Journal of Elementology ISSN 1644-2296

Sojka M., Siepak M., Pietrewicz K. 2019.
Concentration of Rare Earth Elements in surface water and bottom sediments in Lake Wadąg, Poland.
J. Elem., 24(1): 125-140. DOI: 10.5601/jelem.2018.23.2.1648

RECEIVED: 20 March 2018
ACCEPTED: 1 September 2018

ORIGINAL PAPER

CONCENTRATION OF RARE EARTH ELEMENTS IN SURFACE WATER AND BOTTOM SEDIMENTS IN LAKE WADĄG, POLAND*

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Abstract

The paper presents the results of analyses of the content of rare earth elements (REEs) in surface water and bottom sediment in the river-lake system of Lake Wadąg located in the Masuria Lakeland (Poland). The samples were collected in August 2015. The aim of the study was to describe the spatial variation of REEs concentration in the river-lake system, and to identify the hydro-geochemical factors that affect their distribution. Multivariate statistical methods of data analysis, i.e. cluster analysis (CA) and principal component analysis (PCA), were used to analyze similarities and differences in REEs content in water and bottom sediments of the lake-river system. In order to determine the enrichment of the river and lake water and bottom sediments with REEs, their concentrations were standardized in relation to the average concentrations in chondrite. Low concentrations of REEs in water and bottom sediments of the Wadąg river-lake system indicate their geogenical origin. The REE concentrations in the inflows to the lake were higher and more variable than those found in the lake and its outflow. The similarity between the REE content in the water of the Wadąg River and Lake Wadąg results from the long exchange time of water in the lake. Eu anomalies in the river and lake water and Ce anomalies in the lake water were observed. Higher REE concentrations were detected in the bottom sediments of Lake Wadąg and at its outflow. The bottom sediments of the Wadąg river-lake system are characterized by higher enrichment with LREE in relation to HREE.

Keywords: LREE, HREE, river-lake system, aqua regia, ICP-QQQ.

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* This research was supported by financial means granted by the Ministry of Science and Higher Education; Research project No. 215862/E-336/SPUB/2017/1.

INTRODUCTION

Rare Earth Elements include a group of fifteen elements from lanthanum (La) to lutecium (Lu) and yttrium (Y). All REEs have similar physical and chemical properties and for that reason they are usually interpreted together (Zhu et al. 2012). In the geochemical research, owing to their similar behaviour REEs are widely used as a marker of geochemical processes. Characterization of the REE content, its variability in the environment and identification of REEs potential sources typically include three factors: total content, the ratio of normalized content $[La/Tb]_N$ or $[La/Yb]_N$ and the occurrence of anomalies in the content of particular elements. The REE content analysis is often performed on two groups: LREE – light rare earth elements, which include more easily soluble and more alkaline elements, and HREE – heavy rare earth elements, which include less easily soluble and less alkaline elements.

The REE concentration in river waters depends on several factors, such as the watershed's topography, geology, climate and vegetation (Armand et al. 2015, Ilina et al. 2016). The weathering process leads to extensive fractionation between the dissolved REE composition of river water and that of river-suspended particles (Hannigan, Sholkovitz 2001). Generally, the dissolved REE concentrations increase systematically in surface waters as the distance from the upstream to the downstream grows (Sultan, Shazili 2009). The concentration of REEs in stream water varies with respect to physicochemical properties (Eh, pH, total organic carbon, carbonates, Fe, Mn and Al). Armand et al. (2015) showed that Eu, La and Lu are positively correlated with Fe and Mn and negatively to carbonate alkalinity and pH. The pH has a great impact on the speciation and thus the behaviour of REEs (Pourret et al. 2007). Lower pH values contribute to a raised REE concentration through desorption from mineral surfaces (García et al. 2007). The REE pattern in natural water and bottom sediments is modified by the natural and anthropogenic processes. The presence of REEs can be used individually or collectively to identify potential sources of contaminants (Antweiler et al. 2012). Detection of natural processes and assessment of the impact of anthropogenic factors on changes in REE distribution in the environment is mainly performed on the basis of the analysis of anomalies in particular REEs. In natural waters the anomalous behavior of redox-sensitive Ce (de Baar et al. 1988) and Eu (Bau 1991) has been detected. Chen et al. (2017) suggest that Eu-anomalies in water inherit the characteristic of the host rock and indicate that the dissolution of host rock is the main material source for the basin while Ce anomalies reflect the source difference and processes that occurred during the transport of water. Sklyarova et al. (2017) indicate Ce depletion in small stream-water, and suggest that in a large river the water composition is more uniform and the REE patterns more similar to one another and less dependent on local variations in watershed lithology.

Increasing anthropogenic inputs of REEs to natural systems may alter the natural signatures (Noack et al. 2014). The strong increase in the consumption of REEs in high-tech processes and products leads to increased release of REEs into the environment (Kulaksiz, Bau 2013). Rivers draining densely populated and industrialized areas show positive Gd anomalies (Bau, Dulski 1996, Bau et al. 2006). In addition, in recent years, La and Sm anomalies related to anthropogenic sources have been observed in river water (Kulaksiz, Bau 2013) and bottom sediments (Kulaks, Bau 2007, Klaver et al. 2014, Song et al. 2017). The anthropogenic lanthanum is mostly transported adsorbed onto the particulate matter and gadolinium is transported in the dissolved phase (Klaver et al. 2014).

Apart from determining the REE content in the environment, it is also very important, from the scientific point of view, to describe the process of circulation of these elements in the water-bottom sediments system. REEs carried by rivers are deposited in bottom sediments of lakes as a result of sedimentation of debris transported from the catchment area.

Małecka (2012) suggests that REEs are preferentially accumulated in the littoral zone. The sediments from the lakes located on low-permeable glacial sediments are more abundant in REEs in comparison with the sediments from the lakes located on highly permeable glacial sediments. Research shows that river waters registered higher average REE concentrations than lake waters (Sultan, Shazili 2009). In aquatic systems, REE concentrations are low compared to their concentrations in rocks with regards to their slight solubility (Noack et al. 2014).

The aim of the study was: (1) to determine REE content in the water and bottom sediments of the Lake Wadąg river-lake system; (2) to determine REE spatial distribution in water and bottom sediments; (3) to assess REE distribution in the river-lake and water-suspension systems.

MATERIALS AND METHODS

Study area

Lake Wadąg is located in the western part of the Masurian Lake District (Niewolak et al. 2003). The lake is situated in the catchment area of the Wadąg River, which flows into the Łyna River at the 232nd km from the debauchment of the Łyna to the Pregoła. The area of Lake Wadąg is 495 ha, and its average depth is 12.7 m (Niewolak et al. 2003). The maximum depth of the lake is almost 3 times larger and amounts to 35.5 m. The lake basin is of glacial origin – it represents the ribbon and dead-ice type of a lake and is embedded in glacial and fluvial Pleistocene deposits. Lake Wadąg is supplied by five watercourses: the Wadąg (Pisa Warmińska), the Orzechówka, Kanał Elżbiety, an inflow from Tuławka settlement and an inflow from Trackie

Lake. The only watercourse flowing out of Lake Wadąg is the Wadąg River. The water exchange time in Wadąg Lake, calculated as the ratio of lake volume to the yearly average inflow to the lake, is over 100 days. The land use structure in the direct catchment of Lake Wadąg is dominated by forests and meadows that cover 67.4% and arable land and orchards 29.7%. A small part of the catchment is covered by built-up areas of about 2.9%. The anthropogenic impact is predominantly related to agriculture, i.e. farmland and poultry farms situated in the northern and western part of the study area. Another important factor is the influence of industry – mainly its food processing branch, which is located in the area of the southern creek from Lake Trackie. The municipal landfill site, located in Łęgajny (about 4 km from the "Wadąg" groundwater intake) and closed in 2007, also has a significant impact on the natural environment, and primarily the water environment.

Sample collection and preparation

Samples of water and bottom sediments were collected for chemical analysis in August 2015 from Lake Wadąg and its three tributaries: the Wadąg (Pisa), the Orzechówka, an inflow from Trackie Lake and from the Wadąg River flowing out from the lake (Figure 1).

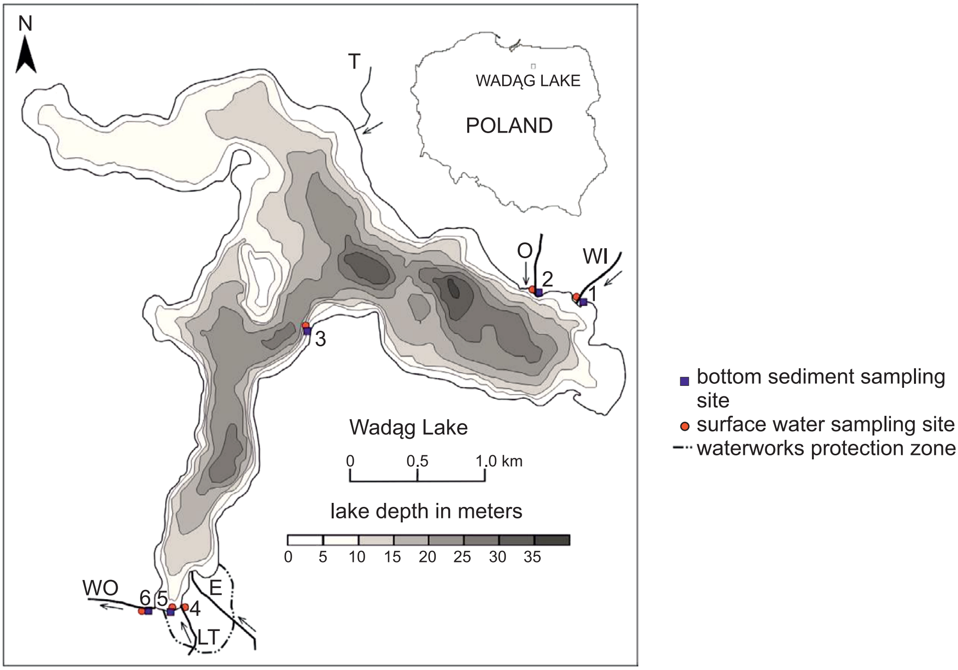

Fig. 1. Study area, on map: WI – Wadąg River – inflow, O – Orzechówka River, T – inflow from Tuławki village, E – Kanał Elżbiety, LT – inflow from Lake Trackie, WO – Wadąg River – outflow

Measurements, taken directly in the field using a multifunctional measuring device, Multi 350i, made by the firm WTW (Weilheim, Germany), included the temperature, pH reaction and electrolytic conductivity of the water. The water samples of the volume of 500 mL were collected in polyethylene bottles (HDPE) produced by Nalgene® using a Toń 2 sampler (Mera Błonie, Gdańsk, Poland). The portions of the samples used for chemical analyses were acidified *in situ*. High-purity 65% HNO_3 (Merck, Darmstadt, Germany) was used for trace element subsamples in an amount needed to obtain a $pH < 2$. After sampling, the samples were taken to the chemical laboratory in a mobile refrigerator at a temp. of 4 ± 2.5°C.

Bottom sediment samples of 10 cm in depth were collected in triplicates at each location by a Czapla-1 core sampler (Mera-Błonie, Gdańsk, Poland) into polyethylene (PE) containers. The sediment samples were dried at the temp. of 105°C in Binder FD 53 (Binder GmbH, Germany). Dry samples were mineralized with aqua regia prepared from HNO_3:HCl (1:3 v/v) by Merck (Merck, Darmstadt, Germany). The samples were extracted using a MARS 5 Xpress (CEM) microwave digester.

Chemical analysis

Concentrations of REEs (La, Pr, Nd, Eu, Gd, Tb, Dy, Ho, Er, Tm, Lu) and additionally Sc, Mo, Rb, Tl, Th and U were determined by inductively coupled plasma mass spectrometry (ICP-QQQ 8800 Triple Quad, Agilent Technologies, Japan). All parameters were manually optimized to achieve the best signal intensity and stability. MassHunter software for ICP-QQQ (Agilent Technologies, Japan) was used to control the instrument and to process the data (Siepak, Sojka 2017). The instrumental operating parameters are given in Table 1.

Table 1

ICP-QQQ operating conditions

Spectrometer	Agilent 8800 Triple Quad
Nebulizer	MicroMist
Interface	Sampler and skimmer cones in Ni
RF power	1550 W
RF matching	1.80 V
Plasma flow rate (L min^{-1})	15
Carrier gas flow (L min^{-1})	1.08
Nebulizer pump (rps)	0.3
S/C temp (°C)	2
Sample depth (mm)	8.0
Gas flow rate He (mL min^{-1})	5.0

Reagents

The determinations by ICP-QQQ were done using calibration curves obtained from diluted stock multi-element standard 100 μg mL^{-1} (VHG Labs, Manchester, USA). The reagents used were ultrapure, and the water was de-ionized to a resistivity of 18.2 MΩ cm in a Direct-Q® 3 Ultrapure Water System apparatus (Millipore, France). Analytical quality control was verified by the analysis of certified reference materials, viz. SPS-SW2 (Spectrapure Standards As, Oslo, Norway).

Statistical analysis

The analysis of the REE content was conducted in the water-bottom sediments and river-lake system. In order to determine the enrichment of river water, lake water and bottom sediments with rare earth elements, their concentrations were standardized in relation to the average concentrations in chondrite (Nakamura 1974).

The REE concentration in water and bottom sediment samples before the statistical analysis using multivariate statistical techniques was log-transformed to obtain a normal distribution. In order to avoid misclassification due to differences in data dimensionality, the CA and PCA were applied on standardized data through z-scale transformation (Sojka et al. 2008, Varol, Şen 2009, Varol et al. 2012, Siepak, Sojka 2017). Cluster analysis (CA) was applied to group samples into categories or clusters on the basis of similarities and dissimilarities between REE concentrations. CA was performed using squared Euclidean distances as a measure of similarity and the Ward's method was used to obtain dendrograms (Li, Zhang 2010). The next stage of statistical analysis involved detrended component analysis (DCA). The obtained gradients of the first axis of DCA were shorter than 3.0 SD, which indicates that the REEs were in linear distribution. Glińska-Lewczuk et al. (2016) suggest that in such cases the principal component analysis (PCA) is recommended for further data analysis. PCA is an ordination method which allows for the interpretation of complex correlations between the analyzed REEs and environmental factors and presentation of the results obtained against the environmental factors. The following environmental factors were considered in two groups: type of water (river-lake) and role in river-lake system (inflow, lake, outflow). Principle component analysis (PCA) was employed to identify a potential source of REEs. The number of significant principal components was selected on the basis of a Kaiser criterion of eigenvalues higher than 1. Apart from this, it was assumed that when factor loadings between the concentrations of selected REEs and principal components are 0.75-1.00, 0.50-0.75, and 0.30-0.50, they are adequately strongly, moderately, and weakly correlated. The CA and PCA were conducted using Statistica 13.1 and Canoco 5.0 respectively.

RESULTS AND DISCUSSION

In the water of the river-lake system of Lake Wadąg, the concentrations of Sc and U were the highest, while those of Tm reached the lowest values. REE concentrations in water were from 0.0006 to 0.0967 μg L^{-1} and can be presented in the following descending order: Ce>Nd>La>Pr>Gd>>Sm>Dy>Eu>Er>Ho>Tb>Lu>Tm. The highest REE concentrations were found in the water of Lake Wadąg inflows (points 1, 2 and 4), and the lowest – in the lake water (points 3 and 5). On the other hand, almost all REE concentrations in the Wadąg River water (point 6) were on the intermediate level between those observed in the inflows and Lake Wadąg (Table 2).

Maximum concentrations were found in point 1 (82%) and in point 2 (12%) – Table 2. Minimum concentrations occurred mainly in the water samples from Lake Wadąg. Almost 67% of these occurred in point 5, while 27% – in point 3 (Table 2). The total content of REEs in the water of inflows ranged from 0.3270 to 0.4780 μg L^{-1}, with the average value of 0.3846 μg L^{-1}, while at the outflow from the lake (in point 6) it was 0.1286 μg L^{-1}. The lowest total REEs content was found in the lake water and amounted to the average value of 0.0823 μg L^{-1}.

Table 2

REE concentration in surface water

Elements	Unit	Sampling site					
		1	2	3	4	5	6
Sc	(μg L^{-1})	1.02	1.90	0.31	0.33	0.31	0.31
La		0.089	0.010	0.072	0.058	0.006	0.021
Ce		0.199	0.159	0.017	0.146	0.011	0.048
Pr		0.023	0.019	0.003	0.016	0.002	0.007
Nd		0.090	0.075	0.011	0.067	0.010	0.027
Sm		0.019	0.014	0.003	0.014	0.002	0.005
Eu		0.008	0.012	0.004	0.008	0.005	0.005
Gd		0.019	0.014	0.004	0.016	0.003	0.006
Tb		0.0028	0.0021	0.0004	0.0021	0.0004	0.0008
Dy		0.0134	0.0111	0.0023	0.0108	0.0024	0.0041
Ho		0.0028	0.0023	0.0006	0.0019	0.0005	0.0008
Er		0.0078	0.0059	0.0014	0.0059	0.0015	0.0024
Tm		0.0013	0.0008	0.0002	0.0009	0.0002	0.0004
Lu		0.0015	0.0009	0.0006	0.0011	0.0004	0.0006
Tl		0.0062	0.0029	0.0021	0.0030	0.0015	0.0012
Th		0.0835	0.0226	0.0194	0.0757	0.0529	0.0186
U		0.5283	0.2726	0.6988	0.5913	0.6234	0.6191

Table 3

REE concentration in bottom sediments

Elements	Unit	Sampling site				
		1	2	3	5	6
Sc	(mg kg^{-1})	0.38	0.21	0.26	0.60	0.52
La		7.40	5.60	9.23	6.42	9.33
Ce		16.1	11.3	19.0	14.3	19.9
Pr		1.95	1.34	2.35	1.70	2.51
Nd		7.19	5.29	8.65	6.69	9.45
Sm		1.39	1.01	1.67	1.36	1.86
Eu		0.22	0.16	0.24	0.28	0.31
Gd		1.32	0.96	1.61	1.37	1.79
Tb		0.17	0.12	0.20	0.19	0.23
Dy		0.86	0.62	1.01	1.09	1.19
Ho		0.15	0.11	0.18	0.20	0.17
Er		0.41	0.30	0.47	0.54	0.38
Tm		0.052	0.037	0.059	0.072	0.074
Lu		0.044	0.031	0.049	0.066	0.064
Tl		0.036	0.015	0.030	0.147	0.035
Th		1.34	0.88	1.71	0.90	1.38
U		0.40	0.25	0.73	1.18	0.39

The REE content in the bottom sediments samples were diversified (Table 3). In the bottom sediments of the Lake Wadąg river-lake system, concentrations of Ce were the highest, and Lu concentrations reached the lowest values. The REE concentrations in water ranged from 0.051 to 16.1 mg·kg^{-1} and they can be presented in the following descending order: Ce>La>Nd>Pr>Sm>>Gd>Tm>Dy>Er>Eu>Tb>Ho>Tm>Lu. The highest REE concentrations occurred in the bottom sediments at the outflow of the lake in the Wadąg River, and the lowest concentrations were found in the bottom sediments of watercourses flowing into the lake (points 1 and 2). The REE concentrations in Lake Wadąg bottom sediments were at the intermediate level.

Maximum concentrations of particular elements occurred 10 times in point 6, located in the Wadąg River (flowing out of the lake). Maximum values occurred eight times in point 5, located in the southern part of the reservoir. The southern part of the study area is characterized by higher REE concentrations in comparison with its northern part. In point 3 one maximum value – of Th – was recorded, while in points 1 and 2 no maximum values were found. Almost all minimum REE concentrations occurred in point 2, in the zone of supplying Lake Wadąg with groundwater. Higher REE concentrations within Lake Wadąg were recorded in point 3, located in the littoral zone, than in point 5, located in the profundal zone. The above results comply with the results obtained by Małecka (2012), who showed that REEs are preferentially accumulated in the littoral zone. The total REE content in the bottom sediments of the Wadąg River at the outflow from the lake was 47.3 mg kg^{-1}, and the content recorded in the inflows amounted to 32.1 mg kg^{-1}. The sum of the REE content in the lake bottom sediments was at the intermediate level and amounted to 39.6 mg kg^{-1}.

The analysis of the content of particular REEs in bottom sediments showed their small variability in particular sampling sites. Variability coefficients for particular REEs ranged from 21 to 29%, with the average value of 23%. Higher REE variability between particular sampling points was observed in water. Variability coefficients for particular REEs ranged from 42 to 84%, with the average value of 68%.

In order to analyze the REE contents jointly in water and bottom sediments, their concentrations were standardized in relation to chondrite. Standardized REE contents in bottom sediments in relation to chondrite indicate their moderate enrichment with the element (Figure 2*a*). In the bottom sediments, a negative anomaly of Eu is clearly visible. Both in the bottom sediments of the lake and its inflows, the enrichment with LREE is visible clearly in comparison with HREE.

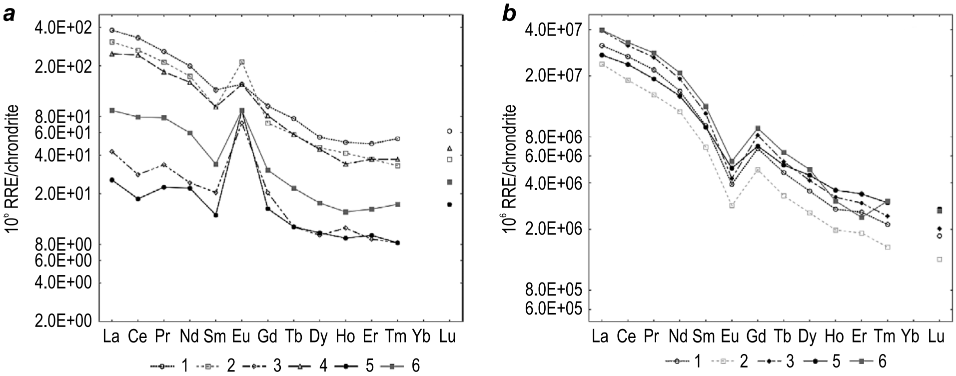

Fig. 2. Chondrite-normalized REE patterns of the river and lake surface waters (*a*) and sediments (*b*)

The lines showing standardized REE contents in bottom sediments in points 1, 2 and 3 are basically distributed collaterally. This is not the case for point 5, in which the size of Eu anomaly is the smallest and concentrations of La, Cr, Pr, Nd, Sm, Eu, Gd, Tb, Dy and Tm in bottom sediments in sampling point 6 were the highest. Additionally, a negative Ho and Er anomaly can be observed. The values of the $(La/Yb)_N$ ratio (Yb values were calculated as an arithmetic mean based on Tm and Lu concentrations) in bottom sediments in points 1, 2, 3 and 6 ranged between 13.3 and 14.6. The lowest $(La/Yb)_N$ ratio of 8.6 was recorded in point 5. The values obtained in this study were lower than those recorded by Sultan, Shazili (2009), who showed that the chondrite normalized high $(La/Yb)_N$ ratios in both river sediments (~18.8) and lake sediments (~20.6) reflected highly fractionated REE compositions.

The chondrite normalized patterns for the lake and river water samples are plotted in Figure 2*b*. The normalized patterns of the REE content in the lake water (points 3 and 5) are different from the ones in the river water. In the pattern of normalized REE concentrations in lake water a positive Eu anomaly is clearly visible as well as a negative Ce anomaly, albeit less distinctly seen. The pattern of curves is also characterized by a smaller gradient. In the case of river water supplying Lake Wadąg, a definitely larger gradient of graphs occurs in group LREE (La, Ce, Pr and Nd). The Eu anomalies in river water are slightly smaller in relation to lake water and there are no Ce anomalies. Normalized REE values for point 6, located at the outflow from the lake were at an intermediate level between those recorded at the inflows to the lake and in the lake.

In the pattern of standardized REE values for rivers, a small increase of values from Er to Lu can be noticed. The Eu anomaly in river waters is likely due to the variation in pH and redox conditions between the river and lake's hydro-chemical compartments (SULTAN, SHAZILI 2009). The chondrite normalized $(La/Yb)_N$ ratio varied between 2.9 to 8.7 with a higher value for river water (average 7.1) than for lake water (average 3.9).

The results show that bottom sediments of the Wadąg river-lake system are characterized by higher enrichment with LREE in relation to HREE. MAŁECKA (2012) showed that the REE contents in lake sediments are diversified similarly to the other environments – lake sediments are richer in LREE than in HREE (excluding Eu) – and that the concentrations of REEs in bottom sediments in Lake Wadąg were lower compared to bottom sediments of 30 other Polish lakes. The patterns of normalized REE concentrations in Lake Wadąg water were at a similar level and differed from the ones in the river water supplying this lake. The REE concentrations in the Wadąg River were slightly higher than those recorded in the reservoir. The greater similarity between the REE content in the water of the Wadąg River and the water in Lake Wadąg results from the exchange time of water in the lake, which is about 100 days. Eu anomalies in the river and lake water and Ce anomalies in the lake water were observed. KULAKS, BAU (2007) showed that large anomalies for cerium (Ce) and europium (Eu) are related to the redox potential. The analysis of the REE content did not show Gd anomalies, which indicates that their nature is mainly linked to the geological structure of the catchment. BAU, DULSKI (1996), BAU et al. (2006), KULAKS, BAU (2007) found that rivers draining densely populated and industrialized areas with advanced medical and healthcare systems show pronounced positive Gd anomalies.

Based on the CA analysis, two groups of sampling points can be distinguished: those with lower REE concentrations – points 3, 5 and 6 – and those with higher concentrations and variability – points 1, 2 and 4. It is clearly visible that REE contents in the lake water and in the Wadąg River

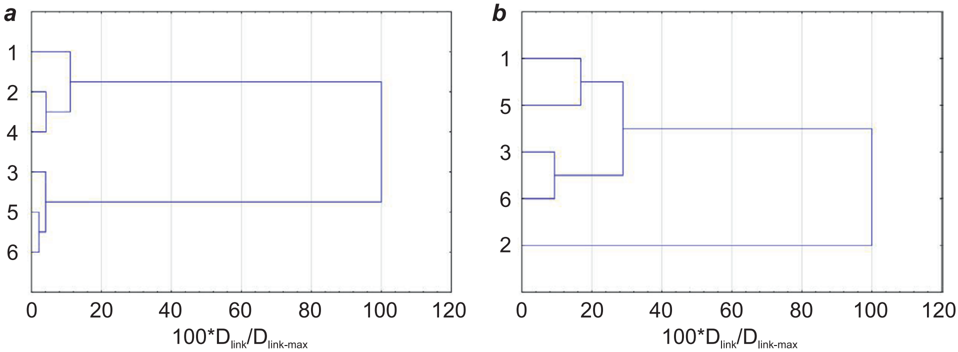

Fig. 3. Division of water and sediment sampling sites into groups based on rare earth elements (REEs) concentration

at the outflow from the lake were more similar (Figure 3*a*). The higher variability of the REE content at the inflows to the lake probably results from the nature of their catchment, i.e. geological structure, topography of the area and the use structure.

The cluster analysis based on the REE content in bottom sediments justified the division of sampling points into three groups. The first group included points 1, 5, the second one – points 3 and 6, and the third one – point 2 (Figure 3*b*). The REE concentrations in point 2 were much lower than in the other sampling points, while in points 1 and 5 the concentrations were on the average level. The most similar, both in terms of REE concentrations and their variability, were the points located in Lake Wadąg (point 3) and in the Wadąg River at the outflow from the lake (point 6). These points were characterized by the highest aggregate REE content, which was 46.1 mg kg^{-1} on average.

The relationship between environmental factors and the REE concentration in water and bottom sediments was determined by principal component analysis (PCA) with multiple scaling. During the analysis, two environmental variables were considered. The first variable is the type of water, in which rivers and lakes were distinguished, while the other one is the influence – in the river-lake system – of hydrological characteristics on the inflows, the outflow and the lake. The results showed that in the case of water, particular REEs were strongly positively correlated with the first component (PC1). The first axis (PC1) explained almost 88.5% of the variance of the original data set. PC2 with 10.1% of the variance explained was moderately positively correlated with Eu. The strong correlation of all REEs with the first component indicates their geochemical origin, while the Eu correlation with the other component is the result of the positive anomaly of this element. The Eu anomalies in water inherit the characteristic of the host rock and indicate that the dissolution of host rock is the main material source for the basin (CHEN et al. 2017). The anomalous behavior of Eu results from the redox conditions (BAU 1991). PCA analysis confirmed higher REE concentrations in water of the inflows and high probability of concentrations at the outflow and in the lake. Generally, the concentrations in rivers are higher than in the lake.

In the case of bottom sediments, PCA showed that the first component (PC1) correlated strongly and negatively with almost all REEs with the exception of Er, which was moderately correlated. The first axis (PC1) explained almost 74.1% of the variance of the original data set. Similarly as in the case of water, all the analysed REEs have the same geogenical origin. The presence of REEs in lake sediments in the area of northern and central Poland is predominantly related to the geological structure, while the anthropogenic impact is of less importance (De Vos, Tarvainen 2006, Małecka 2012). Due to the above, REEs can be used as indicators in assessment of natural concentrations of elements in the studied sediments (Małecka 2012).

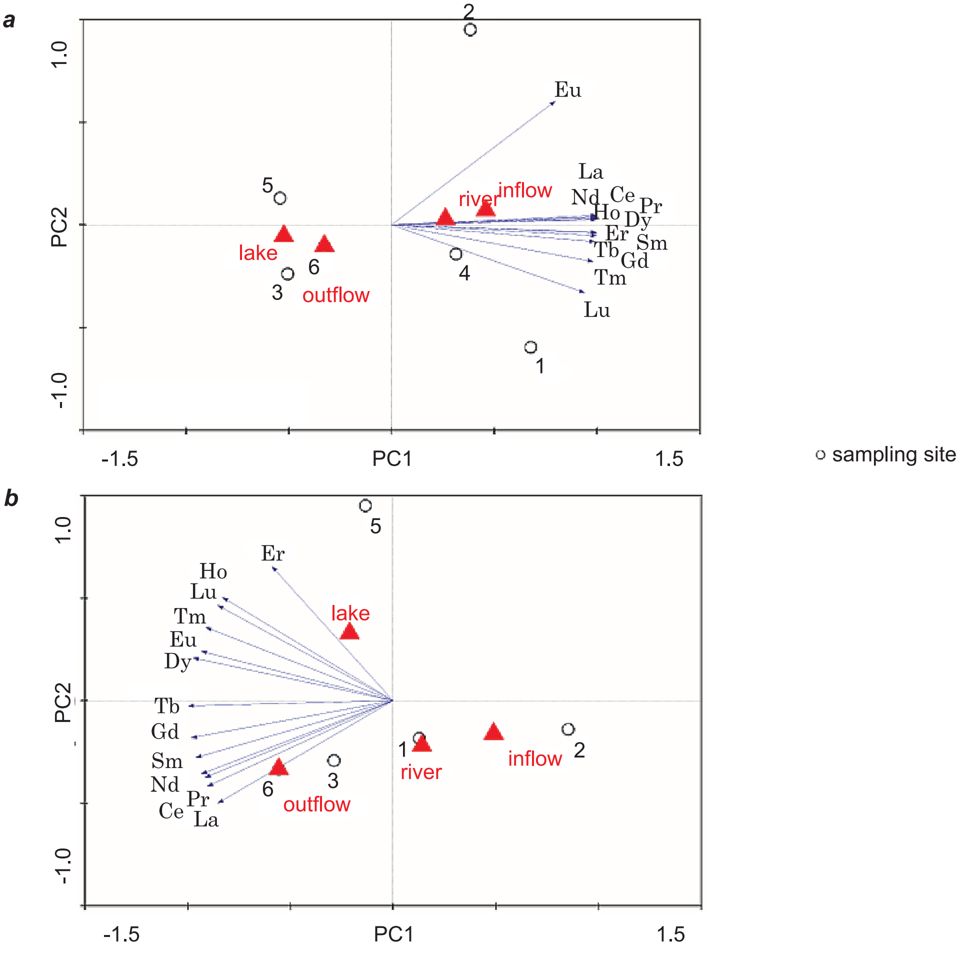

Fig. 4. Ordination diagram of PCA to identify an impact of environmental factors on the REE content in water (*a*) and bottom sediments (*b*)

The other principal component, PC2 with 18.8% of the variance explained, was moderately positively correlated with Er, Ho and Lu, and negatively with La. La, and the neighboring (Figure 4) Ce, Pr, Nd and Sm, belong to the LREE group – light rare earth elements, which includes more easily soluble elements, while Er, Ho and Lu belong to the HREE sub-group – heavy rare earth elements, which includes less easily soluble elements. Due to their limited permeability to water solutions, REEs are subject to very limited migration (Chudaev et al. 2015).

The PCA analysis confirmed higher REE concentrations in lake sediments and in the sediments of the Wadąg River at the outflow from the lake. The relatively highly dispersed distribution of points representing environmental variables (red triangles) (Fig. 4b) indicates higher spatial REE variability in sediments. To sum up, it should be observed that higher REE concentrations in water probably result from the fact that REEs are adsorbed on the debris carried by the flowing water. The debris transported by the inflows is deposited in the lake. This fact confirms the results obtained by Frankowski et al. (2009) that suspension was found to play an important role in the accumulation and transport of pollutants.

CONCLUSIONS

1. The results of the RREs content in waters and bottom sediments presented in the paper were obtained from a single measurement campaign and should be treated as preliminary results. The results could contribute to the future evaluation of the geochemical background.

2. REE concentrations in water and bottom sediments of the Wadąg river-lake system were low, which indicates their geogenical origin. The lowest REE concentrations were found in sampling point 2, where Lake Wadąg is supplied by groundwater.

3. REE concentrations in the water of the inflows of Lake Wadąg were higher and were characterized by higher variability than those found in the lake and its outflow.

4. Higher REE concentrations in the bottom sediments of Lake Wadąg and at its outflow probably result from their accumulation in the debris.

5. The analysis of REE contents in the Lake Wadąg river-lake system, in relation to their content in chondrite, showed the occurrence of a small Ce anomaly in the lake water.

6. The analysis showed higher enrichment with LREE in comparison with HREE in bottom sediments than in water.

7. The PCA analysis showed the same source of REE origin in water and bottom sediments, as well as a similar behaviour of elements from both groups, LREE and HREE.

8. The CA analysis confirmed the higher probability of REE presence in lake water and at the outflow, which is related to the time of water retention in the water body, which is about 100 days.

9. The analysis showed lower variability of particular REEs in bottom sediments than in water.

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