisation analyser (Micromeritics, USA). The specific surface area (SSA) and pore size distribution were determined based on the Brunauer-Emmett-Teller (BET) method and the Barrett-Joyner-Halenda (BJH) equation, respectively. The SSA was evaluated in the limited relative pressure range of 0.05–0.30 p/p₀. The monolayer was assumed to have a close-packed structure giving the nitrogen molecule an area of 0.162 nm² at 77 K. Pore characteristics, including average pore diameter (Dₘᵢₚ), cumulative pore surface area (Sₘᵢₚ), and cumulative pore volume (Vₘᵢₚ) were obtained from the desorption...
isotherm in the hysteresis loop region. The differential curves obtained by mercury intrusion porosimetry and nitrogen adsorption methods were used to analyse diverse pore classes in the following diameter range: macropores (>75 μm), mesopores (75-30 μm), micropores (30-5 μm), ultramicropores (5-0.1 μm), cryptopores (0.1-0.007 μm), and residual pores <0.007 μm (Cameron and BuchanLal, 2006).

2.2.2. Determination of trace element content in bottom sediments

In order to determine the total content of trace elements (As, Cd, Cr, Cu, Ni, Pb, Zn), the sediment samples were digested with a 9 cm³ mixture (1:3 v/v) of concentrated acids (HCl and HNO₃ suprapure, MERCK), by wet method, in a closed system of a microwave oven (Baran et al., 2019; Szara et al., 2020). Trace element concentrations were determined by the ICP-OES method (Inductively Coupled Plasma Atomic Emission Spectroscopy) on Optima 7300 DV (PerkinElmer). The Hg content analysis in sediments was carried out using the Atomic Absorption Spectrophotometer (AAS) (Advanced Mercury Analyser; AMA 20 254). The CRN016-050 reference material was used to assess the analytical procedures. The results showed that the recovery percentage ranged from 86 (Pb) to 119 % (Cr).

3. Results

3.1. Basic properties of bottom sediments and organic matter fraction

In general, the determined properties of bottom sediments from both reservoirs (Ry and Ro) were different (Table 1). Moreover, higher variation in properties was demonstrated for bottom sediments from the Ry (CV = 7–147 %) than from the Ro (CV = 2–68 %). The Roznów reservoir bottom sediments had slightly acidic and basic pH as well as a high content of CaCO₃ (from 9 to 13 %) (Table 1). In addition, the particle size fraction analysis determined the dominance of the silt (from 52 to 87 %) and clay (from 8 to 33 %) fractions in the bottom sediments of the Ro. The Rybnik reservoir bottom sediments contained from 58 to 98 % sand, from 0 to 40 % silt, and from 0 to 5 % clay (Table 1). The pH of sediments turned out to be neutral and alkaline (from 7.1 to 8.5). The CaCO₃ content was low and varied (0–0.3 %) inside the Rybnik reservoir. The TOC ranged from 2.0 (Ry3) to 119 g/kg dm (dry matter) (Ry4) and from 12.5 (Ro1) to 20.0 g/kg dm (Ro4) (Table 1, Fig. 2). The TOC, Cnh, Cha, and Cfa contents were almost 1.4–5.0 times higher in the Ry bottom sediments compared to the Ro bottom sediments (Table 1). The Cnh fraction was dominant in the sediment samples from the Rybnik reservoir, whereas the Cfa fraction dominated in samples from the Roznów reservoir. In samples from the Rybnik reservoir, the Cnh fraction was approx. 11 % (Ry3) – 80 % (Ry1), the Cfa fraction was approx. 19 % (Ry1) – 64 % (Ry3), and the Cha fraction was approx. 1 % (Ry1) – 23 % (Ry3) of the total organic carbon. In the sediment samples from the Roznów reservoir, the fraction of humic substances accounted from 2 % (Ro3) to 6 % (Ro1) Cha, from 26 % (Ro4) to 83 % (Ro1) Cfa, and from 11 % (Ro1) to 70 % (Ro4) Cnh of the total organic carbon (Fig. 2). The study showed a similar mean DOC content in the sediments from both reservoirs. The DOC content in reservoir sediments was from 0.1 to 1.3 g/kg dm (Ry) and from 0.3 to 0.5 g/kg (Ro), respectively (Table 1).

3.2. Trace element content in bottom sediments and ecotoxicity to H. incongruens

The accumulation of trace elements in bottom sediments varied depending on the reservoirs. The content of trace elements (excluding Cr and Ni) in sediments from the Rybnik reservoir was 1.4 (Hg) – 30 (Cu) times higher than from the Roznów reservoir (Table 2). The trace element contents in sediments were ordered decreasingly, as follows, with mean values (mg/kg dm) in brackets: Cu (837) > Zn (692) > Pb (46.0) > Cr (39.3) > Ni (26.2) > As (8.2) > Cd (5.4) > Hg (0.15) (the
The PEC (Probable Effect Concentration) and mean PEC quotient (PECq) were used to determine the risk of trace elements in sediments (Table 2) (Szara et al., 2020; Macdonald et al., 2000). The sediments were classified as toxic if the concentrations of pollutants were above the Probable Effect Concentration (PEC): Zn 459 mg, Cu 150 mg, Pb 128 mg, Cd 4.98 mg, Ni 48.6 mg, Cr 111 mg, Hg 1.1 mg, As 33 mg/kg dm (Macdonald et al., 2000). The mean PECq assesses the potential effect of sediment associated with a specific trace elements when they are present in a complex mixture (Szara et al., 2020). The mean PECq was calculated as the average ratio of each trace element concentration to its corresponding PEC (PECq = \( \frac{\sum c}{\sum PEC}/n \), c - concentration resents of trace elements in the sediments, PEC - Probable Effect Concentration, and n - number of elements). The mean PECq ranked sediments in terms of incidence of toxicity into four categories: non-adverse effect (PECq

### Table 1

| Parameter | Rybnik (Ry) n = 8 | Minimum | Maximum | Roznów (Ro) n = 6 | Minimum | Maximum |
|-----------|------------------|---------|---------|------------------|---------|---------|
| Sand %    | 79               | 56      | 98      | 6                | 4       | 15      |
| Silt %    | 18               | 0       | 40      | 73               | 52      | 87      |
| Clay %    | 2                | 0       | 5       | 21               | 8       | 33      |
| pH        | 7.4 ± 0.5        | 7.1     | 8.5     | 7.1 ± 0.2        | 6.9     | 7.3     |
| CaCO₃ %   | 0.1 ± 0.1        | 0.0     | 0.3     | 10 ± 1.4         | 9       | 13      |
| TOC g/kg dm | 53.1 ± 50.2     | 2.0     | 119     | 16.6 ± 2.9       | 12.5    | 20.0    |
| Cha       | 1.0 ± 0.6        | 0.2     | 2.0     | 0.6 ± 0.2        | 0.3     | 0.8     |
| Cfa       | 11.1 ± 9.1       | 1.4     | 23.3    | 7.5 ± 3.5        | 4.6     | 13.9    |
| Cnh       | 41.0 ± 40.4      | 0.2     | 93.9    | 8.5 ± 5.3        | 1.3     | 14.0    |
| DOC       | 0.51 ± 0.4       | 0.1     | 1.3     | 0.4 ± 0.1        | 0.3     | 0.5     |

Abbreviations: TOC - total organic carbon; Ckh - humic acid carbon; Cfa - fulvic acid carbon; Cnh - non-hydrolysing carbon; DOC - dissolved organic carbon.

### Table 2

| Trace elements mg/kg dm | Rybnik (Ry) n = 8 | Minimum | Maximum | Roznów (Ro) n = 6 | Minimum | Maximum |
|-------------------------|------------------|---------|---------|------------------|---------|---------|
| As                      | 8.2 ± 7.2        | 1.2     | 19.3    | 5.3 ± 0.7        | 4.6     | 6.5     |
| Cd                      | 5.4 ± 4.6        | 0.3     | 11.9    | 0.30 ± 0.1       | 0.2     | 0.4     |
| Cu                      | 39.3 ± 35.7      | 5.0     | 83.5    | 66.9 ± 6.3       | 59.0    | 75.1    |
| Ni                      | 837 ± 863        | 99.4    | 2010    | 28.0 ± 2.1       | 25.3    | 30.6    |
| Pb                      | 26.2 ± 18.1      | 6.1     | 54.8    | 38.3 ± 2.8       | 33.9    | 41.4    |
| As                      | 46.0 ± 37.2      | 5.5     | 89.0    | 12.0 ± 0.7       | 11.4    | 13.2    |
| Zn                      | 692 ± 575        | 62.1    | 1596    | 75.3 ± 4.6       | 69.8    | 80.8    |
| Hg                      | 0.15 ± 0.12      | 0.01    | 0.28    | 0.11 ± 0.02      | 0.08    | 0.13    |
| PECq                    | 1.2 ± 0.8        | 0.2     | 2.7     | 0.27 ± 0.04      | 0.25    | 0.3     |
| Mortality H.i. %        | 35 ± 38          | 0       | 100     | 10 ± 18          | 0       | 45      |
| Growth inhibition H.i. %| 61 ± 26          | 26      | 100     | 40 ± 21          | 17      | 68      |

*H.i. – Heterocypris incongruens.*

Rybnik reservoir and Zn (75.3) > Cr (66.9) > Ni (38.3) > Cu (28.0) > Pb (12.0) > As (5.3) > Cd (0.3) > Hg (0.11) (the Roznów reservoir).

The PEC (Probable Effect Concentration) and mean PEC quotient (PECQ) were used to determine the risk of trace elements in sediments (Table 2) (Szara et al., 2020; Macdonald et al., 2000). The sediments were classified as toxic if the concentrations of pollutants were above the Probable Effect Concentration (PEC): Zn 459 mg, Cu 150 mg, Pb 128 mg, Cd 4.98 mg, Ni 48.6 mg, Cr 111 mg, Hg 1.1 mg, As 33 mg/kg dm (Macdonald et al., 2000). The mean PECq assesses the potential effect of sediment associated with a specific trace elements when they are present in a complex mixture (Szara et al., 2020). The mean PECq was calculated as the average ratio of each trace element concentration to its corresponding PEC (PECq = \( \frac{\sum c}{\sum PEC}/n \), c - concentration resents of trace elements in the sediments, PEC - Probable Effect Concentration, and n - number of elements). The mean PECq ranked sediments in terms of incidence of toxicity into four categories: non-adverse effect (PECq...
(0.1), slightly adverse effect (0.1 < PECq < 0.5), moderate effect (0.5 < PECq < 1.0), and heavy effect (PECq > 1.0) (Szara et al., 2020). The PECq values ranged from 0.2 to 2.7 (the Rybnik reservoir) and from 0.25 to 0.3 (the Roźnów reservoir) (Table 2, Fig. 3). The highest mean PECq was found at Ry1, Ry4, Ry7 and the lowest at Ry 6 (Fig. 3). In the Roźnów reservoir sediments, the highest PECq value was calculated for Ro4 and Ro5, and the lowest for Ro1 (Fig. 3). The study revealed a slightly adverse effect of all samples from the Roźnów reservoir and Ry6, Ry2, Ry3 (the Rybnik reservoir) on the benthic fauna, a moderate effect of sediments from Ry5 and Ry8, and heavy effect of samples from Ry1, Ry4, Ry7 (Fig. 3). The mean PECq for individual trace elements was ordered as follows: Cu > Zn > Cd > Ni > Pb > Cr > As > Hg (the Rybnik reservoir) and Ni > Cr > Cu > Zn, As > Hg > Pb > Cd (the Roźnów reservoir).

The sediment ecotoxicity results are presented in Table 2 and Fig. 3. Generally, sediments from the Rybnik reservoir were more toxic to the organism, while for the Roźnów reservoir sediments, a higher variability was observed in this respect. The H. incongruens mortality was between 0 and 100 % (Ry) and 0–35 % (Ro), whereas the growth inhibition ranged from 26 to 100 % (Ry) and 17–68 % (Ro) with the mean percentage effect of 61 % and 40 %, respectively. It was determined that the high trace element contents in both bottom sediments did not increase the sediment ecotoxicity to H. incongruens (Fig. 3). The ecotoxicity of sediment samples to H. incongruens can be ranked in the following order: Ry3 > Ry6 > Ry5 > Ry7 > Ry4 > Ry2 > Ry1 > Ry8 (the Rybnik reservoir) and Ro4 > Ro5 > Ro3 > Ro2 > Ro6 > Ro1 (the Roźnów reservoir) (Fig. 3). In the Roźnów reservoir, Ro4 and Ro5 samples were toxic, Ro2, Ro3, Ro6 were low toxic, and Ro1 was not toxic to H. incongruens. Most of the examined sediment samples (Ry4, Ry5, Ry6, Ry7) from the Rybnik reservoir were classified as toxic and very toxic (Ry3), while Ry1, Ry2 Ry8 samples were classified as low toxic to H. incongruens.

### 3.3. Sorption capacity of bottom sediments

#### 3.3.1. FTIR analysis

FTIR analysis of the studied bottom sediments revealed the presence of signals typical for inorganic and organic structures, which were observed as: broad absorption band with a peak at 3624 cm⁻¹ assigned to OH groups from the Al-OH and Si-OH vibrations in quartz and kaolinite clays (Waruru et al., 2015); band at 3426 cm⁻¹ related to O-H stretching of carboxylic acids, phenols, alcohols, and water, N-H groups, H-bonded OH, intermolecular bonded OH (da Silva et al., 2018); sharp signals at 2927 cm⁻¹ and at 2854 cm⁻¹ corresponded to the C-H stretching of aliphatic groups (Pospíšilová et al., 2008); medium band at 1639 cm⁻¹ attributed to C=O of deprotonated COO⁻, C-O and C-N stretching in amides as well as vibrations of –C = –C- on benzene rings (da Silva et al., 2018); peak at 1429 cm⁻¹ C-H aliphatic bending, C=C aromatic stretching, Si–O–Si vibrations, at ~1452 cm⁻¹ attributed to soil calcium carbonates (Du and Zhou, 2011); absorption at 1090 cm⁻¹ assigned to C,H₄ aliphatic and cyclic, the presence of polysaccharides, ethers and alcohols, Si–O–Si bonds (Waruru et al., 2015); the intense peak at 1029 cm⁻¹ originated from primary alcoholic OH, CO polysaccharide stretching (Boguta et al., 2019). FTIR spectra also revealed numerous, complex bands below 1000 cm⁻¹, mainly at 797, 527 and 470 cm⁻¹, which were related to aromatic C-H and Si–O–Si vibration. Differences in the intensity of individual bands occurred between the samples from two reservoirs as well as within one reservoir, i.e. between samples from different locations. In samples from the Roźnów reservoir, the highest diversity was observed for the absorption bands at 3624, 1429, and 1029 cm⁻¹, while in samples from the Rybnik reservoir at 3427, 1639, 1090 and at 1029 cm⁻¹. Bottom sediments from the Ro were characterised by higher intensities of bands at 3623, 1429, 1029 cm⁻¹ and in the spectral area below 900 cm⁻¹ as compared to samples from the Ry. These results could indicate higher contents of clay minerals, carbonates, polysaccharides, and aromatic structures in the Ro organic matter. The spectral data for all test samples did not reveal the presence of a band at ~1700 cm⁻¹ characteristic of free COOH groups, which could indicate their occupation by metal cations.

#### 3.3.2. Potentiometric titration

Potentiometric titration of bottom sediments showed differences in the analysed material in terms of the content of functional groups generating a negative surface charge. The negative charge value increased with the increase in the analysis pH, which resulted from the dissociation of subsequent functional groups, ranging from strongly acidic, e.g. COOH, to weakly acidic, e.g. OH groups. The total number of negative charges measured at pH 9.0 was very similar in all Ro samples and ranged from 213 to 255 μmol/g. The parameter was more divergent in samples of the Ry bottom sediments, ranging from 35.3 μmol/g (Ry2) to 711.7 μmol/g (Ry7). This indicated a greater diversification of
porosity properties of the Rybnik reservoir samples in terms of the possibility of binding positively charged substances, for example, metal ions.

3.3.3. Nitrogen adsorption/desorption

Nitrogen adsorption/desorption isotherms obtained for bottom sediments from the Rożnów and Rybnik reservoirs are shown in Fig. 4 A and B, respectively. The isotherms had a shape typical for the physical adsorption process. According to the classification all curves may be assigned to type II, characteristic of non-porous or macroporous adsorbents. Each of the isotherms can be divided into three main parts that include a slight inflexion in the relative pressure range \( p/p_0 \approx 0.05 \), a middle section with a different inclination degree \( p/p_0 \approx 0.9 \), and a part at \( p/p_0 \approx 0.9 \), where a high increase in \( N_2 \) adsorption is observed. The adsorbed gas amount at low \( p/p_0 \) values corresponded to the fine pore volume, while, at higher relative pressure, to the volumes of larger cryptopores and ultramicropores. Condensation of the adsorbate pores was accompanied by a hysteresis loop, with the closing point at a relative pressure of approx. \( p/p_0 \approx 0.4 \). The shape of the hysteresis loop, combined with unlimited adsorption at high relative pressures, allowed to classify them as the H3 type. This type of hysteresis loop is characteristic of aggregates with a predominance of plate-like particles with slit pores formed within them. Small hysteresis loop may indicate inaccessibility of pores for \( N_2 \) molecules within the investigated pore range. The total amount of \( N_2 \) adsorbed by bottom sediments varied considerably across the reservoirs; however, higher quantity of \( N_2 \) adsorbed was characteristic of the Ro samples. The specific surface area determined from the adsorption data ranged from 1.0 to 23.2 m²/g. The higher SSA values could indicate the presence in the material of fine microaggregates or particles of a clay size. These structures may affect the ability of bottom sediments to sorb metals and organic compounds. The pore characteristics are presented in the form of differential pore volume (dV/dlogD) versus the equivalent pore diameter (Fig. 4C and D). The desorption cumulative volume of pores estimated for pore diameters of 2–300 nm ranged from 2.2 to 66.9 nm³/g. In general, the Ro bottom sediments had greater pore volume compared to the Ry bottom sediments, with average values of 48.8 and 23.9 nm³/g, respectively. Pores whose diameter ranged from 7 to 100 nm accounted for ~60%, while pores of >0.1 nm just ~13% of the total pore volume. At the same time, the desorption average pore diameter values were 8.0–12.5 nm, and the desorption cumulative surface pore area ranged from 1.0 to 25.0 m²/g.

3.3.4. Mercury intrusion porosimetry

The average pore diameter observed for the Rożnów reservoir bottom sediments ranged from 60.1 to 126.9 nm, while the total pore area values from 11.2 to 20.8 m²/g. The above parameters exhibited a wider range in the case of the Ry bottom sediments. They varied from 91.3 to 889.8 nm and from 1.0 to 25.1 m²/g, respectively, for an average pore diameter and the total pore area. The dependence of the pore volume on the pore diameter logarithm is shown in Fig. 5 A and B, for the Rożnów and Rybnik reservoirs, respectively. Sigmoidal curves are plotted from the largest pore diameter on the X-axis, so that the course of mercury intrusion can be followed upwards from the lowest pressure. The differential pore size distributions (PSD) in the diameter range from 0.003 to 360 μm are shown in Fig. 5C and D. The analysis of these curves allows the assessment of pores diversity and the visualisation of the main distribution peaks. Similar cumulative curves were obtained for the samples from the Rożnów reservoir. In this case, the total pore volume ranged from 0.31 to 0.35 cm³/g, with an average at 0.33 cm³/g. The maximum value was observed for Ro5 and the minimum for Ro1. The PSD curves were unimodal with narrow peaks of similar magnitudes. This suggests that the samples from the Rożnów reservoir were relatively homogenous and contained particles/aggregates of similar size and shape. The peaks were in the range of ultramicropores, which accounted for as much as 76 % of the total pore volume. Bottom

![Fig. 4. Nitrogen sorption data in the form of isotherms (left) and differential curves (right) obtained for bottom sediments of Rożnów (Ro A and C) and Rybnik (Ry B and D) reservoirs.](https://repo.ur.krakow.pl/Downloaded from Repository of University of Agriculture in Krakow 2022-01-13)
sediments from the Rybnik reservoir were characterised by a wide range of cumulative pore volume from 0.22 to 0.59 cm$^3$/g (average at 0.34 cm$^3$/g). The highest values were observed for Ry7 and the lowest for Ry3. The width of the pore size distributions and the size and location of the main peaks varied greatly. Main peaks were generally observed in the ultramicropore range, where the porosity was determined by the size of the silt and/or clay particles, but also in the micropore and mesopore ranges. Ultramicro pores accounted for an average of 51%, mesopores for 24%, and micropores for 12% of the total pore volume.

3.4. Impact of sediment properties on the trace element content in and ecotoxicity of bottom sediment

Correlation and principal component analyses (PCA) allowed to find interesting relationships between the analysed parameters (Tables 3 and 4). In the bottom sediments the Rybnik reservoir, a significant positive correlation was found between the content of the entire organic matter fraction and the trace element content (Tables 3 and 4). A significant positive correlation was also found for the silt (As, Cd, Ni, Pb, Zn, Hg) and clay. The sand fraction was negatively correlated with the content of trace elements in the Rybnik reservoir. In the bottom sediments of the Roźnów reservoir, less significant correlations between the examined parameters were found. In general, a significant correlation was determined between the contents of clay (positive Cr, Ni, Pb), CaCO$_3$ (positive Cd) and silt (negative, As, Cr, Cu, Ni) (Table 3). The results of correlations between the content of trace elements and fractions of organic matter indicate that the elements content in bottom sediments depends on the labile carbon form – Cfa. The stable form of organic matter (TOC and Chn) was negatively correlated with the trace element content in the Roźnów reservoir (Table 3).

Principal component analysis (PCA) also allowed to find interesting relationships between the content of trace elements and the sediment properties (Table 4). The two PC factors described 86% (the Rybnik reservoir) and 72% (the Roźnów reservoir) of the variances. In the Rybnik reservoir sediments, the first factor (PC1) accounted for 72% of the variance and was significantly positively correlated with the total content of all elements, silt, clay, organic matter fraction, pore size and total pore volume, surface charge Q4, Q7, Q9, MIP ultramicropores, MIP cryptopores, MIP residual pores, surface area, N$_2$ cumulative area of pores, and negatively correlated with the sand fraction, MIP average pore diameter, macropores and micropores. The second factor (PC2, Ry) explained only 9% of the variance with a high positive loading on clay, silt, pH, total content of Pb, and negative correlation with response of H. incongruens and mesopores (Table 4). In the sediments samples from Roźnów reservoir first factor (54% of the total variance) displays high positive loading values of sand, clay, CaCO$_3$, Cfa, the total content of As, Cr, Ni, Cu, Pb, MIP total pore area, cryptopores, residual pores, specific surface area, N$_2$ cumulative surface area of pores, and negative loadings of silt, TOC, Cnh, growth inhibition of H. incongruens, MIP average pore diameter, total pore volume, and ultramicropores. The second factor corresponded to 19% of the total variance and was dominated by DOC, total Zn content, MIP macropores, surface charge Q4, Q7, Q9 (Table 4).

In the case of samples from the Rybnik reservoir, positive correlation coefficients between PC1, metal content and the physicochemical properties of bottom sediments indicated an increased metal accumulation with elevated values of the specific surface area and the volume of pores <0.1 μm (Table 4). These results also showed that the concentration of trace elements increases with the increasing surface charge value and the content of organic matter, clay and silt fractions (Table 4). The macropore volumes and the average pore diameter of the Rybnik reservoir bottom sediments were negatively related to the PC1 component, which indicates the minor importance of these characteristics for the sorption of trace elements in the Rybnik reservoir sediments. Given the positive high correlation coefficients for the parameters describing both the chemical (Q4, Q7 and Q9) and physicochemical properties (SSA, volume of pores <0.1 μm, MIP total pore area, total pore volume...
Table 3
Relationships between content of trace elements and physico-chemical properties of bottom sediment.

|         | Rybnik Reservoir | Roznów Reservoir |
|---------|------------------|------------------|
| As      | Cd               | Cr               | Cu   | Ni   | Pb   | Zn   | Hg   | As      | Cd      | Cr   | Cu   | Ni   | Pb   | Zn   | Hg   |
| Sand    | −0.76            | −0.82            | −0.70 | −0.54 | −0.79 | −0.94 | −0.84 | −0.93 | 0.86    | 0.12    | 0.63 | 0.61 | 0.52 | 0.81 | 0.30 | −0.04 |
| Silt    | 0.73             | 0.81             | 0.67  | 0.50  | 0.77  | 0.93  | 0.82  | 0.92  | −0.91   | −0.34   | −0.97 | −0.91 | −0.91 | −0.91 | 0.26 | −0.05 |
| Clay    | 0.89             | 0.86             | 0.90  | 0.83  | 0.82  | 0.88  | 0.86  | 0.87  | 0.78    | 0.37    | 0.94  | 0.87  | 0.91  | 0.80  | −0.43 | 0.07  |
| CaCO₃   | 0.33             | 0.53             | 0.34  | 0.37  | 0.40  | 0.23  | 0.49  | 0.30  | 0.40    | 0.90    | 0.59  | 0.80  | 0.56  | 0.65  | −0.28 | 0.31  |
| TOC     | 0.97             | 0.96             | 0.98  | 0.95  | 0.95  | 0.89  | 0.95  | 0.92  | −0.21   | −0.52   | −0.57 | −0.55 | −0.65 | −0.38 | 0.77  | −0.05 |
| Chh     | 0.01             | 0.96             | 0.87  | 0.78  | 0.97  | 0.86  | 0.97  | 0.91  | 0.18    | 0.64    | 0.12  | 0.34  | 0.10  | 0.32  | 0.25  | 0.35  |
| Clfa    | 0.97             | 0.96             | 0.98  | 0.95  | 0.95  | 0.88  | 0.96  | 0.92  | 0.89    | 0.51    | 0.80  | 0.91  | 0.66  | 0.99  | 0.08  | 0.06  |
| Chnh    | 0.97             | 0.96             | 0.98  | 0.95  | 0.95  | 0.89  | 0.95  | 0.92  | −0.70   | −0.64   | −0.84  | −0.91 | −0.79 | −0.87 | 0.36  | −0.08 |
| DOC     | 0.94             | 0.90             | 0.98  | 0.99  | 0.90  | 0.75  | 0.89  | 0.80  | 0.35    | −0.30   | −0.69  | −0.01 | −0.27 | 0.29  | 0.75  | −0.24 |
| Q4      | 0.96             | 0.97             | 0.95  | 0.89  | 1.00  | 0.88  | 0.97  | 0.92  | 0.42    | −0.43   | 0.07  | 0.06  | −0.10 | 0.21  | 0.67  | −0.02 |
| Q7      | 0.96             | 0.98             | 0.92  | 0.84  | 0.99  | 0.88  | 0.99  | 0.93  | 0.47    | 0.14    | 0.39  | 0.52  | 0.22  | 0.38  | 0.32  | 0.37  |
| Q9      | 0.96             | 0.99             | 0.93  | 0.85  | 0.99  | 0.87  | 0.99  | 0.92  | 0.65    | 0.26    | 0.46  | 0.66  | 0.26  | 0.54  | 0.56  | 0.51  |
| Macropores | −0.59          | −0.60             | −0.61 | −0.55 | −0.68 | −0.60 | −0.61 | −0.61 | 0.05    | 0.08    | −0.06 | 0.16  | −0.21 | −0.02 | 0.47  | 0.41  |
| Micropores | −0.72          | −0.82             | −0.72 | −0.63 | −0.68 | −0.82 | −0.80 | −0.81 | 0.44    | −0.26   | 0.53  | 0.29  | 0.51  | 0.15  | −0.16 | 0.17  |
| Ultramicropores | 0.95          | 0.99             | 0.93  | 0.87  | 0.97  | 0.89  | 0.99  | 0.94  | −0.62   | −0.31   | −0.78  | −0.65 | −0.81 | −0.76 | 0.61  | 0.30  |
| Cryptopores | 0.98          | 0.97             | 0.94  | 0.86  | 0.98  | 0.82  | 0.98  | 0.87  | 0.79    | 0.38    | 0.81  | 0.76  | 0.78  | 0.90  | −0.29 | −0.19 |
| Others <7 nm | 0.98          | 0.95             | 0.96  | 0.91  | 0.99  | 0.78  | 0.96  | 0.84  | 0.65    | 0.26    | 0.81  | 0.63  | 0.87  | 0.70  | −0.56 | −0.16 |
| Surface area | 0.99          | 0.96             | 0.94  | 0.87  | 0.97  | 0.82  | 0.97  | 0.86  | 0.44    | 0.32    | 0.75  | 0.57  | 0.85  | 0.51  | −0.79 | −0.09 |
| Vp < 7 nm | 0.99             | 0.95             | 0.95  | 0.88  | 0.97  | 0.80  | 0.97  | 0.85  | 0.58    | 0.28    | 0.83  | 0.64  | 0.91  | 0.62  | −0.68 | −0.08 |
| Vp 100-7 nm | 0.99            | 0.98             | 0.97  | 0.92  | 0.98  | 0.86  | 0.99  | 0.90  | 0.75    | 0.39    | 0.83  | 0.76  | 0.83  | 0.86  | −0.41 | −0.18 |
| Vp > 100 nm | 0.92          | 0.91             | 0.84  | 0.73  | 0.93  | 0.78  | 0.94  | 0.83  | 0.75    | 0.43    | 0.83  | 0.80  | 0.81  | 0.90  | −0.40 | −0.19 |
| Pore diameter avg. | 0.99          | 0.98             | 0.95  | 0.88  | 0.97  | 0.81  | 0.97  | 0.86  | 0.60    | 0.34    | 0.83  | 0.67  | 0.89  | 0.67  | −0.65 | −0.11 |

*Correlation coefficients significant at the level of p < 0.05 are shown in bold, Abbreviations: TOC - total organic carbon; Chh - humic acid carbon; Clfa - fulvic acid carbon; Chnh - non-hydrolysing carbon; DOC - dissolved organic carbon; Q4, Q7, Q9, - surface charge at pH 4, 7 and 9 respectively; SSA - specific surface area; S_{avg} cumulative surface area of pores, V_{N2} cumulative volume of pores, D_{N2} average pore diameter.
The relationship between the trace element content, bottom sediment properties and *H. incongruens* response is presented in Table 4. The PCA analysis indicated that ecotoxicity to *H. incongruens* was not related to the trace element content in both sediments analysed. However, the influence of the physicochemical properties of the bottom sediments on the behavior of the test organism was demonstrated. In the sediments of the Rybnik reservoir, the content of sand and mesopores volume (30–75 μm) had a significant impact on the response of *H. incongruens*, while in the sediments of the Roznów reservoir - silt, TOC, Cnh, D_{MIP}, V_{MIP} and ultramicropores volume (Table 4).

### 4. Discussion

Most statistically significant relationships were found for materials collected from the Rybnik reservoir, which was probably due to much higher amounts of TOC (Cha, Cfa, Cnh, DOC) in the Rybnik reservoir sediment. The positive correlation between trace element accumulation and DOC or Cfa, seems to be a quite interesting result, because at a relatively high pH of the studied sediments, the above carbon fractions may be partially mobilized and even reduce the amount of trace element in the sediment due to the formation of soluble chelates (El-Radaideh et al., 2014). In addition, other studies indicate that the reduction in the solubility of trace elements tends to occur with the surface charge of larger particles, e.g. particulate organic carbon (POC) (Zhang et al., 2014). A probable explanation for the positive role of the surface charge of the DOC or Cfa fractions in metal binding at high pH may be the accumulation and blocking of these small organic molecules in the fine pores of the sediment. The results also indicated that PC1, covering the organic matter fraction and the trace element content in the bottom sediment, has the same origin of both natural and anthropogenic sources in bottom sediments of the Rybnik reservoir.

The texture of bottom sediments is a measure of the size of primary particles that are components of aggregates of different sizes. Our study showed that texture was one of the main factors regulating trace element sorption of bottom sediments. In the case of sediments from the Rybnik reservoir, strong and positive correlations were observed between the silt and clay fractions and the content of analysed elements. This indicates the accumulation of trace elements potentially toxic to the aquatic environment in fine-grained sediments. For these reasons, the accumulation of trace metals in systems dominated by riverine inputs depends on the migration and transport of these elements in association with mobilized clays (Zhang et al., 2014; George et al., 2007). Our observations are in line with the conclusions of other authors who analysed the effect of bottom sediment texture on metal content (Basham, 2008; Plathe et al., 2013; Farhat and Aly, 2018; Ivanic et al., 2020; Chen et al., 2020).

For example, Sojka et al. (2019) showed significant relationships between the content of metals with silt and organic matter. These authors concluded that correlations with silt were at a higher level. In turn, Chen et al. (2020) found linear relationships between As, Cd, Co, Cr, Ni, Pb, and Zn and the clay fraction. These results were confirmed by Plathe et al. (2013), who revealed that the main metal-containing mineral phases are nanomaterials and mineral nanoparticles. Our study showed that metals such as Cu and Cr were significantly correlated with the clay fraction (r > 0.83, p < 0.05), which indicates the probable adsorption of metals on the surfaces and edges of clay minerals or their occlusion in the crystalline lattice of fine particles. Correlations for other trace elements, i.e. As, Cd, Ni, Pb, Zn, and Hg turned out to be significant for both the silt and clay fractions (r > 0.73, p < 0.05). At the same time, except for Cu, the trace element content was negatively correlated with sand, suggesting that in the case of the Rybnik reservoir sediments, smooth and larger quartz crystals were not able to provide reactive surfaces for interaction with metals (Guven and Akinci, 2013). In the case of the Roznów reservoir, significant correlations were found only between clay and the Cr, Cu and Ni contents, although fine-grained particles dominated in the sediments. This may be due to the presence of young sediments, characterised by less occlusion of mineral surfaces and poor

| Parameter | Rybnik (Ry) n = 8 | Roznów (Ro) n = 6 |
|-----------|------------------|------------------|
| PC1 | PC2 | PC1 | PC2 |
| Sand | −0.64 | 0.66 | 0.63 | 0.44 |
| Silt | 0.61 | 0.66 | −0.97 | −0.19 |
| Clay | 0.68 | 0.68 | 0.94 | 0.08 |
| pH | 0.00 | 0.68 | 0.02 | −0.05 |
| CaCO₃ | 0.51 | −0.16 | 0.76 | −0.17 |
| TOC | 0.89 | 0.41 | −0.69 | 0.46 |
| Cha | 0.96 | 0.20 | 0.26 | −0.12 |
| Cfa | 0.88 | 0.41 | 0.88 | 0.40 |
| Cnh | 0.89 | 0.41 | −0.96 | 0.00 |
| DOC | 0.88 | 0.26 | −0.13 | 0.79 |
| As | 0.92 | 0.35 | 0.82 | 0.49 |
| Cd | 0.92 | 0.36 | 0.44 | −0.01 |
| Cr | 0.89 | 0.36 | 0.93 | 0.15 |
| Cu | 0.86 | 0.25 | 0.88 | 0.34 |
| Ni | 0.96 | 0.26 | 0.89 | −0.07 |
| Pb | 0.71 | 0.64 | 0.90 | 0.37 |
| Zn | 0.93 | 0.35 | −0.38 | 0.80 |
| Hg | 0.79 | 0.56 | −0.02 | 0.28 |
| Mortality *H. incongruens* | −0.20 | −0.82 | −0.55 | −0.22 |
| Growth inhibition *H. incongruens* | 0.12 | −0.96 | −0.80 | −0.52 |
| Q4 | 0.96 | 0.27 | 0.13 | 0.90 |
| Q7 | 0.95 | 0.30 | 0.22 | 0.77 |
| Q9 | 0.95 | 0.28 | 0.30 | 0.89 |
| D_{MIP} | −0.72 | −0.46 | −0.91 | 0.39 |
| V_{MIP} | 0.88 | 0.26 | 0.96 | −0.17 |
| V_{MIP} | 0.96 | 0.11 | −0.77 | 0.57 |
| MIP macropores volume (>75 μm) | −0.69 | 0.01 | −0.22 | 0.72 |
| MIP mesopores volume (30–75 μm) | −0.54 | −0.73 | 0.24 | 0.36 |
| MIP micropores volume (3–30 μm) | −0.63 | −0.05 | 0.27 | 0.12 |
| MIP ultramicropores volume (0.1–5 μm) | 0.93 | 0.34 | −0.93 | 0.29 |
| MIP cryptopores volume (0.007–0.1 μm) | 0.94 | 0.28 | 0.94 | −0.03 |
| MIP residual pores volume (<0.007 μm) | 0.97 | 0.18 | 0.90 | −0.33 |
| SSA | 0.94 | 0.29 | 0.84 | −0.52 |
| N₂ ultramicropores volume (<0.1 μm) | 0.90 | 0.24 | 0.98 | −0.07 |
| N₂ cryptopores volume (0.007–0.1 μm) | 0.94 | 0.34 | 0.97 | −0.13 |
| N₂ residual pores volume <7 nm | 0.93 | 0.28 | 0.89 | −0.40 |
| S₂C | 0.94 | 0.28 | 0.92 | −0.38 |
| V₂C | 0.94 | 0.32 | 0.97 | −0.20 |
| D_{MIP} | 0.18 | 0.70 | −0.06 | 0.76 |
| Total variance (%) | 77 | 9 | 54 | 19 |
| Cumulative (%) | 77 | 86 | 54 | 72 |

**Loadings >0.60 are shown in bold; Abbreviation:** TOC - total organic carbon; Cha - humic acid carbon; Cfa - fulvic acid carbon; Cnh - non-hydrolysing carbon; DOC - dissolved organic carbon; D_{MIP} - average pore diameter; S_{MIP} - total pore area; V_{MIP} - total pore volume; Q4, Q7, Q9 - surface charge at pH 4, 7, 9 respectively; SSA - specific surface area; S_{MIP} cumulative surface area of pores; V_{MIP} cumulative volume of pores; D_{MIP} average pore diameter.

and N₂ cumulative pore area, cumulative pore volume), it can be concluded that there is a higher elements accumulation on negatively charged functional groups in sediments with a large specific surface area and higher number of fine pores. At the same time, the analysis showed a significant relationship between the PC2 component and Pb. This fact, supported by the relationship between PC2 and pH, indicates that the Pb sorption in the Rybnik reservoir may be pH-dependent. For the Roznów reservoir sediments, the positive correlations of the variables with the PC1 component have a similar meaning as for the Rybnik reservoir sediments. The PC1 of the Roznów reservoir was strongly and positively correlated with the clay fraction and CaCO₃ with a negative relationship found for silt. There was also no significant correlation between the concentration of trace elements and the surface charge value, as well as the organic matter content, except for Cfa; however, these variables, together with DOC and Zn, contributed significantly to the variance of PC2. Positive correlations between PC2 and the total Zn content, DOC, surface charge at pH of 4.0, 7.0 and 9.0 can be interpreted as a set of variables whose high value determines high sorption of Zn ions.
aggregation. We also believe that in this case, the sediment texture similarity with local environmental factors maintained, resulted in no significant relationships with other metals. As shown in the study of Szara et al. (2020), the Roznów reservoir is the fastest silting dam reservoir in Poland. Silting is responsible for the inflow of a fine fraction with a large sorption area in relation to trace elements.

Strong positive relationships observed between the negative surface charge values (Q4, Q7, Q9) and the trace element content in the Rybnik reservoir sediments indicated a significant role of negatively dissociating functional groups. These structures are among the most important in metal binding processes due to preferential interactions by attracting oppositely charged particles in the form of simple cations or hydrolysed species, e.g. Cr(OH)\(^{3+}\), Pb(OH)\(^+\) (Hsu et al., 2016). The main source of negatively charged groups in sediments are clay minerals constituting the surface- and ion-exchange active sites for metals and organic carbon compounds providing ligands for the complexation processes (Zhang et al., 2014; Baran et al., 2019). In the Rybnik reservoir samples, the share of organic matter in the pool of negative charge was strongly related to the high content of Cha, Ca, Cn, and DOC fraction. This type of charge is mainly generated during association of carboxyl, phenolic, alcohol, and carbonyl groups (Sparks, 2003; Skic et al., 2016). It can be assumed that in the analysed samples, the above charged structures formed stable complexes, especially due to the relatively high pH of the sediments, in which a large part of the functional groups was already dissociated, facilitating the metal attraction. According to Grybos et al. (2007), such processes could be even more efficient in metal immobilisation than, for example, adsorption and co-precipitation on Fe hydroxides.

Interestingly, strong correlations were observed in the Rybnik reservoir sediments for negative charge measured at both low and high pH (Q4, Q7, Q9), indicating a significant role of strongly acidic and weakly acidic functional groups of organic compounds (Boguta and Sokolowska, 2020). This may also be due to the significant proportion of clay minerals, especially their active sites in the basal planes which exhibit a constant and pH-independent negative charge. The importance of the clay fraction in the negative charge pool was evidenced by its positive relationships with trace element content – even though the amounts of these minerals in the Rybnik reservoir samples were much lower than in the Roznów reservoir sediments. Given the above, it can be assumed that the strong correlations between the trace element content and the negative charge at pH of 4.0, 7.0 and 9.0 confirm the significant, combined contribution of both clay fractions and organic matter to the trace element retention processes. The study of El-Radaideh et al. (2014) seem to confirm this combined effect, as the authors observed that organic matter was “cemented” by clay and other amorphous components and that the sediment CEC (strongly corresponding to Q) correlated positively with the clay content. The increase in Q had the greatest effect on increasing accumulation of As, Cd, Cr, Ni, Zn, and Hg (r = 0.92–1.00, p < 0.05) and slightly less on sorption of Cu and Pb (r = 0.84–0.89, p < 0.05). The lower correlation coefficients for Q-parameters with Cu and Pb could result from the presence of any additional binding mechanisms, other than through COOH and OH structures. It was reported that functional groups containing organic nitrogen and sulphur could have higher affinity to copper ions than oxygen atoms of carboxyl groups (McBirge and Martinez, 2000; Evangelou et al., 2020). In consequence, the lower effect of Q-parameters on the Pb and Cu contents can be explained by their possible preferential interactions with sulphur and/or the presence of other charged groups for the lower effect of the negative bottom sediment charge on the sorption of the two above metals may be the easy transformation of soluble Pb compounds into relatively insoluble sulphate, carbonate and phosphate derivatives as well as Cu sulphides and carbonates (Loska et al., 2000). Moreover, the Rybnik reservoir bottom sediments had alkaline pH, which might promote formation of hydroxy compounds of Cu and Pb with a lowered positive charge or even electrically neutral forms. The presence of such trace element species could reduce the influence of negative surface charge (Q) on the sorption of these elements.

In the case of bottom sediments from the Roznów reservoir, no significant influence of the Q on the sorption of trace elements was observed. This may be due to the high amount of carbonates and lower content of organic matter. El-Radaideh et al. (El-Radaideh et al., 2014), in their study on sediments from the reservoir in northwestern Jordan, reported a strong, positive correlation between the content of carbonate compounds and Cu, Zn, Cr, Cd, Pb, Co, Mn, and Ni. Indeed, for most of elements of the Roznów reservoir sediments (except for Cd), no significant correlations with CaCO\(_3\) were found. Therefore, it can be assumed that the lack of significant correlations of metals with both Q and CaCO\(_3\) as well as only few significant correlations with clay may result from the combined effect of the above three groups of compounds on metal binding.

The specific surface area (SSA) is the total, available and reactive surface area of a solid phase that determines the adsorption capability (Otuola and Obiobodo, 2020). Therefore, the importance of fine-grained sediment particles in metal accumulation tends to increase with higher SSA and higher cation exchange capacity (Zhang et al., 2014). Our results showed that, except for Ni, there were no significant relations between metals and SSA in the Roznów reservoir sediments. However, strong correlations at the level of \( r \geq 0.82, p < 0.05 \) characterised sediments from the Rybnik reservoir. The affinities of individual trace elements with SSA were As > Ni > Zn > Cd > Cr > Cu > Hg > Pb. Our results are consistent with other studies (George et al., 2007; Ivanić et al., 2020; Zhuang and Yu, 2002) which revealed that distributions of metals are usually controlled by fine-grained sediments with high SSA. Some authors have also shown no or weaker relationship between SSA and the metal content, highlighting the importance of other factors involved in their accumulation. For example, Miranda et al. (2020) noticed that, at upstream sites, metals such as Zn, Ni and Pb were strongly correlated with amorphous matter and SSA, while at downstream locations, these metals presented weak or no correlation with the amorphous matter and SSA. The authors concluded that trace elements may exhibit different adsorption preferences to the weakly-bound fraction depending on the environmental conditions (e.g. competition and ability to bind to different charge sites).

The strong correlations between SSA and the trace element content in the Rybnik reservoir could also result from the presence of Al, Fe and Mn oxides. According to Zhuang and Yu (2002) metal-oxide-coated surfaces as well as primary clay mineral surfaces, contained different types of active sites that preferentially bound to trace elements. These results were confirmed by Farhat and Aly (2018), who concluded that Fe and Mn oxides with high SSA were the dominant factors in the metal immobilisation. As stated by Six et al. (2002) and Skic et al. (2020), structures in the form of aluminosilicates, iron and aluminium oxides allow for the physical protection of organic matter through its encapsulation in aggregates or through the formation of organic-mineral compounds. As numerous studies showed, organic matter affect the SSA values by coating mineral particles (Breiner et al., 2006; Kaiser and Guggenberger, 2007) and thus may determine the reactivity of mineral phase to metals.

The accumulation of trace elements in the analysed sediments is also related to the mineralogical composition of the bottom sediments. Due to the higher SSA, minerals with internal and external layers (such as smectites) have a greater capacity to accumulate metals compared to clay minerals with only external layers (like kaolinite) (Aboudi Mana et al., 2015). In addition, differences in the mineralogical composition of the reservoir sediments, such as mineral surface reactivity, even if they are submicron in size (Ivanić et al., 2020). In the case of the Roznów reservoir sediments, an interesting example of a significant relationship may be that between Cd and the carbonate content. In this particular case, Cd was not correlated with most of the studied variables, which may indicate that it is dependent only on carbonate minerals. These results are consistent with the study of Gober et al. (2014) as well as Farhat and Aly (2018), who showed that low solubility heavy metals, such as Cd, are co-precipitated with carbonates.
and their hydroxides precipitate in warm waters with a pH higher than 8.5.

Since pores are voids between and inside the aggregates as well as between primary particles of the solid phase, the bottom sediment texture, the specific surface area and the pore volumes are closely related. Analysing the results obtained, we found that pores in the clay and silt fraction were an important factor affecting the accumulation of trace elements and organic matter in the bottom sediments. For the Rybnik reservoir, significant correlations were found between metals and pores with diameters of less than 5 μm. These pores included classes of ultramicropores, cryptopores and residual pores. Since the nitrogen adsorption method reflects the presence of fine pores (d ≤ 100 nm), a significant correlation was also found between the trace element content and total pore volume and total pore area (r ≥ 0.84 and r ≥ 0.81, p < 0.05, respectively). In the case of bottom sediments of the Roznów reservoir, positive and significant relationships were only found between the Cr, Ni and Pb contents and volumes of cryptopores and residual pores.

Plathey et al. (2013) and Liu et al. (2009) argued that the accumulation of trace elements in pores of small diameter results from reduced water flow velocity in these limited spaces, leading to a reduced diffusion of ions and electrolytes. Trace elements can be bound to mineral surfaces by accessible reactive sites located on the pore walls and/or pore mouths (Kaiser and Guggenberger, 2007). These locations are also sorption sites for different organic matter fractions (McCarthy et al., 2008), which may consequently affect metal-binding through ion exchange or the metal complexation. The volume of macropores, mesopores and micropores seem to be less important for trace elements binding; however, these pores may participate in the migration within the mineral phase structure, increasing the permeability of sediments rich in quartz and clay minerals (Medina et al., 2011).

Apart from the natural factors mentioned above, anthropogenic factors may also influence the content and mobility of trace elements in sediments. Additionally, anthropogenic factors also indirectly affect the sorption properties of bottom sediments. The PCA indicated the presence of significantly positive correlations between trace elements in the bottom sediments from the Rybnik and Roznów reservoirs (except for Cd, Hg, Zn), which was related to similar sources and distribution routes. In the Rybnik reservoir, sources of trace elements in the bottom sediments are associated with metallurgical industry, coal combustion, municipal wastewater, and wet and dry atmospheric deposition (Baran et al., 2016; Baran et al., 2019; Baran A et al., 2017; Baran et al., 2020).

In the bottom sediment of the Roznów reservoir, the main sources of trace elements include: frequent floods, surface water flowing from agricultural fields and municipal sewage flowing directly into the reservoir (Baran A et al., 2017). In addition, the intense silting process of the Roznów reservoir may be an important source of trace elements, as fine mineral or organic fractions have high sorption capacities for trace elements. Higher content of trace elements caused higher potential toxicity (higher PECs) of bottom sediments of the Rybnik reservoir and lower and medium (lower PECs) in bottom sediments of the Roznów reservoir. However, negative correlations were found between the trace elements content and H. incongruens mortality and growth inhibition in both bottom sediments. Our previous studies also showed that the relationship between the trace element content and A. fischeri response was insignificant in sediments from the Rybnik reservoir (Baran et al., 2019). Szara et al. (2020) found that the trace element content in the Roznów reservoir bottom sediments was not responsible for the toxicity of the sediments to plants. This can be explained by several factors. First of all, the lack of significant relationships between the trace element content in both bottom sediments and H. incongruens response suggest their relatively low mobility and bioavailability. In the Rybnik reservoir bottom sediments, organic matter fractions play a key role in the sorption of trace elements, while in the Roznów reservoir bottom sediments, the clay fraction and the carbonate content are important in this process (Table 4). Moreover, the sediments of the Roznów reservoir were characterised by a low trace element content and low toxicity.

Other authors were observed that content of calcium, sorption properties and pH have significant influence on a decrease in the toxicity of heavy metals (Oleszczuk, 2008; Chial and Persoone, 2003). Charles et al. (2005) observed that metal toxicity is reduced by Ca²⁺, because of competition for cell surface–binding sites or because of solution speciation changes resulting from metal complexation and/or coprecipitation. The influence of grain size is variable on the ostracod response. Results of Casado-Martínez et al. (2006) showed that increasing the presence of clay reduced ostracod growth but mortality of H. incongruens was not affected. Chial and Persoone (2003) indicated that the H. incongruens mortality in Zn-polluted soils was a result of the toxicants bound to the solid-phase particles, rather than of those that had dissolved in the water phase. Kludak et al. (Kludak et al., 2011) showed that the sensitivity of H. incongruens to metal ions is as follows: Cd²⁺ > Hg²⁺ > Cu²⁺ > Cr³⁺ > Ni²⁺ > Mn²⁺ > Zn²⁺ > Pb²⁺ > Li⁺ > Fe³⁺. Higher take up of Cd by invertebrates can be connected with availability of the uptake route through “major ion” channels as Cd can enter into the cell through Ca channels as both elements have very similar ionic radius (Shuhaimi-Othman et al., 2011). In this studies, PC analysis revealed the influence of the physicochemical properties of the sediments (sand, silt, clay, TOC, mesopores, ultramicropores volume) on the sediment eco-toxicity for H. incongruens. The above are important environmental factors determining the conditions for the growth and development of organisms in sediments and have a significant impact on the mobility and bioavailability of elements. What is more, the bioassays integrate the effects of physicochemical properties and all chemical substances present as well as detect possible combinations such as synergistic or antagonistic effects that are difficult to predict and analyse (Baran et al., 2019; Cooman et al., 2015; Apitz, 2011; de Castro-Catala et al., 2016).

Our other studies revealed that contaminants such as PAHs, dioxins, biogens, increased water temperature and may affect the bottom sediment toxicity (Szara et al., 2020; Baran A et al., 2017; Baran et al., 2020). In the Ostracodotoxkit test, crustaceans are exposed to contaminants which are both soluble and absorbed on sediment particles; therefore, this test seems to be valuable for studying the influence of physicochemical parameters on the content and bioavailability of trace elements.

The study assessed different factors affecting the content and sorption of trace elements in the bottom sediments. The interaction between the various physical and chemical processes related to the trace element accumulation is very complex and is highly dependent on the physicochemical properties of bottom sediments. Studies on the effect of sorption properties on the trace element content in bottom sediments are very difficult and require data on the physicochemical properties of sediments, ecotoxicological and environmental characteristics, as well as modern analytical techniques. Only an understanding of the above factors will provide comprehensive information on the content of trace elements in aquatic systems.

5. Conclusions

1. The study found higher content of trace elements caused higher potential toxicity of bottom sediments of the Rybnik reservoir and lower and medium in bottom sediments of the Roznów reservoir. However, the PCA analysis indicated that ecotoxicity to H. incongruens was not related to the trace element content in both sediments.

2. The study revealed a strong variation in the strength and direction of statistical relationships between the properties of different bottom sediments and trace element sorption, which results from significant differences in the carbonate and organic matter contents.

3. Strong positive relationships were observed between the negative surface charge values (Q₄, Q₇, Q₉) and the trace element content in the Rybnik reservoir sediments (r = 0.92–1.00 for As, Cd, Cr, Ni, Zn, Hg and r = 0.84–0.89 for Cu and Pb) indicating high utility of
Boguta, P., Sokolowska, Z., 2020. Zinc binding to fulvic acids: assessing the impact of pH, metal concentrations and chemical properties of fulvic acids on the mechanism and stability of formed soluble complexes. Molecules 25 (6), 1292.

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Potentiometric titration parameters. The obtained relationships showed a significant role of negatively dissociating functional groups (carboxyl, phenolic, alcohol, and carbonyl groups) of Cha, Cfa, Cach and DOC fraction and of clay minerals.

4. We demonstrated a positive correlation between the metal content and the volume of ultramicrocrystals, cryptocrystals and residual pores. Our observations suggest that these pore groups contain reactive sites capable of effective trace element sorption. In contrast, larger pores turned out to be of marginal importance in metals sorption, probably participating only in their migration within the bottom sediment structure.

5. The results showed that the mercury porosimetry, which provides relevant information about a wide range of pore diameters, can be a useful tool for characterising the trace element sorption capacity of bottom sediments.

Credit author statement
Patrycja Boguta: Methodology, Investigation, Writing – original draft, Visualization, Conceptualization, Writing – review & editing. Kamil Skic: Methodology, Investigation, Writing – original draft, Visualization, Formal analysis. Agnieszka Baran - Methodology, Investigation, Writing – original draft, Visualization, Formal analysis, Conceptualization, Project administration, Funding acquisition, Magdalena Szara-Bak – Investigation

Declaration of competing interest
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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