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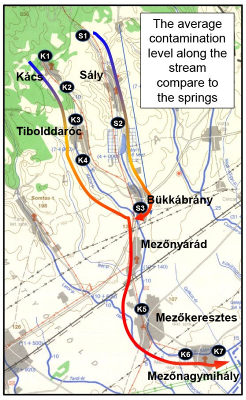

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ABSTRACT

The fact that freshwaters are becoming affected increasingly by a wide range of stressors, mainly because of various human activities, is acknowledged by many national and international organizations. Thus, not only the protection and quality management of natural waters but the examination and identification of the origin of the contaminants are relevant research topics. In the article, the main correlation between the anthropogenic activities and stream water quality are observed in case of Kácsi Stream in Northeast Hungary. Based on the chemical properties and contaminants, it can be stated that mainly the agricultural effects can be observed on the water quality. Furthermore, the use of fertilizers with different compositions can also be detected.

1. Introduction

Various water bodies, depending on the geographical locations, can be subjected to different natural (e.g. drought) and anthropogenic stressors (e.g. urbanization), the result of which can be such severe issues as freshwater scarcity, pollution and subsequent loss of biodiversity. Thus, the analysis of water quality and water quality trends is essential, as the appropriate management and protection of natural resources is a crucial element to sustainable development. The importance of this topic has already been recognized by the United Nations and was included in the Millennium Development Goals as *Goal 6: Ensure availability and sustainable management of water and sanitation for all* [1, 2, 3].

The examination and monitoring of water quality are relevant and widely researched topics in each part of the world, in continental [3], national [1, 4] and regional [5, 6] levels as well.

Water quality parameters can be divided into three categories: physical (e.g. temperature, total suspended solids), chemical (e.g. pH, electrical conductivity), and biological. These parameters change not only over time but depending on the sampling point, especially in the case of rivers and streams [5, 7].

To determine the chemical status of drinking water, 125 parameters are listed by WHO. These substances can be divided into two categories: chemicals that should be assessed for possible health effects, and others that can affect the acceptability of drinking water (e.g. taste or appearance). Guideline values have been established for actual or potentially toxic chemicals that can occur in drinking water. If the value of a certain constituent is below the given value, the prolonged consumption does not pose a significant health risk. On the other hand, no values have been established for substances due to their natural occurrence in drinking water or occurrence at concentrations well below those of health concern [8].

The examined area is located in Northeast Hungary, near the base of the Bükk Mountains. The main characteristic of the topography is the transition from mountainous regions to plains towards the south. The karst springs of Kács and Sály can be found in forested areas and agricultural production is more significant in the southern parts. The most common crops are wheat, barley, corn, and sugar beet. The karst springs are used to provide drinking water for the local settlements. The stream is considered to be intermittent, with up to 40 km long watercourse [4].

According to the data of the European Environmental Agency on the chemical status of surface water bodies, the concentration of the priority hazardous substances (based on the Environmental Quality Standards Directive 2008/105/EC) is unknown in case of 44.9% of Hungarian rivers, the length of which is over 6500 km [9]. Certain parameters of the karst springs of Kács and Sály have already been investigated during the last decades [6, 10]. However,

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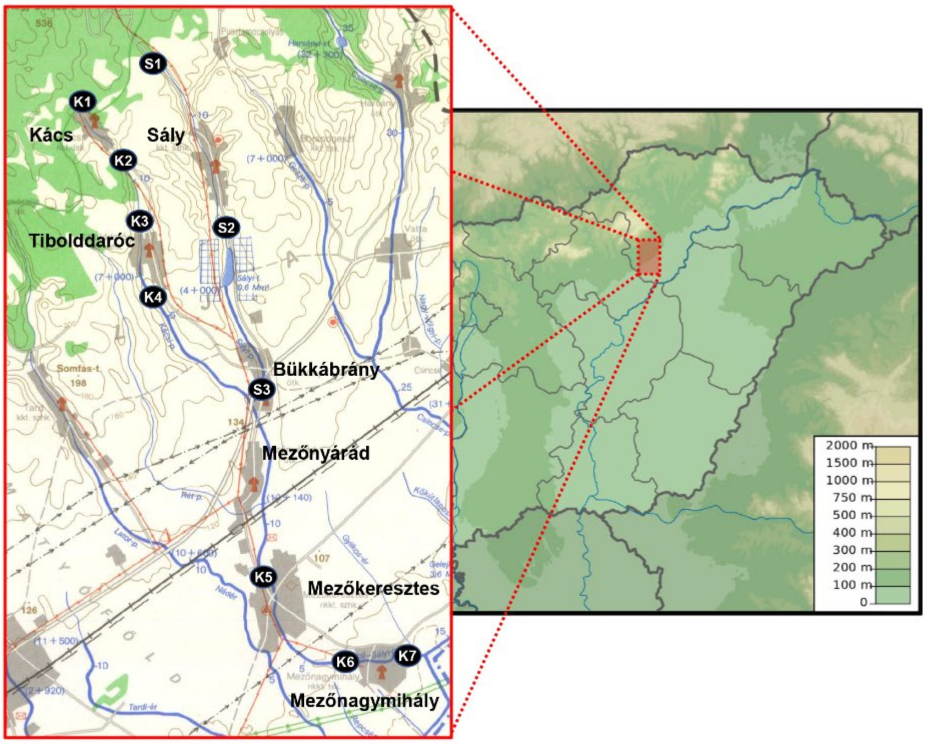
no data is known about the quality changes along the whole watercourse of the Kácsi Stream.

The aim of the article is to examine the effect of urbanized, mining and agricultural (farming) areas on some water quality parameters of the Kácsi Stream.



Sampling point	Sample	Coordinates
Kács – spring	K1	N 47°57'51.13" E 20°36'17.86"
After Kács	K2	N 47°57'3.55" E 20°37'23.49"
Before Tibolddaróc	K3	N 47°55'54.96" E 20°38'4.72"
After Tibolddaróc	K4	N 47°54'23.97" E 20°38'35.00"
Mezőkeresztes	K5	N 47°49'50.36" E 20°41'6.70"
Mezőnagymihály	K6	N 47°48'25.96" E 20°43'18.47"
After Mezőnagymihály	K7	N 47°48'32.95" E 20°44'19.75"
Sály – spring	S1	N 47°58'55.80" E 20°37'54.88"
After Sály	S2	N 47°56'6.23" E 20°39'58.63"
Bükkábrány – mining area	S3	N 47°52'38.05" E 20°41'14.98"

Figure 1. The sampling points

2. Methods

During the examinations, both the status of the water resources and the quantity of certain harmful substances were evaluated and tested for a better understanding of the anthropogenic effect on the Kácsi Stream. The sampling points and coordinates are illustrated in Figure 1.

The samples were taken during the summer period. The tests were performed either in situ or at the laboratory of the University of Miskolc. Samples were held at 4 °C until the laboratory analyses in plastic canisters, which were used for sampling.

A Hanna HI 9142 instrument was used for the in-situ measurement of dissolved oxygen (DO) content and water temperature, from which the dissolved oxygen saturation (DOS) can be calculated. The pH values were also measured at the sampling points, using a combined electrode Orion model 210a pH meter.

Table 1. The parameters of the springs compared to the WHO guideline values for drinking water quality

	Temperature, °C	pH	COD_{Cr}, mg/L	EC, µS/cm	TDS, mg/L	DO, mg/l	DOS, %	M-alkalinity, mmol/L	Hardness, mg/L
Sample – K1	16.5	7.23	10	609	247	8.2	84	6.1	167
Sample – S1	16.4	7.32	10	656	256	9.1	94	5.7	167
WHO values	-	-	-	-	-	-	-	-	-

	Ammonium, mg/L	Chloride, mg/L	Nitrite, mg/L	Nitrate, mg/L	Phosphate, mg/L	Sulfate, mg/L	Hydrogen carbonate, mg/L	Ca, mg/L	Mg, mg/l
Sample – K1	0.01	0.50	<0.01	2.66	0.05	6.56	372	97.34	13.55
Sample – S1	0.01	0.36	<0.01	2.90	2.76	3.84	348	86.31	20.06
WHO values	-	5	3	50	-	-	-	-	-

	K, mg/L	Na, mg/L	Mn, mg/L	Pb, µg/L	Cd, µg/L	Zn, µg/L	Cu, µg/L	Cr, µg/L	Ni, µg/L
Sample – K1	9.13	4.30	<0.08	<163	<8	8	<23	<41	<43
Sample – S1	8.82	1.05	<0.08	<163	<8	28	<23	<41	<43
WHO values	-	50	0.4	10	3	-	2000	50	70

Specific conductivity (EC) was determined during sampling with a Mettler Toledo MC 126 portable conductivity meter, which was suitable to measure the total dissolved solids (TDS) as well.

The rest of the parameters were examined in the laboratory. COD was measured using potassium dichromate in a sulfuric acid medium. The ammonium ion content was tested with a Spekol 10 photometer at 670 nm wavelength. A nitrite, nitrate, orthophosphate, chloride and sulfate ions were determined with an HP HPLC 1050 chromatograph (Asahipak ODP-50 column, UV-VWD detector). The examination of Cr, Ni, Cu, Cd, Zn, Pb, Mn, K, Na content was carried out with a Philips PU 9100 type flame atomic absorption spectrophotometer. Through complexometric titration, the Mg and Ca could be determined. Titration was carried out with methyl orange indicator and hydrochloric acid solution to determine the M-alkalinity, which was used to calculate the quantity of hydrogen carbonate. The hardness values were calculated based on Ca and Mg values.

3. Results

The examined parameters of the spring of Kács and Sály and the WHO guideline values for drinking water quality [8] are summarized in Table 1. It can be observed that most of the examined parameters meet the WHO criteria for drinking water quality. In case of lead and cadmium, however, the limit of detection of the analyzer was higher than the WHO limit. Thus, the accurate value of Pb and Cd could not be determined.

To assess the anthropogenic effects, the described parameters were also examined at each sampling points. The quantity of nitrate, manganese, lead, cadmium, copper, chromium and nickel were under the detection limit at all sampling points. Table 2 contains the ratio of the rest of the parameters in relation to the concentrations measured at the springs.

The temperature of the stream increased during its course, from the approximately 16 °C at the springs to 20 (S3) and 26 (K7) °C.

The pH of the water was slightly increased or had only a small deviation from the original values. Such slightly alkaline pH is natural in case of surface waters.

The higher amount of total dissolved solids is in the water, the higher the electric conductivity is. It can be observed that when samples were taken before and after a settlement (K1-K2, K3-K4, K6-K7, S1-S2), the EC was always higher after the settlements. Between settlements (K2-K3) the TDS and EC decrease to a minor extent. The reason for this might be the lower salt load outside of settlements, and runoff water from the surroundings can dilute the stream water.

COD was significantly higher at two sampling points compared to the springs, at K2 and K7, which represents the organic matter content of the water. The higher COD at K7 may be the result of heavy livestock farming in the area.

Table 2. The ratio of contaminants at the sampling points in relation to the springs

Parameter	Ratios in relation to the parameters of the springs									
	K1	K2	K3	K4	K5	K6	K7	**S1**	S2	S3
Temperature	**1.00**	1.21	1.12	1.17	1.32	1.29	1.49	**1.00**	1.28	1.14
pH	**1.00**	1.15	1.14	1.13	1.12	0.95	1.02	**1.00**	0.98	1.02
EC	**1.00**	1.07	1.02	1.04	1.28	1.40	1.48	**1.00**	1.13	1.48
TDS	**1.00**	1.02	1.00	1.11	1.27	1.37	1.45	**1.00**	1.14	2.57
COD_{Cr}	**1.00**	4.00	1.00	1.00	1.00	1.00	3.00	**1.00**	1.00	2.00
DO	**1.00**	1.37	1.27	1.21	1.15	1.13	1.41	**1.00**	1.00	0.46
DOS	**1.00**	1.47	1.32	1.28	1.28	1.25	1.67	**1.00**	1.10	0.48
Nitrate	**1.00**	1.00	0.72	0.47	0.22	0.81	0.81	**1.00**	0.47	0.27
Ammonium	**1.00**	1.00	3.00	8.00	8.00	1.00	1.00	**1.00**	1.00	2.00
Phosphate	**1.00**	36.20	42.40	135.20	194.80	115.40	41.80	**1.00**	1.05	1.08
Sulfate	**1.00**	1.00	1.00	0.99	2.02	0.82	0.71	**1.00**	2.86	7.04
Chloride	**1.00**	3.40	2.22	1.46	4.82	17.58	21.76	**1.00**	14.92	17.25
Hydrogen carbonate	**1.00**	0.87	0.84	0.89	0.93	0.93	1.15	**1.00**	1.00	1.23
M-alkalinity	**1.00**	0.89	0.85	0.90	0.98	0.97	0.97	**1.00**	1.00	1.23
Hardness	**1.00**	0.96	0.92	1.05	1.13	1.09	1.21	**1.00**	0.89	1.20
K	**1.00**	2.11	2.13	4.85	6.57	11.25	11.17	**1.00**	8.61	10.39
Ca	**1.00**	0.92	0.89	1.01	0.98	1.08	1.03	**1.00**	0.80	1.23
Mg	**1.00**	1.11	1.08	1.22	1.78	1.12	1.99	**1.00**	1.13	1.13
Na	**1.00**	1.20	1.07	1.98	2.49	3.15	3.02	**1.00**	4.70	19.00
Zn	**1.00**	2.50	1.88	1.13	1.00	2.03	2.38	**1.00**	0.71	0.46

The amount of dissolved oxygen is dependent on many other factors and chemicals in the water, all of which should be examined together. DO in the water is essential for living organisms and is inversely proportional to the temperature of the water. Furthermore, the increase in dissolved salt content may decrease the DO value. Moreover, DO can be also increased by the organic matter content of water which is present due to the photosynthesis of plants. As a consequence, DO is also in relation to the COD, as the higher COD, i.e. more organic material in the water, is beneficial for the reproduction of aquatic plants which results in higher oxygen content.

The changes of the abovementioned parameters can be observed in Figure 2. As there was no significant temperature change in the examined areas, the connection with the DO value is not observable. As TDS increased, the quantity of DO decreased. It can be seen in Figure 2 that the highest TDS was obtained at the S3 point, along with the lowest DO value. The highest COD was found at K2 and K7 points, parallelly with the highest DO content. It can be assumed that the number of aquatic plants is higher at these sampling points which may have a negative impact on water quality during autumn and winter time due to the decay and decomposition of plants. However, no effect of human activities can be observed in relation to these parameters.

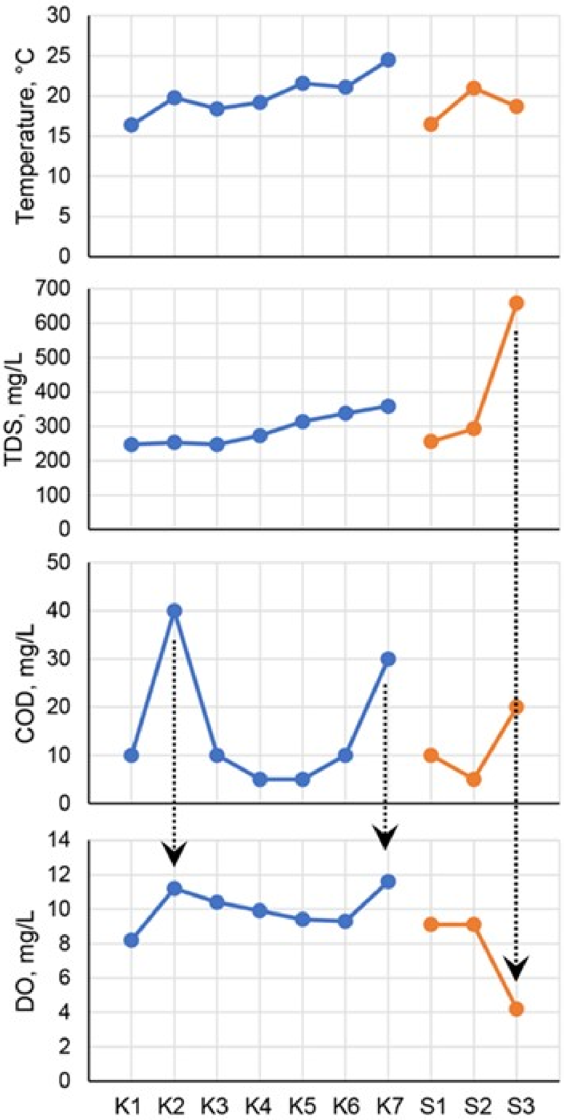


Figure 2. The obtained DO values and its possible influencing parameters

Various anions and cations should be examined along with sodium and phosphorous, as a heavy agricultural activity is prevalent in the basin and the components of fertilizers may be dissolved in surface waters due to overfertilization. These components can change the quality of the water body. The most common potassium compounds used as fertilizers are KCl and K_2SO_4, the phosphorous compounds are mainly calcium phosphates and superphosphates, while $(NH_4)_2SO_4$, $NaNO_3$, NH_4NO_3 or $(NH_2)_2CO$ are suitable for sodium supplement. Certain compounds, e.g. $(NH_4)_3PO_4$ or NPK compound fertilizers are applicable to replenish several nutrients at once. Thus, the examination of these components together can indicate the use of various types of fertilizers and should be analyzed collectively.

The quantity of nitrite was always below the detection value, but nitrate could be observed at every sampling point. The concentration continuously decreased in comparison to the spring until it started increasing at K6 and K7. The quantity of ammonium slightly increased first and then peaked at K4 and K5, reaching eight times higher value than at the spring. However, by the next sampling point, the concentration decreased back to the original value. The most significant increase could be observed in the phosphate value, becoming almost 200x higher at K5 than at K1. Then the phosphate content started decreasing from K6. In the case of the Sályi Stream, only a small increase could be observed. On the other hand, the sulfate content slightly rose along the Kácsi Stream but significantly increased in the Sályi Stream. At S3, the sulfate content was 7x higher than at S1. No clear tendencies could be observed for the chloride content, but the values at K6, K7, S2, and S3 was exceptionally high – 15-22x higher than at the springs. The concentration of potassium slowly increased moving away from the springs and doubled after K5.

There is a significant correlation between cultivation and the occurrence of these components in the water, as it indicates the use of various types of fertilizers. Along the Kácsi Stream, the phosphate content is the most significant which increases until K5. This tendency is similar in the case of ammonium. In Hungary, the use of superphosphates is common which, in many cases, contains $(NH_4)_3PO_4$. After the K6 sampling point, the phosphate and ammonium content decreased but the potassium and chloride increased, indicating the change of fertilizer type. Superphosphates are replaced with potash with KCl content. The use of KCl can also be detected in case of the Sályi Stream.

The amount of sodium in the Kácsi Stream was up to three times higher than the value of the stream. On the other hand, the sodium value rapidly increased in the samples of Sályi Stream. At S3, the sodium content was 19 times higher than at S1. This increase might be the effect of the mining activities in the vicinity of the sampling point.

The quantity of hydrogen carbonate and the M-alkalinity at the K2-K7 sampling points were usually lower than at the spring, while in case of the S sampling points, the values were higher.

Examining the hardness of the springs in degree of General Hardness (°dH, where 1 °dH = 10 mg/L CaO) and the rest of the samples, the stream water can be classified as very hard.

Among the inorganic microcontaminants, zinc was the only one with observable changes. Certain organic manures contain high quantities of zinc and the leaching of components may result in the increased zinc content of K samples. This assumption is further strengthened by the fact that the samples with the highest organic matter content, i.e. COD value (K2 and K7) also contained the highest amount of zinc. The zinc content was lower at S2 and S3 than it was at the S1 spring.

4. Conclusions

The small water system at Northeast Hungary was examined to identify the effect of human activities on the chemical status of the water. Some of the examined characteristics were suitable to indicate the anthropogenic impact, mainly the effect of agriculture.

Moving south from the spring of Kács, the phosphate content showed the highest increase. Parallelly, the ammonium content increased as well, possibly due to the fertilizers containing $(NH_4)_3PO_4$. After K5 sampling point, these values decreased but the potassium and chloride rose. Thus, instead of phosphorous-based fertilizers, the KCl-based ones are used. The used of KCl can be observed in the samples from Sályi Stream.

The highest CDO was measured at K2 and K7, along with the highest zinc content, which might be the result of leaching into the water.

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