

Article

Water Quality Assessment of a Meromictic Lake Based on Physicochemical Parameters and Strontium Isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$) Analysis: A Case Study of Lubińskie Lake (Western Poland)

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Abstract: In 2017, hydrochemical surveys of meromictic Lubińskie Lake (W Poland) and its water inflows were carried out. The lake experienced complete mixing in 2008 due to a series of orkan winds, and since 2015, intensifying worsening of water quality in the lake has been observed. Our aim was to determine the degree of transformation of Lubińskie Lake based on water chemistry and to identify the source of pollution of the lake using strontium isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$) as a new chemical tracking tool. The physicochemical analysis confirmed the meromictic character of the lake. The comparison with previous studies (2003 and 2008) showed significant year-to-year differentiation, indicating intensifying eutrophication of the lake's water, both in the epilimnion and the hypolimnion. Nine spring niches, directly supplying the lake, provide water with very high phosphorus and nitrogen concentrations (up to 10 kg of nitrogen and 0.9 kg of phosphorus daily). The strontium isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$) analysis indicated that the lake's water was supplied mostly by the springs, and recharge from deep aquifers is of secondary importance. Moreover, strontium isotope data and the relationship between Sr and Cl content support the finding that the high load of nutrients is of anthropogenic origin and reaches the lake through springs.

Keywords: water quality; strontium isotopes; springs; meromictic lake; eutrophication

1. Introduction

Climate changes triggered by human activity have caused profound alterations in lake ecosystems, including imbalances in the water budget, eutrophication, and increased sediment resuspension, which lead to the worsening of water quality and the loss of habitats [1–3]. These negative changes have affected both large water bodies, such as the Great Lakes or Lake Chad [4,5], and small lakes in remote areas [6,7]. Anthropogenically driven eutrophication is considered as one of the most critical threats for water quality in lakes, resulting in plankton blooms, decreased water clarity, oxygen deficiencies, and finally, loss of habitats [8]. It is mostly induced by an increased supply of nutrients coming from manure and mineral fertilizers applied on crop fields. Nutrients reach the lake through ground water

recharge and surface runoff [9]. They can also be delivered to the lake by sublacustrine springs supplying some lakes of early post-glacial areas [10,11]. This applies in particular to the springs whose alimentation area is located within the zone of strong anthropogenic influence [12].

In addition to external supply, an important source of nutrients is also internal loading from sediments [13]. This is particularly important in deep, stratified lakes, in which the decomposition of organic matter under anaerobic conditions causes the release of various substances, such as ammonia, sulfur, or heavy metals, which endanger the quality of water [14]. Thus, stratification and the associated cyclic mixing regime are important for the functioning of lake ecosystem and water quality as well.

The meromictic type is very special and rare with regards to natural lakes. Unlike dimictic lakes (a type of holomixis), in these lakes the deepest stratum of water (monimolimnion) remains isolated from the upper mixing stratum (mixolimnion) by a stratum called chemocline [15]. Hutchinson [16] distinguished three types of meromictic lakes: (i) Ectogenic meromictic lakes with meromixis caused by external events (e.g., the inflow of saline water), (ii) crenogenic meromictic lakes (inflow of saline spring water at a constant, low temperature), and (iii) biogenic meromixis, where differences in water density leading to limited mixing result from the decomposition of organic matter at the bottom. In all these types, stratification may be aided by the morphometric characteristics of the lake as well as shelter from the prevailing wind by surrounding hills or tall vegetation at the shore [9].

Due to permanent density stratification within the monimolimnion, there is no direct supply of oxygen from the atmosphere and the vertical transport of solutes is limited. As a result, sedimentary substances are trapped and accumulated for a long time in anoxic conditions. In holomictic lakes there is a systematic exchange between surface and bottom waters. In meromictic lakes hypolimnion water accumulates huge amounts of ammonia, carbon dioxide, and hydrogen sulfide, which may pose an internal threat to the stability of the ecosystem [17]. Consequently, if the meromixis is disturbed, substances accumulated in the monimolimnion for a long time, including substantial amounts of nutrients, can be rapidly released and cause negative changes within the whole ecosystem. This negative process may be accelerated by external supply from the catchment, e.g., via springs or surface runoffs [13].

Nowadays, water quality assessment of the lakes, mostly based on trophy-related parameters, has been replaced by ecological status assessment, whose main tools are bioindicators [18]. However, the parameters that directly determine water quality (i.e., visibility, nutrient concentration, and chlorine concentration) are still widely used and largely reflect the quality and functioning of the ecosystem as a whole. This is particularly important for assessing the degree and sources of pollution, given the simple and relatively quick analytical methods [19].

Numerous studies show that radiogenic strontium isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$) have the potential to fingerprint anthropogenic additives (typically, mineral fertilizers, municipal sewage, and industrial emissions) in aquatic systems [20–26]. Moreover, strontium isotopes proved to be a reliable tool for the identification of water reservoirs and interactions between water bodies in various aquatic systems [27–31]. They are also a valuable tracer of water-rock interactions and are widely applied in weathering studies [32–37].

The strontium isotope method utilizes differences in relative concentration of two strontium isotopes, ^{87}Sr , and ^{86}Sr . As the amount of ^{87}Sr increases with time due to the decay of rubidium isotope ^{87}Rb , rocks of different age develop different $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. Strontium is released from rocks by weathering into water and soil and becomes available for further uptake by plants and animals [38]. Since the strontium isotope composition of surface water results from the mixing of strontium derived from various natural (bedrock, soil, precipitation, sea spray) and anthropogenic (industrial emissions, sewage, mineral fertilizers) sources with different isotopic ratios, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio might be applied to trace strontium sources [39–41]. Although strontium isotopes are commonly applied in studies of lakes, works investigating meromictic lakes are scarce [42].

In 2004, Pełechaty et al. [43] described a new meromictic lake in mid-Western Poland: Lubińskie Lake. According to Pełechata et al. [44], this lake experienced complete mixing in 2008 due to a series of storm winds. Since then, intensifying worsening of water quality (i.e., increase in nutrient

concentration, phytoplankton blooms, decrease of water visibility) in the lake has been observed. Additionally, in 2015, increased fertilization of fields, mainly with liquid manure, occurred within the catchment area.

Our aim was to determine the degree of transformation of Lubińskie Lake based on water chemistry and to identify the source of pollution of the lake using strontium isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$) as a new chemical tracking tool. We hypothesized that complete mixing of the water column after storm winds triggered the eutrophication process, which was then reinforced by the inflow of nutrients from the catchment.

2. Study Object

Lubińskie Lake is a small lake with the surface area of 22.7 ha located in western Poland ($52^{\circ}18'32''$ N, $14^{\circ}54'25''$ E), in Lubuskie Lakeland (Figure 1). Its catchment area only covers 5.5 km². It is one of 21 lakes located in the post-glacial tunnel valley running by Gronów, Rzepin, and Torzym towns. The valley spreads NW-SE but in the southern part, its direction changes to W-E, so the basin of the water body has an arched shape. In the southern part of the lake, a bay has formed, separated from the main pool with a 60 m wide isthmus [45]. The maximum depth of the lake is 21.6 m [46,47], whereas the mean depth is 8.8 m [47]. This results in steep slopes of the lake bottom. Detailed parameters and morphometric indices of the lake are presented in Table 1. The west and north-east slopes are particularly steep. The slopes of the bay, however, are gentle, and its depth does not exceed 5 m. The north and west shores of the lake are directly adjacent to the edge of the valley and have the form of steep scarps, over a dozen meters high. The south and north sides are milder.

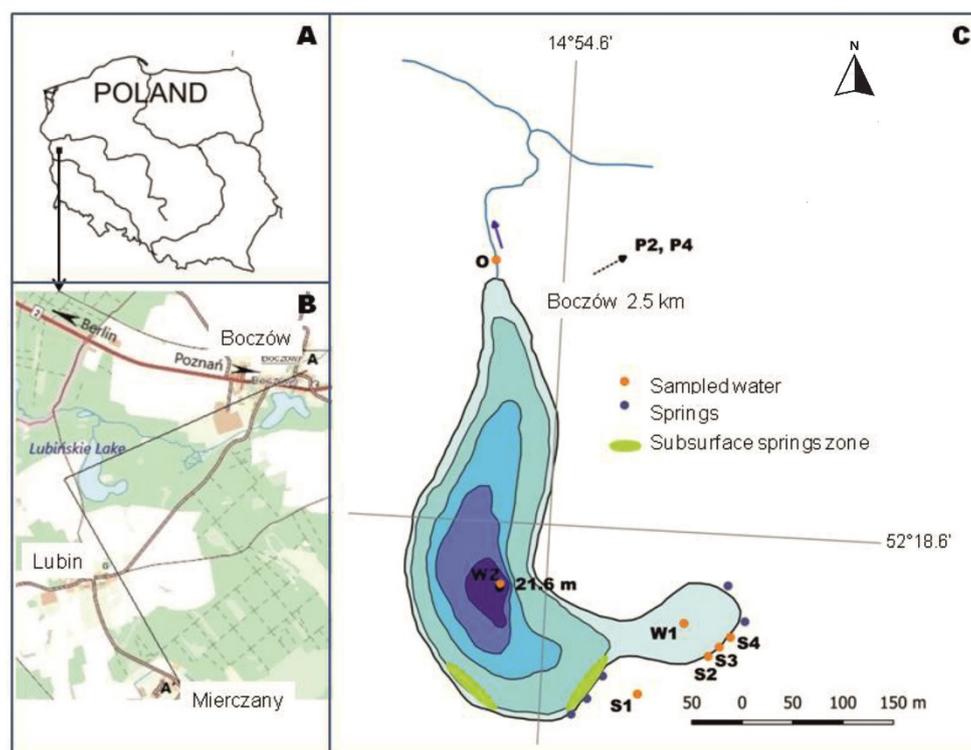


Figure 1. Location of Lubińskie Lake and the points of water samples intake from: The lake (W1 and W2), outflow (O), springs (S1–S4), and wells P2 and P4 (A,C). The line A–A' shows the line of hydrogeological cross-section (B).

Table 1. Parameters and morphometric indices of Lubińskie Lake (according to Jańczak [47]).

Parameters and Indices	Unit	Value
Surface area	ha	22.7
Maximum length	m	1130
Maximum width	m	270
Mean width	m	200
Length ratio	-	4.2
Shoreline length	m	2950
Shoreline development	-	1.75
Volume	10 ³ m ³	1997.6
Maximum depth	m	21.6
Mean depth	m	8.8
Relative depth *	-	0.0453
Depth ratio	-	0.41
Exposure ratio	-	2.6

* Maximum depth (m)/surface area (km²).

The bottom of the lake is mostly made of fine- or medium-grained sands, and at some points also of gravels. In the bay and in the north part of the lake, the bottom is mostly covered with gyttjas [45]. The lake basin cuts through alternating deposits of fluvial sands and gravels [48] whose thickness fluctuates between several and over a dozen meters, which facilitate the infiltration of water from the catchment. In the lower part, the basin probably also cuts through the deposits of post-glacial clay (Figure 2), whose thickness in the open pit located approximately 1 km north of the lake is up to 35 m. Above and below the layer of clay there are approximately 10 m thick deposits of fine- and medium-grained sands, whose waters directly feed the lake in the form of groundwater upwellings [48].

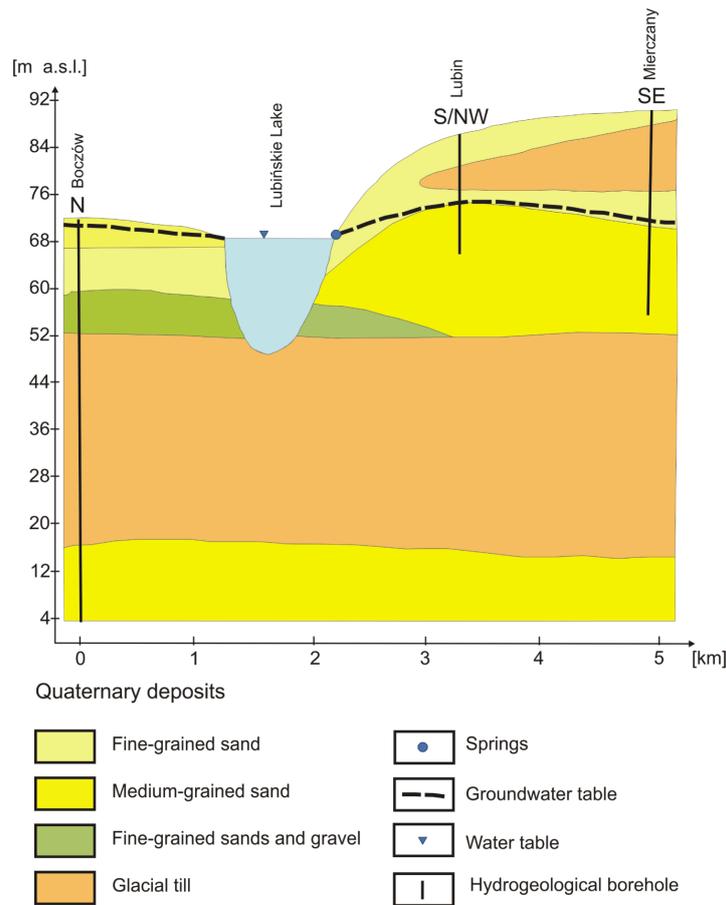


Figure 2. Hydrogeological cross-section of Lake Lubińskie drainage basin along the line Boczów—Lubińskie Lake—Mierczany.

As evidenced on an orthophotomap made in 2010 [49], woodlands and farmlands prevail in the catchment, covering the area of 2.7 and 2.6 km², respectively (Figure 3). The remaining area is covered by waters and the urban territory of Lubin town. The lake is surrounded by forests from all sides, but on the west and south side the forest buffer is very narrow, only between about a dozen and several dozens of meters from the lake shore. Woodlands predominantly occur in the eastern part of the catchment, while arable lands are located in the western part.

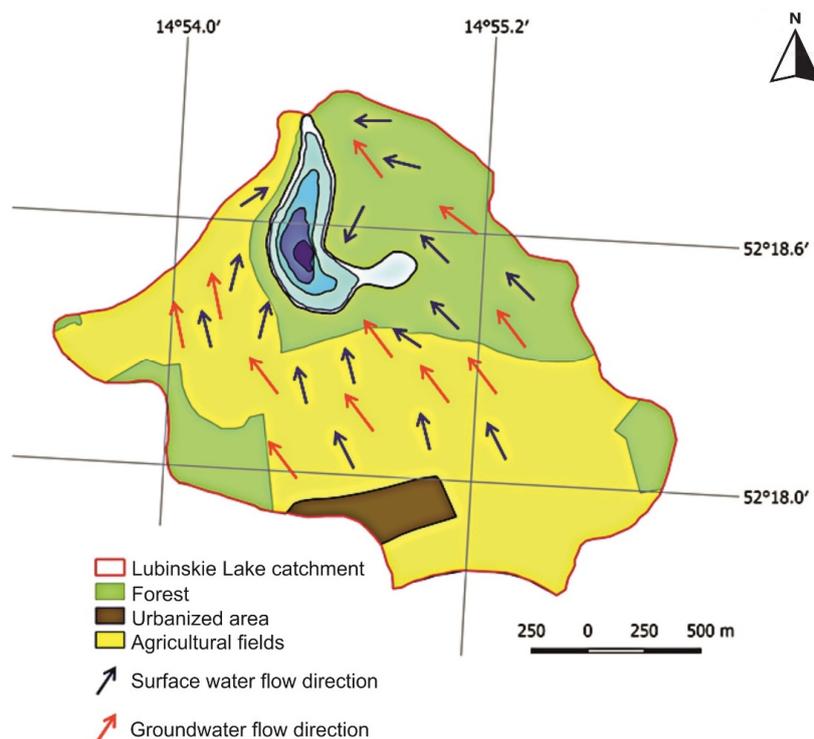


Figure 3. Structure of land use in the catchment of Lubińskie Lake based on the orthophotomap.

3. Materials and Methods

The lake was investigated in April and August 2017, both for comparison with the previous results in 2003 [43] and 2008 (unpublished data) and with regard to the potential meromictic nature of the lake. In both months, the electrolytic conductivity (EC) and pH were measured in the deepest part of the lake, using an Elmetron CX-701 meter (Elmetron Sp.j.). The Secchi disk was used for visibility. Oxygen concentration and temperature were measured in the vertical profile using an Elmetron CX-401 meter. In order to confirm the mixing type, additional measurements for oxygen and temperature were taken at the end of November 2017.

For further chemical analysis, the samples were collected in 1-l plastic bottles (one from the surface and one from the above-bottom layer—using an electric pump) and kept in a portable refrigerator. Then, the samples were kept in a refrigerator (at 4 °C) until the remaining chemical analyses were performed at the Department of Water and Soil Analysis, Faculty of Chemistry, Adam Mickiewicz University in Poznań.

Concentrations of total nitrogen (TN) were determined in the filtered samples by high-temperature combustion (HTC) using a Shimadzu TOC-L Total Organic Carbon analyzer (Shimadzu, Japan). For TN determination, the analyzer was equipped with a TNM-L TN unit (Shimadzu, Japan). The concentrations of NO_2^- , NO_3^- , and NH_4^+ ions were determined by the ion chromatography method with a conductivity detector (Shimadzu, Japan), using Dionex AS22 with AG22 columns. Total water hardness was determined by the versenate method. In order to determine Ca^{2+} and Mg^{2+} ion concentrations, a Shimadzu ion chromatograph with conductivity detection was applied, using Dionex IonPac SCS 1 Silica Cation Separator Column.

The inductively coupled plasma optical emission spectrometer (ICP-OES) ICPE-9820 (Shimadzu, Japan) was used for the qualitative and quantitative detection of total phosphorus (TP). Prior to the analysis, the Sigma-Aldrich (USA) containing 1000 mg L^{-1} P in 10% nitric acid (comprising hydrofluoric acid traces) was used for the calibration of ICP-OES. In order to preserve the standard/sample conditions, the matrix match method was used.

Soluble reactive phosphorus (SRP) in the water was determined by the molybdate method with ascorbic acid as a reducer. Prior to the analyses, the water samples were filtered through a rinsed 0.45 µm pore size filter (Macherey-Nagel, Germany).

Based on Secchi disc visibility and the concentration of TP in water, Carlson's trophic state index (TSI) was calculated [50]. The TN and TP concentrations were used for the N:P ratio.

The same methodology as above was applied in the case of the analysis of physicochemical parameters of water in springs feeding the lake, also carried out in April and August 2017. Methods described by Pełchaty et al. [43] were applied with regard to the compared years 2003 and 2008.

The flow and discharge of springs flowing out of the lake were measured three times: On 15 March, 15 April, and 15 August, using an electromagnetic flow meter Valeport model 801 with measurement accuracy of ± 0.5% of reading plus zero stability < 0.005 m s⁻¹.

Separate samples were taken for ⁸⁷Sr/⁸⁶Sr analysis of the dissolved strontium load. Additionally, rain water was collected at Słubice, about 30 km to the west, and groundwater was collected at Boczów (about 2.5 km to the north-east) in order to evaluate its contribution to the Sr budget of the lake. A total of 16 samples were taken. Grab samples were taken from the springs. Lake water was sampled with an electric pump from the deepest part of the lake and from the south-eastern bay (Figure 1). In the former, it was gathered at points from the surface up to the depth of 20 m in 4 m intervals, whereas in the latter, samples were collected from the surface and the depth of 4 m. The rain was caught on the roof of Collegium Polonicum of Adam Mickiewicz University to a precleaned rain collector. The obtained sample encompass rainwater from several rain events during two weeks. The groundwater was collected from water intakes. All the samples were taken unfiltered to precleaned polyethylene bottles (250 mL) after flushing the bottles with the sampled water. The samples were filtered through Rotilabo cellulose syringe filters (0.45 µm), acidified with Merck sub-boiled ultrapure HNO₃ (1 mL of acid per 100 mL of water), and stored at 4 °C immediately after returning to the laboratory.

The analytical part of this work, including chemical separation of Sr and the measurements of Sr isotope ratios, were carried out in the Isotope Laboratory of the Adam Mickiewicz University in Poznań. About 15 mL of water was evaporated on a hot plate in PFA vials. Subsequently, a 340 µL portion of 2N HNO₃ was added to the sample and left overnight to equilibrate. The Sr was separated from matrix elements on PFA columns filled with Sr.Spec resin using the miniaturized chromatographic technique described by Pin et al. [51]. Some modifications in the column size and concentration of reagents were introduced by Dopieralska [52]. Strontium was loaded with a TaCl₅ activator on a single W filament and analysed in the dynamic collection mode on a Finnigan MAT 261 mass spectrometer. During the course of this study, the NBS 987 Sr standard yielded ⁸⁷Sr/⁸⁶Sr = 0.710210 ± 10 (2σ mean on thirteen analyses). The measured ratios were normalized to the nominal value of 0.710240 for the standard NBS 987. Total procedure blanks were below 83 pg.

Statistical analyses were performed using STATISTICA 12 (StatSoft, Kraków, Poland) software. The normality of distributions of the analyzed variables and the homoscedasticity of the samples were tested with the Shapiro-Wilk and Levene tests, respectively. The significance of differences was tested by ANOVA with the Kruskal-Wallis test. *p* < 0.05 was accepted as being statistically sound. The principal components analysis (PCA) was performed for the statistical analysis of the physicochemical parameters data set. Prior to this analysis, the data (except pH values) was subject to logarithmic transformation (log (1 + x)) to minimize the discrepancies between the empirical distribution of the variables and their theoretical normal variation. Out of the studied environmental variables, speciation forms of nutrients that were highly interrelated were reduced to TP and TN and included in the PCA. Additionally, to reduce the number of variables, a simple factor analysis was applied. Covariation was tested using non-parametric Spearman rank correlation. The significant levels were set to α = 0.05.

4. Results

4.1. Lake Physio-Chemical Characteristics

The thermal and oxygen profiles (Figure 4) performed during the spring overturn and summer stagnation and repeated during the autumnal overturn indicate the meromictic character of Lubińskie Lake. In all seasons, the monimolimnion zone began at 13 m, which was indicated both by a constant temperature (approx. 4.5 °C) and by anoxia.

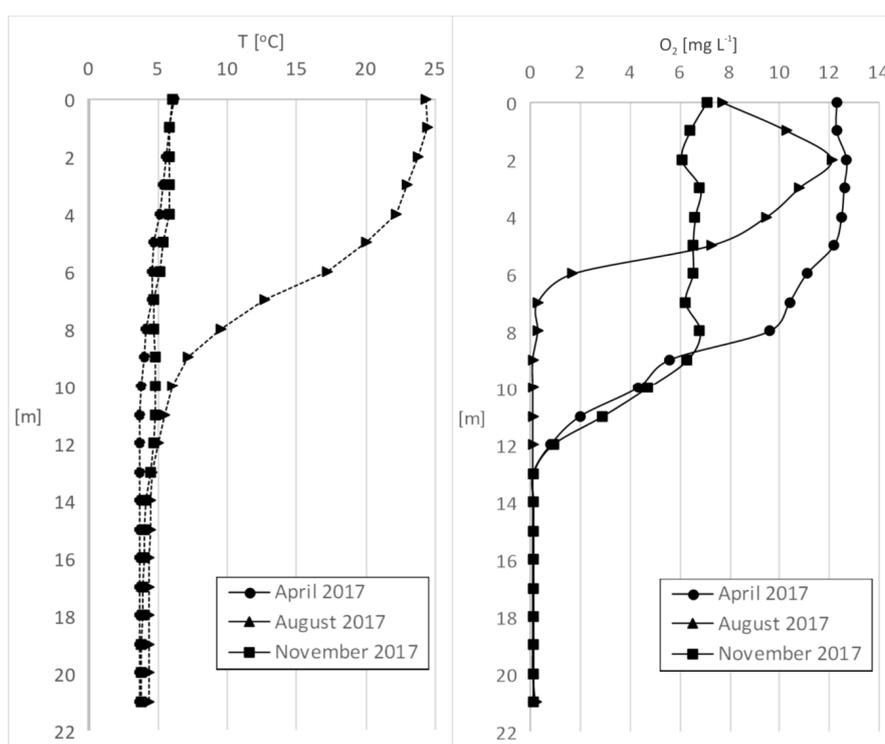


Figure 4. Vertical variability of temperature and oxygen concentration in Lubińskie Lake studied in 2017.

The analyzed water properties were typical for eutrophy (TSI = 61), with high nutrients concentration (TN = 3.81 mg N L⁻¹ and TP = 0.13 mg P L⁻¹, on average), high water mineralization (mean EC = 380 μS cm⁻¹), and poor light conditions (mean SD visibility = 2 m; Table 2).

Comparison with the previous studies showed significant ($p < 0.05$) year-to-year differentiation for three parameters only: Hardness, TN, and NO₃⁻. For all of them, a significant increase in values was observed between 2003, 2008, and 2017. A similar pattern of increase was also observed for TP concentration and trophic indicators: TSI and N:P. The results indicate intensifying eutrophy, both in the epilimnion and hypolimnion waters. Interestingly, in the epilimnion, the N:P ratio increases with increasing TSI (phosphorus limitation), while in the hypolimnion, N:P decreases (nitrogen limitation). Although similar differentiation between the surface (epilimnion) and the above-bottom (hypolimnion) layer was observed in all the study years, the results from 2017 are the most divergent, indicating the highest mineralization and trophic.

The factor analysis showed that pH, EC, hardness, Ca²⁺, Mg²⁺, TN, and TP were the variables significantly differentiating the physicochemical composition of water within the studied periods. Based on these variables, the PCA analysis was performed (Figure 5). The first two main components explained almost 80% of the observed variance. The PCA output proved pH, hardness, Mg²⁺, TN, and TP (correlated with the first axis, $r > 0.80$) as well as EC (correlated with the second axis, $r > 0.80$) to be primarily responsible for the observed variance.

Table 2. Physicochemical characteristic of Lubińskie Lake epilimnion (E) and hypolimnion (H) water over three years of study: 2003 [43], 2008 (unpublished data) and 2017. The mean value \pm standard deviation is given for each year.

Parameter	(unit)	2003		2008		2017	
		E	H	E	H	E	H
SD	(m)	3.2 \pm 0.5		2.5 \pm 0.9		2 \pm 0.1	
Temp.	(°C)	14.4 \pm 10.7	4.4 \pm 0.1	13.4 \pm 9.8	4.3 \pm 0.8	15.3 \pm 12.7	4 \pm 0.5
EC	($\mu\text{S cm}^{-1}$)	416 \pm 11.3	452 \pm 19.8	442 \pm 15.6	485 \pm 28.3	380 \pm 7.1	460.5 \pm 0.7
pH	(mg L^{-1})	8.4 \pm 0.6	7.5 \pm 0	8.6 \pm 0.3	7.7 \pm 0.6	8.4 \pm 0.2	7.2 \pm 0
O ₂	(mg L^{-1})	14 \pm 2.2	0 \pm 0	12.2 \pm 1.5	2.8 \pm 3.9	8.2 \pm 0.6	0.2 \pm 0.1
Ca ²⁺	(mg L^{-1})	70 \pm 8.06	76.4 \pm 7.07	77.3 \pm 13.72	67.45 \pm 0.49	74.16 \pm 2.76	90.26 \pm 1.75
Mg ²⁺	(mg L^{-1})	4.3 \pm 0	5.05 \pm 2.19	1.91 \pm 1.33	3.29 \pm 0.79	3.54 \pm 0.15	6.81 \pm 0.11
Hard.	(dH)	10.8 \pm 1.13	12.2 \pm 0	9.05 \pm 1.49	10.2 \pm 0.14	12 \pm 0.14	12.8 \pm 0.14
TP	(mg L^{-1})	0.08 \pm 0.025	0.199 \pm 0.106	0.088 \pm 0.071	0.834 \pm 0.069	0.13 \pm 0.02	0.998 \pm 0.04
TN	(mg L^{-1})	1.524 \pm 1.561	4.357 \pm 1.008	1.964 \pm 0.31	4.008 \pm 3.029	3.812 \pm 0.173	5.844 \pm 0.047
N _{org} -N	(mg L^{-1})	1.252 \pm 1.177	3.194 \pm 0.504	1.335 \pm 0.064	2.605 \pm 1.563	3.029 \pm 0.033	3.804 \pm 0.157
NO ₃ -N	(mg L^{-1})	0.1 \pm 0.141	0 \pm 0	0.199 \pm 0.177	0.148 \pm 0.209	0.467 \pm 0.195	0.656 \pm 0.109
NO ₂ -N	(mg L^{-1})	0.002 \pm 0.003	0.004 \pm 0.005	0.005 \pm 0.004	0.003 \pm 0.004	0.001 \pm 0.001	0 \pm 0
NH ₄ -N	(mg L^{-1})	0.17 \pm 0.24	1.16 \pm 0.509	0.426 \pm 0.555	1.253 \pm 1.679	0.316 \pm 0.013	1.384 \pm 0.218
SRP	(mg L^{-1})	0.011 \pm 0.016	0.127 \pm 0.051	0.036 \pm 0.009	0.126 \pm 0.096	0.089 \pm 0.012	0.858 \pm 0.084
N:P*		6.8	18.5	15.8	7.8	33.9	6.0
TSI		52.8		59.5		61	

* For epilimnion water only.

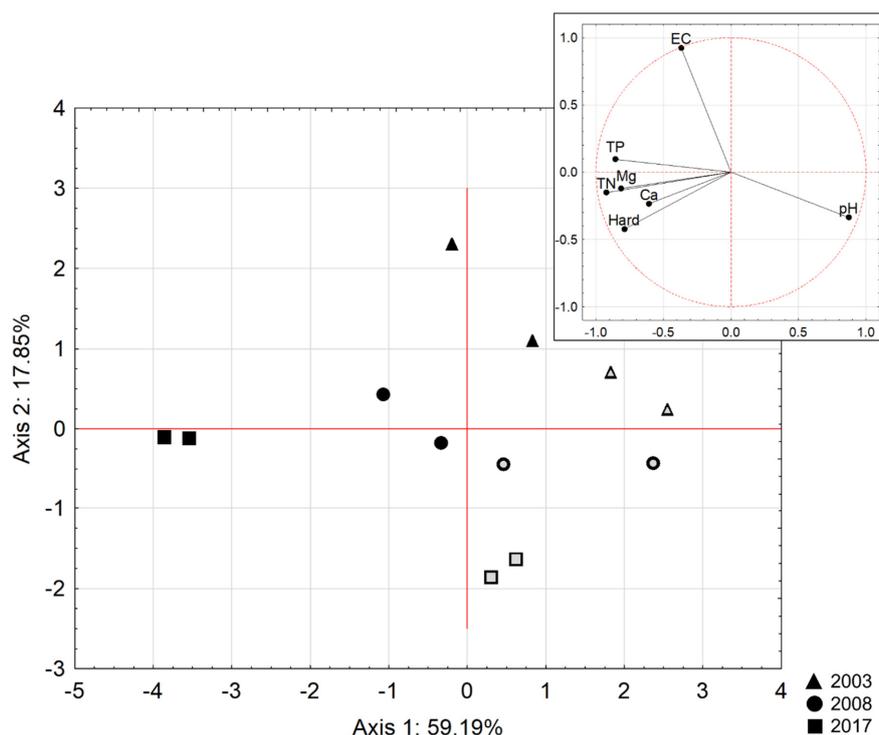


Figure 5. The principal components analysis (PCA) for water analyses in Lubińskie Lake performed in 2003 [43], 2008 (unpublished data), and 2017—differentiation across the selected hydrochemical characteristics (preceded by factor analysis). Gray color indicates samples taken in August, and black—those taken in April.

4.2. Site-to-Site Differentiation of Water Chemistry

The water analyses showed that springs provide water with a significantly lower temperature (from about 10 °C in winter to 12 °C in summer) and much higher mineralization (about 50 $\mu\text{S cm}^{-1}$ higher in spring and about 100 $\mu\text{S cm}^{-1}$ in summer) than in the lake's water (Figure 6). This was also

reflected in the values of total hardness and concentrations of Ca^{2+} and Mg^{2+} . In the case of pH and oxygen, however, the lowest values were found in spring waters and the highest in the outflow waters.

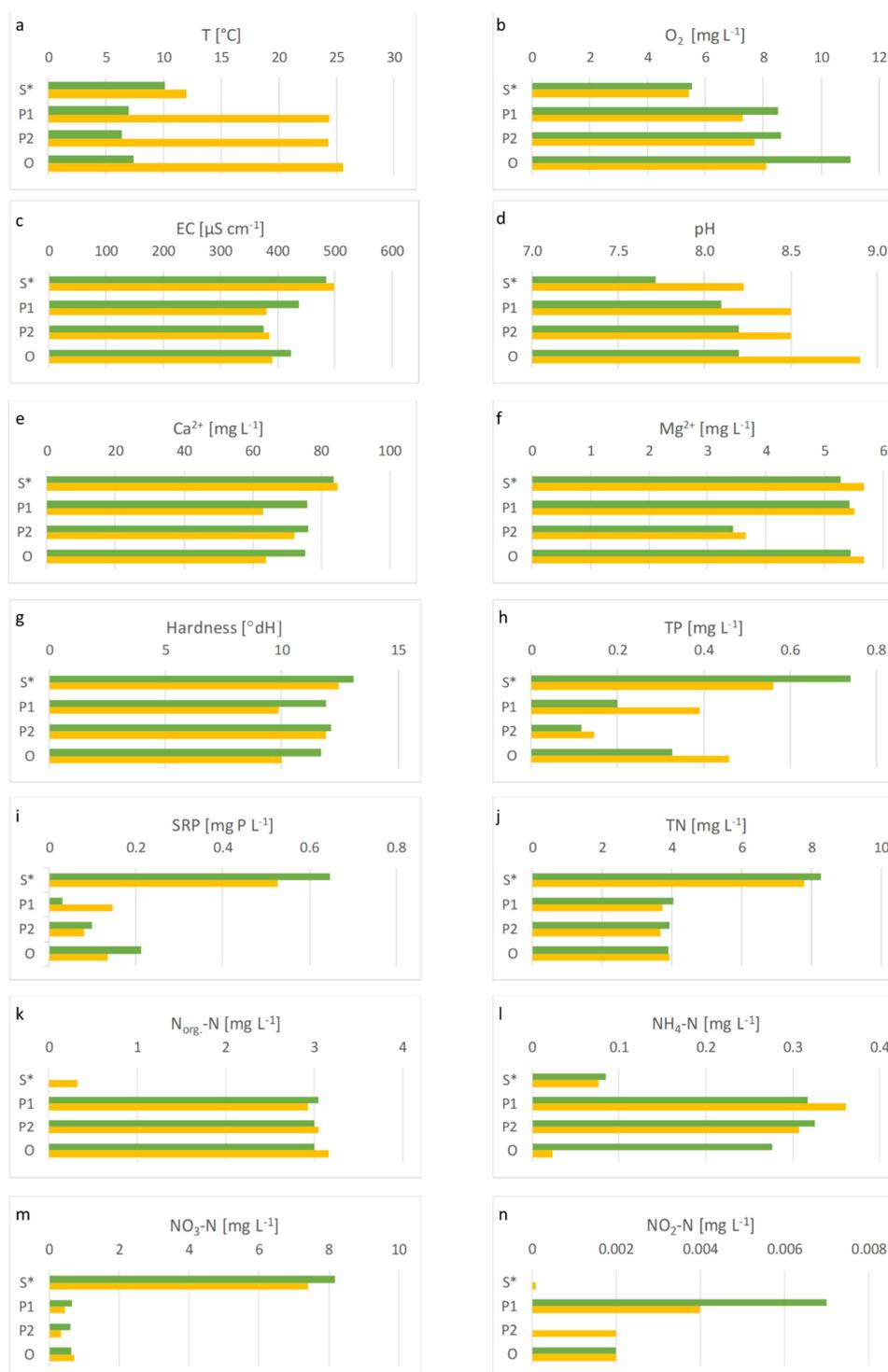


Figure 6. Differentiation of water properties between the studied sites. P1—pelagial 1, P2—pelagial 2, O—outflow, S—spring, *—mean values for all springs. Green bars—April, yellow bars—August.

The spring waters were characterized by much higher nutrient concentrations. This is particularly noticeable in the case of TP and SRP as well as TN and $\text{NO}_3\text{-N}$ concentrations (Figure 6). It is worth noting that the waters of the bay directly fed by springs (site P1) had higher values than the waters in site P2. Even higher values were found in outflow waters (site O). Total nitrogen concentrations

in spring were almost twice as high (up to 8.2 mg L^{-1} on average) as in lake waters. The majority of this load was $\text{NO}_3\text{-N}$, the highest values of which were found in spring S1, both in the spring and the summer (24.13 and 22.86 mg L^{-1} , respectively). The exceptions were: $\text{NO}_2\text{-N}$ and $\text{N}_{\text{org.}}\text{-N}$, which was found to be almost non-existent in spring waters, and lower concentrations of $\text{NH}_4\text{-N}$.

4.3. Water Inflow to the Lake

Groundwater upwellings occur both in the littoral zone and in the pelagic zone (Figure 1). They are fed from the shallow aquifer at the depth of 2 to 5 m below ground level and from the aquifer occurring at the depth below 10 m and isolated from the surface with post-glacial clay deposits. The gravity springs feeding the lake are permanent. In the littoral zone of the lake, nine spring niches were recorded, from which waters are directly supplied to the lake. The flow discharge rate of the four measured springs was in the range of 1 to $8 \text{ dm}^3 \text{ s}^{-1}$ (Table 3). The other flow discharge rates were estimated at below $0.5 \text{ dm}^3 \text{ s}^{-1}$. The total flow discharge rate of all the springs is on average $20 \text{ dm}^3 \text{ s}^{-1}$. In the southern part of the lake, two zones of sublacustrine springs were also recorded. They are approximately 10–20 m from the shoreline. However, it is difficult to measure their flow discharge. It is estimated to be about 50% of the inflow from overground springs, but this value may be underestimated. The discharge rate of the stream flowing out of the lake in the spring, directly after the disappearance of the ice cover was $40 \text{ dm}^3 \text{ s}^{-1}$, and in the summer, $21 \text{ dm}^3 \text{ s}^{-1}$. The difference between the amount of water feeding from the springs and the outflow from the lake indicates additional feeding with groundwater from aquifer outcrops on the bottom of the lake.

Table 3. Efficiency of the springs and discharge of the outflow from the lake in 2017.

Discharge	Q ($\text{dm}^3 \text{ s}^{-1}$)			
	Date	15.03	12.04	02.08
Spring (S1)		6.0	4.0	4.0
Spring (S2)		8.0	8.0	7.0
Spring (S3)		1.0	5.0	4.0
Spring (S4)		1.0	2.0	1.0
Outflow (O)		29.0	40.0	21.0

4.4. Strontium Isotope Composition in Water

The profiles of $^{87}\text{Sr}/^{86}\text{Sr}$ and Sr content for Lubińskie Lake are shown in Figure 7, and Sr isotope and elemental characteristics for components of the hydrologic system of the lake are given in Table 4. Since the bay yields a uniform Sr isotope composition and Sr concentration throughout the water column, it will not be discussed in detail. The lake is characterized by a narrow range of $^{87}\text{Sr}/^{86}\text{Sr}$ values, between 0.710741 and 0.710798. Thus, it is isotopically homogeneous throughout the water column (Figure 7a). Similarly, Sr content of lake water is highly uniform in the profile and changes from 0.124 to 0.148 mg L^{-1} (Figure 7b). It is worth mentioning that the highest concentration of dissolved Sr occurs in the lower part of the water column. As can be expected, the stream draining the lake has the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio close to that of surface lake water, but is enriched in Sr (Figure 7).

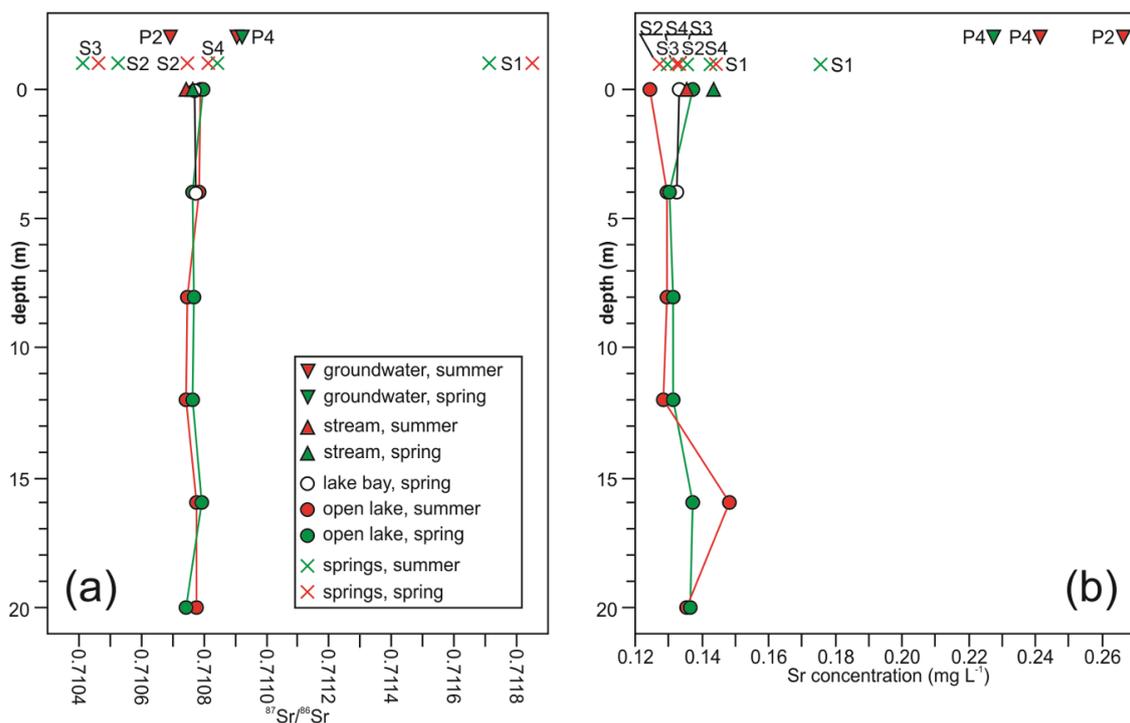


Figure 7. Depth profiles for (a) $^{87}\text{Sr}/^{86}\text{Sr}$ and (b) Sr content of the lake water. Data for the springs, the stream, and the groundwater is also shown for comparison. Explanations for panel (a) also refer to panel (b).

Table 4. Strontium isotope composition ($^{87}\text{Sr}/^{86}\text{Sr}$) and Sr content of components of the Lubińskie Lake hydrologic system.

Component	$^{87}\text{Sr}/^{86}\text{Sr}$		Sr Content (mg L^{-1})	
	Spring	Summer	Spring	Summer
Lake water—open lake				
0 m	0.710798 ± 10	0.710790 ± 10	0.137	0.124
4 m	0.710764 ± 10	0.710784 ± 9	0.130	0.129
8 m	0.710770 ± 10	0.710748 ± 11	0.131	0.129
12 m	0.710762 ± 10	0.710744 ± 8	0.131	0.128
16 m	0.710791 ± 12	0.710775 ± 9	0.137	0.148
20 m	0.710741 ± 9	0.710776 ± 10	0.136	0.135
Lake water—bay				
0 m	0.710770 ± 10	ND	0.133	ND
4 m	0.710771 ± 10	ND	0.132	ND
Stream				
	0.710765 ± 10	0.710741 ± 9	0.143	0.135
Springs				
S1	0.711851 ± 10	0.711710 ± 10	0.175	0.144
S2	0.710746 ± 10	0.710525 ± 10	0.135	0.127
S3	0.710463 ± 11	0.710412 ± 9	0.129	0.133
S4	0.710813 ± 11	0.710844 ± 16	0.142	0.132
Groundwater				
P2	ND	0.710693 ± 10	ND	0.266
P4	0.710922 ± 10	0.710906 ± 10	0.227	0.241
Rain				
	0.708879 ± 11	ND	ND	ND

ND—no data.

The springs show a wide range of $^{87}\text{Sr}/^{86}\text{Sr}$ values from 0.710412 to 0.711851 and relatively diverse Sr dissolved load (0.127–0.175 mg L⁻¹). The strontium isotope composition of the groundwater falls within the range for the springs ($^{87}\text{Sr}/^{86}\text{Sr}$ values of 0.710693–0.710906), yet it has a clearly higher Sr content (0.241–0.266 mg L⁻¹). Finally, the rain is the least radiogenic component (with the lowest $^{87}\text{Sr}/^{86}\text{Sr}$ ratio) and yields $^{87}\text{Sr}/^{86}\text{Sr}$ value of 0.708879.

5. Discussion

5.1. Water Chemistry Analysis

The conducted research showed that Lubińskie Lake is currently in the state of higher trophy, which is indicated by the concentrations of nutrients and low Secchi disk visibility. The comparison with previous years of research shows clearly worsening of the water quality. In 2003, despite high nutrient concentrations, the lake maintained the clean water state (visibility over 4 m) and was classified as a charophyte lake [43,53].

The results of the physicochemical and algological tests showed that the meromictic character of the lake maintained since 2003 was disturbed between January and March 2008 [44]. At the end of February 2008, the waters in the lake mixed completely. At that time, a series of storm winds went across the western part of Poland (“Paula”, “Zizi”, and “Emma”). The complete restoration of the meromictic conditions lasted until June 2008 [54] (Pukacz et al. 2010). Although the complete mixing of lake waters lasted only a few months (which is confirmed by measurements carried out in the subsequent years), it probably contributed to the release of nutrients and other substances (e.g., methane and hydrogen sulfide) deposited for years in the monimolimnion [55]. This resulted in gradual worsening of the condition of the whole ecosystem. One of the visible effects was the worsening of light conditions and gradual disappearance of submerged vegetation (Pukacz 2008–2018, unpublished data).

Although meromictic stratification was restored in the lake, further increase in nutrients concentration was observed. The study showed that an important source of phosphorus and nitrogen (especially in the form NO₃-N and NH₄-N) supplied to the lake is the spring waters. Based on the average concentrations and water supply from the springs, it can be estimated that each day, approximately 10 kg of nitrogen and 0.9 kg of phosphorus can be introduced to the lake. However, these values may be underestimated by approximately 25%, because they do not take into account the load supplied with discharges for which the volume was estimated, and the load supplied through the springs in the bottom of the lake.

The increased supply of those elements must be associated with the change in the use of land in the catchment area of Lubińskie Lake. Since 2015, in the fields located in the SE part of the catchment, corn, and rapeseed have been cultivated, which are not only fertilized with mineral fertilizers but also, in the spring, with organic fertilizers (own observations). Taking into account the directions of inflow of groundwater and the very high concentrations of nutrients in spring waters, it is a very probable cause of the increased inflow of nutrients to the lake.

Interestingly, the values of the studied parameters in the SE bay, where most springs are located, were not significantly higher than in the central basin. This may result from the small surface area of the lake and from feeding it with inflows located in the slope of the basin. Feeding the lake through springs located in the bottom of the lake basin may have an impact, not only on the lower quality of the lake waters, but also on disturbed stratification and crenogenic meromixis [56].

5.2. Strontium Isotopes Perspective

Strontium isotope composition coupled with Sr content enables the identification of reservoirs controlling the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of water and mixing processes involved [27,36,57]. There is a strong correlation between $^{87}\text{Sr}/^{86}\text{Sr}$ and 1/Sr for the springs dataset, which points to mixing between the two Sr reservoirs (Figure 8). The first reservoir is characterized by a relatively radiogenic $^{87}\text{Sr}/^{86}\text{Sr}$ ratio

and moderately low $1/Sr$ (high Sr concentration), whereas the second reservoir has a less radiogenic $^{87}Sr/^{86}Sr$ ratio and higher $1/Sr$ (lower Sr content). Since the springs emerge from shallow Quaternary aquifers, the first reservoir is represented by silicates, mostly glacial deposits. It controls the isotopic composition of the S1 spring. Since the investigated springs are charged by atmospheric waters [58], we identify the second reservoir with rainwater, which strongly influences the Sr isotope budget of the S2-S4 springs. As shown by Raiber et al. [59], rain can be an important source of Sr to shallow groundwater. Strontium isotope composition of rainwater at Słubice ($^{87}Sr/^{86}Sr$ value of 0.708879) is less radiogenic than that of modern seawater ($^{87}Sr/^{86}Sr$ about 0.70917; [60]) being the source of rainwater, likely due to the addition of atmospheric dust. Inland deviation of precipitation $^{87}Sr/^{86}Sr$ ratio is a well-documented phenomenon [59,61,62]. Typically, rainwater is not rich in Sr [59,61,63]. Zieliński et al. [25] provide Sr concentration of about 0.001 mg L^{-1} for rain and snow at Poznań, about 140 km east of Lubińskie Lake. However, the admixture of dust elevates the Sr content [59]. Therefore, Sr dissolved load of tens of $\mu\text{g L}^{-1}$ for the rain at Słubice can reasonably be assumed.

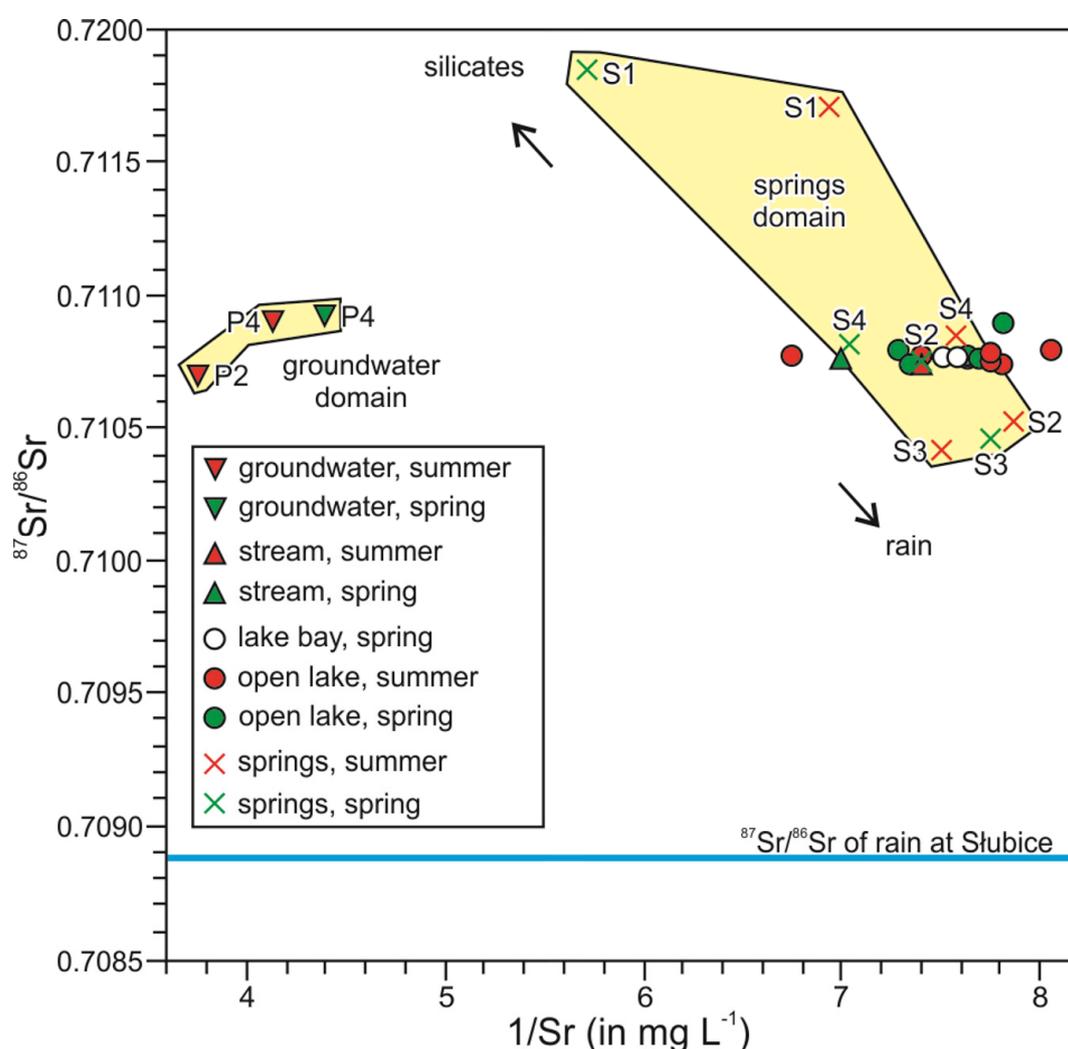


Figure 8. $^{87}Sr/^{86}Sr$ versus $1/Sr$ mixing diagram of the Lubińskie Lake hydrologic system. Note a binary mixing trend for the springs dataset and the deviation of data points for lake water from mixing paths between the springs.

The role of rain as one of the major sources of Sr for the springs is supported by a clear relationship between Cl and Sr in the springs dataset (Figure 9), indicating their common origin. Chloride ions are a useful atmospheric input reference to the hydrosystem, because in the dissolved load of the hydrosystem they originate from seasalt and saltrock dissolution [64,65].

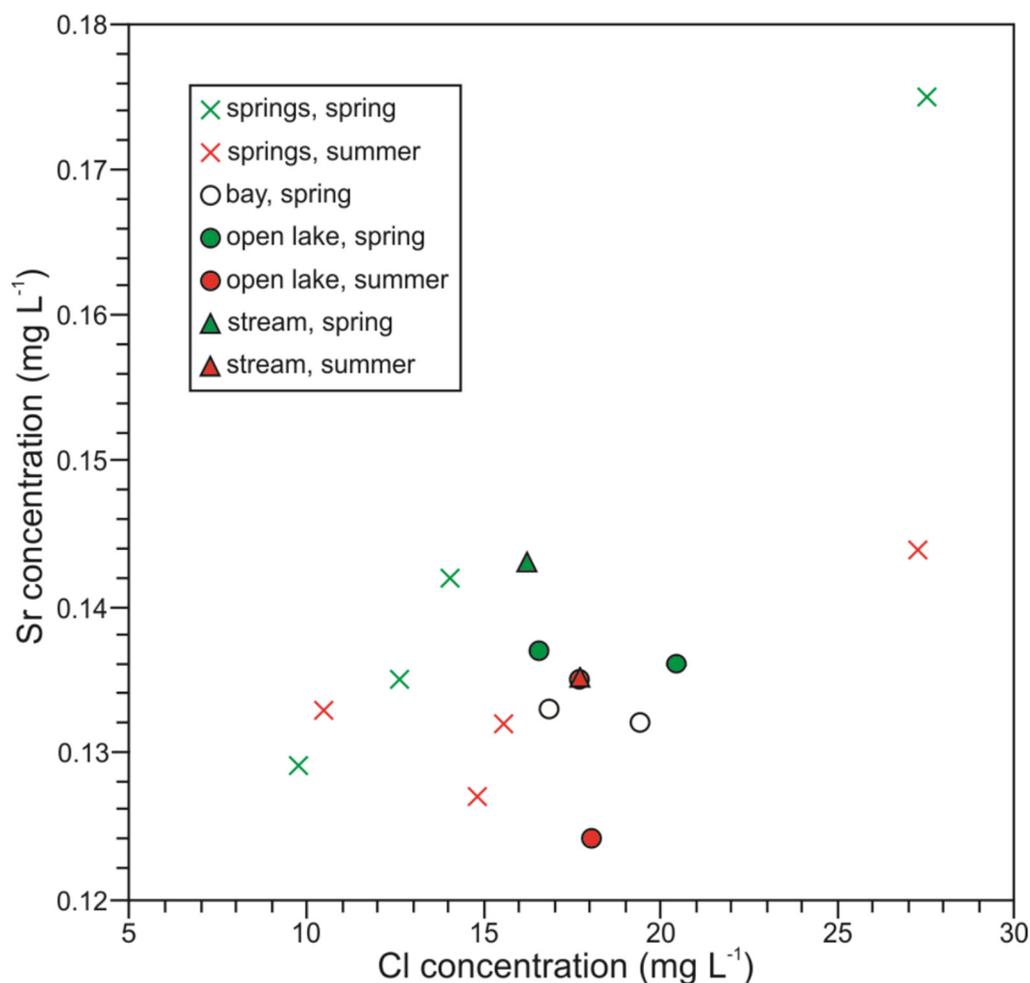


Figure 9. Relationship between Cl and Sr in samples collected from the springs and Lubińskie Lake. Chlorine content in the lake was measured only for surface and near bottom waters (see Table 4).

However, they can also result from various human activities (domestic sewage, fertilizers, and deicing salts) [66]. Since the Lubińskie Lake drainage basin is free of evaporates, they do not participate in the weathering reactions. Consequently, the general trend of relationships between Cl and Sr can be explained by the contribution of Cl from the atmospheric and anthropogenic sources. Since crop fields occur in hinterland of the spring area, the latter is likely represented by mineral fertilizers. This assumption is supported by the high load of nitrates (NO_3) carried by the springs (Figure 6). Additionally, sewage leaking from surrounding villages may also provide some load of Cl.

Recently, Zieliński et al. [25] provided evidence for the common lowering of the present-day $^{87}\text{Sr}/^{86}\text{Sr}$ values of Noteć River water in western Poland due to the impact of fertilizers used in agriculture. The estimated scale of the lowering was not higher than 0.0006 to 0.0007 of the observed $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the downstream portion of the Noteć River. Given that the input of fertilizers-related Sr to the springs waters was recognized, the lowering of the lake water isotopic ratio should be assumed.

Figure 8 shows that data points for Lubińskie Lake in general plot in the springs domain on the $^{87}\text{Sr}/^{86}\text{Sr}$ versus $1/\text{Sr}$ diagram; thus, crucial contribution of spring-derived Sr is identified. Surprisingly, spring S1, the second largest yet richest in Sr, has a negligible impact on the Sr isotopic composition of the lake. Instead, springs S2–S4 with lower flow rates and Sr contents seem to contribute to it the most. This suggests additional input of shallow groundwater with $^{87}\text{Sr}/^{86}\text{Sr}$ ratios similar to these springs below the water table due to the lack of other springs along the lake's shore. Indeed, we found several seepages at the bay's bottom.

If the isotopic composition of Lubińskie Lake was solely related to the springs-derived Sr, data points for the lake water would lie on paths between the springs. Most of the data points, however, are moved aside the mixing trends, mainly towards lower Sr concentrations but without noticeable changes in $^{87}\text{Sr}/^{86}\text{Sr}$, and evidence the contribution of less concentrated waters. Apart from rainwater supplied to Lubińskie Lake through the springs, as inferred above, it also reaches the lake directly. Therefore, it is likely responsible for the dilution of the lake's Sr dissolved load.

The input of dust-derived Sr can account for differences in Sr content between Lubińskie Lake and the stream originating from it. Graustein and Armstrong (1983) [39] show that coniferous foliage is more effective in dust trapping than deciduous foliage. As the stream flows in a coniferous forest surrounding the northern fringe of the lake, dust deposited on the foliage and then incorporated into the soil by throughfall seems to charge soil waters and hence the stream by additional Sr.

Although the lake basin cuts deeply into the aquifer (Figure 2), and the recharge of the lake by groundwater arguably occurs, its impact on Sr isotope composition of the lake water seems negligible. Nonetheless, this impression is only apparent, because $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of the groundwater fall within the $^{87}\text{Sr}/^{86}\text{Sr}$ range for the springs, so the contribution of the former will be masked. The input of groundwater-derived Sr to Lubińskie Lake is suggested by the rise of Sr concentration several meters above the bottom, which is consistent with the lateral input of groundwater enriched in Sr and its downward descend. Due to the meromictic character of the lake, it is, however, limited to its deepest part.

6. Conclusions

The results of the study indicate that Lubińskie Lake has regained its meromictic character after complete mixing in 2008. That sudden event probably led to the release of nutrients from the monimolimnion layer, which resulted in an increase in trophy and deterioration of water quality in subsequent years. An additional, significant factor affecting the lake's water quality is the nutrient inflow from the catchment. Although the lake is insulated with a belt of trees, water polluted with fertilizers infiltrates into the first aquifer and enters the lake through springs. The difference between the lake supply from springs and the outflow from the lake indicates lake charging with groundwater from underwater outcrops of aquifers. That was also confirmed by strontium isotopes ($^{87}\text{Sr}/^{86}\text{Sr}$) analysis. It indicates that water is supplied to Lubińskie Lake mostly by the springs, and recharge from deep aquifers is of secondary importance. Moreover, strontium isotope data and the relationship between Sr and Cl content support finding that high load of nutrients is of anthropogenic origin and reach the lake through springs. We show that the $^{87}\text{Sr}/^{86}\text{Sr}$ composition of lake water supplemented by major ion chemistry is a valuable tool in the investigation of meromictic lakes.

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