Quality of the Surface Water in the Ratka Small Water Reservoir

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Abstract. The aim of the contribution is to evaluate the state of the quality of the surface water in the Ratka small water reservoir and its surroundings. The Ratka small water reservoir is included in fishing grounds; it is therefore necessary to know the quality of the surface water. The work is focused on an evaluation of the surface water quality indicators, i.e., the water temperature, pH reaction, content of the nitrate nitrogen, nitrite nitrogen, and the ammonia nitrogen, the chemical oxygen demands, and the total organic carbon. The analysis was divided into field measurements and laboratory measurements. Three sampling points were identified, from which samples were regularly taken. For water temperature and pH reaction, the field measurements were performed every month during 2019 and for other selected indicators of water quality, the field measurements were performed during April – September 2019. The laboratory analyses were realized in 2019 (summer, winter) and were focused only on samples from the Ratka small water reservoir. To evaluate the results, they were compared with the recommended values found in the valid Regulation of the Government of the Slovak Republic No. 269/2010 Coll. After evaluating the results of the study, increased values indicators of quality of the surface water were found water temperature, pH reaction, $N\text{–}NO_2$, chemical oxygen demands and total organic carbon. Phosphate contents are also present in the water. The results showed that the Ratka small water reservoir, due to the increased values of the mentioned indicators of the quality of the surface water, does not meet the set conditions of the Government of the Slovak Republic. The significance of this study can be seen not only in the importance of water quality assessment from the practical point of view, but also in the need to perform these analyses, especially in areas where no water quality assessments have been performed so far, an example of which is the Ratka small water reservoir assessed in this study.

1. Introduction

The goal of the work is to evaluate the state of the quality of the surface water in the Ratka small water reservoir. To achieve the aim, it was necessary to perform measurements in the field and in the laboratory. The work focuses on indicators of the quality of the surface water, i.e., the water temperature, pH reaction, content of the nitrate nitrogen, nitrite nitrogen, and the ammonia nitrogen, the chemical oxygen demands, and the total organic carbon.

The article is divided into 4 chapters: introduction, material and methods, results and discussions, and conclusions. The chapter 2 “Material and methods” deals with selected theory of the issue, study site and input data, and measurements (field, laboratory). The chapter “Results and discussions”
summarizes all the results of the field measurements and analyses performed in the laboratory. Evaluations of the results are also part of this section.

2. Material and methods

The current processes of climate change negatively affect the basic components of the environment and the existence of humanity (water supply, food production, land use, etc.). The consequences of climate change are beginning to manifest themselves, especially in water distribution [1]. The construction of small water reservoirs on rivers in Slovakia began where additional irrigation was needed and where there was not a sufficient water source in places where hydrological and morphological conditions were suitable for the construction of dams [2]. Small water reservoirs perform many important functions due to the importance of water in the agricultural landscape and the protection and creation of the environment. Their important functions include storage, protection, economics, ecology and landscaping, hygiene, remediation, recreation, aesthetics, and rainwater capture and use [3].

Small water reservoirs are part of our lives, so we must take care of them and monitor the quality of the water in their storage spaces. As early as the 1970s, the deterioration of the surface and groundwater quality due to agricultural activity began to manifest itself. Even in the 1960s, there was an intensification of agricultural production through the chemicalization and management of large areas of agricultural land [4].

2.1. Study site and input data

The Ratka small water reservoir was constructed in the years 1965–1966 in the village of Ratka, the district of Lučenec, in the region of Banská Bystrica, which is located in the southern part of the Slovak Republic (Figure 1) [5]. It was created due to a need for the accumulation of water for irrigation, but irrigation systems were never built. The Ratka small water reservoir is currently declared a fishing area, and swimming is prohibited. The owner, and administrator, is the Slovak Water Management Company. It belongs to the IV. category of water construction [6].

Figure 1. Location of the village of Ratka in the district of Lučenec [7]

The basic technical parameters of the Ratka small water reservoir include: the constant accumulated volume – 17,000 m³; \( Q_{100} \) – 7.0 m³.s⁻¹; specific runoff – 1.71 l.s⁻¹.km⁻²; dimensions of the dam’s crown – 102.10 m.a.s.l.; length of the dam crown – 83 m; width of the dam in the crown – 3.2 m; and maximum height of the dam in the axis – 4.5 m [6].
The source of the water for the Ratka small water reservoir is the Cerová stream, which contains insufficient water in the summer months. Therefore, the main source of water is a well, which is in front of the Ratka small water reservoir; it is located on private land.

In 2008, the Ratka small water reservoir was reconstructed [8]. During the reconstruction, it was determined that the bottom of the reservoir contained approximately 60 – 80 cm of sediments [5]. The sediments in the reservoir have not yet been removed, so the results of the work on the indicators of nitrate compounds, phosphates, the chemical oxygen demands, and total carbon content may be affected by this fact. Intensive timber harvesting is another big problem in the basin as it changes the characteristics of the outflow regime and increases the soil erosion.

2.2. Measurements
The following section describes the field and laboratory measurements that were performed in this study in 2019. The procedures, methods, and aids used in the measurements are mentioned. The analyses aimed to determine the quality of the surface water in the small water reservoir Ratka and its surroundings. The research was carried out because no analysis of quality of the surface water has been carried out in the area so far.

2.2.1. Field measurements
Measurements were performed at 3 sampling points (1st sampling point – Cerová stream, 300 m upstream the Ratka small water reservoir; 2nd sampling point – directly in the reservoir; 3rd sampling point – Cerová stream, 300 m downstream the reservoir). In figure 2 we can see all sampling points in the Cerová stream and in figure 3 we can see the state of the sampling points in 2019.

Field measurements were performed in the months of April – September, as an increased amount of compounds (the amount of nitrates, and phosphates in the water) was expected in the summer months. All field measurements were taken from the surface of water to a depth approximately to 10 cm.

Quantofix test strips, which record the presence of nitrate and nitrite nitrogen, ammonia nitrogen and phosphates in water, were used for the field measurements. These are test strips for the semi-quantitative determination of ions and other substances in water. They consist of a plastic strip on which a test paper is glued at the lower end. The presence of the mentioned compounds in the aqueous sample is deducted from any changes in colour.

The advantages of using the test strips include:

- easy and fast handling,
- the rapidity of the results obtained directly on-site immediately after collection.

The disadvantages of using the test strips include:

- high ranges of measured (the indication of the presence of only higher values of the individual parameters; for this reason, the results are low, and the limit values are difficult to interpret).

To better explain the changes in the contents of the above-mentioned compounds, the study also focused on basic indicators of the quality of the surface water, especially on the water temperature and pH reactions. A portable multimeter, i.e., a Pocket Pro+ Multi 2 from Hach, was used for the measurements.
2.2.2 Laboratory measurements

After the amounts of the nitrate and phosphate compounds in the water were determined, laboratory analyses were undertaken. A water analysis was performed for the first time in the summer months (once) and for a second time in the winter months (once). The analysis of the sample was as follows: the day before the analysis in the laboratory, a sample was taken from the reservoir; the analysis was then performed in the laboratory of the Department of Landscape Engineering, Faculty of Horticulture and Landscape Engineering, the Slovak University of Agriculture in Nitra, in cooperation with Ing. Tatiana Kaletová, PhD.

In addition to the parameters such as the nitrate nitrogen, nitrite nitrogen and ammonia nitrogen, and the phosphate contents in the water, the laboratory analyses focused on other parameters, including the chemical oxygen demands (COD) and total organic carbon (TOC).

The chemical oxygen demand was analysed by dichromate method (COD$_c$) from unfiltered samples. The samples were heated at 175 °C for 15 min, and cooled samples were analysed by spectrophotometer DR6000 (Hach company). The amount of total organic carbon (TOC) was analysed from unfiltered samples by purging method and persulphate digestion. A digestion cuvette with reagent and sample was shaken for 5 min, after the preparation the digestion cuvette was immediately closed by an indicator cuvette and heated at 95 °C for 120 min. The cooled sample were analysed by spectrophotometer DR6000 (Hach company). Both methods correspond to methods required by Slovak Technical Standards.
3. Results and discussions

3.1. Field measurements

As already mentioned, field measurements were performed at three sampling points. For the indicators of the quality of the surface water, the water temperature, and the pH reaction, three measurements were always made with the portable multimeter, from which the arithmetic mean was subsequently derived. This arithmetic mean determined the final value of the measurements in each month. The resulting measured values of the water temperature can be seen in Table 1 and pH reaction can be seen in Table 2. A better illustration of the increases in the water temperature and pH reactions can be seen in Figure 4, which is an evaluation of the 2nd sampling point, where the water abstractions were available throughout the study period.

**Table 1. Results of the field measurements of the water temperatures [°C] in 2019**

| Month    | 1st sampling point | 2nd sampling point | 3rd sampling point |
|----------|--------------------|--------------------|--------------------|
|          | Measured values    | Mean               | Measured values    | Mean               | Measured values | Mean               |
| January  | 6.4 5.9 5.3        | 5.9                | 4.5 3.7 3.7        | 4.0                | 6.5 5.4 4.8    | 5.6                |
| February | 9.7 7.9 7.1        | 8.2                | 7.6 6.3 5.9        | 6.6                | 7.4 6.8 6.5    | 6.9                |
| March    | 16.6 15.5 13.9     | 15.3               | 19.0 17.9 16.9     | 17.9               | 19.7 18.5 18.1 | 18.8               |
| April    | 15.2 13.7 13.2     | 14.0               | 18.8 18.8 18.4     | 18.7               | 19.7 19.4 19.1 | 19.4               |
| May      | 14.8 13.5 13.4     | 13.9               | 18.9 19.2 19.0     | 19.0               | 19.8 20.0 20.1 | 20.0               |
| June     | - - -              | -                  | 26.3 26.1 26.1     | 26.2               | - - -          | -                  |
| July     | - - -              | -                  | 27.0 27.1 27.4     | 27.2               | 24.1 22.8 22.6 | 23.2               |
| August   | - - -              | -                  | 25.9 25.8 25.8     | 25.8               | 26.0 25.6 25.4 | 25.7               |
| September| 14.4 13.0 12.9     | 13.4               | 14.4 14.0 14.1     | 14.2               | 15.2 13.8 13.7 | 14.2               |
| October  | - - -              | -                  | 12.3 10.2 11.6     | 11.4               | 10.3 9.4 9.3   | 9.7                |
| November | 6.1 5.7 5.2        | 5.7                | 5.6 5.3 5.2        | 5.4                | 8.6 8.5 8.1    | 8.4                |
| December | 5.0 4.7 4.5        | 4.7                | 3.3 2.7 2.3        | 2.8                | 6.6 4.7 4.5    | 5.3                |

*a If the symbol [-] appears in the resulting tables, it means that sampling in the given month was not possible due to a lack of water at the sampling point.

*b Yellow colour means exceeded limit value of Government Regulation No. 269/2020 Coll.

**Table 2. Results of the field measurements of the pH reactions [-] in 2019**

| Month    | 1st sampling point | 2nd sampling point | 3rd sampling point |
|----------|--------------------|--------------------|--------------------|
|          | Measured values    | Mean               | Measured values    | Mean               | Measured values | Mean               |
| January  | 7.9 7.8 7.8        | 7.9                | 8.2 8.2 8.2        | 8.2                | 8.2 8.2 8.3    | 8.2                |
| February | 8.7 8.5 8.3        | 8.5                | 8.3 8.7 8.7        | 8.5                | 8.5 8.8 8.8    | 8.7                |
| March    | 8.3 8.0 8.0        | 8.1                | 8.2 8.3 8.2        | 8.2                | 8.3 8.3 8.3    | 8.3                |
| April    | 8.8 8.2 8.1        | 8.4                | 8.5 8.6 8.6        | 8.6                | 8.2 8.3 8.2    | 8.2                |
| May      | 8.1 8.2 8.1        | 8.1                | 8.5 8.6 8.5        | 8.5                | 8.2 8.2 8.2    | 8.2                |
| June     | - - -              | -                  | 8.5 8.5 8.5        | 8.5                | - - -          | -                  |
| July     | - - -              | -                  | 8.5 8.6 8.5        | 8.5                | 7.6 7.6 7.6    | 7.6                |
| August   | - - -              | -                  | 9.1 8.9 9.0        | 9.0                | 7.7 7.6 7.6    | 7.6                |
| September| 8.1 8.0 8.0        | 8.0                | 8.3 8.4 8.4        | 8.4                | 8.4 8.2 8.2    | 8.3                |
| October  | - - -              | -                  | 8.4 8.3 8.4        | 8.4                | 8.1 8.1 8.1    | 8.1                |
| November | 7.2 7.2 7.1        | 7.2                | 8.6 8.5 8.5        | 8.6                | 8.2 8.2 8.3    | 8.2                |
| December | 6.3 8.1 7.1        | 7.2                | 8.7 8.6 8.7        | 8.7                | 9.0 8.7 8.7    | 8.8                |
3.1.1. Upstream the Ratka small water reservoir (1st sampling point)
In June, July and August, it was not possible to take readings due to a shortage of water in the Cerová stream. In terms of the presence of test compounds, the 1st sampling point was the least contaminated. Table 3 summarizes the monthly analyses from the 1st sampling point.

| Month   | $N - NO_3$ | $N - NO_2$ | $N - NH_4$ | $PO_4^{3-}$ |
|---------|------------|------------|------------|-------------|
| April   | 0 - 10     | 0 - 1      | 0          | 0 - 3       |
| May     | 0 - 10     | 0 - 1      | 0          | 3 - 10      |
| June    | -          | -          | -          | -           |
| July    | -          | -          | -          | -           |
| August  | -          | -          | -          | -           |
| September | 0         | 0          | 0          | 0 - 3       |

The first sampling point, which is located upstream the small water reservoir, confirmed the presence of nitrate nitrogen (0-10 mg.l$^{-1}$), a small amount of nitrite nitrogen (0 – 1 mg.l$^{-1}$), and the presence of phosphates (0 - 10 mg.l$^{-1}$). The presence of ammonia nitrogen contamination was not confirmed.

3.1.2. Directly in the Ratka small water reservoir (2nd sampling point)
Due to pollution, the second sampling point was the most polluted sampling point. For this reason, samples were also taken from it for laboratory analysis. The increased pollution could be caused secondarily by the presence of the sediments in the reservoir. The results of the field measurements from the 2nd sampling point can be found in the following table (Table 4).

| Month   | $N - NO_3$ | $N - NO_2$ | $N - NH_4$ | $PO_4^{3-}$ |
|---------|------------|------------|------------|-------------|
| April   | 0 - 10     | 0 - 1      | 0          | 0 - 3       |
| May     | 0 - 10     | 10 - 25    | 0          | 3 - 10      |
| June    | 0          | 0          | 0          | 3 - 10      |
| July    | 0 - 10     | 0          | 0          | 10 - 25     |
| August  | 0          | 0          | 0          | 3 - 10      |
| September | 0        | 0          | 0          | 0 - 3       |
Sampling was possible in each selected month from the 2nd sampling point located directly in the Ratka small water reservoir. The presence of nitrate nitrogen (0–10 mg.l\(^{-1}\)), nitrite nitrogen (maximum amount in May: 10–20 mg.l\(^{-1}\)), and an increased amount of phosphates (maximum amount in July: 10–25 mg.l\(^{-1}\)), were detected. This higher amount may have been caused by increased logging in the Cerová stream basin and increased agricultural activity on the surrounding land. The presence of ammonia nitrogen was not confirmed.

3.1.3. Downstream the Ratka small water reservoir (3rd sampling point)

It was not possible to measure the 3rd sampling point in June, due to a lack of water in the Cerová stream. The results of the field measurements from the 3rd sampling point are shown in the following table (Table 5).

| Month   | \( N - NO_3 \) [mg.l\(^{-1}\)] | \( N - NO_2 \) [mg.l\(^{-1}\)] | \( N - NH_4 \) [mg.l\(^{-1}\)] | \( PO_4^{3-} \) [mg.l\(^{-1}\)] |
|---------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| April   | 0–10                          | 0–1                           | 0                             | 0–3                           |
| May     | 0–10                          | 0–1                           | 0                             | 3–10                          |
| June    | -                             | -                             | -                             | -                             |
| July    | 0–10                          | 0                             | 0                             | 10–25                         |
| August  | 10–25                         | 0                             | 0                             | 0–3                           |
| September | 0                            | 0                             | 0                             | 0                             |

The presence of nitrate nitrogen (maximum amount in August: 10–25 mg.l\(^{-1}\)), nitrite nitrogen (0–10 mg.l\(^{-1}\)), and phosphates (maximum amount in July: 10–25 mg.l\(^{-1}\)), was also detected downstream the reservoir. The presence of ammonia nitrogen was not detected.

The measured values of the indicators were subsequently compared with the valid Regulation of the Government of the Slovak Republic No. 269/2010, which lays down the requirements for achieving good water quality, as amended 1.1.2013 [9]. The limit values for the water quality indicators examined are set out in table 6.

| Indicators of the quality of the surface water | Recommended value | Government Regulation No. 269/2010 |
|-----------------------------------------------|-------------------|-----------------------------------|
| Water temperature                             | < 26 °C           |                                   |
| pH                                            | 6 – 8.5           |                                   |
| \( N - NO_3 \)                                | < 5 mg.l\(^{-1}\) |                                   |
| \( N - NO_2 \)                                | 0.02 mg.l\(^{-1}\) |                                   |
| \( N - NH_4 \)                                | 1.0 mg.l\(^{-1}\) |                                   |
| \( PO_4^{3-} \)                                | -                 |                                   |
| COD                                           | 35 mg.l\(^{-1}\)  |                                   |
| TOC                                           | 11 mg.l\(^{-1}\)  |                                   |

As to the water temperature, the limit value was exceeded in June and July; the maximum measured temperature was 27.17 °C in July. The limit values within the pH reaction were in a range of 6 – 8.5. In this respect, the values that were exceeded were recorded at the 2nd sampling point for the
entire monitored period (except for September). For the other measured indicators of the quality of the surface water, i.e., the content of the nitrate nitrogen, nitrite nitrogen and ammonia nitrogen, and the content of the phosphates in the water, it was not possible to evaluate compliance with the recommended values for the individual parameters using the test strips. For this reason, the research was moved to the laboratory, which yielded accurate values of the surface water quality indicators.

3.2. Laboratory measurements
As a part of the laboratory measurements, the study focused on the 2nd sampling point, because the largest amount of pollution in the area investigated was found there.

As can be seen from the previous tables, the field measurements yielded results in the form of ambiguous intervals. The limit values of the Government of the Slovak Republic are often in intervals of the measured indicators of the quality of the surface water. For this reason, it is not possible to objectively assess whether or not the limit values were reached. To ensure the accuracy of the results, two analyses were performed in the laboratory. For the first analysis, the sampling was performed in the summer months; for the second analysis, the sampling was performed in the winter months.

It was assumed that the summer months would show higher values of the individual indicators of the quality of the surface water. In the summer months, the water in the reservoir is naturally heated. This increase in temperature causes a transformation of the substances and the development of vegetation, which leads to an increase in eutrophication reactions and an increase in the concentration of nutrients. Agriculture in the vicinity of the Ratka small water reservoir also plays an important role in increasing the content of nitrate and phosphate compounds in the water. In the summer months, the incidence of storms is increased, which along with torrential rain, causes the substances to flush into the aquatic environment. An uncommon phenomenon occurs in a drought when the wind can also carry soil particles and other substances into the water. The chemical oxygen demand and total organic carbon were also analysed. All the resulting values are contained in Table 7. The results measured were evaluated according to the recommended values of Government Regulation No. 269/2010, which are summarized in Table 6.

### Table 7. Results of the laboratory measurements from the 2nd sampling point

| Season | $N{\text{O}}_3$ | $N{\text{O}}_2$ | $N{\text{H}}_4$ | $PO_4^{3-}$ | Chemical oxygen demand | Total organic carbon |
|--------|----------------|----------------|--------------|-------------|----------------------|---------------------|
|        | [mg.l$^{-1}$]  |                |              |             |                      |                     |
| Summer | Below the measuring range, less than 5 mg.l$^{-1}$ | 0.048 | 0.039 | 6.43 | 46.4 | 21.1 |
| Winter | 0.017 | 0.015 | 0.26 | 77.7 |

The content of nitrate nitrogen in the samples taken in both periods examined was below the measured range; the recommended value of 5 mg.l$^{-1}$ was met. During the laboratory research, it was determined that the content of nitrite nitrogen in the water was twice as high as that allowed by the government regulation in the summer months. In the winter months, the content of $N{\text{O}}_2$ decreased to the limit value. The presence of ammonia nitrogen was zero according to the test strips. The laboratory analysis revealed the minimal presence of the compounds. The recommended value for $N{\text{H}}_4$ is 1.0 mg.l$^{-1}$. In this respect, ammonia nitrogen does not cause water pollution in the reservoir.

The increased occurrence of phosphates was already demonstrated during the field measurements. The laboratory analysis confirmed the presence of phosphates in the sample. In the summer months, their incidence increases, for the reasons already mentioned. In the winter months, the occurrence of phosphates in the sample decreased.
The analysis performed in the summer showed an increased value of the chemical oxygen demand up to 46.4 mg.l\(^{-1}\). In the winter analysis, the value almost doubled, which could be caused by background chemical processes in the sample, that could not be detected.

The total organic carbon value approximately twice exceeded the required recommended value, which is 11 mg.l\(^{-1}\). The total organic carbon could have been increased in particular by the presence of sediments in the water reservoir.

3.3. Discussion

An evaluation of the quality of the surface water has not yet been carried out in the surroundings of the Ratka small water reservoir. Due to this fact, no data from the addressed area are available. Exploring the quality of surface water in small water reservoirs in Slovakia should be enhanced, because people use the water for recreation and irrigation of small agricultural parcels. Small water reservoirs are most often used as ponds, and the water can be chemically contaminated.

In 2016, a revision of vulnerable areas was carried out in Slovakia due to low nitrate concentrations in the monitoring facilities in cadastral areas. According to the revision, the village of Ratka comes within the vulnerable areas [10]. Not only nitrates but also phosphorus from agricultural land cause significant surface water pollution and pose an environmental problem resulting from their participation in the eutrophication of surface waters. In Slovakia, a decisive source of phosphorus is the application of fertilizers to agricultural land. The most significant occurrence of water erosion in Slovakia occurs in the summer months (June – August) [11].

Of course, we cannot forget about climate change, which also affects the characteristics of the quality of the surface water. Elevated air temperatures cause the water temperature to rise, and as the water temperature increases, the indicators of the quality of the surface water change. As the water temperature increases, values of the pH reaction increase, the contents of the nitrate nitrogen and many other nutrients in the water increase. Nitrogen is one the main nutria that limit and support the eutrophication process of surface waters.

The year 2019 was assessed as very dry. Below-average precipitation totals occurred in the summer to the autumn months [12].

4. Conclusions

The paper aims to evaluate the quality of the surface water in the Ratka small water reservoir and its surroundings. The study found the presence of contaminants in the water samples taken. According to the results of the measurements, the least polluted water flowing into the reservoir is contaminated directly in it; after passing through the small water reservoir, the water is more polluted than at the inflow. The water flowing into the small water reservoir indicates pollution, especially from phosphorus, which is caused by farming in adjacent land. The most polluted water was confirmed directly in the Ratka small water reservoir. This is stagnant water, which is naturally heated in the summer and thus the water temperature affects the changes in the contents of the investigated parameters in the water. In order to find out the exact values of selected indicators of quality of the surface water, the work was moved to the laboratory. It found increased amounts of nitrite nitrogen, a content of phosphates in the water, and an increased chemical oxygen demand and total organic carbon. The results could also be affected by the presence of sediments with a thickness of approximately 60 – 80 cm, which may have increased since 2008. Improving the water quality in the reservoir could be ensured by extracting these sediments. Intensive timber harvesting in the river basin, which will affect the characteristics of the river basin in the future, also contributes to the water pollution. The water remains considerably polluted after passing through the reservoir. In particular, there is a content of phosphates, which are indicated across the entire observed section. A more proper
use of fertilizers is needed to ensure a smaller loss of fertilizer by entrainment in the water stream. Because of the results of the study, it is recommended that an analysis of the quality of the surface water in the Ratka small water reservoir be performed again soon.

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