# Assessment of water quality in Blinaja River Basin (Kosovo) using the Canadian Water Quality Index (WQI)

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Received: 15-09-2022 Accepted: 19-11-2022


## Abstract

Kosovo has limited natural water resources which should be well managed. This is recently realised through quantitative and qualitative monitoring of both surface and groundwater and by characterizing their quality according to their destination. In this paper, the Water Quality Index (WQI) developed by the Canadian Council of Environment Ministers (CCME WQI) was applied to evaluate the groundwater quality of the River Blinaja Basin, Kosovo. For calculating the WQI, sixteen (T, Turbidity (TUR), DO, CODMn, BOD5, pH, TDS, TH, Na+, $Ca^{2+}$, $Mg^{2+}$, $K^{+}$, $HCO3^{-}$, $Cl^{-}$, SO4 $^{2-}$ and $NO3^{-}$) physic-chemical parameters were analysed. The WQI in Blinaja Basin groundwater ranges from 66.52 to 100.00 ranking these waters from fair to excellent classes. Bicarbonate, dissolved oxygen, Ca2+, Mg2+ and total hardness have higher values in the north-eastern part of the basin affecting the water quality and having the most influence on the WQI. Based on the results obtained and compared with the WHO standard, it was found that groundwater of River Blinaja Basin is mainly within the allowed limit values to be used for drinking water. The application of the Brown WQI method gave similar results, classifying the groundwater from good to excellent. Both WQI methods showed that these waters are of better quality because the relatively protected groundwater is hosted by a weakly affected peripheral area by human activities.


**Keywords:** Groundwater, Water Quality Index, Basin, Blinaja, Kosovo.

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## Introduction

Groundwater is an important source of water supply to the local community of the Blinaja region. The recent demographic growth and economic development of the Region conditioned an increase of the demand for water. On the other hand, as reported by Foster et al. (2002) and Nair et al. (2015), the residential, industrial, commercial, agricultural and other anthropogenic activities along with changes in natural conditions often lead to deterioration of groundwater quality. In recent times, developing countries have faced significant problems in protecting water quality when trying to improve water supply and sanitation (Debels et al., 2005; Kannel et al., 2007; Carvalho et al., 2011; Ortega et al., 2016). The physic-chemical properties of water, compared with approved norms according to its destination, help to distinguish drinking water from technological, agrarian or curative water. In this regard, the quantitative and qualitative knowledge of water is of particular importance to every community in the world. The Water Quality Index (WQI) model is one tool among several that have been developed to evaluate water quality data. WQI models are based on an aggregation function which allow analysis of large temporally and spatially-varying water quality datasets to produce a single value, i.e., the water quality index, that indicates the quality of the waterbody (Uddin et al., 2021).

Most of WQI models have the same basic structure that is composed of four major structural elements: (1) parameterisation, (2) parameter sub-indexing, (3) parameter weighting and (4) index aggregation (Uddin et al., 2021). Water quality assessment takes into consideration the physical, chemical and biological properties of water, its intended use and human effects that may affect the health of water systems (Bartram et al., 1996). Almost 100% of the inhabitants who live in the area of the River Blinaja Basin provides their needs for water (drinking, irrigation, technological) by pumping the groundwater of the local Blinaja alluvial aquifer. Groundwater quality in the Blinaja River Basin is affected by different factors, including wastewater runoff, drainage from manure, agriculture diffuse pollution due to artificial fertilizers application and drainage of wastewater from road network. To estimate the suitability of groundwater for human consumption, it is essential to determine and assess their quality. In general, water engineering professionals compare individual chemical parameters with recommended allowable limits to interpret water quality. Horton (1965) proposed a water quality index (WQI) to describe the suitability of water for human consumption, distinguishing five water classes according to water quality - excellent, good, weak, very weak and unusable - which is easy to understand for decision makers and consumers. The same WQI method was used (Çadraku et al., 2013) for the assessment of the surface water quality of the Drini i Bardhë Basin (Kosovo) which found that surface water of Drini i Bardhë basin mostly fall in medium (WQI=50-70) and good (70-90) water

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quality categories. Despite the studies conducted so far on the quantitative and qualitative assessment of water in Kosovo (Çadraku and Beqiraj, 2013; Çadraku et al., 2013; Çadraku, 2014; Rizani et al., 2016; Çadraku et al., 2016; Çadraku, 2018, 2021), other studies should be carried out on the physic-chemical and biological parameters of water. This study tends to assess the quality of groundwater of the Blinaja basin according to CCME Water Quality Index (CCME, 2005a). The CCME model was developed from the British Colombia WQI Model (BCWQI) in 2001 (Lumb et al., 2011). Worldwide, the CCME WQI model has been applied to a wide range of surface water bodies (Abbasi and Abbasi, 2012; Uddin et al., 2017). The purpose of this study is: a) to assess the quality of groundwater in the River Blinaja Basin, through 28 water samples collected in four wells and four water springs. b) highlight the suitability of groundwater for human consumption using the WQI method. c) construct a map of the spatial distribution of groundwater quality in the Blinaja river basin based on the WQI values.

## Materials and methods

Study area

The study area is located in the central part of the Republic of Kosovo (Fig. 1), between the geographical coordinates 20º 57'30", 21º 04'00" (E) and 42º 28'20", 42º 33'50" (N), covering a surface of 31.43 km2.

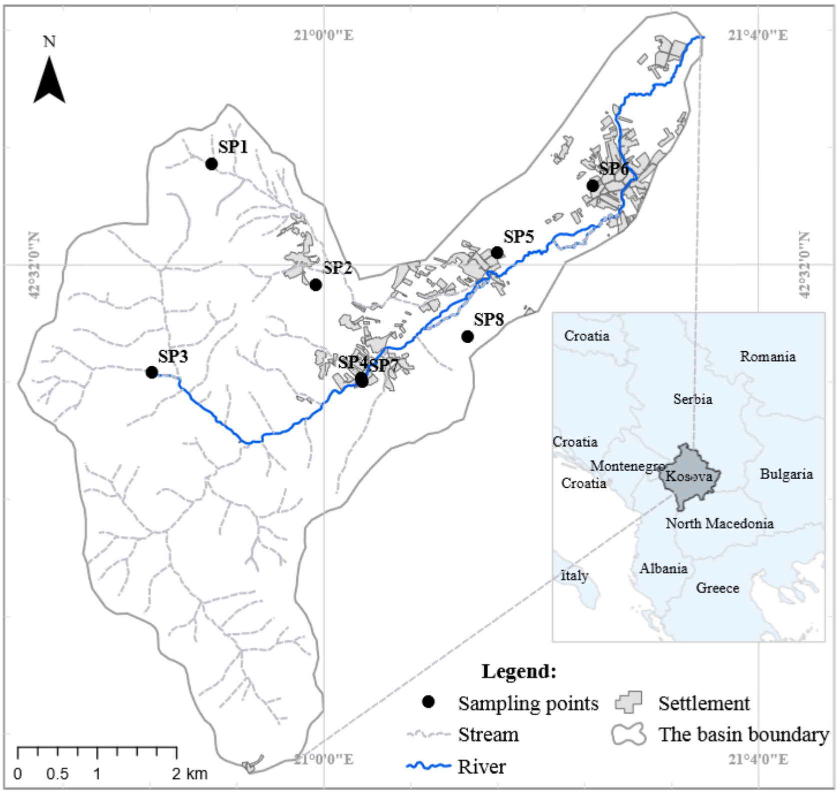


**Figure 1: Geographical of sampling location at the study area (2015-2019).**

In the River Blinaja Basin live 5169 inhabitants (KAS, 2011) with a density of 165 inhabitants per/km2. Residents mainly deal with farming and some craft activities, but there is no any industry activity. Morphologically, two units can be distinguished, the mostly mountainous western part ranging in altitude from 670 m to 884 m

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(Neck of Goleshi) and the valley part ranging from 530 m to 670 m a.s.l. The fluvial processes, which were developed from west to east, shaped the relief of this area, creating erosion forms in the upper western part of the basin, and depositing the material downstream. The catchment area is covered by forests (64.86%), agriculture land (17.37%), mountain pastures (9.21%), inhabited area (5.02%), meadows (2.32%), road infrastructure (0.86%) and water area (0.14%) (Çadraku et al., 2016). The climate of the Blinaja catchment is continental (Pllana, 2015), with average annual air temperatures ranging from -0.24°C to 22.14°C, while the average annual rainfall is 656.4 mm (Hydrometeorological Institute of Kosovo, station Prishtina, period 2001-2019). The river Blinaja is the main surface water body and its water is mainly used for irrigation, whereas groundwater from springs and wells provides drinking water needs of the local community. The river shows a typical seasonal water regime that is closely related to the intensity of rainfalls. Measurements carried out in the frame of this study showed that water yield of springs ranges from 0.1 to 7.0 l/s, and its regime depends on precipitation. The groundwater level ranges from 0.50 to 25.60 m, while its seasonal variation, as from the measurements of groundwater level in about 263 wells, is about 2 m which shows that groundwater is mainly fed by atmospheric precipitation (Çadraku et al., 2016). The Water quality upstream is evaluated as good, in the centre as excellent and north-eastern plain area as fair. Surface waters in this basin are subject to pollution from urban discharges and agricultural pollution.

Geology and hydrogeology

The study area is characterized by three rock complexes. The western and southwestern part is composed of Paleozoic rocks, represented by quartzite, quartzite-conglomerate, sandstone, sericitic shale, quartz-sericite, limestone quartz, biotitic, gneiss and marble (Lončarević 1971; Pavić et al., 1980; Meshi et al, 2012). The north-western part consists of Jurassic ultrabasic rocks represented by serpentinites, peridotites, harcburigites, etc. Neogene formations are widespread mainly on the eastern side (Fushë Kosovë) of the basin and are represented by clays, partly by lignite, etc. Quaternary formations spread out along both sides of the river Blinaja and its eastern tributaries and are represented by prolluvium, alluvium and vegeTable soils (Meshi et al., 2012), ranging in thickness from 0.5 to 3.5 m. The hydrogeological features of the region are closely related with the geological context that is lithology, tectonics, compactness, etc. Three aquifer types are distinguished: a) the aquifer related to fissured rocks, b) the porous – fissured aquifer related to Neogene and Quaternary deposits and c) the aquifer related to Palaeozoic rocks (Knobloch and Orana, 2006). The Palaeozoic rocks of the western and southwestern area possess very weak aquifer potential and they may be considered as aquiclude.

Data collection and procedures

Totally 28 water samples were taken for chemical analysis, from both spring and wells (Fig. 1). The research started with field activity-identification and determination of

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sampling location where some physic-chemical parameters were measured in situ and continued with laboratory analysis and interpretation and control of results. The main difficulty in sampling process is representation and integrity (Madrid and Zayas, 2007). In order that samples to be more representative, the selection of their location is made according to hydro-geological and geological context. The" GPS" instrument of the type Garmin 79C is used for the measurement of coordinates and altitude. Water samples were taken in polyethylene bottles, with a volume of 1 litter, closed with pressured cork and fillet cap. The bottles were filled, leaving a space under the compressed cap, about 1 mm, to eliminate the possibility of the pollution of the sampled water. Samples are stored in the field refrigerator in order to preserve natural conditions until they are sent to the laboratory. Water parameters were analysed in the laboratory for main anions and cations, while physic-chemical parameters such as temperature, pH and TDS were measured directly in the sampling location. Water parameters were analyzed in the laboratory for major anions and cations, while physico-chemical parameters such as temperature, pH and dissolved oxygen in water were measured directly at the sampling site. pH was determined with the CONSORT C830 pH-meter; Total alkalinity was determined with standard 0.155 mol/dm3 HCl solution, using US Geological Survey methodology. For the determination of total hardness, the titration method with complexometric EDTA (K III) was applied. The Ca2+ ion was determined by nitration of the sample with standard EDTA solution in the presence of the MUREXID indicator. The Mg2+ ion was determined by taking 100 ml of water for analysis in erlenmeyer where 5 cm3 ammonia buffer and a little black eryochrome were added and the whole was titrated until the colour changed from red to light blue. Cl- is determined by the photometric method which is analogous to standard methods such as EPA 325.1 and US-Standard Methods 45000-Cl-E. The determination of SO42- was done by the photometric method. Nitrate ion (NO3-) is defined in H2SO4 and H2PO4 by 2,6-Dimethylphenol (DMF) and 4,6-Dimethylphenol-photometric method which is analogous to standard method ISO7890/1 and DIN38405 D9. Water data are elaborated and interpreted by using graphs, charts, maps and statistical analysis (Hounslow, 1995). The Inverse Distance Weighted (IDW) interpolation method was used for construction of maps in the Arc Map 10.5 program (Schut, 1976; Burrough, 1986).

Water Quality Index (WQI)

The current formulation of the WQI is based on three measures of non-compliance or deviation from established water quality guidelines (CCME, 2001; CCME, 2005a; Lumb, 2006). The first component of the index is referred to as scope, and it measures the number of parameters out of

compliance with objectives as a percentage of the total number of parameters measured. The second component is referred to as frequency and measures how often a water quality objective is exceeded. The final component is referred to as magnitude, and measures by how much the objectives are exceeded. The three components are assembled into a unitless number scaled from 0 to 100. Higher index

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numbers reflect higher water quality, while lower numbers reflect poorer water quality. There are three factors in the index, and each of them has been scaled to range between 0 and 100 (Table 1).

**Table 1: Canadian Water Quality Index (CWQI) designation.**

| Index value | Designation | Interpretive Description |
|---|---|---|
| 95-100 | Excellent | Water quality is protected with a virtual absence of threat or impairment; conditions very close to natural or pristine levels. |
| 80-94 | Good | Water quality is protected with only a minor degree of threat or impairment; conditions rarely depart from natural or desirable levels. |
| 65-79 | Fair | Water quality is usually protected but occasionally threatened or impaired; conditions sometimes depart from natural or desirable levels. |
| 45-64 | Marginal | Water quality is frequently threatened or impaired; conditions often depart from natural or desirable levels, |
| 0-44 | Poor | Water quality is almost always threatened or impaired; conditions usually depart from natural or desirable levels. |

Since the index is designed to measure water quality, it was felt that the index should produce higher numbers for better water quality. The index equation is based on the water quality index (WQI) endorsed by the Canadian Council of Ministers of the Environment (CCME, 2001). The index allows measurements of the frequency and extent to which parameters exceed their respective guidelines at each monitoring station. Therefore, the index reflects the quality of water for both health and acceptability, as set by the World Health Organisation (WHO, 2004; 2007, 2011). The index is determined on an annual basis, taking into consideration not the mean of values but all the monitoring data (Table 2), thus resulting in an overall rating for each station per year.

**Table 2: Physic-chemical parameters of the groundwater (TDS-total dissolved solids, TH-total hardness, TUR-turbidity, DO-dissolved oxygen, COD-chemical oxygen demand, BOD5-biochemical oxygen demand, five days after sampling, ND-Not determined.**

| No. | Water point | Date of Sampling | T (°C) | TUR (NTU) | DO (mg/L) | COD (mg/L) | $BOD_5$ (mg/L) | pH | TDS (mg/L) |
|---|---|---|---|---|---|---|---|---|---|
| 1 | SP1 (Spring) | 13April.2015 | 14.20 | ND | 6.80 | 5.40 | 0.20 | 7.58 | 292.48 |
| 2 | | 08Aug.2015 | 15.70 | ND | 7.13 | 3.40 | 0.10 | 7.80 | 347.52 |
| 3 | | 8.Jan.16 | 11.10 | 1.91 | 7.67 | 3.70 | 0.40 | 8.03 | 339.84 |
| 4 | | 22Sept.2019 | 14.40 | 0.70 | 7.40 | 6.40 | 0.30 | 7.51 | 370.56 |
| 5 | SP2 (Well) | 13Apri.2015 | 13.60 | ND | 5.30 | < 0.10 | < 0.10 | 6.91 | 338.56 |
| 6 | | 08Aug.2015 | 15.70 | 2.30 | 2.08 | < 0.10 | < 0.10 | 6.94 | 295.04 |
| 7 | | 8.Jan.16 | 5.40 | 5.00 | 3.67 | 1.00 | 0.30 | 6.93 | 199.68 |
| 8 | | 22Sept.2019 | 13.10 | 2.50 | 3.50 | 3.80 | 1.70 | 7.02 | 279.68 |
| 9 | SP3 | 13Apri.2015 | 10.80 | ND | 7.60 | < 0.10 | < 0.10 | 7.03 | 225.92 |

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| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| 10 | (Spring) | 08Aug.2015 | 10.40 | 2.10 | 6.45 | 0.10 | < 0.10 | 7.01 | 382.72 |
| 11 | | 8.Jan.16 | 4.90 | 7.40 | 10.30 | 2.30 | 0.90 | 7.30 | 120.96 |
| 12 | | 22Sept.2019 | 9.90 | 2.20 | 6.00 | 1.30 | 0.50 | 6.82 | 494.72 |
| 13 | | 13Apri.2015 | 12.50 | ND | 3.60 | < 0.10 | < 0.10 | 6.92 | 361.60 |
| 14 | | 08Aug.2015 | 16.30 | 3.50 | 2.54 | 0.80 | < 0.10 | 7.18 | 369.28 |
| 15 | SP4 (Well) | 8.Jan.16 | 5.40 | 1.55 | 6.27 | 4.50 | 1.50 | 7.49 | 410.88 |
| 16 | | 17 Feb.2018 | 11.40 | 2.80 | 2.22 | 63.80 | 33.20 | 7.26 | 595.20 |
| 17 | | 22Sept.2019 | 19.60 | 0.70 | 3.20 | 3.80 | 0.20 | 6.38 | 330.88 |
| 18 | | 13Apri.2015 | 14.60 | ND | 4.30 | < 0.10 | < 0.10 | 7.21 | 513.28 |
| 19 | SP5 | 08Aug.2015 | 15.70 | 3.10 | 2.89 | < 0.10 | < 0.10 | 7.18 | 645.12 |
| 20 | (Well) | 8.Jan.16 | 10.40 | 0.82 | 3.89 | 4.50 | 2.10 | 7.50 | 664.32 |
| 21 | | 22Sept.2019 | 12.90 | 1.60 | 4.20 | 0.60 | 0.20 | 6.69 | 698.88 |
| 22 | | 13Apri.2015 | 14.00 | ND | 1.10 | 5.30 | 0.20 | 7.30 | 622.08 |
| 23 | SP6 | 08Aug.2015 | 15.00 | 4.20 | 1.60 | 5.30 | 0.20 | 7.33 | 668.16 |
| 24 | (Well) | 8.Jan.16 | 7.90 | 1.51 | 4.14 | 5.80 | 2.60 | 7.57 | 844.16 |
| 25 | | 22Sept.2019 | 14.10 | 2.10 | 0.20 | 2.70 | 0.10 | 7.11 | 744.96 |
| 26 | SP7 (Well) | 17-Feb-18 | 12.10 | 2.50 | 1.68 | 48.00 | 10.10 | 6.85 | 554.24 |
| 27 | SP8 | 17 Feb.2018 | 12.50 | 2.80 | 4.67 | 9.20 | 6.10 | 6.50 | 117.76 |
| 28 | (Spring) | 22Sept.2019 | 13.90 | 1.90 | 9.00 | 4.30 | 0.20 | 5.92 | 106.88 |

| No. | Water point | Date of Sampling | TH (ºdH) | $Na^+$ (mg/L) | $Ca^{2+}$ (mg/L) | $Mg^{2+}$ (mg/L) | $K^+$ (mg/L) | $HCO_3^-$ (mg/L) | $Cl^-$ (mg/L) | $SO_4^{2-}$ (mg/L) | $NO_3^-$ (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | | 13April.2015 | 20.44 | 1.74 | 48.90 | 82.06 | 0.05 | 408.70 | 6.44 | 117.00 | 3.20 |
| 2 | SP1 | 08Aug.2015 | 21.67 | 1.45 | 26.90 | 108.60 | ND | 457.60 | 28.60 | 76.40 | 2.70 |
| 3 | (Spring) | 8.Jan.16 | 21.50 | 1.12 | 34.50 | 72.43 | ND | 427.00 | 8.60 | 62.00 | 2.40 |
| 4 | | 22Sept.2019 | 18.80 | 2.06 | 14.00 | 73.10 | 0.06 | 402.70 | 4.62 | 10.70 | 4.60 |
| 5 | | 13Apri.2015 | 15.90 | 12.04 | 60.90 | 44.57 | 1.94 | 244.00 | 8.59 | 129.00 | 25.80 |
| 6 | SP2 | 08Aug.2015 | 14.00 | 10.25 | 56.90 | 33.40 | 2.03 | 221.60 | 8.59 | 110.00 | 25.00 |
| 7 | (Well) | 8.Jan.16 | 16.07 | 13.22 | 64.20 | 30.87 | 4.23 | 233.00 | 11.46 | 112.00 | 26.00 |
| 8 | | 22Sept.2019 | 11.20 | 11.90 | 43.70 | 22.10 | 2.77 | 195.20 | 9.23 | 41.40 | 26.10 |
| 9 | | 13Apri.2015 | 13.16 | 2.46 | 82.20 | 10.13 | 0.69 | 213.50 | 4.30 | 76.00 | 0.20 |
| 10 | SP3 | 08Aug.2015 | 17.86 | 2.38 | 146.40 | 8.10 | 0.83 | 393.20 | 10.70 | 69.00 | ND |
| 11 | (Spring) | 8.Jan.16 | 7.73 | 3.80 | 44.90 | 3.89 | 2.20 | 122.00 | 4.30 | 58.00 | ND |
| 12 | | 22Sept.2019 | 23.00 | 9.75 | 143.60 | 12.60 | 0.90 | 512.40 | 3.55 | 11.50 | 2.80 |
| 13 | | 13Apri.2015 | 18.87 | 18.53 | 97.80 | 31.40 | 31.08 | 274.50 | 34.01 | 169.00 | 52.00 |
| 14 | | 08Aug.2015 | 15.68 | 13.60 | 67.40 | 37.80 | 24.20 | 229.30 | 17.54 | 129.00 | 10.00 |
| 15 | SP4 (Well) | 8.Jan.16 | 18.48 | 15.27 | 87.40 | 34.20 | 27.38 | 250.00 | 32.90 | 145.00 | 55.50 |
| 16 | | 17 Feb.2018 | 23.30 | 9.59 | 95.80 | 38.90 | 23.50 | 263.18 | 36.10 | 25.56 | 44.20 |
| 17 | | 22Sept.2019 | 13.50 | 12.80 | 50.70 | 27.80 | 5.10 | 298.90 | 16.33 | 11.50 | 1.70 |
| 18 | | 13Apri.2015 | 29.68 | 18.72 | 72.20 | 108.20 | 0.73 | 436.80 | 47.98 | 161.00 | 48.50 |
| 19 | SP5 | 08Aug.2015 | 30.91 | 19.26 | 75.80 | 122.60 | 0.88 | 512.40 | 15.18 | 174.00 | 65.50 |
| 20 | (Well) | 8.Jan.16 | 34.22 | 21.18 | 69.80 | 106.21 | 4.32 | 491.00 | 60.87 | 159.00 | 54.50 |
| 21 | | 22Sept.2019 | 28.60 | 38.10 | 57.60 | 89.30 | 5.56 | 500.20 | 49.70 | 90.50 | 39.90 |
| 22 | | 13Apri.2015 | 36.23 | 26.44 | 97.40 | 113.40 | 1.95 | 640.50 | 41.53 | 179.00 | 14.70 |
| 23 | SP6 | 08Aug.2015 | 37.35 | 25.11 | 99.40 | 141.50 | 3.11 | 664.90 | 16.60 | 248.00 | 37.00 |
| 24 | (Well) | 8.Jan.16 | 44.13 | 32.80 | 115.90 | 121.30 | 5.42 | 683.00 | 40.80 | 269.00 | 33.00 |
| 25 | | 22Sept.2019 | 31.10 | 38.40 | 89.30 | 80.60 | 3.47 | 585.60 | 77.40 | 43.31 | 42.00 |
| 26 | SP7 (Well) | 17-Feb-18 | 22.20 | 7.63 | 107.90 | 30.90 | 4.85 | 261.40 | 36.50 | 19.88 | 42.10 |
| 27 | SP8 | 17 Feb.2018 | 3.70 | 4.76 | 18.00 | 9.70 | 3.07 | 81.50 | 19.50 | 3.91 | 4.10 |
| 28 | (Spring) | 22Sept.2019 | 3.40 | 4.99 | 19.00 | 3.10 | 4.55 | 84.20 | 0.71 | 11.30 | 3.20 |

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This will allow both spatial and temporal assessment of Blinaja basin water quality to be monitored and evaluated. Brown WQI was achieved after a critical study on the Horton index (Brown et al., 1970). In their study they concluded that the index only shows gradations in water quality. Brown (Year??) also reviewed the model parameters taking into account the expert opinions and their recommended weight values and proposed a weighted average index formula for stream water as follows (Uddin et al., 2021):

$$Brown\ WQI = \sum_{i=1}^{n} w_i S_i$$

Where the weight values summed to 1. Brown (Year??) concluded that this index function worked well if all water quality parameters were considered independent of each other.

## Results and discussion

The method of water quality index was applied for quality evaluation of rivers water in the territory of Kosovo by several authors (Bytyqi et al., 2018; Shala-Abazi et al., 2020). According to Bytyqi et al. (2018) founded that the WQI of the river Lepenc and Nerodime water (southern part of Kosovo) ranged between 36 to 76, classifying their water quality to vary from moderate to poor (bad). Shala-Abazi et al. (2020) evaluated the water quality index (WQI) for the river Sitnica water (central part of Kosovo) and showed that WQI ranges from 46 to 95 classifying these waters as to marginal category. The Blinaja study area drains water into the Sitnica River. For evaluation of Blinaja water quality two WQI methods are applied; the Canadian Water Quality Index (CWQI) method (2001) and the method according to Brown et al. (1972).

Chemical composition of groundwater

Groundwater chemistry is result of different factors contribution, like physical, chemical, geographical, geological, hydrogeological, biological and anthropogenic factor. In general, the natural chemical quality of groundwater is good, but high concentrations of the different components in certain situations may be a concern for their use by people. The groundwater of River Blinaja Basin has generally good physic-chemical parameters (Table 2) and is odourless, colourless and tasteless (Çadraku et al., 2016).

Temperature (T) In Blinaja groundwater it ranges from 4.90 to 19.60°C having an average value of 12.41±3.46°C (Table 3). There is a correlation between temperature of groundwater and air temperature (the lowest and highest temperatures in groundwater are met in January 2016 and August 2015, respectively) showing that shallow groundwater temperature is affected by air temperature throughout the hydrological year. The temperature of groundwater is lower in the mountainous western part, while the highest temperatures are met in the northern, eastern and central part of the basin.

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**Table 3: Descriptive statistics of physical-chemical parameters of groundwater (28 samples).**

| Parameters | Minimum | Maximum | Mean | Median | Standard Deviation | Variance | Skewness |
|---|---|---|---|---|---|---|---|
| T (°C) | 4.90 | 19.60 | 12.41 | 13.00 | 3.46 | 11.95 | -0.63 |
| TUR (NTU) | 0.70 | 7.40 | 2.53 | 2.20 | 1.55 | 2.39 | 1.72 |
| DO (mg/L) | 0.20 | 10.30 | 4.62 | 4.17 | 2.53 | 6.38 | 0.37 |
| COD (mg/L) | 0.10 | 63.80 | 6.66 | 3.55 | 14.28 | 203.89 | 3.48 |
| $BOD_5$ (mg/L) | 0.10 | 33.20 | 2.21 | 0.20 | 6.45 | 41.58 | 4.48 |
| pH | 5.92 | 8.03 | 7.12 | 7.15 | 0.44 | 0.19 | -0.49 |
| TDS (mg/L) | 106.88 | 844.16 | 426.26 | 369.92 | 200.99 | 40397.16 | 0.28 |
| TH (ºdH) | 3.40 | 44.13 | 21.17 | 19.66 | 10.01 | 100.20 | 0.35 |
| $Na^+$ (mg/L) | 1.12 | 38.40 | 13.55 | 11.97 | 10.86 | 117.90 | 0.92 |
| $Ca^{2+}$ (mg/L) | 14.00 | 146.40 | 71.02 | 68.60 | 34.87 | 1215.97 | 0.34 |
| $Mg^{2+}$ (mg/L) | 3.10 | 141.50 | 57.10 | 38.35 | 42.92 | 1841.85 | 0.45 |
| $K^+$ (mg/L) | 0.05 | 31.08 | 6.34 | 3.09 | 9.02 | 81.35 | 1.97 |
| $HCO_3^-$ (mg/L) | 81.50 | 683.00 | 360.30 | 346.05 | 172.38 | 29714.80 | 0.25 |
| $Cl^-$ (mg/L) | 0.71 | 77.40 | 23.31 | 16.47 | 19.69 | 387.57 | 1.05 |
| $SO_4^{2-}$ (mg/L) | 3.91 | 269.00 | 96.86 | 83.45 | 72.74 | 5290.69 | 0.63 |
| $NO_3^-$ (mg/L) | 0.20 | 65.50 | 25.64 | 25.90 | 20.87 | 435.50 | 0.24 |

Biochemical demand for oxygen (BOD5) ranges from 0.1 to 33.2 mg/L with an average value of 3.06±7.51 mg/L. The highest (33.2 mg/L) value is found at the measuring station SP4, while the minimum (0.1 mg/L) value is found at the station SP1 and SP6 (Table 3). 15 water samples or 75% of them fall within the BOD5 range 1-2mg/L.

Chemical Oxygen Demand (COD) ranges from 0.10 to 63.80 mg/L with an average value of 8.45±15.70 mg/L. The highest (63.80 mg/L) value is found at the station SP4, while the minimum (0.10 mg/L) is found at the stations SP2 and SP3. Besides a very few cases, most of COD values fall within WHO standard values (Table 2 and 5).

Turbidity ranges from 0.70 to 7.40 NTU having an average value of 2.53±1.55 NTU. The minimum (0.70 NTU) value is found in station SP1, while the maximum (7.40 NTU) value is found in station SP3 which represents a water source that drains from carbonate rocks. 20 water samples or 95.24% of them fall within WHO standard values.

Dissolved oxygen (DO) ranges from 0.20 to 10.30 mg/L with an average value of 4.62±2.53 mg/L. This wide variation of DO values indicates an extremely variable “state of purity” of groundwater. 16 samples or 57.14% of them fall within the WHO standard values, while 12 samples or 42.86% of them show lower DO values and mostly belong to groundwater from north-eastern part of the basin.

pH is controlled by the carbon dioxide-bicarbonate-carbonate equilibrium system (WHO, 2007) and indicates the acidity or alkalinity of a solution (Prasanth et al., 2012). In the groundwater of the River Blinaja Basin, the value of pH ranges from 5.92 to 8.03, with an average value of 7.12±0.44 (Table 3), showing a decline trend north-eastward. Thus, pH values (Table 2 and Fig.1) are higher in the northern part and eastern, while lower values are found in southern part of the basin.

Total dissolved solids (TDS), that represent the degree of salinity of a medium (Mitra et al., 2007), range from 106.88 to 844.16 mg/L, with an average value of 426.26±200.99 mg/L

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(Table 3). The highest TDS values are found at measuring stations SP5 and SP6 (Table 2). There is an increasing trend of the TDS values from the recharge western and south-western parts towards the north-eastern area (Table 2 and Fig. 1). Among others, this trend may be related with longer residence time of groundwater and higher temperatures of groundwater. TDS values in the

groundwater of Blinaja basin fall within the WHO standard guideline values (Table 5).

Total hardness (TH) ranges from 3.40 to 44.13°dH (German degrees), with an average value of 21.17±10.05°dH (Table 3). Higher TH values are found at measuring stations (SP1, SP5 and SP6), while lower ones at stations SP2, SP3, SP4, SP7 and SP8 (Table 2). Based on TH values the groundwater in this basin belongs to hard and very hard water. This might be conditioned by aquifer medium and especially by groundwater residence time, as it might be expected from the strong correlation between TH and TDS in SP5 and SP6 groundwater (Fig. 2a).

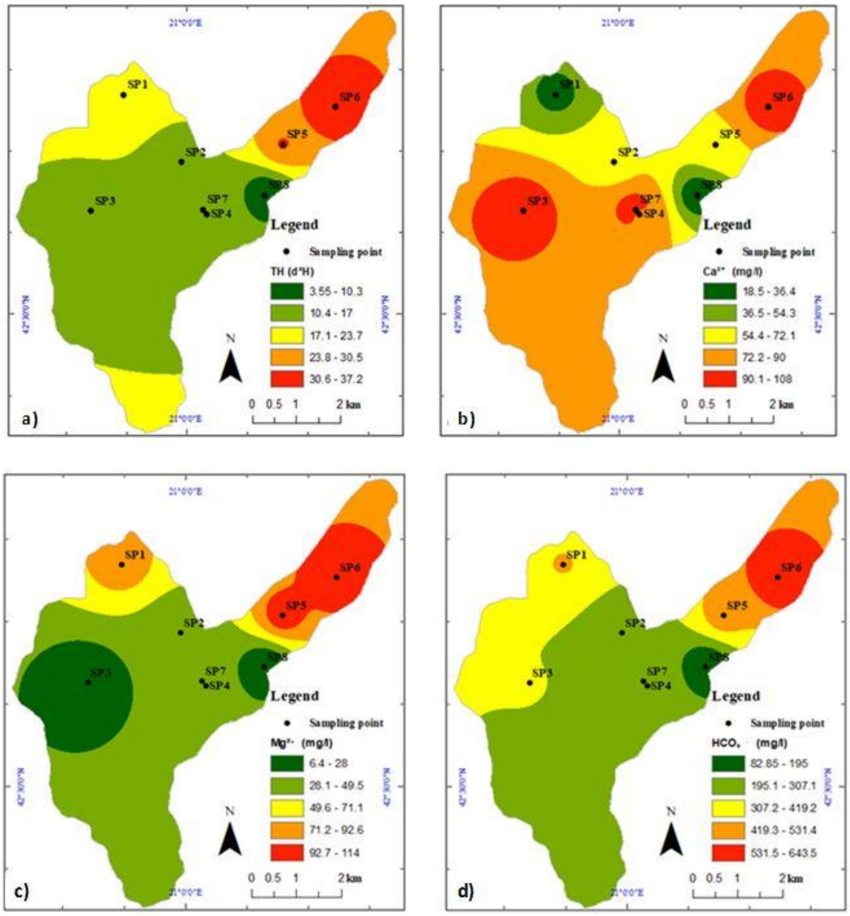


**Figure 2: Spatial variation of TH (a) Ca2+ (b), Mg2+ (c) and HCO3- (d).**

Sodium (Na+) ranges from 1.12 to 38.40 mg/L, with an average value of 13.55±10.86 mg/L (Table 3). The lowest Na + content is found in springs SP1 SP3 and SP8, while the maximum (38.40 mg/L) value is found in the well SP6 (Table 2 and Fig. 1). The sources of Na+ in the groundwater come probably from the assemblage of sodium aluminosilicate minerals, due to ion-exchange processes

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between $Ca^{2+}$ in water with $Na^+$ in aluminosilicate minerals, characterized by negative Chloride Alkaline Index (Schoeller, 1965). All samples analysed have shown $Na^+$ values within the WHO standard limits.

Calcium ($Ca^{2+}$) along with magnesium are essential to human health (Cotruvo and Bartram, 2009). The calcium concentration varies from 14.00 to 146.40 mg/L, with an average value of 71.02 ± 34.87 mg/L (Table 3 and Fig. 2b). The high values of calcium belong to the dry season and are introduced to the groundwater by limestone solution, fostered by pH lowering due to dissolved $CO_2$ and/or hydrolysis of silicate minerals, such as pyroxene, plagioclase, etc. 85.72% of water samples are within WHO standard values (Table 5), while 14.28% of them have higher $Ca^{2+}$ content.

Magnesium ($Mg^{2+}$) ranges from 3.10 to 141.50 mg/L, with an average value of 57.10±42.92 mg/L (Table 3). The highest values are found in the north-eastern and eastern areas of the basin (Fig. 2c). Magnesium comes from dolomite solution and from hydrolysis of olivine, pyroxene, serpentine (northeast basin), and of amphiboles and mica, as well (western basin). In the eastern part $Mg^{2+}$ probably derives from the solution of the magnesium sulphate and chloride salts. 12 samples or 42.86% of them are above, while 16 samples or 57.14% are below the WHO standard values.

Potassium ($K^+$) ranges from 0.046 to 31.08 mg/L with average value of 6.34±9.02 mg/L (Table 3). The highest $K^+$ values are found in the station SP4 in the central part of the basin (Table 2 and Fig. 1). Potassium entered the groundwater mainly from the decomposition of organic matter. 4 samples or 14.28% have $K^+$ content above WHO standard values, while 24 samples or 85.72% have lower values.

Bicarbonates ($HCO_3^-$) varies from 81.50 to 683.00 mg/L, with an average value of 360.30±172.38 mg/L (Table 3). Higher values are found at spring SP1 and wells SP5 and SP6 (Table 2) and belong to the northeast and east parts of the basin (Fig. 2d). This ion is probably related to dissolved $CO_2$ in water but mostly derives from dissolution of limestone and dolomite. 18 samples or 64.27% of them have bicarbonate content above the WHO standard values, while 10 samples or 35.73% are lower.

Chloride ($Cl^-$) ranges from 0.71 to 77.40 mg/L with an average value of 23.31±19.69 mg/L (Table 3). The highest (77.4 and 60.87 mg/L) values were found at well SP6 and SP5, respectively, while the lowest (0.71 mg/L) value was found in spring SP8 (Table 2 and Fig. 1). The chloride in groundwater is probably released from the smelting as sodium chloride used for snow and ice smelting on the road. Chlorides can also enter a watershed through water softener discharge or sewage contamination. All the $Cl^-$ values are within the WHO standard values (Table 5).

Sulphates ($SO_4^{2-}$) range from 3.91 to 269.00 mg/L, with an average value of 96.86±72.74 mg/L (Table 3). The maximum (269.00 mg/L) value was found at the well SP6, while the minimum (3.9 mg/L) value was found at the spring SP8 (Table 2 and Fig. l). High content of sulphate in the River Blinaja Basin groundwater are due to atmospheric deposition, sulphate mineral dissolution, and sulphide mineral oxidation (Krouse and Mayer, 1999). The $SO_4^{2-}$ values mostly fall

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within the WHO standard (Table 5).

Nitrates (NO3-) range from 0.20 to 65.50 mg/L with an average value of 25.64±20.87 mg/L (Table 3). The maximum (65.50 mg/L) value was found at the well SP5, while the minimum (0.2 mg/L) value was found at the spring SP3 (Table 2 and Fig. 1). The main source of nitrates in groundwater of the north-eastern plain area could be from the use of chemical fertilizers in agriculture. The decomposition of organic matter might be another source of nitrate's entrance into the groundwater. 4 samples or 14.28% of the total, are above, while 24 samples or 85.72% of them, are below the WHO allowed values (Table 5).

In the Table 3, where the descriptive statistics of physical-chemical parameters are shown, it may be seen that mean values are larger than median as indicated by positive skewness for most elements except temperature and pH which have negative skewness. The positive skewness and large outliers are generally characteristic for distribution of geochemical data (Rock, 1988). In fact, TUR, BOD5 and K+ that have higher positive skewness values (Table 3) have also larger boxplot outliers (not shown).

The correlation matrix of the physic - chemical parameter values is given in the Table 4, where TH has strong (R=0.95) correlation with HCO3- and high (R=0.87) correlation with Mg2+ indicating that TH is mostly represented by temporary carbonate hardness of magnesium. This is also confirmed by high (R=0.84) correlation between Mg2+ and HCO3- which entered the groundwater through dissolution of carbonates and hydrolyses of silicates, respectively. TH has a moderate (R=0.72 and 0.71) correlation with Na+ and SO42-, respectively, indicating that permanent sulphate hardness is of lesser importance to the TH. A moderate (R=0.74) correlation between Na+ and Cl- and a low to moderate (R=0.67) one between Mg2+ and SO42- is indication of both the hydrolysis of the silicate minerals and cation exchange processes in groundwater (Table 4).

The physic-chemical parameters do not show the same variation extent throughout the basin as it could be seen by values of variance and/or standard deviation (Table 3). Thus, temperature and pH values are characterized by low variance, while HCO3 and TDS contrast them having high values of variance (Fig. 3).

**Table 4: Correlation Matrix of the physic - chemical parameter values.**

| | **pH** | **TDS** | **TH** | **$Na^+$** | **$Ca^{2+}$** | **$Mg^{2+}$** | **$K^+$** | **$HCO_3^-$** | **$Cl^-$** | **$SO_4^{2-}$** | **$NO_3^-$** |
|---|---|---|---|---|---|---|---|---|---|---|---|
| pH | 1 | | | | | | | | | | |
| TDS | 0.31 | 1 | | | | | | | | | |
| TH | 0.50 | **0.90** | 1 | | | | | | | | |
| $Na^+$ | 0.03 | **0.78** | **0.72** | 1 | | | | | | | |
| $Ca^{2+}$ | 0.04 | 0.55 | 0.46 | 0.34 | 1 | | | | | | |
| $Mg^{2+}$ | 0.55 | **0.72** | **0.87** | 0.55 | 0.05 | 1 | | | | | |
| $K^+$ | 0.09 | 0.03 | 0.10 | 0.09 | 0.16 | 0.18 | 1 | | | | |
| $HCO_3^-$ | 0.48 | **0.83** | **0.95** | 0.61 | 0.43 | **0.84** | 0.24 | 1 | | | |
| $Cl^-$ | 0.16 | **0.71** | 0.59 | **0.74** | 0.26 | 0.48 | 0.22 | 0.47 | 1 | | |
| $SO_4^{2-}$ | 0.40 | 0.50 | **0.71** | 0.53 | 0.33 | 0.67 | 0.14 | 0.54 | 0.27 | 1 | |

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|---|---|---|---|---|---|---|---|---|---|---|---|
| $NO_3^-$ | 0.12 | 0.60 | 0.45 | 0.58 | 0.44 | 0.35 | 0.34 | 0.24 | 0.60 | 0.48 | 1 |

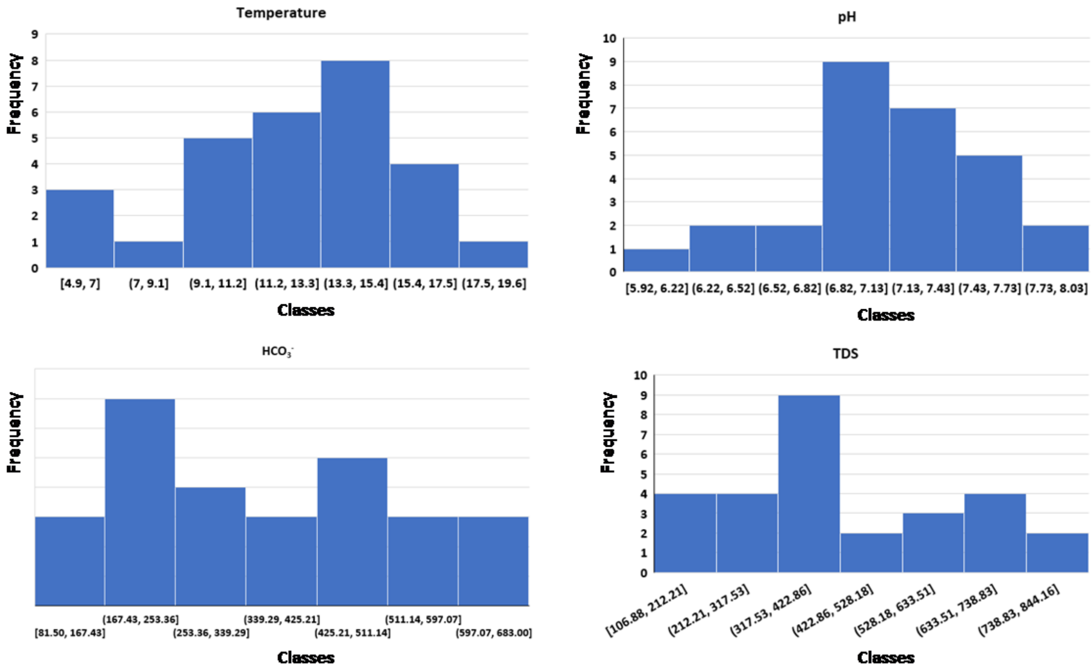


**Figure 3: Histograms of temperature pH, TH and TDS values.**

Such a variation of the physic-chemical parameters is reflected in the groundwater hydro-chemical types which are represented by HCO3-Mg, HCO3-Ca, HCO3-Mg-Ca and HCO3-$SO_4$-Mg-Ca, distributed to the north-northwest, west, southeast and east, respectively (Çadraku, 2018).

Assessment of groundwater quality by means of WQI

The WQI was calculated according to the method of the Canadian Council of Environment Ministers (CCME, 2001, 2005) and referring to the limit values of WHO standard (Table 5). The relevance of the WQI is given by the importance as instrument in the authorities' management plans to improve water quality in the area, including the citizens' information concerning the water resources quality in their living area (Oişte, 2012).

**Table 5: WHO standard values (WHO, 2009).**

| Parameters | Units | WHO standards |
|---|---|---|
| T | °C | 12 - 25 |
| TUR | NTU | 1.0 |
| DO | mg/L | 4.0-6.0 |
| COD | mg/L | 5.0 |
| $BOD_5$ | mg/L | 6.0 |
| pH | - | 6.5 - 8.5 |
| TDS | mg/L | 500 |
| TH | $^0$dH | 10-17 |
| $Na^+$ | mg/L | 50 |
| $Ca^{2+}$ | mg/L | 75 |
| $Mg^{2+}$ | mg/L | 50 |
| $K^+$ | mg/L | 12 |
| $HCO_3^-$ | mg/L | 250 |
| $Cl^-$ | mg/L | 250 |
| $SO_4^{2-}$ | mg/L | 150 |
| $NO_3^-$ | mg/L | 50 |

WQI values in groundwater of the River Blinaja Basin range from 66.52 to 100, classifying the collected groundwater samples in the River Blinaja Basin from fair to excellent. In four monitoring stations (SP1, SP3, SP4, SP7) or in 50% of them, the water quality is ranked to good category, in two stations (SP5, SP6) or in 25% of the them the

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water is ranked as Fair, and in the well SP2 and spring SP8 is ranked as excellent (Table 6). In spatial terms (Fig. 4), the lower WQI values of groundwater correspond to the north-eastern part of the basin, while the highest WQI value belong to groundwater from its central part. The low values of WQI in the north-eastern part are due to both longer residence time of groundwater and probably the interference of different human activities.

**Table 6: Calculation of CCME water quality index.**

| Station/ Source | F1 | F2 | F3 | CCME WQI | Designation |
|---|---|---|---|---|---|
| SP1 (Spring) | 15.38 | 16.00 | 9.90 | 85.97 | Good |
| SP2 (Well) | 0.00 | 0.00 | 0.00 | 100.00 | Excellent |
| SP3 (Spring) | 15.38 | 8.00 | 4.80 | 89.61 | Good |
| SP4 (Well) | 23.08 | 13.85 | 7.53 | 83.86 | Good |
| SP5 (Well) | 30.77 | 26.92 | 14.87 | 74.88 | Fair |
| SP6 (Well) | 46.15 | 28.85 | 20.02 | 66.52 | Fair |
| SP7 (Well) | 15.38 | 15.38 | 0.95 | 87.43 | Good |
| SP8 (Spring) | 0.00 | 0.00 | 0.00 | 100.00 | Excellent |

In Figure 5, are plotted the parameters that exceed the WHO guideline in order to understand which parameters were contributing the most to the WQI. From the figure is evident that bicarbonate, dissolved oxygen, Mg2+, Ca2+ and total hardness account for over 60% of the exceedances observed in the WQI suggesting that they are the most common, and maybe having the most influence on the index. In fact, this complies with the prevalence of the HCO3-Mg-Ca hydro-chemical type of the groundwater which correlates with very hard waters in the north-eastern

part of the aquifer. The lowest content of DO also belongs to groundwater of the north-eastern part of the aquifer, probably due to its long distance from the recharge area and/or anthropogenic contaminations.

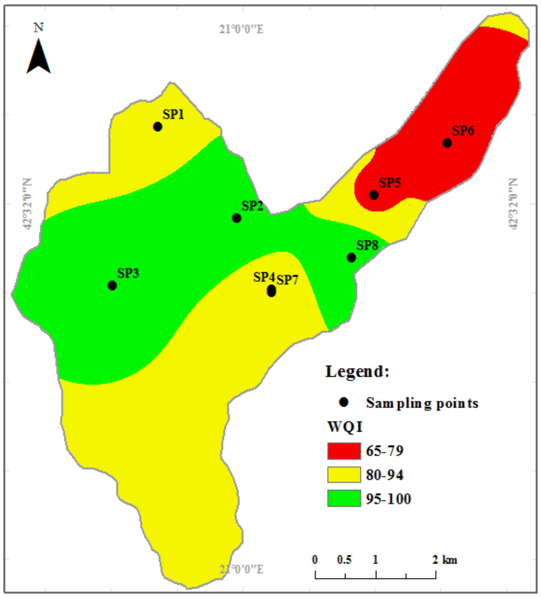


**Figure 4: Map of the spatial distribution of CCME WQI in Blinaja river basin.**

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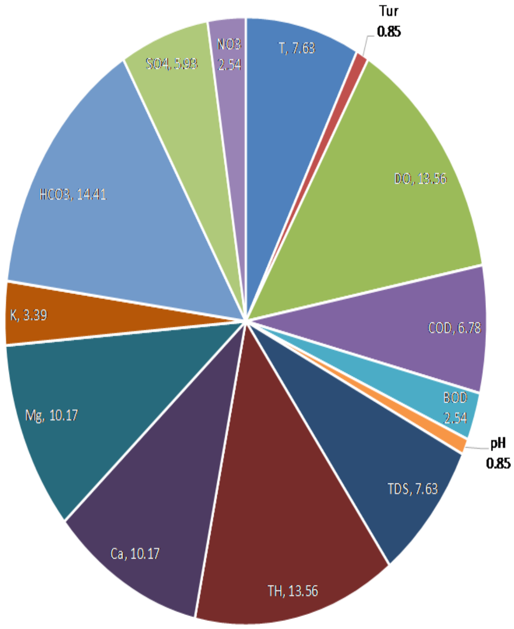


**Figure 5: Parameters that exceeds the WHO guideline (percentage of total exceedances) for WQI.**

Alertatively, the method of Brown et al. (1972) was applied for the evaluation of water quality in the River Blinaja Basin, which was considered as the water quality index which can be used efficiently in improving the water quality programmes (Saleem, et al., 2016). According to this method, the water quality was ranked in five categories: Excellent, Good, Poor, Very poor, Unfit for consumption that corresponds to the following categories in the Canadian WQI: Excellent, Good, Fair, Marginal, Poor, respectively. Based on the method of Brown et al. (1972), the groundwater in the River Blinaja Basin was classified from good to excellent besides station SP4 whoose groundwater quality was assessed very poor (Table 7). Comparing the results of Tables 6 and 7 it is evident that there is a complete match of water quality status in stations SP1, SP2, SP7 and an incomplete match in the others. In conclusion, the water quality classification by Canadian WQI method seems to fit better with the hydrogeological context of the River Blinaja Basin.

**Table 7: Water quality classification according to the method of Brown et al. (1972).**

| Water point | WQI | WQI |
|---|---|---|
| SP1 (Spring) | 41.38 | Good |
| SP2 (Well) | 21.7 | Excellent |
| SP3 (Spring) | 14.99 | Excellent |
| SP4 (Well) | 81.75 | Very Poor |
| SP5 (Well) | 46.59 | Good |
| SP6 (Well) | 48.28 | Good |
| SP7 (Well) | 33.82 | Good |
| SP8 (Spring) | 35.42 | Good |

## Conclusions

Groundwater from eight water points, was sampled during the period between April 2015 and September 2019. In River Blinaja Basin, groundwater is odourless, colourless and tasteless. Most of values of the physic-chemical parameters are within the WHO standards, while a few exceed these limits.

The physic-chemical parameters show different variation throughout the basin which is indicated by their respective values of variance and/or standard deviation. The most prevalent hydro-chemical types are represented by HCO3-Mg, HCO3-Ca, HCO3-Mg-Ca and HCO3-SO4-Mg-Ca.

According to the CWQI method the groundwater quality index (WQI) in Blinaja basin ranged from 66.52 to 100, while according to Brown et al. (Year??) method, the WQI varied from 21.7 to 81.75. Both the above mentioned WQI methods showed that these waters are of better quality, which should be expected due to two factors: firstly, groundwater is to some extent protected by surface contaminations and secondly, the study area is a peripheral area of the Sitnica River basin and is not highly exposed to agricultural, industrial and civil pollutants.

The spatial distribution of the WQI showed that most of the groundwater in the study area fall within the “Fair” to “Excellent”

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categories. Bicarbonate, dissolved oxygen, Mg2+, Ca2+ and total hardness account for over 60% of the exceedances observed in the WQI having the most influence on the index.

Both methods of WQI evaluation showed that groundwater of River Blinaja Basin is mainly within the allowed limit values to be used for drinking water. However, the groundwater of the north-eastern part, needs some treatment before consumption, and it also needs to be protected from surface contamination hazards.

This study could be a baseline for the authorities to establish a groundwater management plan in the study area in the future.

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