SEASONAL WATER CHEMISTRY VARIATIONS IN THREE SLOVENIAN MOUNTAIN LAKES

Gregor Muri and Anton Brancelj

National Institute of Biology, Večna pot 111, 1000 Ljubljana, Slovenia

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Abstract

Water quality was analyzed in three Slovenian mountain lakes (i.e., Krnsko jezero, Jezero v Ledvicah and Jezero na Planini pri Jezeru) situated in the Julian Alps, NW Slovenia. Water samples were collected monthly in the ice-free period. The water was examined from chemical, physical and biological points of view to assess the overall status of these lakes. In this paper, only a chemical aspect is reported. Water quality in remote Jezero v Ledvicah is good, while in Krnsko jezero and especially in Jezero na Planini pri Jezeru, both situated close to mountain huts, is worse.

Introduction

High altitude mountain lakes represent one of the most remote and least disturbed environments found on Earth. These lakes are more vulnerable to any atmospheric input into their catchment areas than lowland area lakes, since they commonly have shallow soil covers, modest dimensions of watershed and rapid flushing rates. Atmospheric deposition of pollutants thus strongly influences on these systems, in terms of changing acidity of lakes and input of toxic air pollutants into lakes' catchment and lakes themselves. Consequently, mountain lakes have been frequently used as reliable sensors of environmental change, providing valuable information on the consequences of human impact on pristine environments, since their sensitivity can be used as a proxy for the speed, direction and impact of changing air quality and climate.[1,2,3] Therefore, several research projects on a European-wide scale were conducted in the last decade to assess condition of these systems.

There are 14 mountain lakes in Slovenia, situated in the Julian Alps (NW Slovenia) and located at elevations from 1325 m to 2150 m. Most of them lie above the tree level. The main bedrock is limestone. All the lakes are of glacial origin, small (surface area of 0.3 to 4.6 ha), shallow (2 to 15 m) and surrounded by steep slopes.[4] The annual precipitation rate is high, exceeding 3000 mm per year in the western part of the Julian Alps and decreasing in the easterly direction.[5] In most cases, there are no permanent surface inflows into these lakes. From early November until late April/May, the lakes are normally covered by ice.[4] All the lakes are situated in the Triglav National Park where human activities are limited by law. The only exception is Jezero na Planini pri Jezeru, where there is a mountain hut situated just above the lake.

First attempts to analyze water quality of Slovenian mountain lakes started in 1991. Initially, a few mountain lakes were sampled once per year. From 1995 onwards, a series of national as well as international research projects was initiated, in order to assess the condition of these lakes. Water samples were collected regularly twice per year, in the late spring and early autumn. However, the three, above mentioned, lakes were monitored at shorter intervals. Hence, water samples were collected every month in the ice-free period and some samples were also taken in the winter when lakes were covered by thick ice. Chemical and physical determinants were measured in the lake water and biological samples were also taken. Additionally, on-site meteorological data were also collected using an automated weather station, situated near Jezero v Ledvicah to assess the overall condition of Slovenian mountain lakes.

The objective of this work was to determine basic water chemistry parameters in selected Slovenian mountain lakes and to follow their temporal changes. Three mountain lakes were selected, i.e. Krnsko jezero, Jezero v Ledvicah and Jezero na Planini pri Jezeru (site description in Table 1), representing lakes of different trophic status. Krnsko jezero and Jezero na Planini pri Jezeru are eutrophic to highly eutrophic lakes, while remote Jezero v Ledvicah is still a pristine, oligotrophic lake.

Table 1: Sampling site description.[4]

	Altitude [m]	**Surface area** [ha]	**Max. depth** [m]
Krnsko jezero	1383	4.53	18
Jezero v Ledvicah	1830	2.19	15
Jezero na Planini pri Jezeru	1430	1.56	11

Experimental

Sampling

Water sampling was carried out from the deepest basin of the lakes using a Van Dorn sampling device (Wildco, USA). Samples of the water column were collected at every 2.5 m and filtered in the field using an 0.2 μm filter (Fluropore membrane filters, Millipore) to eliminate solid particles and to reduce biological activity. Samples were stored in plastic containers (PP, Brand). Conductivity, oxygen concentration/saturation and temperature were also measured in the field using a WTW Multiline P4 universal instrument. These parameters were measured at 1 m intervals. The samples were delivered to the laboratory within one or two days after collection and analyzed immediately after arrival of the samples at the laboratory.

Analyses

The pH was measured using a digital WTW pH 540 GLP instrument, equipped with a SenTix 81 glass electrode. Standard buffer solutions of pH 4 and 7 were used to calibrate the instrument. Alkalinity was determined by the Gran titration method.[6] Total nitrogen and phosphorus were analyzed in two steps. Both samples were first oxidized with persulphate. Subsequently, total nitrogen was determined by measuring the nitrate concentration in the digestate[6] using an UV-VIS spectrophotometer (Lambda 12, Perkin Elmer). Total phosphorus was also spectrophotometrically determined by analyzing the ortho-phosphate in the digestate.[6] Major anions and cations were determined using an ion chromatograph (761 Compact IC, Metrohm), equipped with high-pressure pump, pulsation dampener, separation columns and conductivity detection cell. Standard laboratory procedures were followed for analyses of ions in water samples, according to APHA *et al.*[6] Chloride, nitrite, nitrate, phosphate and sulphate were analysed using a METROSEP A Supp 5 separation column (150 × 4.0 mm), followed by a chemical suppressor module. Sodium, ammonium, potassium, calcium and magnesium were determined on a METROSEP C_2 150 separation column (150 × 4.0 mm). In the case of cations, suppression was not used. Detection limits were in the range 30-50 μg/L.

Standard solutions and blank samples were used to calibrate the instruments and check the calibration curves. Analytical results were validated using calculations and controls proposed by APHA *et al.*[6] Once the sample data were completed, an ionic balance was calculated, as a further check on the data quality. The difference between the total anions and total cations was within 5-10%.

Results and discussion

Physical parameters

Characteristic water temperature profiles in Jezero v Ledvicah and Jezero na Planini pri Jezeru are shown in Figure 1. All the lakes were thermally stratified in summer. Water temperature varied most at the surface. The lakes are relatively small, so that the water temperature depended strongly on weather conditions. Surface temperatures as high as 19 °C were observed in Krnsko jezero and Jezero na Planini pri Jezeru. In Jezero v Ledvicah, surface temperatures were lower and did not exceed 14 °C, since the lake is situated at higher altitude. In the deeper water layers, the temperature was quite uniform throughout the summer, ranging from 4 to 7 °C. In winter, uniform temperature profiles were observed in all the lakes. The temperature averaged 4 °C, except in the surface water layers which were a few degrees cooler due to their immediate contact with ice. In spring and late autumn, mixing of the whole water column occurred. As a consequence, the temperature profiles were uniform at around 4 °C in all the lakes.

Dissolved oxygen concentrations varied considerably in these lakes (Figure 1). Jezero v Ledvicah was normally rich in oxygen throughout the year, with concentrations ranging from 9 to 12 mg O_2/L. In Krnsko jezero and Jezero na Planini pri Jezeru however, the dissolved oxygen concentration decreased markedly during the summer stratification. Suboxic conditions were frequently observed in the deeper water layers of these two lakes, where the dissolved oxygen concentration dropped below 2 mg/L. In late summer, anoxic conditions were occasionally observed in the bottom water layers. Severe oxygen depletion in Krnsko jezero and Jezero na Planini pri Jezeru was induced in summer by increased primary production in these lakes. In contrast, no oxygen depletion was found in Jezero v Ledvicah, due to its oligotrophic status. The only exception was the winter when the latter lake was covered by thick ice, preventing exchange of oxygen between the atmosphere and the lake water and lowering the dissolved oxygen concentration. During the overturn, the whole water column was mixed and became rich in oxygen in all three lakes.

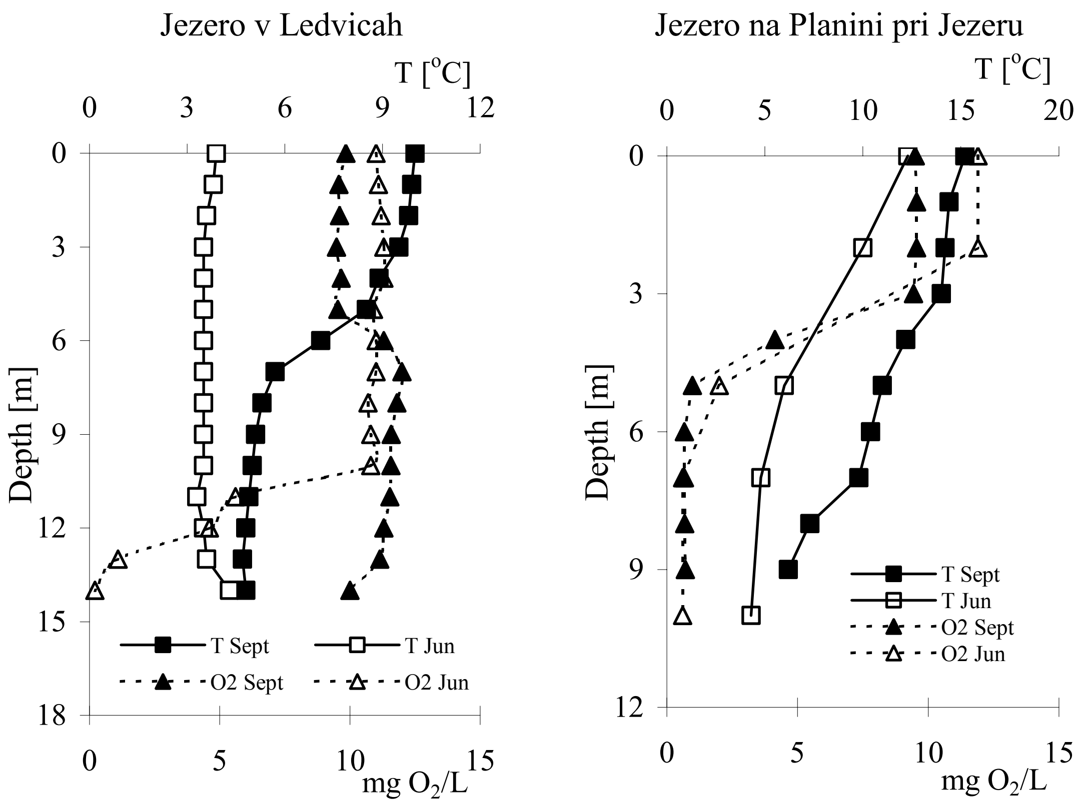

Figure 1: Water temperature and dissolved oxygen profiles in Jezero v Ledvicah and Jezero na Planini pri Jezeru in the year 2000.

The water conductivity ranged between 140 and 170 µS/cm. In eutrophic lakes (Krnsko jezero and Jezero na Planini pri Jezeru), a considerable increase of conductivity with depth was observed, reaching 350 µS/cm in the deeper water layers in the latter. This remarkable increase in conductivity was caused by a shift of the carbonate equilibrium and subsequent dissolution of $CaCO_3$,[7] as will be discussed later.

Chemical parameters

The pH in all the lakes was slightly basic throughout the year, ranging from 7 to 8.5 (Figure 2), showing the absence of acidification at all sites. The total nitrogen and total phosphorus concentrations in Jezero v Ledvicah were usually low, rarely exceeding 1.5 mg N/L and 20 µg P/L (Figure 3). The eutrophic lakes, Krnsko jezero and Jezero na Planini pri Jezeru, were again exceptions, since the total phosphorus concentrations in the bottom layers of the water column reached 100 µg P/L, and even 350 µg P/L in autumn, respectively.

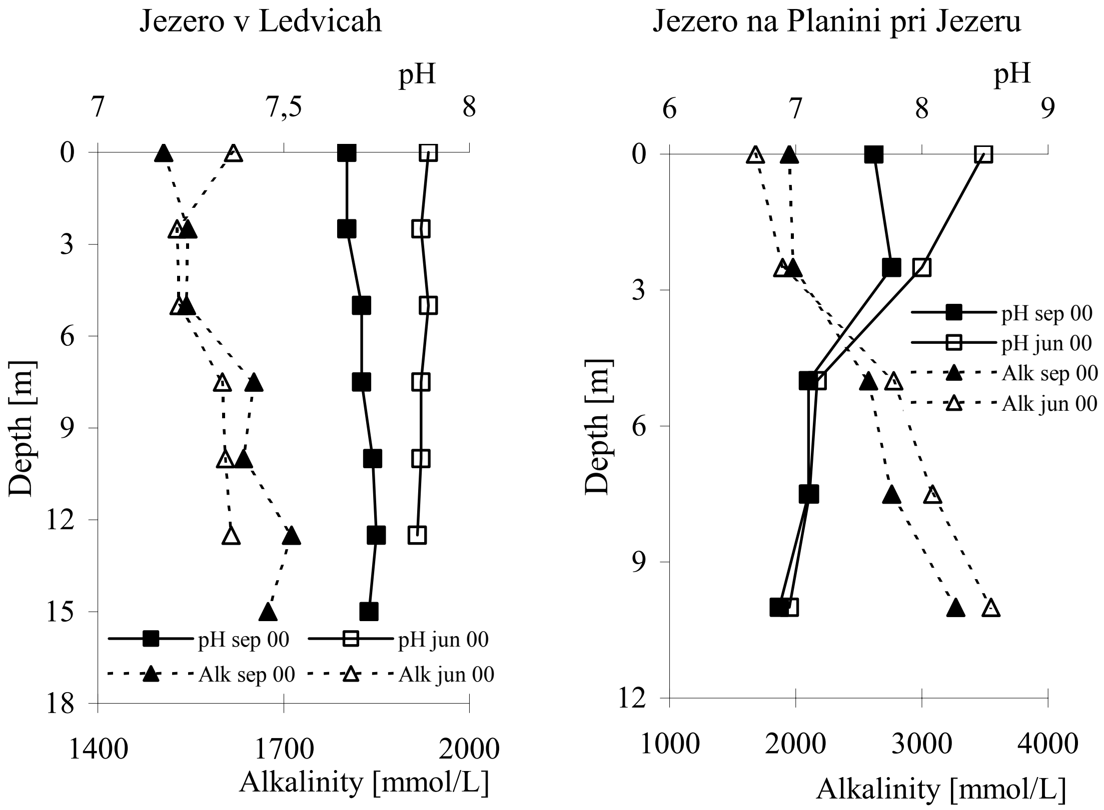

Figure 2: pH and alkalinity profiles in Jezero v Ledvicah and Jezero na Planini pri Jezeru in the year 2000.

Hydrogen carbonate/carbonate ions were the most abundant anions, accounting for the high alkalinity. In general, the alkalinity ranged from 1 to 2 mmol/L, but frequently exceeded 3 mmol/L in Jezero na Planini pri Jezeru during the late summer period. Nitrate and sulphate concentrations ranged from 0.2 to 0.4 mg NO_3^--N/L and around 1-2 mg SO_4^{2-}/L. The concentrations were usually higher in spring during snowmelt but decreased afterwards. In the lakes with high primary production i.e., Krnsko jezero and Jezero na Planini pri Jezeru, nitrate concentrations were below 0.1 mg NO_3^--N/L during summer. The chloride concentration was around 0.5 mg Cl^-/L. Nitrite and phosphate concentrations were below the limits of detection for most of the year.

Of the cations, calcium was the most abundant, constituting more than 90% of the total cation concentration. Its concentration normally ranged from 15 to 30 mg/L (Figure 3). The magnesium concentration was much lower, around 4 mg/L, while potassium and sodium concentrations generally did not exceed 1 mg/L. Ammonium concentration was below the limit of detection for most of the year, but increased in eutrophic lakes during the late summer stratification, even reaching 1.5 mg NH_4^+-N/L in Jezero na Planini pri Jezeru.

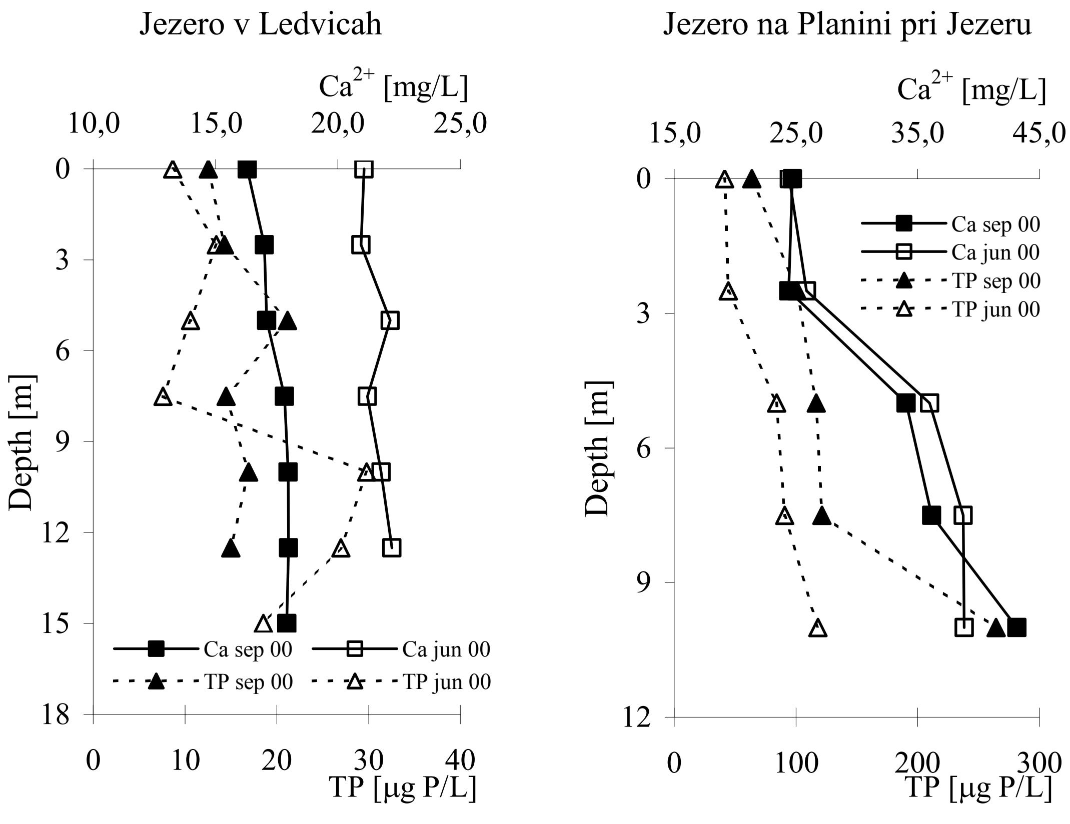

Figure 3: Calcium and total phosphorus (TP) profiles in Jezero v Ledvicah and Jezero na Planini pri Jezeru in the year 2000.

All the studied lakes are situated on limestone bedrock, which explains their high calcium concentration, alkalinity and pH. In carbonate watersheds, weathering is the main source of calcium and carbonate (related to alkalinity) in the water column,[8] both constituting over 90% of the total cation and anion concentration in the lake water. In some cases, the alkalinity was extraordinarily high in the bottom water layers, exceeding 3 mmol/L in Jezero na Planini pri Jezeru in which there is an abundant population of primary producers. The increase of alkalinity down the water column in Krnsko jezero was lower but concentrations as high as 2.3 mmol/L were still observed. In stratified eutrophic lakes, this phenomenon is observed regularly. The concentration of CO_2 is enriched in the deeper layers of the water column due to decomposition of organic matter and respiration. The enrichment of CO_2 shifts the carbonate equilibrium and consequently, $CaCO_3$ is redissolved from the water column and sediment,[7] leading to a rise in the hydrogen carbonate/carbonate, as well as calcium concentrations. Calcium contents as high as 55 mg Ca^{2+}/L were observed in Krnsko jezero and Jezero na Planini pri Jezeru (Figure 3). The nitrate and sulphate concentrations correlated well with precipitation. Atmospheric deposition is their most important source in remote mountain areas, given that nitrate and sulphate are the most abundant anions in rain and snow in continental regions.[9,10,11] In addition, nitrate and sulphate concentrations rose after snowmelt since these anions were accumulated in the snowpack and released during snowmelt.[12] Nevertheless, the nitrate concentration varied remarkably in oxygen depleted lakes during the year. When lake stratification occurred, the nitrate concentration decreased below 0.1 mg NO_3^--N/L, since nitrate is used by aquatic organisms.[11] In contrast, concentrations of reduced forms of nitrogen, particularly ammonium, increased. The ammonium concentration in the bottom water layers in Jezero na Planini pri Jezeru reached 1.5 mg NH_4^+-N/L. No such extreme behavior was observed in Jezero v Ledvicah. The detection limit of ammonium was exceeded only on rare occasions, indicating that ammonium is completely oxidized.

Seasonal variations

All three lakes are similar in size and depth (Table 1). However, they differ markedly in productivity. Jezero v Ledvicah is relatively clean and oligo- to mesotrophic, while Krnsko jezero and Jezero na Planini pri Jezeru are eutrophic. A short overview of selected parameters in Krnsko jezero, Jezero v Ledvicah and Jezero na Planini pri Jezeru in the period 2000-2002 is presented in Table 2. No strong variations of parameters were found in Jezero v Ledvicah. In contrast, in Krnsko jezero, and especially in Jezero na Planini pri Jezeru, some parameters, such as alkalinity and calcium content, varied considerably during the year.

Table 2: Seasonal variation of selected parameters in Krnsko jezero, Jezero v Ledvicah and Jezero na Planini pri Jezeru in the period 2000-2002.

	pH	**TP [µg P/L]**	**Alk [mmol/L]**	**NO_3^--N [mg/L]**	**Ca^{2+} [mg/L]**
Krnsko jezero					
2000	7.1-8.4	9-74	1.2-2.2	0.01-0.32	12.0-43.5
2001	7.5-8.8	14-34	1.1-2.0	0.02-0.22	17.7-37.7
2002	7.5-8.8	15-59	1.2-2.1	0.01-0.15	17.3-42.4
Jezero v Ledvicah					
2000	7.7-7.9	9-30	1.5-1.7	0.24-0.31	16.3-23.9
2001	7.9-8.2	9-30	1.4-1.6	0.27-0.35	22.5-25.2
2002	7.9-8.3	9-39	1.4-1.6	0.34-0.45	24.1-29.9
Jezero na Planini pri Jezeru					
2000	6.9-8.5	41-265	1.7-3.5	0.01-0.19	22.0-45.3
2001	7.5-8.1	14-381	1.4-3.3	0.03-0.23	26.1-54.2
2002	7.3-8.5	23-108	1.7-3.1	0.01-0.26	33.0-56.2

TP = total phosphorus; Alk = alkalinity

Atmospheric deposition, main bedrock and soil cover play a key role in determining lake water chemistry.[11,13,14] Atmospheric deposition is particularly important for lakes with a watershed composed of acidic rocks.[11,13] All three lakes considered in this study are situated on limestone bedrock. Hence, their capacity to buffer acidic inputs is high and acidification of the lake water was not observed. Soil cover could also affect certain lakes, especially those which are situated below the tree line.[15] Two of the lakes, Krnsko jezero and Jezero na Planini pri Jezeru, are located below the tree line. Unfortunately, data concerning soil characteristics in the Julian Alps are too scarce to assess their contribution to changes in lake water chemistry.

Seasonal changes of parameters were more pronounced in eutrophic lakes. In general, the values were in the ranges presented in Table 2 and discussed above. Alkalinity, calcium, oxygen and total phosphorus concentrations varied most. In years with long duration of snow and ice cover, and consequently cold lake water, primary producers were less abundant. Hence, the overall condition of the lakes improved, since nutrient concentrations were lower. High altitude lakes are particularly sensitive to changes in the duration of snow and ice cover. Even small temperature changes of 1 to 2 °C can result in extensive hydrological, physical, chemical and biological effects in these systems, and can lead to changes in water chemistry, hydrology and biota.[16, 17]

Conclusions

The remote lake Jezero v Ledvicah is a pristine lake. The water quality is good and the lake is oligo- to mesotrophic. No strong changes of parameters in the water column were observed. Also, seasonal changes of parameters were not pronounced. In the lakes located close to trails and mountain huts, however, local human influence is evident and the condition of these lakes has deteriorated, as is seen clearly in the cases of Krnsko jezero and, particularly, Jezero na Planini pri Jezeru. Concentrations of some parameters e.g., alkalinity, calcium and total phosphorus, varied considerably with depth. Nevertheless, seasonal variations of parameters were moderate, mostly depending on climatic effects (the temperature and duration of snow and ice cover) and in-lake productivity.

Altitude, affecting temperature and snow and ice cover duration, trophic status of the lake, its morphometry (size and depth) and catchment characteristics, appear to play a dominant role in determining lake water chemistry and its seasonal variations.

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Povzetek

Analizirali smo kvaliteto vode v treh slovenskih visokogorskih jezerih, in sicer v Krnskem jezeru, Jezeru v Ledvicah in Jezeru na Planini pri Jezeru, ki ležijo v Julijskih Alpah, SZ Slovenija. Vzorce vode smo pobirali mesečno v času, ko je bilo jezero brez ledenega pokrova. Jezersko vodo smo analizirali iz kemijskega, fizikalnega in biološkega vidika, da smo lahko ocenili celotno stanje, v katerem se ta jezera nahajajo. V tem prispevku je obravnavan samo kemijski del. Kvaliteta vode v odmaknjenem Jezeru v Ledvicah je dobra, medtem ko je v Krnskem jezeru in še posebno v Jezeru na Planini pri Jezeru, ki se nahajata blizu planinskih koč, slabša.