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# Some preliminary investigations of water quality parameters in a Hungarian thermal lake, Hévíz

# A Hévízi-tó vízminőségi paramétereinek előzetes eredményei

Szabina SIMON (✉), Brigitta SIMON, Gábor SOÓS, Tamás KUCSERKA, Angéla ANDA

Department of Meteorology and Water Management, Georgikon Campus, Szent István University, Keszthely 8360, Hungary

✉ Corresponding author: simonszabina95@gmail.com

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## ABSTRACT

Recently, there were only a few investigations published related to thermal waters in all over the world. In this study, an assessment on lake water quality was carried out in Lake Hévíz and its effluent, to provide valuable information about the present lake water quality in the winter season. In Hévíz, the thermal lake has an economic, geological and medical significance, and plays an important role in the tourism industry. Monitoring the quality of water resources - where thermal waters are present - is of primary importance. The chemical composition of geothermal waters often differs markedly from surface waters. The direct drainage of used geothermal waters getting into freshwaters is usually not authorized, so the excess thermal water of Lake Hévíz dilutes in the outflow effluent. A principal component analysis (PCA) was applied to explore the surface water quality dataset. Three sampling points were chosen from the effluent characterized by different water temperatures. The study took place between 9$^{th}$ December, 2019 and 16th March, 2020. There were 9 sampling times to measure conductivity, pH, biological and chemical oxygen demand, total organic carbon, ammonium-, phosphate-, sulphate concentration at the same sampling time. The highest water quality values were determined in the third sampling point of the outflow effluent, where the water temperature was the lowest. Temperature is an important factor in the aquatic environment since it affects directly or indirectly the aquatic flora and fauna. This study is important in providing comprehensive information on water quality for decision makers in particular the thermal waters and valuable reference for international researchers.

**Keywords:** Lake Hévíz, Hévíz effluent, water quality, principal component analysis (PCA)

## ÖSSZEFOGLALÓ

A közelmúltban alig végeztek néhány vizsgálatot a termálvizekkel kapcsolatban világszerte. Jelen kutatásban a Hévízi-tó vízminőségének felmérését végeztük el, ami értékes információkat nyújthat a tó jelenlegi vízminőségéről a téli szezonban. A hévízi termálfürdő gazdasági, geológiai és orvosi jelentőséggel bír, valamint fontos szerepet játszik az idegenforgalmi ágazatban. A termálvízzel rendelkező vízkészletek minőségének ellenőrzése elsődleges fontosságú. A geotermikus vizek kémiai összetétele gyakran jelentősen eltér a felszíni vizektől. Az elhasznált geotermikus vizek édesvizekbe történő közvetlen vízelvezetése nem szabályozott, így a Hévízi-tó felesleges termálvize egy kifolyóba áramlik. A felszíni vízminőség értékek vizsgálata céljából PCA-t (fő komponens analízist) alkalmaztunk. A kifolyón három különböző hőmérsékletű mintavételi helyet választottunk ki. A vizsgálatra 2019. december 9. és 2020. március 16. között került sor. A vezetőképesség, a pH, a KOIp, a BOI5, a TOC, az ammónium-, foszfát- és szulfátkoncentráció mérésére 9 egyidejű mintavételi időpontot jelöltünk ki. A legmagasabb értékeket a kifolyó 3-as mintavételi pontjánál mértük, ahol a víz hőmérséklete a legalacsonyabb volt. A hőmérséklet fontos tényező a vízi környezetben, mivel közvetlenül vagy közvetve hat a vízi növény- és állatvilágra. Jelen kutatás fontossága, hogy átfogó tájékoztatást nyújt a vízminőségről a termálvizekkel kapcsolatos döntéshozók számára, valamint nemzetközi kutatások esetében összehasonlítás alapját képezheti.

**Kulcsszavak:** Hévízi-tó, Hévízi-kifolyó, vízminőség, PCA (fő komponens analízis)

## INTRODUCTION

Water is the prime natural resource, which is the prime constituent of the ecosystem. Sources of water may be mainly in the form of lakes, rivers, rainwater, ground- and underground water. Besides the use of water for drinking, water resources play a highly important role in several sectors of economy such as agriculture, forestry and industrial activities. A decrease in water quality and availability are mainly caused by some important factors like increasing population, industrialization, urbanization, etc. It is very important to gain access to reliable information on natural and anthropogenic factors, which are the most determining factors for quality parameters as long as water resource conservation and management planning are affected from the local to the global scale (Hamid et al., 2020).

Water quality is commonly determined by measuring the following parameters: water temperature ($T_w$), pH, conductivity, biological and chemical oxygen demand ($BOD_5$, $COD_p$), total organic carbon (TOC) and ion concentrations [ammonium ($NH_4^+$), phosphate ($PO_4^{3-}$), sulphate ($SO_4^{2-}$)].

$T_w$ is a critical component of aquatic ecosystems. It affects the chemical processes occurring in waters, and more directly for aquatic biota it impacts abundance, distribution, vitality, growth, survival and phenological indices.

$T_w$ is in a very close correlation with the local air temperature (Ficklin et al., 2012, Yearsly, 2012). This means, that the higher solar radiation increases in $T_w$s (Morrison et al., 2002).

The impact of $T_w$ on abundance is well studied. $T_w$ is a main phenological indicator for aquatic species, for example fish. Ebersole et al. (2001) observed an inverse correlation between mean ambient maximum $T_w$ and abundance of rainbow trout.

Water quality indicators are usually more closely monitored in the period between spring and autumn (Hatvani et al., 2020) as $T_w$ is high at this time of the year in case of non-thermal waters. However, the water of Lake Hévíz and its effluent are also of higher temperature in the winter period, so the water quality should be varied in the non-thermal water during this time of the year. As Hévíz effluent flows into Keszthely-Bay of Lake Balaton, it directly affects the water quality of the bay. Even minor changes can influence the water quality of Lake Balaton, thus taking into account every factor which could affect on the lake's water quality should be of high priority.

## MATERIALS AND METHODS

### *Study sites*

Four sampling points were designated, one of them in the Lake Hévíz, and three points in the connected effluent (Figure 1):

- Lake Hévíz (LH): N 46.787° E 17.194°,
- Hévíz effluent 1 (He1): N 46.784° E 17.194°,
- Hévíz effluent 2 (He2): N 46.782° E 17.198°,
- Hévíz effluent 3 (He3): N 46.761° E 17.205°.

Lake Hévíz is the deepest thermal lake in Europe, which contains volcanic and marsh components and has a very rich microbial community (Krett and Palatinszky, 2009). The water of the lake comes from two crater springs, which have different temperatures (26 °C and 41 °C). The $T_w$ never falls below 22 °C in the lake (annual mean $T_w$ : 30.7 °C). The temperature of the lake is evenly distributed due to the vapor layer ("mist") covering the water surface. The oligotrophic water of the lake is poor in nutrients mainly in forms of nitrogen, but rich in sulphur compounds and can be characterized as calcium–magnesium–hydro carbonate type (Krett et al., 2013). The average summer and winter temperatures are 33-35 °C and 24-28 °C, respectively.

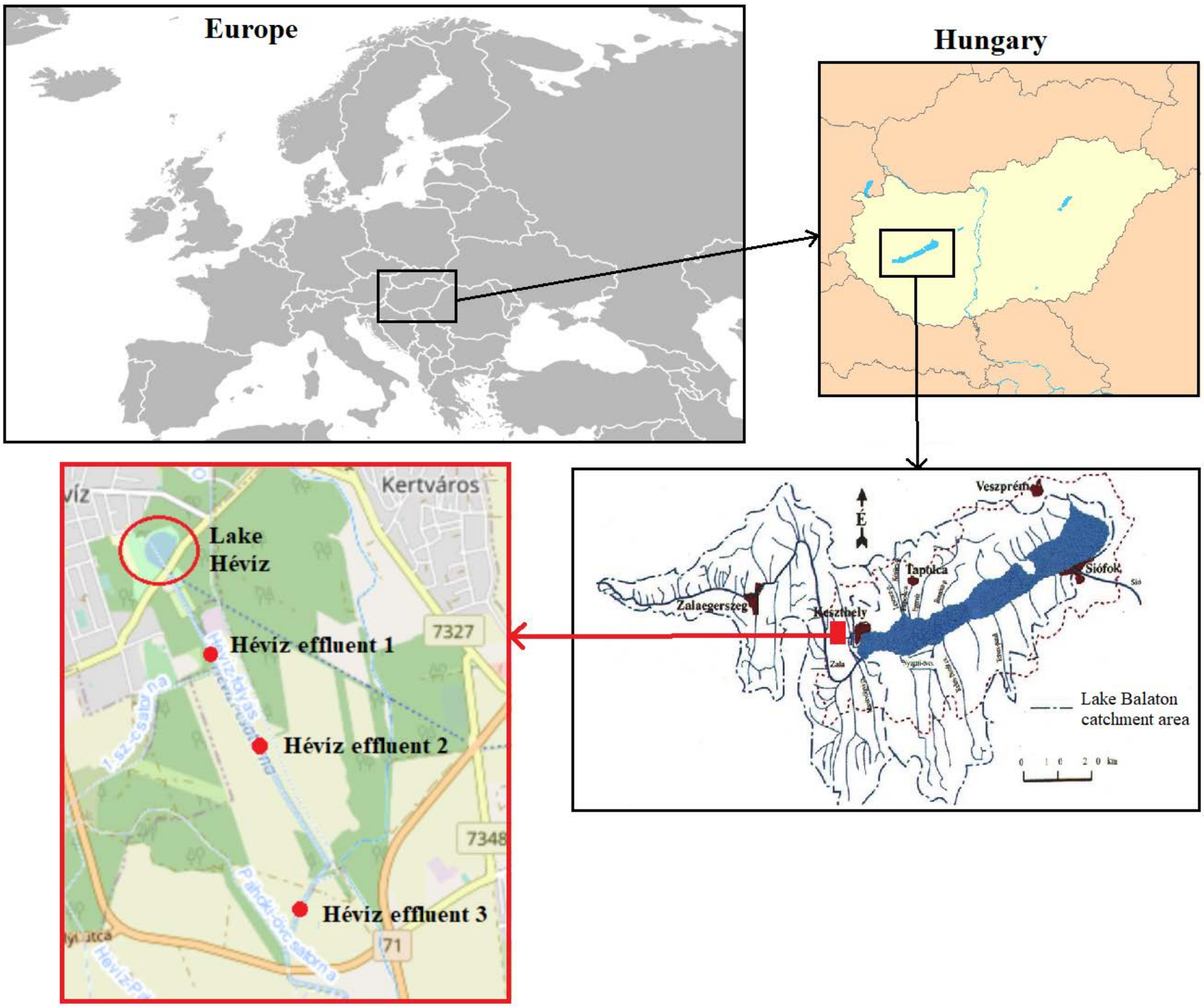


**Figure 1.** The location of the study sites

Dominant minerals in the water are $Ca^{2+}$, $Mg^{2+}$, $HCO_3^-$, S, Ra and also organic compounds (Varga et al., 2013). The vegetation of the lake consists of water lily species, the common surrounding trees are *Salix* and *Taxodium*. The lake has a special microbial community.

Lake Hévíz covers a relatively small area of 47 500 m$^2$. The water supply of Lake Hévíz is abundant (more than 500 L/s). The lake is completely replenished every third day. The balanced $T_w$ is the result of mist forming over the surface of the lake, which acts as a cover, keeping heat at the lake surface. The lake is fed by two thermal springs in an underwater cave. The warmer one has a temperature of 40 °C. Its flow rate is about 450 L/s. The cooler spring has a temperature 26.3 °C. Its flow rate is 60 L/s. The water of the two springs merge in the cave and gets into the lake. The chemical composition of the lake's water is slightly radioactive and contains reduced sulphuric compounds, as well as oxygen in solution (Rybach and Muffler, 1981).

***Sample collection and measurements of the physical and chemical parameters***

Water samples were taken from 9 December 2019 on the 1$^{st}$, 2$^{nd}$, 3$^{rd}$, 5$^{th}$, 7$^{th}$, 21$^{th}$, 42$^{nd}$, 70$^{th}$ and 98$^{th}$ days after starting the observation. The sample taking finished on 16 March, 2020.

$T_w$ was continuously registered *in situ* with a HOBO UA-002-64 data logger. Conductivity and pH were measured *in situ*, using Adwa AD111 and AD310 field equipment. $NH_4^+$, $PO_4^{3-}$ and $SO_4^{2-}$ were determined in the laboratory, using a Lovibond MultiDirect (type 0913462) spectrophotometer. Dissolved oxygen, biological oxygen demand ($BOD_5$), chemical oxygen demand ($COD_p$) and total organic carbon (TOC) were measured after the procedure of the following standards: MSZ ISO 5813, MSZ EN 1899-1:2000, ISO 15705 and MSZ EN ISO 5667-3-1998, respectively.

### *Statistical analysis*

Student's t-test was used to evaluate the difference in the parameters averages between samples of different sampling points. The resulted probabilities (p-values) from sample data occurred by chance are indicated.

PCA (Principal Component Analysis) is one of the most common multivariate statistical techniques to determine linear relationships (Simeonov et al., 2003). PCA is a dimensionality reduction technique helping to simplify the data and making it easier to visualize by defining a set of principal components (Joliffe, 2002, Yídana et al., 2008). Principal components (PCs) are orthogonal variables calculated by multiplying the original correlated variables with a list of coefficients, which can be described as

$$z_{ij}=a_{i1}x_{1j}+a_{i2}x_{2j}+...+a_{im}x_{mj} \quad (1)$$

where z represents the component score, a represents the component loading, x represents the measured value of the variable, i represents the component number, j represents the sample number, and m represents the total number of variables (Duan et al., 2016).

In this study, PCA scores of all 9 water quality parameters were used as independent variables in multiple linear regression analysis.

PCA analysis was conducted in R (R Core Team, 2020) and the biplot plot (Gabriel, 1971) was produced using the package ggbiplot based on ggplot2 (Wickham, 2009).

## RESULTS AND DISCUSSION

The $T_w$s of the four sampling points during the investigated period are presented in Figure 2.

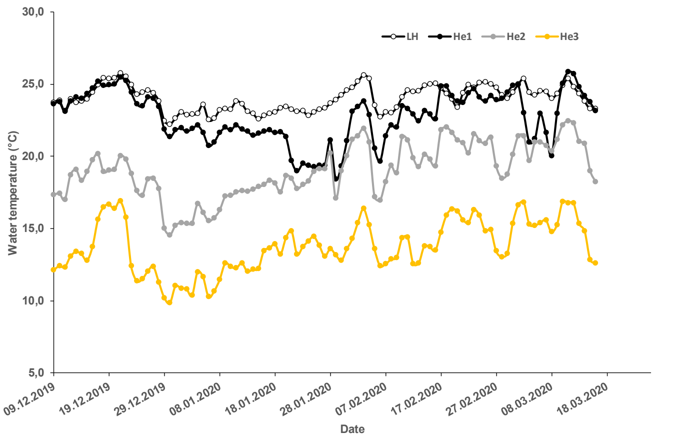


**Figure 2.** The water temperature values of the four sampling points in the studied period (Lake Hévíz - LH, Hévíz effluent 1 - He1, Hévíz effluent 2 - He2, Hévíz effluent 3 - He3)

The daily average of the $T_w$ varied in 22.2 °C and 25.7 °C between the sampling points. The $T_w$s measured from He1 to He3 are gradually decreasing. Except for LH and He1 (p=0.566), $T_w$ of every sampling points differed significantly (P<0.001). On account of the distance from the lake, the $T_w$ of the effluent continuously decreased. The temperature was lower by 22.0% between He1 and He2 and by 29.5% between He2 and He3. Between the warmest (Lake Hévíz) and coldest (Hévíz effluent 3) measuring points a temperature difference of 10.8 °C was observed.

The conductivity, pH, $COD_p$, $BOD_5$, TOC, $NH_4^+$-, $PO_4^{3-}$-, $SO_4^{2-}$ concentration values of the four sampling points are presented in Figure 3.

Conductivity in natural water bodies is affected primarily by the geology of the area through which the water flows (Bhateria and Jain, 2016). Conductivity shows a significant correlation with many parameters, such as chloride, phosphate and nitrate, resulting a raise in conductivity and oil presence decreasing the conductivity (Gupta and Paul, 2010, Bhateria and Jain, 2016).

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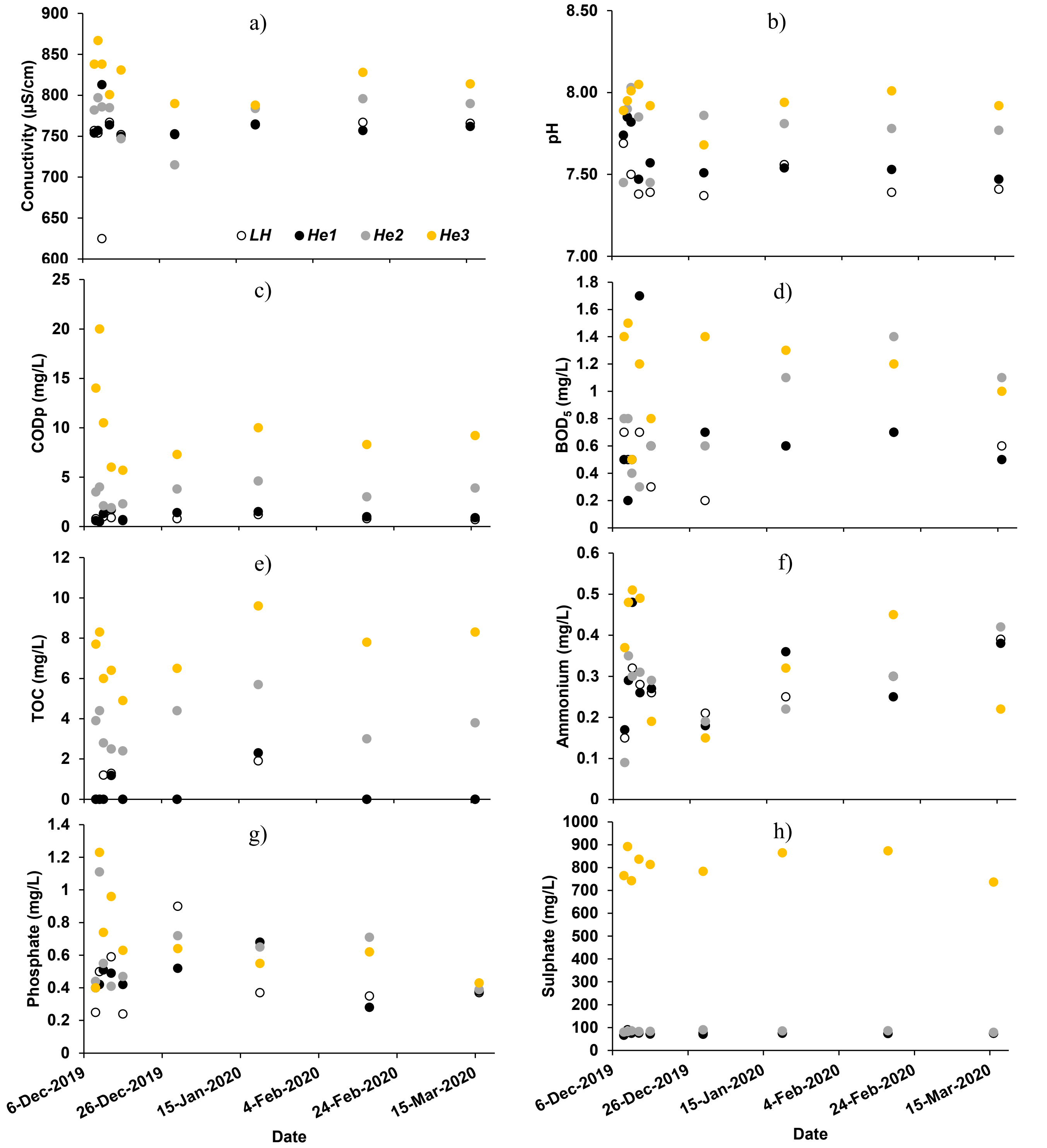


**Figure 3.** The a) conductivity, b) pH, c) $COD_p$, d) $BOD_5$, e) TOC, f) ammonium-, g) phosphate-, h) sulphate concentration values of the four sampling points in the studied period

As given in Figure 3 (a), conductivity in the water samples ranged from 715 to 867 µS/cm. Conductivity of He3 and the other sampling points, moreover HL and He2 also differed significantly ($P<0.001$) in the investigated period. In general, the average values did not differ significantly corresponding to similar values measured in the Carpathian Basin (Krutilla and Logan, 2009).

The pH can affect the ability of trace metals and minerals to dissolve (Sungsitthisawad and Pitaksanura, 2013), which property is of paramount importance for thermal waters. The pH of different sampling sites of the study varied significantly ($P<0.001$). The pH (Figure 3 b) of the study sites occurred in the range of 7.37–8.05, indicating slightly alkaline nature of the water quality. The higher pH tends to have negative impacts on skin and eyes (Rao and Rao, 2010).

The nitrogen is a key factor in aquatic environments (Carpenter, 2008). There were no significant differences between the sampling points regarding ammonium ($NH_4^+$) (Figure 3 f). Nitrate ($NO_3^-$) was under the measuring range of the instrument during the study period. Nitrification and denitrification may significantly influence the $NH_4^+$ and $NO_3^-$ concentration ratio. In the surface layers, where nitrification can take place, there is an accumulation of nitrate (Noori et al., 2018). Garnier et al. (2000) and David et al. (2006) reported about the importance of denitrification on nitrate removal. However, the other water quality characteristics such as $T_w$, pH and total suspended solids also affect the concentration of $NH_4^+$ and $NO_3^-$ in water bodies (Kim et al., 2006).

The phosphorus is quite rare element. In nature, phosphorus is usually present as part of a phosphate molecule ($PO_4^{3-}$). In aquatic systems phosphorus occurs as organic phosphate and inorganic phosphate (Spellman, 2014). The phosphorus plays an important role in the overall nutrient dynamics of surface waters (Bloesch, 1995). In case of $PO_4^{3-}$ (Figure 3 g) He3 differed significantly from LH ($p=0.049$) and He1 ($p=0.026$).

The concentration of $SO_4^{2-}$ in He3 (Figure 3 h) was about ten times higher in the studied period, than in the other sampling points. Except of HL and He1 ($p=0.4726$), there were significant differences in $SO_4^{2-}$ contents ($P<0.001$) between all sampling points. After the winter experiment (in the summer period) an additional sampling was made and the $SO_4^{2-}$ concentration of He3 point in the effluent water was measured. At this time the mentioned ion content of the water (73.2 mg/L) did not differ significantly from the previously measured data. Many $SO_4^{2-}$ compounds are readily soluble in water. $SO_4^{2-}$ ions can usually be found in natural waters. In the weathering process, gypsum (calcium sulphate) is dissolved and sulphide minerals are partially oxidized, giving rise to a soluble form of $SO_4^{2-}$ which is then carried away by water. In a humid environment, $SO_4^{2-}$ is readily leached from the zone of weathering by infiltrating waters and surface run off but in semiarid and arid regions the soluble salts may pile up within a few tens of feet of land surface (APHA, 2005). Land use activities have a prominent effect on the physicochemical properties of water bodies. The extremely high level of $SO_4^{2-}$ at He3 may be attributable to the inflow of fertilizers ($NH_4^+$- $SO_4^{2-}$ or gypsum) from the surrounding agricultural areas.

$COD_p$ is defined as the amount of oxygen required for chemical oxidation with the sample under controlled conditions. Furthermore, $BOD_5$ is a measure of oxygen consumed by microorganisms under specific conditions (APHA, 2012). Actually, $COD_p$ and $BOD_5$ are indicators representing organic contamination (Li et al. 2016, Ravikumar et al. 2013, Wu et al., 2017). $COD_p$ (Figure 3 c) and TOC (Figure 3 e) were much higher in He3, than at the other three points. $COD_p$ of the water samples was detected in the range from <15 to <80 mg/L and $BOD_5$ (Figure 3 d) ranges from <3 to <6 mg/L (10/2010 (VIII. 18.) VM decree). All sampling points differed significantly regarding $COD_p$ ($P<0.001$) and TOC ($P<0.001$), except for HL and He1 ($COD_p$ $p=0.1264$, TOC $p=0.7867$).

Waters with $BOD_5$ of less than 1 mg/L can be subjected to minimum human impact and are primary candidates for conservation (Magara, 2002). If $BOD_5$ exceeds 3 mg/L, it affects coagulation and rapid sand-filtration processes in conventional water treatment plants, requiring expensive advanced water treatment (Magara, 2002).

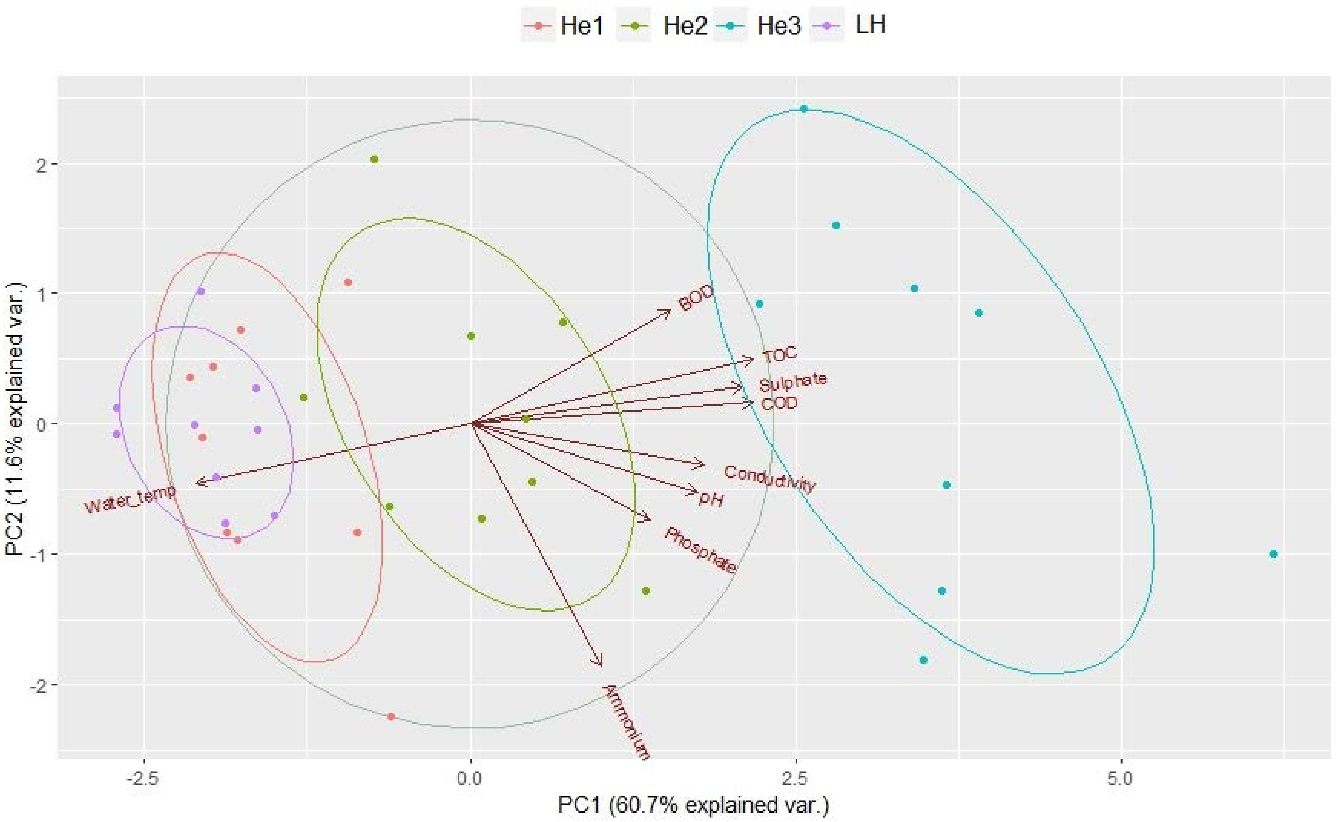


**Figure 4.** PCA biplot displaying the first two axes with water quality variables and sample sites (Lake Hévíz - LH, Hévíz effluent 1 - He1, Hévíz effluent 2 – He2, Hévíz effluent 3 - He3)

Therefore, BOD5 standards are set at 2 and 3 mg/L, respectively, for Class I and II waters (Magara, 2002). BOD5 varied from 0.2 to 1.7 mg/L in the investigated period. He3 differed significantly (P<0.001) from all of the other points.

The PCA biplot (Figure 4) shows that the eigenvalues of the two first principal components represent up to 72.3% of the total variance (PC1 60.7%, PC2 11.6%) of the observations. The PCA plot shows the four clusters of samples based on their similarity, which is the sampling place. The loading plot shows how strongly each characteristic influences a principal component. The projected values on each PC show how much influence they have on that PC. Many factors contribute to PC1, including $T_w$, $BOD_5$, TOC, $SO_4^{2-}$, $COD_p$, Conductivity, pH and $PO_4^{3-}$. The only factor accounting for PC2 is $NH_4^+$.

The $T_w$ shows the highest variance. The angle between TOC, $SO_4^{2-}$ and $COD_p$ is small, so they are strongly associated. There is also a strong relationship between conductivity and pH. There is a weak relationship between $BOD_5$ and $NH_4^+$. The correlation between $T_w$ and each of the other variables is negative.

The projection of LH onto the vector for variable of $T_w$ falls on the positive direction of the variable vector, which means that values in LH had higher than average values for the $T_w$. He2 and He3 onto variable $T_w$ falls on the opposite direction, therefore, the average value for them is less than the mean $T_w$. He2 and He3 are positive to other variable vectors, so those representing an increased value in both clusters.

## CONCLUSION

The present study reflects the chemical and physical quality in the surface waters of the Lake Hévíz and its effluent in the winter season. The quality of the lake water is influenced by intense human activities (tourism). All water quality parameters of the Lake Hévíz and effluent water samples fell within the limits of recommendations by the national standards of Hungary (10/2010. (VIII. 18.) VM decree). The results obtained on all the physical-chemical parameters of surface water of the Lake Hévíz and its effluent revealed that the quality of the water is "excellent" following the standards of EU Water Framework Directive (2000/60/EC) during the winter time.

The PCA analysis showed that the $T_w$ negatively correlated to physico-chemical variables, because of the lower the $T_w$ is, the more intense the appearance of soluble oxygen form. The reason of low correlation of $NH_4^+$ to the other parameters could be the presence of other nitrogen forms produced by the widely variable microbiological communities in the effluent.

Hamid et al. (2020) found that local determinants significantly contribute to the spatiotemporal variation of water quality. Natural determinants relating to geology, atmospheric deposition associated with precipitation, weather processes and anthropogenic inputs regarding urban, industrial and agricultural activities were determined as potential factors to induce spatiotemporal variations in water quality. Anthropogenic activities and catchment characteristics drive spatial variability in water quality parameters. In case of He3 there was an increase in $SO_4^{2-}$ concentration probably due to a temporary artificial fertilizer depot. This minor change in the environment of the effluent impacted the water quality. The agriculture is a significant factor in threatening the quality of surface waters, mainly on such a protected area as the Lake Hévíz.

This preliminary-study on the assessment of water quality of the Lake Hévíz can be a good reference for further studies on the thermal waters in Hungary.

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