1. INTRODUCTION

Accurate assessment of the quality of the aquatic environment is related to the analysis of contamination of bottom sediments, as they reveal the essential features of aquatic ecosystems. Bottom sediments constitute a habitat of many organisms, they participate in the biogeochemical process of elements circulation and they are the place of deposition and chemical changes of many compounds entering the waters. Due to the structure of sediments they form a natural geosorbent, in which pollutants introduced into the aquatic envi-
The chemical composition of the matter lying on the bottom of water reservoirs is conditioned by both natural and anthropogenic factors. An important role is played, among others, by the geological structure of the basin, the type of soil cover, terrain and climatic conditions. Additionally, the chemical analysis of bottom sediments is a source of information on human activity in a given region. The most frequently observed forms of anthropogenic impact affecting the quality of sediments are discharges of municipal and industrial sewage, atmospheric and gaseous pollution of the atmosphere as well as leaks from landfills. In agricultural areas, additionally, contaminants introduced into the basin of the reservoir (fertilisers, plant protection chemicals), as well as sewage sludge, which is used to fertilize the arable land. As a result of the total effect of the presented factors, the material deposited on the bottom of water reservoirs may contain significant loads of organic (e.g. PAH, pesticides) and inorganic (e.g. trace elements) pollutants, which accumulate in sediments and may subsequently pose a threat to water quality due to remobilisation. A feature of these compounds is that they can remain active for a long period of time and constitute a secondary source of water contamination.

Modern studies on trace elements in bottom sediments are often related to ecological risk, toxicity evaluation, health risk caused by trace elements and geochemical cycling. Sediment quality guidelines (SQGs) and potential ecological risk index (PERI) are group of useful methods which allows assessment of pollution risk of an aquatic system by integrating total trace element content. The main aim of this study was to evaluate the quality of bottom sediments of water reservoir Poraj by applying a set of sediment quality guidelines, potential ecological risk and spatial analysis. Toxicity effect and total trace element content were described in previous studies.

2. MATERIALS AND METHODS

2.1. Study area and bottom sediments sampling

Sampling of bottom sediments from the Poraj Reservoir was conducted in August 2016. The analysed reservoir is located in the Poraj and Koziegłowy municipality in the Myszków County, in the northern part of the Silesian Voivodeship. It has an area of 550 hectares. It was created in 1978 in order to build a reservoir of water for Huta Czestochowa. Currently, it is the subject of interest to local residents because it could be used for water sports and tourism, as well as recreation in the region. The Warta River is the main tributary directly supplying the Poraj water tank. For this reason, it substantially affects the quality of the water and bottom sediments of the reservoir. The waters of the river are polluted inter alia by sewage, which are supplied mainly from the area of Zawiercie and Myszków. They originate mainly from rural areas without a sewerage system. Domestic wastewater is directly introduced into the surface waters, which are located in the catchment area of the reservoir. Numerous resorts are present in the immediate vicinity of the lake, because of its recreational character. They constitute point sources of pollution, which directly participate in shaping the quality of water and sediment tank.

Samples of bottom sediments were collected at 46 measuring points (determined by ArcGIS software) with depths ranging from 0.4 m to 7.4 m below the water table, Fig. 1. The research material was collected using a specialized hook for bottom sediments of Van Veen’s KC Denmark type.
2.2. Laboratory analysis

The samples were first dried under dry-air conditions and then sieved through a 2 mm screen. They were then dried in an oven at 105°C to constant weight and ground in a vibrating mill until the grain size was lower than 0.2 mm [2, 14]. Prepared samples were used to determine the total trace element content in accordance to Polish Standard PN-ISO 10390:1997 and 11466:2002. Aqua regia (a mixture of concentrated hydrochloric acid and nitric acid in a volumetric ratio of 3:1) was used for trace element extraction (Zn, Cd, Pb, Ni, Cu, Cr). Mineralisation was carried out at 180°C, for 30 minutes in a high pressure microwave mineraliser from the German company Berghof GMBH. A plasma spectrometer (IRIS ICP-OES Thermo) was used to determine the trace element content. (Rozpondek, Wancisiewicz, 2016). Total nitrogen were determined by Kjedahl method. Organic matter content were determined in accordance to PN-ISO 11465:1999. Toxicity effect of bottom sediments was determined by *Alivibrio fischeri* bacteria bioassay using Microtox M 500 Analyzer (in accordance to PN-ISO 11348-2:2008). Water extracts were prepared by mixing one volume of bottom sediments and four of distilled water [17]. Total trace elements concentration, percentage toxic effect, organic matter and total nitrogen was described in previous studies [2, 14].

2.3. Indexes of ecological risk

Sediment quality guidelines (SQGs) were applied to evaluate the degree to which the sediment-associated chemical status might adversely affect aquatic organisms and to aid in the interpretation of sediment quality [9, 10, 18]. These guidelines have been widely used to screen sediment contamination by comparing sediment contaminant concentrations with the corresponding quality guidelines in aquatic ecosystems [9, 10, 11, 12, 17]. The assessment of sediment contamination with trace elements was based on threshold effect concentration (TEC) and probable effect concentration (PEC) methods. To determine potential risk to the benthic fauna, values of trace elements were compared to corresponding TEC and PEC values (Table 1). For each of the studies, trace elements concentration and mean PEC were determined (PECQ). PECQ was calculated by the average of the ratio of PEC of each element concentration. There are two crucial values for indication potential environmental risk: 0.5 and 1.0. If values of PECQ are lower than 0.5 then bottom sediments sample are predicted to be non-toxic. If it exceeds value of 1.0 then it indicates that the bottom sediments are predicted to be toxic and pose a threat to benthic fauna [10, 18, 19].

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Zn</th>
<th>Cd</th>
<th>Pb</th>
<th>Ni</th>
<th>Cu</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEC</td>
<td>459</td>
<td>5</td>
<td>128</td>
<td>49</td>
<td>149</td>
<td>111</td>
</tr>
<tr>
<td>TEC</td>
<td>121</td>
<td>1</td>
<td>35.8</td>
<td>23</td>
<td>32</td>
<td>43.4</td>
</tr>
</tbody>
</table>

The potential ecological risk index (PERI) is also a method that allows assessment of potential harmfulness of trace elements contained in bottom sediments. The potential ecological risk index for trace elements was calculated based on the formula developed by Håkanson [20, 21]. It consists of: potential ecological risk of the trace elements, contamination factor, measured background values of the trace elements in studied area. The toxic response factor of the trace elements depends on the sedimentological toxic factor (STF) and bioproduction index (BPI) [20, 23, 24]. STF of individual elements is as follows: for Zn = 1; Cu, Pb, Ni = 5; Cr = 2, Cd = 30; [20, 21]. Bioproduction index is a factor that affects the bioavailability of trace elements. BPI was calculated as the nitrogen content in the regression line for the organic matter content value of 10% (Fig. 2) [20, 21]. The content of total nitrogen and organic matter was described in previous studies [2, 14].

The value of BPI was equal to 37.7. Contamination factor for each of the studied trace elements was estimated on the basis of geochemical background of the bottom sediments: Zn 48 [mg·kg⁻¹], Cu 6 [mg·kg⁻¹], Ni, Cr 5 [mg·kg⁻¹], Pb 10 [mg·kg⁻¹] and Cd 0.5 [mg·kg⁻¹] [10, 21, 22].
2.4. Statistical and spatial analysis

The performed descriptive statistics included determining mean value, standard deviation, median, minimum and maximum, kurtosis and skewness. Coefficient of determination was also performed. Statistical analysis was performed with Statistica software.

Spatial distributions of PERI, PECQ and TEC were generated with ArcGIS software. Location of points was defined before bottom sediments sampling. For purpose of generating spatial models, inverse distance weighted interpolation method was used. Spatial distributions allow determining the areas with highest ecological risk [2,10,14].

3. RESULTS AND DISCUSSION

Statistical analysis for total trace element content in bottom sediments are presented in Table 2. Data is characterized by significant difference between min and max value, high value of standard deviation compared to mean and high skewness and kurtosis (except Ni). Those factors indicate that total trace element content in bottom sediments was not normally distributed. Distribution is characterized by strong right-sided asymmetry which is typical for environmental studies. Similar results were obtained for PECQ, PERI and TEC values (Table 3). Normal distribution can be crucial for some of geostatistical methods.

Considering PEC and TEC value we can distinguish three primary groups:
- if measured value of concentration of trace element is higher than corresponding TEC (Table 1), sample of bottom sediments is predicted to be non-toxic,
- if measured value of concentration of trace element is higher than corresponding PEC (Table 1), sample of bottom sediments is predicted to be toxic,
- if measured value of concentration of trace element is higher than corresponding TEC and lower than corresponding PEC (Table 1), sample of bottom sediments is predicted neither to be toxic or not [10,18].

Concentrations of three trace elements were above PEC value: Zn (22% of samples), Pb (17%) and Cd (17%). Based on TEC value, 76% of bottom sediment samples were predicted to be non-toxic.

Mean PECQ value provides a basis for assessing the potential effect of sediment-associated contaminants when they occur in a complex mixture [10,23]. Values of PECQ ranged from 0.04 to 2.08 with mean of 0.38. PERI values ranged from 4.36 to 323.62 with mean of 55.35. PERI of less than 150 indicates low potential ecological risk, and PERI above 150 indicates moderate potential risk [10,20,21,24,25]. Both mean values of PERI and PECQ indicate low potential risk, but it should be mentioned that PERI above 150 was observed in 17% of collected samples. By considering mean PECQ value, 17% of samples were predicted to be toxic. The Coefficient of determination was determined between studied factors: PERI and PECQ ($R^2 = 0.98$), PECQ and TEC ($R^2 = 0.99$), PERI and TEC ($R^2 = 0.98$), PERI and PE ($R^2 = 0.06$), PECQ and PE ($R^2 = 0.07$). High correlation between PERI, TEC and PECQ indicates that both factors are characterized by similar results and they can be used interchangeably in terms of assessing quality of bottom sediments (same results were obtained by other authors [10]). Low correlation between toxic effect and PERI or PECQ indicated that there are other factors that contribute to the toxicity of the sediments. [2,10]. Additionally, the BPI value of 38 indicates that water reservoir Poraj is an eutrophic basin [27]. In eutrophic basins trace elements are often characterized by low bioavailability, which can directly influence the response of *Alivibro fischeri* bacteria [27]. Also other studies showed that specific bacteria can have different responses to various factors [28].

Values of mean PECQs can be classified to four class-
es [29]: below 0.1, 0.1 to 0.5, 0.5 to 1.0 and above 1.0. Those classes indicate probability that respectively 10, 17, 56 and 97% of samples are toxic. On this basis, classification of obtained spatial distribution was generated (Fig. 2. and Fig. 3.).

Spatial distributions of PECQ, PERI and TEC were generated (Figure 2, 3 and 4). The area is characterized by significant diversity in terms of localization of contaminants. Highest values of PECQ and PERI occurred in points 1, 2, 3, 8, 12, 17, 26 and 45 which are mainly localized in the northern part of water reservoir Poraj. This part of the reservoir is also the deepest [14]. The lowest values were observed in central and east region. Maximum values of PERI and PECQ were observed in point number 45 (PECQ 2.08 and PERI 323.62).

The distribution of the indicators to a large extent coincides with the dominant current in the reservoir what can be an indication of the mobility of the analysed material. The increased content of the trace elements in the bottom sediment of the water reservoir Poraj can stem from the fact that the analysed reservoir and its basin are exposed to the harmful influence of anthropogenic activities.

Additionally, the increased content of trace elements in the tested object can also be related to the surface runoff, which introduces pollution from agricultural areas (fertilizers, pesticides) as well as sewage sludge, with which fields are fertilized [2, 14, 16, 30].
Coefficient of determination was calculated between PECQ, PERI, TEC and studied trace elements (Table 4). The highest values were observed between Zn, Cd, Pb, Cu and calculated indexes, the lowest concentration was found between Cr and analysed factors. It can lead to an assumption that in terms of water reservoir Poraj Cr was not directly correlated with PERI and PECQ. Thus, Cr should be considered separately. Other trace elements are strongly correlated with applied rules of evaluation of quality of bottom sediments.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>PECQ</th>
<th>PERI</th>
<th>TEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>0.99</td>
<td>0.96</td>
<td>0.99</td>
</tr>
<tr>
<td>Cd</td>
<td>0.97</td>
<td>0.99</td>
<td>0.97</td>
</tr>
<tr>
<td>Pb</td>
<td>0.99</td>
<td>0.98</td>
<td>0.99</td>
</tr>
<tr>
<td>Ni</td>
<td>0.77</td>
<td>0.77</td>
<td>0.75</td>
</tr>
<tr>
<td>Cu</td>
<td>0.97</td>
<td>0.95</td>
<td>0.97</td>
</tr>
<tr>
<td>Cr</td>
<td>0.52</td>
<td>0.47</td>
<td>0.51</td>
</tr>
</tbody>
</table>

Despite the dominating low ecological risk, the Poraj water reservoir, due to its function (including recreational aspects), should be constantly monitored due to the threat to the health of people resting there [2, 14]. In particular due to high concentrations of trace elements as well as locally occurring toxicity effect. The drawn maps of spatial distribution (Figures 2 and 3) can form the basis for undertaking activities aimed at planning prevention, protection and processes aimed at improving the current state [2, 14].

4. CONCLUSIONS

On the basis of conducted studies, following conclusions were established:
1. 76% of bottom sediments samples are predicted to be non-toxic, 17% are predicted to be toxic and 7% is neither toxic or non-toxic,
2.sediments quality guidelines and potential ecological risk index due to high correlation and similar spatial distribution can be used interchangeably for the assessment of quality of bottom sediments,
3. highest values of PERI, PECQ and TEC occur mainly in northern part of water reservoir Poraj, which is also the deepest area [16],
4. lowest values of PERI, PECQ and TEC were observed mainly in south-eastern part of reservoir,
5. low correlation between toxic effect and PERI or PECQ indicated that there are other factors that contribute to the toxicity of the sediments,
6. the main contaminants in studied water reservoir are zinc and lead,
7. spatial distributions can be crucial for proper understanding of contamination in bottom sediments of water reservoirs,
8. based on the obtained results and recreational function of water reservoir, a need of constant monitoring and improving quality of bottom sediments has been established,
9. there was no correlation between PECQ, PERI and Cr ($R^2 \sim 0.5$).

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REFERENCES


