Toxic metal pollution of aquatic ecosystems of European Union nature protection areas in a region of intensive agriculture (Lake Gopło, Poland)

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Abstract
The paper presents the results of research into toxic metal concentrations in the surface layer of bottom sediments in Lake Gopło. The research objectives were to identify the levels and spatial variability of Cu, Pb, Cd, Zn, Ni, Cr, As and Hg concentrations, their potential sources and the determinants of pollution levels. Metal contamination of the sediments was assessed using the geoaccumulation index (Igeo), pollution load index (PLI) and ecological risk index (RI). Chemometric methods (Pearson correlation, principal component analysis (PCA) and cluster analysis (CA) were used to determine the relationship between sampling sites and concentrations of toxic metals, thereby identifying the sources of contamination. The research found that grain-size composition, carbonate content and organic matter content in the bottom surface sediments of Lake Gopło are all characterised by low diversity. Therefore, the lithological features of the sediments are not a major factor in the concentrations and spatial variability of the metals. It was found that the metal concentrations in the great majority of samples were above regional geochemical background levels. The geochemical indices (Igeo, PLI, RI) indicate that the degree of toxic metal pollution in the sediments is slight in the central and southern parts of the lake and high in the northern part. The chemical analysis results showed that the samples in the central and southern parts of the lake differ little in their shares and concentrations of individual metals. This provides evidence that, as well as geogenic sources, their presence in sediments can be associated with non-point sources related to agricultural activities and with atmospheric sources (mainly the products of fossil fuel combustion). The higher concentrations of metals (especially Ni, Cd, Cr and Hg) in the northern part of the lake are influenced by the supply of industrial and communal pollutants from the lakeside town of Kruszwica. A factor limiting the migration of pollutants from the northern part of the lake towards the south is the lake’s morphology of the lake, which hinders water exchange between the northern part and the rest of the lake.

Keywords Toxic metals · Bottom surface sediments · Lake · Co-occurrence · Spatial patterns · Contamination-ecological risk assessment

Introduction
The toxic metal pollution of aquatic ecosystems is a global problem that results from increasing industrialisation, urbanisation, and the intensification and chemicalisation of agriculture (Foster and Charlesworth 1996; He et al. 2005; Häder et al. 2020; Xia et al. 2020). The changes caused by the industrial revolution, and especially the significant increase in extraction and processing of metal ores in the early twentieth century, were marked by, among other things, a significant increase in metal concentrations in soil profiles and sub-aqueous sediment cores (Nriagu 1996; De Vleeschouwer et al. 2009).

The toxic metal pollution of the environment, and especially of aquatic ecosystems, is dangerous because of the environmental persistence of toxic metals, their toxicity and their potential for biological accumulation (Varol 2011; Copat et al. 2012; Jiang et al. 2012; Singh and Kumar 2017; Zhao et al. 2017; Chen et al. 2018). Toxic metals pass through the environment in different ways to ultimately reach water bodies, where they accumulate...
in bottom surface sediments (Foster and Charlesworth 1996; Cai et al. 2015). Their path from source of emission to water body depends on the form in which they are introduced into the environment. Toxic metals can enter the hydrological network directly in soluble form (Wang et al. 2018; Wilson 2018). They can also be emitted to the atmosphere as dust or gases, and then fall to the surface as liquid or solid precipitation (Gunawardena et al. 2013; Sarkar et al. 2015; Chang and Yingxia 2020).

Toxic metals contained in soil, both those of anthropic origin and those that are a natural component of the substrate, participate in adsorption and desorption processes, which determine their bioavailability and mobility in the environment (Violante et al. 2010). They can then be leached by infiltrating precipitation water or pass in insoluble form with mineral-organic suspended matter and in surface runoff to reach the channels of watercourses and onwards to natural and artificial water bodies (Foster and Charlesworth 1996; Garrett 2000; Sharma 2001; Siegel 2002).

Toxic metal concentrations in bottom surface sediments are conditioned by volume of supply, but also by their physical properties and mineral composition, the dynamics of the aquatic environment, and the physico-chemical properties of the water (Förstner 1982; Dickinson et al. 1996). In this case, the sediment properties that are of fundamental importance in affecting the efficiency of sorption processes are: the grain size of clastic material; the mineral composition of the sediment; the organic matter and carbonate contents in the sediment material; and their concentration of Al, Fe, Mn and P compounds (Helios-Rybicka 1986, 1997; Foster and Charlesworth 1996; Kabata-Pendias and Pendias 1999; Brekhovskikh et al. 2001; Canavan et al. 2007). Large water bodies usually exhibit significant spatial differentiation in the metal content in the bottom surface sediment layer (Håkansson and Jansson 1983). This reflects not only the location of the sources supplying pollutants to the water body, but also the effects of internal hydrodynamic processes that cause both the re-suspension of accumulated sediment and post-depositional bioturbations (Zhang et al. 2014). These processes change Eh and pH values, potentially causing mobile metal forms to be released from bottom surface sediments into the water (Eggleton and Thomas 2004; Atkinson et al. 2007; Cantwell et al. 2008).

Previous studies indicate that the scale and spatial variability of toxic metal concentrations in the bottom surface sediments of water bodies are influenced by many factors and processes:

(1) The environmental diversity of the catchment area (e.g. relief, substrate lithology, soil type), (Abraham et al. 1998; Wiechula 2003; Wang et al. 2014; Sojka et al. 2019; Kostka and Leśniak 2021),

(2) The form of land use (Lindström 2001; Skwierawski, Sidoruk 2014; Zemelka et al. 2019; Zeng et al., 2020),

(3) The location and type of point pollution sources (Cobelo-Garcia, Prego 2004; Sojka et al. 2013; Wu et al. 2014; Smal et al. 2015; Kuriata-Potasznik et al. 2016),

(4) Water body characteristics (shape, morphology, depth, hydrodynamics), (Smal et al. 2015; Zhu et al. 2017; Gierszewski 2018; Sojka et al. 2018; Sahoo et al. 2019),

(5) Bottom surface sediment properties (grain sizes, mineral composition, organic matter content) (Foster and Charlesworth 1996; Kabata-Pendias and Pendias 1999; Tao et al. 2015; Lin et al. 2016; Gierszewski 2018; Kostka and Leśniak 2021),

(6) Chemical and biochemical processes in bottom surface sediments (Salomons and Stigliani 1995; Zhang et al. 2014),

(7) Climate change (Zhang et al. 2018).

Due to the multiplicity of these factors, analyses of the factors determining the variation in toxic metal contamination of bottom surface sediments should consider the specific features of individual water bodies and their catchments (Sojka et al. 2019).

Here, we present the results of studies on toxic metal concentrations in the surface layer of bottom surface sediments in Lake Gopło. It is one of the Poland’s largest lakes by surface area and lies in a region of highly developed agriculture and extensive agricultural-food industry. It also lies within a zone of influence of lignite mines and coal-fired power plants. Despite the lake’s catchment area containing many sources of supply of hazardous pollutants, no comprehensive studies have yet been undertaken to identify the sources of supply of toxic metals or the spatial distribution of toxic metals in the bottom surface sediments, nor to assess pollution. Therefore, the aim of the research was: (i) to determine the spatial distributions of selected toxic metals (Cu, Pb, Cd, Zn, Ni, Cr, As and Hg) in surface sediments of Gopło Lake; (ii) to assess the degree of contamination of the toxic metals using indices of contamination; and (iii) to evaluate the relationship between toxic metals and define their possible sources (natural and/or anthropogenic) by the application of chemometric analysis. Chemometric methods such as Pearson’s correlation analysis, principal component analysis (PCA) and cluster analysis (CA) are considered to be effective at discovering sources of contamination and have been used successfully in many studies of the contamination of bottom sediments with toxic metals (e.g. Loska and Wiechula 2003; Larrose et al. 2010; Chabukdhara and Nema 2012). The authors’ use of a complementary approach that integrates chemometric analyses and geochemical methods increased the accuracy of the assessment of sediment contamination.
contamination with metals and helped determine the sources of their supply.

**Materials and methods**

**Study area**

Located in the Kuyavian lake district (central Poland), Gopło Lake has an area of 21.5 km², placing it ninth in Poland by area. It occupies a 25-km-long channel that splits into two arms in the middle of the lake. The shape of the lake and the presence of numerous islands and inlets mean that its shoreline is over 90 km long (Fig. 1). The lake depth is 16.6 m at its deepest point and averages 3.6 m. Its different depths mean that summer thermal stratification occurs only in its deepest, southern part (Goszczyński, Jutrowska 1996).

The relief of the lake’s 1342 km² catchment area was formed during the Weichselian glaciation. It consists of morphologically diverse post-glacial moraine plateaus. In the northern part, these are mainly flat surfaces of sandy clay ground moraine. In the southern part, the relief is more...
diverse, consisting of an undulating moraine plateau, marginal hillocks and ridges, and sandy outwash plains. The moraine plateau is incised in many places by subglacial channels, the centrally located Gopło channel, and marginal valleys (Molewski 1999). The predominance of poorly permeable sediments limits the migration of pollutants to the groundwater, and the relatively low energy of the relief restricts surface runoff (Fig. 1). The dominant land-use type in the lake’s catchment area is agricultural, covering as much as 82.6% of its area. The share of other forms of land use is: 11.4% forests; 1.5% urban and industrial areas; 4.5% water and wetlands (Fig. 1). The lake area and adjacent farmland, meadows and pastures, forests, swamps, reeds and other wastelands constitute a protected area that functions partly as a landscape park and partly as a nature reserve (Gopło Millennium Landscape Park). It is also a Natura 2000 area (an area of EU nature protection; SPA PLB040004 Ostoja Nadgoplańska and SAC PLHO40007 Jezioro Gopło, established pursuant to Council Directive 2009/147/EC on the conservation of wild birds (EU 2019) and Council Directive 92/43/EEC on the Conservation of natural habitats and of wild fauna and flora (EU 2013)). The toxic metal content in soils and sediments in the lake's catchment area does not exceed geochemical background values (Atlas Geochemiczny Polski 2012). Concentrations of Ni and Pb can be locally elevated (Cieślak et al. 1994).

The shallow depths of the lake, the large area of the bottom that lies within the range of the epilimnion, the large size of the catchment area relative to the lake area, and the catchment relief and land management all make Gopło Lake highly susceptible to the supply of pollutants from the catchment area and to the redistribution of autochthonous matter (Goszczyński and Jutrowska 1996). Some pollution is brought to lakes in the waters of tributaries. In this case, this is the Noteć River, which flows into Lake Gopło from the south and whose average flow at the Łysek gauge was 0.89 m³ s⁻¹ in 1961–2000 (Graf 2003). In addition to the main tributary, the lake is supplied with water from 72 small streams and drainage channels and ditches, though these do not flow for most of the year (Juśkiewicz 2014).

Large-scale drainage works at the turn of the twentieth century were fundamental to the economic development of this part of Poland (Kaniecki 2011). They allowed intensive agriculture to develop in the Gopło Lake catchment, this practice being associated with the use of crop protection products and large amounts of mineral and organic fertilisers. The consumption of the latter is equivalent to 170–232 kg of NPK per 1 ha of agricultural land, which is among the highest such consumptions in Poland and Europe (GUS 2008; IERiGŻ 2015). This agricultural activity led not only to the rapid eutrophication of the lake (Wiśniewski 1992), but also to the supply of many toxic substances, including toxic metals. Since the early twentieth century, agricultural-food industries based on a range of crops has been established in the catchment area; these, together with industrial animal husbandry centres and domestic and municipal pollutants, constitute the main point sources of pollution. At various times, over 38 such sources have existed in the lake catchment area (Fig. 1). A large number of food industry plants (fat, wine, sugar factories) have been built in Kruszwica. The town lies immediately lakeside on the northern shore. In the early 1990s, sanitary sewerage systems and related sewage treatment plants were built. Gradually, they have extended their coverage to serve Kruszwica and other towns in the lake’s catchment area. Lake Gopło is also within the zone of influence of open-cast lignite mines that have been operating in this region since the 1950s. They are located about 10–18 km as the crow flies to the south-east and west of the lake. The drainage of the open-cast mines has contributed to changing the lake’s groundwater supply conditions (Przybytek 2020). Another potential source of pollution is the air pollution that results from coal mining and coal combustion in three thermal power stations 21 km from the lake.

Sediment sampling and analytical methods

Twenty sediment cores were collected using a Uwitec Corer. The locations of the sample points (SP) were determined using a Garmin dual-beam GPS sonar. The sites were selected based on a bathymetric plan such that the SPs were evenly distributed across the entire lake area, while maintaining principles that ensure the collecting of samples of undisturbed structure (Fig. 2). From each core, from its upper 10-cm layer, four sediment samples were collected for sedimentological and geochemical analyses, providing eighty samples in total. Metal concentrations averaged from the four samples were used both to analyse the spatial variation in the selected metal concentrations in the sediments and to assess the degree of contamination and ecological risk. The content of organic matter and carbonates in the sediments was determined by loss on ignition (Heiri et al. 2001). The particle-size composition was determined by laser diffraction on a Fritsch Analysette 22 device. After mineralisation of samples in concentrated nitric acid, the concentrations of the toxic metals (copper [Cu], lead [Pb], cadmium [Cd], zinc [Zn], nickel [Ni], chromium [Cr], arsenic [As] and mercury [Hg]) were determined in a microwave oven by atomisation atomic absorption spectrometry methods in the accredited "Labor-test" laboratory in Toruń; depending on the element to be determined, this was done in a graphite furnace, in a flame, by hydride technique or by cold vapour technique.
The grain-size analysis results were statistically processed in GRADISTAT software (Blott and Pye 2001), which calculated grain-size indicators according to Folk and Ward (1957).

The contamination of bottom sediments with toxic metals was assessed using the common geochemical index, which is Müller’s (1979) geoaccumulation index (Igeo):

\[ I_{geo} = \log_2 \left( \frac{C_m}{1.5GB} \right) \]  

where \( C_m \) concentration of the analysed metal (mg·kg\(^{-1}\)), \( GB \) geochemical background (mg·kg\(^{-1}\)).

The index value was then assigned to one of the seven purity classes according to Müller (1981): class 0 (Igeo < 0) uncontaminated; class 1 (0 < Igeo ≤ 1) uncontaminated to moderately contaminated; class 2 (1 < Igeo ≤ 2) moderately contaminated; class 3 (2 < Igeo ≤ 3) moderately to heavily contaminated; class 4 (3 < Igeo ≤ 4) highly contaminated; class 5 (4 < Igeo ≤ 5) heavily to extremely contaminated; class 6 (5 > Igeo) extremely contaminated. We adopted the geochemical background values that represent the geometric mean concentration of toxic metals in lake and river water sediments in Poland from Bojakowska and Sokólowska (1998).

The summative assessment of sediment contamination with all analysed metals was presented using the pollution load index (PLI) (Tomlinson et al. 1980):

\[ PLI = \sqrt[2n]{CF_1 \times CF_2 \times CF_3 \times \ldots \times CF_n}, \]  

where \( n \) number of elements, \( CF \) the ratio of selected elements to their background values. The PLI results were used to divide the sediments into three purity classes: PLI ≤ 0, no pollution; PLI = 1, background pollution; and PLI > 1, elevated pollution.

The potential ecological effects of the toxic metal contamination of lake sediments are described in the ecological risk index (RI) (Häkanson 1980). The RI is the sum of the toxic effects of individual metals expressed by the risk factor (ER):

\[ ER_i = TR_i \times CF_i, \]  

where \( TR_i \) is the biological toxic factor of element \( i \), which is determined for Cu = Pb = Ni = 5, Cd = 30, Zn = 1, Cr = 2, Hg = 40, As = 10 (Häkanson 1980); and \( CF_i \) – contamination factor of element \( i \). Due to the set of metals being different in this study, the original (Häkanson 1980) classification of ecological risk indicators (Li et al. 2012) was modified. The risk factor (ER\(i\)) is classified as: low risk (ER\(i\) < 40), moderate risk (40 ≤ ER\(i\) < 80), considerable risk (80 ≤ ER\(i\) < 160), high risk (160 ≤ ER\(i\) < 320), or very high risk (ER\(i\) ≥ 320); whereas, ecological risk index is categorised as: low risk (RI < 100), moderate risk (100 ≤ RI < 200), considerable risk (200 ≤ RI < 400), or very high risk (RI ≥ 400). A set of TEL / PEL guidelines was also used (MacDonald et al. 2000).

Chemometric analyses of toxic metal concentrations in sediments were performed using Pearson’s correlation analysis, Principal Component Analysis (PCA) and Cluster Analysis (CA) in the software package Statistica. Pearson correlation analysis was applied to identify the co-occurrence correlations between toxic metals and the nature of the relationship of metal concentrations to the physical properties of sediments and environmental parameters. To identify the possible sources of toxic metals in the Lake Gopło catchment and to discover the similarities and differences in toxic metal concentrations in sediments at each sampling point, PCA and CA analyses were performed. Cluster Analysis (CA) helped identify the measurement points that...
were most similar to one another in terms of toxic metal concentrations. The most similar points are grouped into one cluster. PCA reduced the number of variables describing a given point (in this case to eight variables—i.e. metal concentrations) and 20 sample points, to several indirect factors, the so-called principle components (PCs) to analyse the relationship between the observed variables. This provides information on the relationship between sampling sites and pollutant concentrations. Cluster analysis was performed by z-scale transformation were used to avoid the potential for misclassification due to large differences in data dimensionality (Liu et al. 2003). Cluster analyses were performed by Ward’s method, using Euclidean distances as a measure of similarity. The PCA was calculated based on a correlation matrix of measured parameters. The number of significant principal components was selected based on the Kaiser criterion of eigenvalues higher than 1 (Kaiser 1960). The correlation between principal component and concentration of toxic metals was classified according to values > 0.75, 0.75–0.50 and 0.50–0.30 as strong, moderate and weak, respectively (Liu et al. 2003). Multivariate statistical analysis is an alternative methods of identifying pollution sources that can determine anthropogenic or geogenicity (Yalcin et al. 2010, Huang et al. 2017). Combining PCA analysis with CA ensures that sources for a given metal distribution pattern in the sediment will be correctly identified (Upadhyay et al. 2006; Zhou et al. 2008).

Results

General description of lake sediments

The grain-size composition, organic matter content of the bottom surface sediments of Lake Gopło are all characterised by low diversity. Only the share of calcium carbonate in the analysed sediment samples ranged widely, from 20 to 74%, averaging 58%. The content was found to be lower in the sediments in the north of the lake (SP1–SP5), where it averaged 45% of sample mass. In the rest of the lake, the share of CaCO$_3$ in the sediments averaged 63%, and the maximum (SP16) even exceeded 70%. The calcium carbonate that precipitates from the lake water due to biogeochemical and physico-chemical changes mainly derives from young glacial sediments (e.g. Mazurek 1999). The average organic matter content in the sediments is 13.8% and is relatively poorly diversified (8–20%). In the very north of the lake (SP1–SP5) and in the bay on its western side (SP13, SP15, SP17), organic matter constitutes an average of 16% of dry matter, and a maximum of 20%. The share of clastic material in the tested samples ranged from 13 to 62% (averaging 28%), and the grain size was in the range of 8–38 μm. The dominant fraction was silt, which constituted as much as 98%, complemented by clay. The highest number of grains of the corresponding clay fraction was found in sediment samples from the western, bay part of the lake (SP15, SP17). Fifty-nine percent of the silt fraction was coarse grained, 7% very coarse grained, and 34% medium grained. Despite organic matter and carbonates having been removed before grain size was measured, the tested mineral material still contained biogenic silica and metal hydroxides, which probably somewhat affected the grain-size measurement (Żarczyński et al. 2019).

Based on the share of the main components, the bottom surface sediments of Gopło Lake are—according to the Succow’s classification (1988) with modifications by Kaiser (2001)—carbonate gyttja. Only in the north of the lake (SP1, SP5) was the mineral–organic/carbonate gyttja.

Concentrations of toxic metals in bottom surface sediments

The basic statistics related to toxic metals in bottom surface sediments of Gopło Lake, as well as regional and local values of geochemical background, sediment quality guidelines (SQGs) TEL (Threshold Effect Level) and PEL (Probable Effect Level) is summarised in Table 1. The variability in concentrations of analysed metals at individual sample points is shown in Fig. 3. The mean concentration of all analysed metals except Cd, Cr and As exceeded regional geochemical background, as did all maximum values (including for those three elements). The degree of enrichment of the studied toxic metals in Lake Gopło decreased in the order of Cu > Pb > Zn > Ni > Cd > Cr > Hg > As. The concentration of toxic metals in sediments in Lake Gopło is similar to or below that of other lakes in the region, with the exception of Cu and Zn. Similarly, in comparison to the lakes of post-glacial origin in northern Poland, the concentration of most of the analysed metals is lower. The opposite case only held for copper and mercury contents in the sediments (Table 1). Except for mercury, the mean content of other metals in the sediments was lower than the corresponding TEL values. In a few sediment samples, the concentrations of all metals exceeded TEL values, and lead, zinc, nickel and mercury also exceeded PEL values (Table 1). PEL values were exceeded by nickel in SP1, mercury in SP1 and SP5, and zinc and lead in SP5. It follows that, in the north of the lake, the concentrations of Pb, Zn, Ni and Hg may be causing adverse biological effects (Fig. 3).

The coefficients of variation (CV) of all metals (except arsenic) indicate high variability of concentrations (Table 1). The distribution pattern of toxic metals in the lake sediments is presented in Fig. 3 indicates the presence of very high concentrations of all metals at the sampling points in the
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Pollution levels of the toxic metals of the sediments

The toxic metal contamination of bottom surface sediments in Lake Gopło is assessed as low according to the Igeo index, except at three SPs in the north of the lake (Table 2). Of these three, the most highly contaminated sediments are found in SP5, where the concentration of Cu, Zn and Pb corresponds to purity class 3 (moderately to heavily contaminated), and the Hg contamination is extremely high (class 6). There is also a moderate degree of contamination in the sediments at the second point (SP1), where Ni and Hg concentrations are purity class 3, and Cu, Zn and Pb are class 2. There were also moderate Cu contamination of sediments at the third point (SP2) (Table 2). The summative assessment of sediment contamination with all analysed metals according to the PLI index confirms the results of the geoaccumulation index. The PLI values are above 1 at SP1–3 and SP5, which indicates metal contamination of the sediments. Also noteworthy are the elevated PLI values in the south of the lake (Table 2).

Geochemical indicators that assess the potential ecological and toxicological impact of the total presence of toxic metals in bottom surface sediments have been proposed.

Table 1 Summary statistics of toxic metal contents in bottom surface sediments from Gopło Lake compared against regional and local geochemical background (RGB, GL, KL, ML) values, sediment quality guidelines for freshwater ecosystems (TEL, PEL) and average metal concentrations in selected lakes of western and northern Poland [mg·kg⁻¹; n = 80], matrix of Pearson correlation coefficients between toxic metal contents in sediments and sediment features influencing their sorption properties (n = 20; *correlation significant at the 0.05 level) and results of the PCA for data of sediments of Lake Gopło

| Summary statistics of toxic metals | Cu     | Pb     | Cd     | Zn     | Ni     | Cr     | Hg     | As     |
|-----------------------------------|--------|--------|--------|--------|--------|--------|--------|--------|
| Minimum                           | 0.25   | 0.92   | 0.03   | 9.5    | 0.25   | 0.06   | 0.01   | 0.69   |
| Maximum                           | 83.0   | 130.0  | 1.3    | 605.0  | 80.0   | 19.0   | 2.7    | 5.2    |
| Average                           | 14.84  | 19.4   | 0.23   | 87.26  | 6.9    | 2.28   | 0.21   | 2.01   |
| Coefficient of variation [%]      | 121.81 | 134.98 | 104.7  | 150.8  | 200.22 | 133.12 | 238.67 | 46.56  |
| RGB¹                              | 6.0    | 10.0   | <0.5   | 48.0   | 5.0    | 5.0    | <0.05  | <5.0   |
| TEL²                              | 35.7   | 35.0   | 0.596  | 123.0  | 18.0   | 37.3   | 0.174  | 5.9    |
| PEL²                              | 197.0  | 91.3   | 3.53   | 315.0  | 36.0   | 90.0   | 0.486  | 17.0   |
| GL³                               | 11.0–7.5 | 33.8–26.0 | 0.6–0.4 | 80.9–56.4 | 7.6–7.0 | 9.7–6.5 | –       | –      |
| KL⁴                               | 11.0   | 36.0   | 0.7    | 126.0  | 7.0    | 18.0   | 0.06   | 7.3    |
| ML⁵                               | 10.0   | 34.0   | 0.7    | 83.0   | 6.0    | 10.0   | <0.05  | <5.0   |
| Pearson correlation               |        |        |        |        |        |        |        |        |
| Sand                              | 0.65*  | 0.55*  | 0.41   | 0.59*  | 0.34   | 0.46*  | 0.52*  | 0.40   |
| Silt                              | −0.51* | −0.48* | −0.27  | −0.46* | −0.17  | −0.34  | −0.47* | −0.03  |
| Clay                              | −0.36  | −0.27  | −0.12  | −0.32  | −0.16  | 0.01   | −0.26  | −0.38  |
| Average Diameter                  | 0.63*  | 0.53*  | 0.35   | 0.58*  | 0.29   | 0.41   | 0.50*  | 0.63*  |
| Organic Matter                    | 0.42   | 0.44   | 0.52*  | 0.46*  | 0.49*  | 0.61*  | 0.39   | 0.48*  |
| Calcium Carbonate                 | −0.77* | −0.78* | −0.69* | −0.78* | −0.46* | −0.75* | −0.75* | −0.48* |        |
| Total Phosphorus                  | 0.35   | 0.27   | 0.31   | 0.35   | 0.25   | 0.43   | 0.22   | 0.69*  |

Rotated component matrix

| PC1 factor loadings | 0.98  | 0.96  | 0.88  | 0.97  | 0.64  | 0.83  | 0.89  | 0.77  |
|--------------------|------|------|------|------|------|------|------|------|
| Eigenvalue         | 6.07 |      |      |      |      |      |      |      |
| % of variance      | 75.92|      |      |      |      |      |      |      |
| % of cumulative    | 75.92|      |      |      |      |      |      |      |
| PC2 factor loadings| −0.05| −0.21| 0.44 | −0.20| 0.75 | 0.09 | −0.39| −0.21|
| Eigenvalue         | 1.04 |      |      |      |      |      |      |      |
| % of variance      | 13.03|      |      |      |      |      |      |      |
| % of cumulative    | 88.96|      |      |      |      |      |      |      |

1—RGB (Regional Geochemical Background) Bojakowska, Sokołowska 1998; 2—TEL (Threshold Effect Level) and PEL (Probable Effect Level) Smith et al. 1996; 3—GL (local geochemical background—Gniezno Lakeland) Sojka et al. 2019; 4—KL (local geochemical background—Kashubian Lakeland) Bojakowska, Sokołowska, 1996; 5—ML (local geochemical background—Mazovian Lakeland) Bojakowska, Sokołowska 1997.
by Häkanson (1980). The potential ecological risk index (RI) values confirm the poor condition of the bottom surface sediments in the north of Lake Gopło (Table 2). Specifically, at SP5 and SP1, the RI indicator reaches values corresponding to class 4, which means that the excessive concentration of metals is a very high ecological risk. In turn, at SP2 and SP3 the index is high (class 3), and at SP6, SP16 and SP20, it is moderate. However, it should be clearly indicated that, at all the aforementioned SPs, the poor ecological state of bottom surface sediments was due in each case to high mercury contents. At most other SPs, mercury contamination corresponds to a moderate threat, but considerable at SP6 (Table 2). The ER values calculated for this metal at SP1 and SP5 correspond to class 5 (classification of ecological risk indicators, Li et al. 2012), which represents a very high ecological threat, and in the case of SP2 and SP3 a high threat.

Mercury contamination aside, the high RI index values at SP1 and SP5 are also influenced by the sediments’ average level of contamination with copper and cadmium at both locations, plus with lead at SP5 and with nickel at SP1.

Results of chemometric analysis

The Pearson correlation analysis results show a strong cross-correlation between most of the analysed metals (Fig. 3). The six pairings Cu–Pb, Cu–Zn, Cu–Hg, Pb–Zn, Pb–Hg and Zn–Hg are very strongly positively correlated ($r > 0.9$) at $p < 0.05$. Also strongly correlated ($r = 0.7–0.9$) are: Cu–Cd, Cu–Cr, Pb–Cd, Pb–Cr, Cd–Zn, Cd–Ni, Cd–Cr and Cr–Hg. Moderate correlations ($r = 0.7–0.4$) were found for the pairings Cu–Ni, Cu–As, Pb–As, Pb–Ni, Cd–Hg, Cd–As, Zn–Ni, Zn–As, Ni–Cr and As–Cr. Correlations were weak or absent for the relationships Ni–Hg, As and Hg–As. The principal component analysis identified two significant PCs for sediments. The distinguished components meet the Kaiser criterion and that explain 89.96% of the total variance in the variables (Table 1). The first component (PC1) accounts for 75.92% of the variance and is strongly positively correlated with all metals except nickel (which correlates only moderately with the component values).

The second component explains 13% of the geochemical variability of the sediments and correlates moderately with nickel concentrations, weakly positively with cadmium, and weakly negatively with mercury. The principal component analysis results agree closely with the Pearson correlation analysis results.

The results of cluster analysis confirmed the earlier described picture of the spatial differentiation of toxic metal concentrations in the bottom surface sediments of Lake Gopło. However, this analysis also distinguished an additional group consisting of four points: two in the north of the lake (SP4 and SP6) and points SP13 and SP18 (characterised by deep water conditions in the central and southern part of the lake) (Fig. 3). In these places, concentrations of Zn and Pb were higher than at other points in the central and southern parts of the lake.

Discussion

The analysis of the concentration of toxic metals in the bottom sediments of Lake Gopło showed that most metals except Cu, Pb and Hg correlate positively (not very strongly, but statistically significantly) with the organic matter content in the sediments (Table 1). Such relationships have also been described in other water bodies (Bartoli et al. 2012; Gierszewski 2018; Saleem et al. 2018; Wakida et al. 2008). Many study results have indicated that the fine-grained fraction in the sediments, especially clay, contributes greatly to an increased accumulation of metals (Rubio et al. 2000; Fukue et al. 2006; Dung et al. 2013). This is associated with,
The unusual nature of the relationship between metal concentrations and grain size of the sediments results from the sediments' low lithological diversity and, at the same time, their toxic contamination with metals of anthropogenic origin. This blurs the relationship between grain size and metal concentration in the sediment (Abracham 1998; Gierszewski 2018). This may explain, too, why the textural composition does not correlate with the spatial variability of metal concentrations in the bottom surface sediments (Lin et al. 2016). Such a situation occurs in the northern part of Lake Gopło, where the bottom sediments are more mineral in nature. These sediment properties were influenced by the discharges of wastewaters from the Kruszwicka sugar refinery, which until 1993 were discharged into the lake. Wastewater from sugar refineries usually contains large amounts of total suspended matter (Kocaturk and Erguder 2015). Although the sorption properties of sediments in this part of the lake are slightly worse, it is here that the toxic metal concentrations were highest. Their source, until the municipal wastewater treatment plant in Kruszwicka was established in 1993, was point discharges of industrial and municipal wastewater that flowed into the lake directly or through the hydrographic network. After these sources were eliminated, after 1993, pollutants were supplied only from non-point sources. One factor contributing to the accumulation of pollutants in this part of the lake is its impeded water exchange with the main lake basin.

By contrast, the metal concentration levels were not affected by other substances included in the analysis that participate in toxic metal adsorption, i.e. phosphorus and calcium carbonate compounds (Sigg et al. 1997; Kabata-Pendas and Pendias 1999; Thakur et al. 2006; Reddy et al. 2014). The negative correlation between the content of metals and the share of calcium carbonate in the sediments is primarily the result of there being a large supply of metals to the north of the lake, where carbonate sediments happen to occur least.

Toxic metals that accumulate in bottom surface sediments are variously interrelated. The nature and strength of these relationships can indirectly inform on their origins and migration routes (Håkanson and Jansson 1983; Sutherland 2000; Yang et al. 2009). High values of positively correlated metals generally indicate a common source of origin and similar behaviour during transport (Lu et al. 2010; Chen et al. 2012; Wang et al. 2016). The nature of the relationships between pairs of metals in the bottom sediments of Lake Gopło, considering the low toxic metal contamination of the sediments at most sampling points, indicates their geogenic origin and possible delivery from non-point sources (Wang et al. 2015; Guan et al. 2016). In the case of the lake under study, these are mainly inter alia, the high sorption capacity of clay minerals (Foster and Charlesworth 1996; Kabata-Pendas and Pendias 1999; Canavan et al. 2007). However, no such relationship was found in the bottom surface sediments of Lake Gopło. Indeed, the opposite was observed: the metal concentrations were higher in samples containing a greater sandy fraction or with a dominant coarse-silt fraction (Table 1). The unusual nature of the relationship between metal concentrations and grain size of the sediments results from the sediments' low lithological diversity and, at the same time, their toxic contamination with metals of anthropogenic origin. This blurs the relationship between grain size and metal concentration in the sediment (Abracham 1998; Gierszewski 2018). This may explain, too, why the textural composition does not correlate with the spatial variability of metal concentrations in the bottom surface sediments (Lin et al. 2016). Such a situation occurs in the northern part of Lake Gopło, where the bottom sediments are more mineral in nature. These sediment properties were influenced by the discharges of wastewaters from the Kruszwicka sugar refinery, which until 1993 were discharged into the lake. Wastewater from sugar refineries usually contains large amounts of total suspended matter (Kocaturk and Erguder 2015). Although the sorption properties of sediments in this part of the lake are slightly worse, it is here that the toxic metal concentrations were highest. Their source, until the municipal wastewater treatment plant in Kruszwicka was established in 1993, was point discharges of industrial and municipal wastewater that flowed into the lake directly or through the hydrographic network. After these sources were eliminated, after 1993, pollutants were supplied only from non-point sources. One factor contributing to the accumulation of pollutants in this part of the lake is its impeded water exchange with the main lake basin.

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Toxic metals that accumulate in bottom surface sediments are variously interrelated. The nature and strength of these relationships can indirectly inform on their origins and migration routes (Håkanson and Jansson 1983; Sutherland 2000; Yang et al. 2009). High values of positively correlated metals generally indicate a common source of origin and similar behaviour during transport (Lu et al. 2010; Chen et al. 2012; Wang et al. 2016). The nature of the relationships between pairs of metals in the bottom sediments of Lake Gopło, considering the low toxic metal contamination of the sediments at most sampling points, indicates their geogenic origin and possible delivery from non-point sources (Wang et al. 2015; Guan et al. 2016). In the case of the lake under study, these are mainly

| Table 2 | Pollution of bottom sediments of Lake Gopło according to geochemical and ecotoxicological indices |
|---|---|
| Indicator | Cu | Pb | Cd | Zn | Ni | Cr | Hg | As | Igeo | PLI | ER | RI |
| Average | 1.66 | 1.08 | 0.42 | 1.13 | 0.26 | 0.20 | 0.11 | 0.39 | 41.5 | 26.9 | 63.5 | 5.6 | 61.3 | 2.6 | 438.0 | 5.5 | 224.7 |
| Max | 2.05 | 0.72 | 0.14 | 0.73 | 0.65 | 0.25 | 0.09 | 0.92 | 17.5 | 17.0 | 12.6 | 3.6 | 1.2 | 1.1 | 100.0 | 4.4 | 272.4 |
| Min | 1.50 | 0.28 | 0.03 | 0.26 | 0.18 | 0.04 | 0.03 | 0.77 | 8.5 | 6.9 | 5.0 | 1.3 | 4.5 | 0.4 | 60.2 | 3.6 | 90.3 |
| Median | 1.50 | 0.28 | 0.03 | 0.26 | 0.18 | 0.04 | 0.03 | 0.77 | 8.5 | 6.9 | 5.0 | 1.3 | 4.5 | 0.4 | 60.2 | 3.6 | 90.3 |
| Upper 95th | 1.50 | 0.28 | 0.03 | 0.26 | 0.18 | 0.04 | 0.03 | 0.77 | 8.5 | 6.9 | 5.0 | 1.3 | 4.5 | 0.4 | 60.2 | 3.6 | 90.3 |
| Lower 5th | 1.50 | 0.28 | 0.03 | 0.26 | 0.18 | 0.04 | 0.03 | 0.77 | 8.5 | 6.9 | 5.0 | 1.3 | 4.5 | 0.4 | 60.2 | 3.6 | 90.3 |
| Standard deviation | 0.55 | 0.11 | 0.02 | 0.11 | 0.02 | 0.01 | 0.01 | 0.39 | 3.9 | 3.5 | 2.2 | 0.8 | 0.5 | 0.2 | 23.8 | 0.9 | 23.8 |

**Notes:**
- **Igeo:** Pollution index, modified after Jacka (1982) and based on Igeo (Yao 1989).
- **PLI:** Pollution level index, according to Brown et al. (1990).
- **ER:** Environmental risk index, according to Parent et al. (1999).
non-point pollutants related to more than a century of intensive agriculture in the catchment. The very strong correlations between Pb, Zn, Cu, and Hg indicate that their concentrations in the sediments were also influenced by supply from a specific anthropogenic source.

Conclusions drawn from the analysis of dependencies between the analysed metals confirm and complement the PCA analysis results. This shows that all elements, especially Cu, Zn, Pb, Hg and Cd, achieved high loads in the first component (PC1). In the second principle component (PC2), Ni had a higher content than in the first principle component (Table S1). This means that the nickel in certain parts of the lake was also supplied from point sources. The distribution of sample points on a coordinate system defined by the two principal components clearly distinguishes SP1–SP3 and SP5 from the others (Fig. 3). These samples are located in the north of the lake, which is surrounded by municipal and industrial buildings of Kruszewica. This part of the lake consists of two pools separated by narrow straits and a shallow bay of approx. 2 m deep, which impedes water exchange with the rest of the lake. Bottom surface sediments from SP1 and SP2 contain significantly more nickel, cadmium and chromium than the other points. The nickel is being supplied to the very north of the lake by Kujawskie Zakłady Tłuszczowe (Kuyavian manufacture of oils and fats). The concentration of this metal increased significantly in the 1960s (Juśkiewicz et al. 2015), when a margarine factory was established in a company expansion (Komosiński 2007). The production of margarine from liquid vegetable fats uses nickel as a catalyst in the hydrogenation reaction (Tarrago-Trani et al. 2006). In addition to the nickel levels, the mineral–organic sediments here were found to have much higher concentrations of Cu, Pb, Zn, Hg, at SP3 and SP5 (and additionally of Cr and As at SP5) than in the central and southern parts of the lake. The remaining SPs form one cluster of points with a very similar geochemistry of toxic metals (Fig. 3). It can be identified with the supply of metals from non-point agricultural sources, but also with the deposition of atmospheric pollutants (combustion products, traffic pollution) and above all with a geogenic source. Many agricultural chemicals contain toxic metals. For example, Cu, Zn and As are present in fungicides, pesticides and herbicides (He et al. 2005). Meanwhile, mineral fertilisers may contain contaminants in the form of Cd and Pb or additions of Cu and Zn. Furthermore, many toxic metals (Cu, Zn, Pb, Cd, Ni, Cr) also derive from organic fertilisers (farm manures, biosolids, composts). They feature much more richly in these products than in most agricultural soils (He et al. 2005). Long-range atmospheric transport followed by wet and dry deposition is responsible for the accumulation of many metals (As, Cd, Cu, Zn and Pb) in soil and subaqueous sediments (Sarkar et al. 2015).

The ecological effects of the toxic metal contamination of the bottom surface sediments are varied. Some metals (e.g. Zn, Cu, Fe, Mn, Mg) are essential to biological systems. However, they can also be toxic when critical concentrations are exceeded (Magnitsky 2011; Chen et al. 2018). Cadmium, lead, arsenic, chromium and mercury have no practical biological significance when contained in sediments at natural levels, but when present in high concentrations they are toxic to organisms (Alloway 2013; Zheng et al. 2013). For all the sediments, the elevated (and in some parts of the lake, high) concentrations of mercury have the greatest potential impact on the functioning of Lake Gopło’s ecosystem.

Besides its supply in the municipal and industrial wastewater that affects the north of the lake, this element also probably derives from atmospheric supply as airborne ash that is a by-product of lignite combustion (Lorenz and Grudziński 2007). Research has shown that the lignite extracted from the mines to the south of the lake has the highest mercury content in Poland. Its concentration in the fuel supplied to the Adamów power plant was 442 ppb (parts per billion) (Bojakowska and Sokolowska 2001). Another source of mercury is agricultural pesticides (Sojka et al. 2019).

The results showed that more than a century of intensive agricultural activity in the catchment area of Lake Gopło has not significantly contaminated the bottom surface sediments with toxic metals. The way the soil has been fertilised has had some part to play in this. In Poland, including in the Kuyavia region, artificial fertilisers have been used (Jankowiak et al. 2003; Dach and Starmans 2005). Such fertilisers contain significantly lower levels of toxic metals than do organic fertilisers (especially liquid manure) (Kabata-Pendias and Pendias 1999). However, it cannot be ruled out that the use of crop protection products, especially herbicides (Piwowar 2021), combined with the deposition of pollutants from fossil fuel combustion processes, has contributed to the increased accumulation of mercury in the bottom surface sediments.

**Conclusion**

Based on the analysis of the differentiation of toxic metal concentrations in the surface layer of bottom sediments of Lake Gopło and chemical analyses, the factors determining the levels, origins and probable sources of supply of metals to the lake were determined. It was shown that the average concentrations of the analysed metals (except Cd, Cr and As) exceeded regional geochemical background levels. The content of toxic metals in the sediments of Lake Gopło was similar to or even below that of many other lakes in central and northern Poland (except for Cu,
Zn and Hg). The low variation in the lithological features of the bottom surface sediments means that the size of the clay fraction and the levels of carbonates and organic matter content do not affect the metal content in the sediments in Lake Gopło, nor, consequently, their spatial diversity. The significantly greater concentration of toxic metals in the north of the lake is due to their supply in municipal and industrial pollution from Kruszwica, and to the fact that the restricted water exchange between the north of the lake and the rest of the lake limits the transfer of pollutants to other parts of the lake. As shown by the PCA analysis, the bottom surface sediments in the north of the lake have significantly higher contents of Ni, Cd, and Cr. The strong correlation between most of the analysed metals and the results of the factor analysis indicate a similarity of source and method of supply to the lake. Except in the north of the lake, the metals are from agricultural area sources, atmospheric pollution (mainly fossil fuel combustion products) and natural sources. The weaker correlation of Ni with other metals indicates that this metal has a different source. The PCA analysis results indicate that the source is in the northern part of the lake. There, the sources of Ni, but also of Cd, are industrial pollutants from food industry plants (fat plants, sugar plants).

Compared to the rest of the lake, the sediments in the northern part are heavily polluted according to Igeo and PLI values. These values indicate moderate and moderate-to-toxic contamination of sediments with Cu, Pb and Zn, Ni and Hg. The most polluted sediments were those in the lake bay that protrudes into the town area. The values of contamination indices were highest there for most of the analysed metals, and the contamination of the sediments with mercury, which is ecologically dangerous, was extremely high. Compared to mercury, the copper, cadmium, lead and nickel contamination of the sediments in the north of the lake has a lesser average impact on the index of potential ecological threat.

The relatively low toxic metal contamination of the bottom surface sediments in the southern and central parts of the lake contrasts with the contaminated sediments in the north of the lake, which receives industrial and municipal pollution from the town of Kruszwica. However, the morphology of the lake basin and the restricted water exchange between the north of the lake and the rest of the lake prevent these pollutants from being transmitted southwards. Despite the previous intensive use of the lake and adjacent areas, the condition of the bottom surface sediments of Lake Gopło is good. Now that the site is managed in an ecologically sustainable manner, it has a full chance of ensuring the long-term survival of some of Europe’s most valuable and endangered species and habitats listed in both the Birds and Habitats Directives.

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**Availability of data and materials**  The datasets supporting the conclusions of this article are included within the article and its additional files.

**Declarations**

**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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