UNIVERSITY OF SZEGED

EARTH SCIENCES DOCTORAL SCHOOL

Summary of Ph. D. thesis

Water quality assessment of the lakes on the Gömör-Torna Karst with particular regard on the nutrient load

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2011

1. INTRODUCTION, AIMS AND BACKGROUND

Research focusing on the recent processes of karst areas is still current and of particular importance. Such research is justified by the changes in the state of karst environment and its sensitivity; the latter is due to special karst features such as the special wildlife, hydrological system, morphological elements and their sensitivity. In karst areas, water quality is a cardinal issue, as it is a link between the elements of the karst system. Its use varies on a very wide range, however its usage as drinking water is the most significant. Nowadays, however, preserving the quality of our waters has become an increasing challenging task. With the contamination of waters usage possibilities are also reduced. However, the growing population and limited supplies require the preservation of the available resources in their original state.

In the Gömör-Torna Karst some relatively small lakes occur. Nowadays many of them are in a very advanced trophic stadium. In the last decades the filling up of the lakes has accelerated as a result of intensified human impact. The more and more frequent weather extremes have been accompanied by a change in the water balance. Inadequate water management, tillage practices, fertilizer use and grazing resulted in further adverse effects.

The presence of karstic lakes is an interesting and valuable hydrological and geomorphological phenomenon; because of their unique formation, biotic environment and fragile ecosystem they would deserve more protection and care. Former research has shown human-induced accelerated filling up processes and water quality deterioration. However, the prevention of adverse effects has rarely been effective.

The study objectives were as follows: a historical overview of the lakes in the Gömör-Torna Karst, an assessment of the changes in their state which took place as a result of human intervention, treatment, and natural influences; a comparison of the lakes and their surroundings and also with former conditions and state; baseline survey of the water quality of the lakes and connected springs in the frames of a monitoring programme between 2008-2010; an analysis of the impact of land use and climate phenomena on the water quality and quantity; the determination of eutrophication inducing factors; an evaluation of the degree of the external and internal load on the basis of lake sediments and soil samples.

2. THE STUDY AREA

The Gömör-Torna karst can be listed as ‘low mountain hills’; it is a part of the NW ridge of the inner part of the Carpathians. It is located in NE Hungary and SE Slovakia. Nowadays the official name of the Hungarian part is Aggtelek Karst, while the Slovak part is named Slovak Karst. It represents a geologically and geographically uniform karst plateau. It can be listed as one of the best-developed karst plateaus of Central Europe. It is bordered in the west by the Revúca-mountains and the Rimava basin, in the north by the Rožňava basin and the Volovec mountains, in the east by the Košice basin, while in the south by the Putnoki hills and the Bódva valley. Most of the surface is typical middle-mountain karst covered by thin soil, characterized by a lot of limestone outcrops. The climate is humid continental, with annual precipitation sums of 600-800 mm, with long summers and cold winters. The Gömör-Torna karst is built of blocks of chalk which were slipped in the middle Cretaceous. These different Triassic limestones are of a thickness exceeding 100 m, while Werfen sandstone and clay is located below them. The Triassic limestones of the area have good water-conducting properties; the dissolving residue is below 1%. There are numerous streams fed by karst springs, of which several are used as drinking water sources for the local villages. In the area several small water bodies also occur, which were formed in old clogged sinkholes. Of the studied lakes Lake Papverme (Farárova jama) is situated on the Silica plateau, in Slovakia, and the associated hydrologic system consists of the Gyökérréti (Jašteričie) wells (NE of the village Silica) and the Spring Fekete (Čierna) (Gombasek, Slovakia), which were also included in the examinations. The Lakes Aggteleki, Kender and Vörös are situated in the vicinity of Aggtelek village, while Lake Tengerszem is located next to the exit of Baradla cave near Jósvafő village. The Jósva spring, flowing into the Lake Tengerszem, and the Jósva stream, which is flowing out from the lake, were also included in the study.

3. METHODS

3. 1. Historical analysis

The lakes' history and the various land use examinations were based on various maps (I., II., III. Military mapping of the Austro-Hungarian Monarchy, map of Imre Vass (1829), Google Earth). Besides the summary of the related articles I also evaluated archive materials from the Aggtelek and Slovak National Parks adding also information received from local people and experts.

3. 2. Sampling methods

The water sampling was performed monthly between 2008 and 2010, except in the winter months. The water sampling points were fixed according to the points of the compass in the vicinity of the coast – in 2 or 4 directions, depending on the size of the lake – and at any existing inflows. Sediment sampling was carried out once in a year. The sampling points were fixed as far as possible near the water sampling points. I took mixed surface samples. Soil sampling was carried out in 2008, by the same principles as sediment sampling.

3. 3. The water quality assessment

The evaluation of the water quality was carried out according to the operative Hungarian standard MSZ 12749:1993. The ecological status of the water was also assessed.

3. 4. Field and laboratory studies

The field and laboratory measurements were carried out according to the Hungarian standards. The following parameters were included in the investigations: in the case of water: dissolved oxygen, oxygen saturation, chemical oxygen demand, NO_3^-, NO_2^-, PO_4^{3-}, total phosphorus, NH_4^+, a-chlorophyll, pH, Ca^{2+}, Mg^{2+}, K^+, Na^+, Fe, Mn, HCO_3^-, CO_3^{2-}, Cl^-, SO_4^{2-}, conductivity, air and water temperature, transparency, turbidity, depth, air pressure, hardness, alkalinity. In the case of the sediment: P, N, dry matter content, pH, total salinity, heavy metals (total and mobile), and organic matter content. In the case of the soils: P, N, heavy metals.

3. 5. Statistical analysis and climatological studies

For the statistical tests PASW Statistics 18 and MATLAB 7. 5. 0. softwares were used. The impact of dry and wet periods on water quality were examined with drought indices like SPI (Standard Precipitation Index), Lang's Rainfall Index, the De Martonne's Index of Aridity and Thornthwaite's Agrometeorological Index.

4. RESULTS

4. 1. Historical analysis

4. 1. 1. The first descriptions of the lakes in the Gömör-Torna Karst were recorded from the late 1700s in various written sources from different aspects of use and function. *Their main functions at first were the support of different human activities* (depending also from other characteristics of the area): metallurgy, hemp-soaking (Lake Kender), fishing (Lakes Gyökérréti-, Papverme), watering of animals (typical usage of most of the lakes), *later a morphological specialty and landscape value* (as rare and unique forms) while *the current focuses are tourism and recreation, the maintenance of the integrity of the ecosystem, the conservation of biodiversity and the karst system. Although in different eras different functions have predominated, the lakes have always played an important role in the area.*

4. 1. 2. *In the same places, adapting to the local and global conditions or sudden changes lakes had disappeared, and though less frequently, also re-established* (possible reasons are e.g. the opening of the obstructed bottom or climate cycles). However *the influence of human activities on faster eutrophication processes can not be disputed* (*Samu, Keveiné 2008*).

4. 1. 3. Besides different water usage in the case of the different lakes, the land use characteristics (highways, agriculture, village, forest) also vary. In some cases, a more extensive (underground) catchment area affects the water quality uniquely. As a consequence their development and processes are fairly different. *In response to the variety of different human impacts the natural processes are shortened and drastically change*d (eg. Lake Gyökérréti, Lake Aggteleki). *The state of Lake Vörös could be stabilized with rehabilitation works but in the case of Lake Aggteleki its continued existence and quality is doubtful due to the improper execution of the dredging.*

4. 1. 4. *The preservation of the water quality of Lake Papverme is an important task since it is part of the largest hydrological systems of the Silica karst plateau in which the permanent contamination may have adverse effects on the underground formations and wildlife.*

4. 2. The water quality assessment

4. 2. 1. *The overall water quality of Lake Papverme moves in all three years on average between the water quality classes III. and V. Oxygen saturation (high chlorophyll concentrations, high levels of organic matter production), chemical oxygen demand (larger organic matter content), ammonium concentration (continuous fresh organic matter load), pH (slightly alkaline, especially in the vegetation season) and iron content play an important role in this process*. Other parameters such as *nitrite, total phosphorus and chlorophyll-a concentrations also contribute to the deterioration of the water quality*. *The oxygen conditions and nutrient concentrations suggest external loads. The water quality is variable, according to the above-mentioned criteria in early spring and late autumn it improves, but then the nitrate load increases due to the rainy weather. The inflow from the direction of the agricultural settlement and the village proved to be a significant pollution source in the whole measurement period, which certainly contributes to the deterioration of the water quality and endangers the cave systems connected to the lake*. However *the pollution stress has been lately reduced, which manifests also in Spring*

Fekete primarily in the nitrate and ammonium content (indicating that "supplies" come also from other sources), *which are considerably lower than in 1982 (e.g. from the direction of the Wells Gyökérréti nitrate comes in lower concentrations)* (*Samu, Keveiné 2010*).

The total phosphorus and orthophosphate concentrations are lower than before but the chlorophyll-a values are higher. The nitrate content is similar as in 1982 – in the Fekete spring it has been reduced, but it is still higher than the lake levels. The increased algae-amount reflect the annual oxygen saturation data (oversaturation during the day) and oxygen profiles in April (unstable oxygen conditions reflected) as well. The alkalinity and total hardness decreased since 1982 and it is similar to the values measured in 1992. For the pH is characteristic a slightly alkaline range. Especially during the summer season a higher proportion of toxic ammonia was typical, which at times reached certain levels already toxic to fish. The water quality of Spring Fekete in 2010 was at least one to two grades higher than the lake's water quality, but overall it moved between the middle (III.) and polluted (IV.) classes.

4. 2. 2. *The water quality of Lake Vörös is in all three years mainly in the polluted (IV.) and the heavily polluted category (V)*. This is mainly *a result of the high iron content of geological origin, and the total phosphorus content*. *If we don't take the iron-content into account, the overall water quality is generally tolerable due to the values of the chemical oxygen demand, chlorophyll-a concentration, and also the oxygen saturation*.

4. 2. 3. *The water quality of Lake Kender is mainly contaminated (IV.) or highly contaminated (V.). The iron content is permanently high here too, which is just a consequence of the geological environment, so it can't be considered as pollution. Sometimes manganese levels were also higher. The internal load of the lake is high (large total phosphorus concentrations, chemical oxygen demand) but for 2010 it improved in spite of the oxygen saturation, which deteriorated.*

4. 2. 4. *The overall water quality of Lake Aggteleki is in the heavily polluted category in all three years, except the early spring period; nearly*

all parameters are in this category. The high orthophosphate and manganese content is a proof for the diffuse pollution coming from the lake's environment and the village. The lake's water quality did not improve even in the unusually wet year of 2010, since more pollution was washed down. The fate of the lake seems doubtful even after the dredging. An exception were the oxygen balance parameters in a short period from the autumn of 2009 until the summer of 2010 and the dissolved oxygen, the nitrate / nitrite content, the ammonium concentration, the conductivity and the iron content from the spring of 2010. *The lake clearly has the worst water quality of all the examined lakes and there was no sign of improvement in the examination period* (*Samu, Keveiné 2009, 2010*).

4. 2. 5. *The water quality of Lake Tengerszem falls into the tolerable (III.) category especially due to the nitrate amount present almost during the whole year. Sometimes the contaminated (IV.) class is reached, due to the higher nitrate loads collected through the Jósva spring from the catchment area of the Baradla cave, especially in the spring and autumn periods. In 2010 orthophosphate and total phosphorus were also present in higher amounts.* The ammonium concentration permanently fell into the II. (good) category in 2009, whereas the same is true to the conductivity in both years. *The values of the Jósva spring and Jósva stream did not differ significantly from those measured in the lake.*

4. 2. 6. *Lake Papverme has the worst trophic state according to the chlorophyll-a amount – probably because of the lack of macro-vegetation (except for the coastal part), which could discourage algae growth. Thus, this lake is mostly eutrophic and polytrophic, whereas Lake Aggteleki is meso-eutrophic and the Lakes Kender and Vörös are mezotrophic. Lake Tengerszem can be considered ultra-oligotrophic. The saprobity state of the first four mentioned lakes is similar: they are in all three years of the alpha-mezosaprobic type, while the Springs Jósva and Fekete, the Stream Jósva and the Lake Tengerszem are oligosaprobic. In 2010 a deteriorating trend is clearly shown so the organic load seems to have increased with the larger amount of precipitation. The halobity-degree of the Lakes Vörös and Kender is in average beta-oligohalobic, the Lakes Papverme and*

Tengerszem are alpha-oligohalobic and Lake Aggteleki is changing from oligo-mesohalobic in 2008 to alpha-oligohalobic in 2010 as a result of being diluted due to the precipitation.

4. 3. The connection of the climate and water quality

4. 3. 1. *The amount of precipitation decreased after 1980 compared to the previous years, and according to the SPI drought index the number of drought periods was also higher than the number of wet periods.*

According to the Lang Index the amount of summer rainfall increased in the late 1980s, and since then it shows a relatively permanent cyclicity. In the case of spring and autumn precipitation almost all the extremes and outliers disappeared from the beginning of the 2000's .

The DeMartonne Index shows that outliers still appear in winter; dry periods, together with the decrease of wet periods, are typical only in the 1990s. 2010 is characterized by extreme values again. In terms of the summer season there are more drought periods from the 2000's. Outliers can only be observed in the late 1980s, no extremes occurred in this season in the presented period. Despite 2010 being a very wet year there was a drought in summer. In case of the autumn season wet extremes occurred until the 2000's but not after whereas the proportion of drought periods increased. In 2010, however, a wetter autumn came again. The springs were similar.

4. 3. 2. *A strong, significant correlation was found between the water quality parameters and the different drought indices, which, depending on the lake's state and position, affect them in different ways. Where the inflow is more significant or the catchment area is larger, with more rainfall events the concentration of especially the inorganic components will be higher (eg.* NO_3^-*), while the organic pollution is going to be diluted (eg. KOIps,* NH_4^+*), the trophy and saprobity degree is lower (Lakes Aggteleki, Kender, Vörös).*

Most of the correlations occurred with medium duration SPI indices (6-12 months), these events affect the processes of all lakes, so *this is a very significant period length for these water bodies (eg. KOIps,* NO_2^-*,*

NH_4^+, Ca^{2+}, hardness, transparency) but in the case of Lake Aggteleki almost all major changes in ion concentration are related to this period. Especially the values of Lake Tengerszem are correlated with the shorter-term indices; this lake has the most constant inflow. The amount of Cl^- behaves very conservatively, except in the case of Lake Papverme; by all the other lakes it was correlated with the 25-month SPI, changes in its amount are very slow.

There were some parameters which were correlated only with the drought indices that include the temperature too, these are the dissolved oxygen, oxygen saturation (this is a result of the temperature dependence of these parameters). *There were some parameters that correlated only with the SPI (thus the shorter or longer term rainfall conditions), these include: PO_4^{3-}, Mn, transparency, hardness, K^+, HCO_3^-, chlorophyll-a. The other parameters showed connections in both cases.* Therefore *temperature changes have a greater impact on the first group of variables, while the second group was equally affected by the rainfall amount and temperature, and on the third group rainfall has greater influence.*

Since most water chemistry parameters are affected by extreme weather events, their increasing frequency could cause sudden extreme changes in water quality and quantity, which in the case of these shallow and unstable lakes may trigger irreversible changes. (*Samu, Bárány-Kevei 2010b*).

4. 3. 3. *Based on a larger scale perspective, both positive and negative extreme values of water quality parameters can be associated with weak or breaking-up warm fronts passing over the region. On the contrary, the role of anticyclones or anticyclone ridge weather situations is supposed to be irrelevant. According to the average ranks of importance of the meteorological variables in determining the factors temperature and relative humidity are the most significant, while air pressure and global solar flux are the least relevant explanatory variables in determining the five factors overall.*

The application of the two-stage factor analysis involves both benefits and disadvantages. Its benefit is that it substantially reduces the *number of resultant variables. In this way, the information loss of the retained factors is around 20%.*

4. 4. Statistical evaluation of the similarities and differences characterizing the lakes

The heterogeneous geological environment of the catchment, the degree of the level of organic material and the nitrate load of the water have an important role in the differentiation of the lakes' profiles even within a small area. In addition, if only the averaged values are considered, orthophosphate, iron and manganese content play an important role as well. The reason is that from the results of the factor analysis in the first case the discriminant analysis identified *conductivity, nitrate and CODps as the strongest classification factors while in the second case nitrate, CODps, Fe and Mn, furthermore factors related to conductivity and ortophosphate proved to be the most important.*

The organic matter originating from different sources as well as the load of nitrate vary between water bodies, and in the efforts to prevent the groundwater and undersurface environment from pollution they should have high priority.

Typically, in both classifications *3 separate groups* were distinguished: *the first* consists of the *Wells Gyökérréti, the Spring Fekete, the Stream Jósva and Lake Tengerszem*, the second of the *Lakes Kender and Vörös*. The values of *Lakes Papverme and Aggteleki are often in the same (the third) group, but their values have bigger variance*.

Strong seasonality can be observed at the monthly level; seasonal trends and different characteristics in different years (climatic, pollution, etc.) play an important role (*Samu, Bárány-Kevei 2010*).

4. 5. Results of the lake sediment and soil investigation

4. 5. 1. *The tested soils have no heavy metal concentration values above the threshold limit. However in the case of sediments some concentrations are above the limits; in the case of the Lakes's Papverme, Vörös, Aggteleki,*

Gyökérréti sediment the Ni concentrations, in Lakes Vörös and Aggteleki the Cr-, and in the Lake Vörös, the Cd concentrations exceed the limit.

However, the mobility of these heavy metals was also tested using sequential extraction. The results show that *in most cases the heavy metals are not mobile under natural conditions*. The *highest rate of mobility was observed by the Lakes Gyökérréti, Kender and Aggteleki, and the most mobile metals are Cd, Co and Cr. From the mobile fractions of the mentioned three lakes and in the case of Lake Tengerszem the fraction binding to the oxidizable , fraction (thus the organic material) is greater and it is also greater in the case of the exchangeable and carbonate bound fractions. By the other two lakes the mobility of heavy metals is around 50% and this amount is divided between the three mobile fractions. Cr can be problematic, since it is relatively mobile and sometimes exceeds the background concentration*.

4. 5. 2. *Changes in the heavy metal content in sediments of Lake Aggteleki in comparison with year 2000: in 2002 the lake was dredged and the surrounding area was filled with the sludge. The nickel content of the silt has doubled compared to the year 2000, as well as the lead and chromium content - but these do not exceed the limit. The cadmium and zinc content decreased, the cobalt had roughly similar values. This may be due to the previously larger quantity of nickel, chromium and lead accumulation (from transport, atmospheric deposition* - there are factories within a 60 km zone like cement factory, U.S. Steel); this contamination dropped in the 1990's, and the layers from which samples were taken, were less loaded with these contaminants. The dredging, however, could resurface the previously polluted layer that I measured. In addition, since the dredging there might have been a greater amount of accumulation as well. It can be also *of natural origin due to the higher heavy metal content of the bedrock*.

4. 5. 3. The *organic matter of sediments* was measured and characterized with Rock Eval pyrolysis, and the following can be concluded: *In order the Lake Kender, the Lake Aggteleki, Lake Vörös, Lake Tengerszem and then the Lake Papverme have the highest organic matter content*. Since *the*

thermal maturity indicators of organic matter in sediments hardly differ from each other, a similar quality can be considered. I have got indicators which suggest that there is external inflow in the case of the Lakes Tengerszem and Papverme. In the case of Lake Tengerszem the Jósva spring brings supply, while by the Papverme it is the pollution inflow from the village and the highway-transport which delivers pollution.

In the Lakes Aggteleki, Kender and Vörös the indices indicated a higher rate of transformation of the initial phase of the incoming fresh plant material, and in all three cases, this represents a very significant amount. The organic matter of the sediment of the Lake Papverme is characterized by the higher presence of the inert fraction, originating from the carbonate bedrock.

The smaller proportion of the relative evolution of the organic macromolecules classes in Lake Aggteleki, and especially in Lake Vörös, is an indication of the effect of dredging because by these the layer containing more immature organic material was removed with the dredging.

4. 5. 4. *From the aspect of the P and N load it can be concluded that in the case of Lakes Papverme and Vörös the amount of soluble* PO_4^{3-} *content present in the soil is higher than the amount in the sediment and especially in the case of Lake Papverme it is in a strong correlation with concentrations found in the water ,so it can be concluded that in both cases the external load plays the major role in the eutrophication processes. Lake Papverme has a special situation as the* PO_4^{3-} *concentration in the wastewater inflow (sampling point P6) is higher than it is in the sediment and in the soil, which shows that there is clearly point-source pollution in this case.*

All the PO_4^{3-} *values at Lake Aggteleki are similar. This can be explained by the lake filling up its environment with its sediment, so it gets almost the same load from inside and outside. In the case of Lake Kender, the sediment's* PO_4^{3-} *concentration is higher, so in this case, the internal load is higher. The sediment of the Lake Gyökérréti is similar to the sediment of Lake Kender from this point of view, while Lake Tengerszem shows similarity with the Lake Papverme. The* NO_3^- *content is higher everywhere in the soil (except in the case of the Lake Kender), but in this* *case a weaker correlation can be detected, so it can be concluded that the nitrate washout does not directly constitute a hazard. However it does pose a threat indirectly, by getting into the underground karst water system and to the springs which bring pollution particularly in the spring and autumn. The NO_3^- content of the sediment of the Lakes Tengerszem, Gyökérréti and Vörös is low.*

4. 5. 5. *The state of the Lake Aggteleki after dredging shows that the pH of the sediment corresponds to that measured 10 years ago and the dry matter content is slightly higher. All nutrient concentrations of the sediment also decreased after the dredging, but it shows an upward trend again. In the case of Lake Aggteleki dredging has reduced the amount of accumulated sediment, but a layer with higher heavy metal content emerged, which may come from past atmospheric deposition. Probably due to the dredging the amount of immature organic matter in the sediment has been reduced. Because the area around the lake was filled with the dredged sediment, the external load can reach the degree of the internal load, which inhibits the improvement of the water quality.*

The water quality of Lake Vörös can be considered good, the dredging reduced the internal pressure, as it removed the upper layer which contained more organic matter, and the lake's surroundings are steadily maintained by Aggtelek National Park, through which the external load is also minimized.

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