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Application of the Water Quality Index (WQI) model for groundwater quality estimation on urban mixed area

Tsetska Simeonova* **and Lyuba Nenova**

Agricultural Academy, „N. Poushkarov" Institute of Soil Science, Agrotechnologies and Plant Protection, 7 Shosse Bankya str., 1331 Sofia, Bulgaria
**Corresponding author:* cecka_simeonova@abv.bg

Abstract

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In recent decades, groundwater has been affected by the growth of urban areas, which causes serious environmental problems such as its enrichment with nitrates and many elements and deteriorates its quality. In the present study, an attempt was made to assess the groundwater quality of a mixed urbanized area by using the Water Quality Index (WQI), by weighted arithmetic mean index method. The monitoring was conducted in the period of 2022, on the watershed of the village of Lozen (near the city of Sofia). Mixed urban areas, where intensive vegetable crops were grown are included in the scheme of the study. The physico-chemical indicators such as (pH, electrical conductivity – EC, total dissolved solids – TDS, total hardness – TH) were studied on the underground waters and their cation-anion composition was determined. It was found that groundwaters were characterized by alkaline reaction and higher content of chemical elements some of which exceed the Maximum Permissible Concentration Level (MPCL) for drinking water. The groundwater was observed to have a calcium-hydrocarbonate-sulfate composition. According to the results of the WQI model, the groundwater quality status could be classified into following categories: excellent and good quality (33% of the investigated wells), poor (42% of the domestic wells), while the remaining samples very poor quality and unsuitable. It was established that the water sources with degraded quality are located mainly in a mixed urban area, where the accumulated amounts of residual nitrogen in the soil will continue to play the role of a point source of nitrates in groundwater due to soil and hydrological characteristics and intensive vegetable grown. The dynamics of the processes causing enrichment of groundwater with various elements and their redistribution in space require periodic monitoring of their chemical composition with a view to updating the information on their condition.

Keywords: chemical composition; groundwater; mixed urban area; Water Quality Index (WQI)

Introduction

The water quality has a significant impact on human health, economic and social development. It influences on agricultural production, livestock farming, food production, industry, forestry and many other areas (Khatri and Tyagi, 2014; Ariza-Restrepo et al., 2022). The chemical composition of groundwaters and surface waters depends on various factors: natural (soil and geological profiles, groundwater flow velocity, groundwater-rock interaction); dynamic natural factors such as climate and precipitation, anthropogenic (fertilization, septic systems, livestoc wasters, industry, land use, pollution with heavy metals), etc. (Sánchez et al., 2007; Stoicheva et al., 2013; Lobato et al., 2015; Uddin et al., 2018; Uddin et al., 2021; Hrelja et al., 2022). The water quality is followed through the constant monitoring, which is important for determining the spatial and temporal trends of physico-chemical characteristics and the composition of surface waters and groundwaters. Many groundwater quality monitoring programs have been developed to prevent

water pollution due to intensive anthropogenic loading of catchments (Council Directive 91/676/EEC, Council Directive 98/83/EEC and Directive 2000/60/EC). Water quality, measured by assessing the physico-chemical and biological properties of water against a set of standards, is used to determine whether water is suitable for consumption or safe for the environment. (Khatri and Tyagi, 2014). These indicators are different depending on the purposes for which the water is used.

In their research (Qin et al. 2013) use principal component analysis (PCA) to identify various major natural and anthropogenic factors and processes that influence water status and explain about 82% of the total variation in water quality parameters. According to the authors, by analyzing the distribution of factor scores combined with geological, hydrogeological and hydrological cycles the main factors are: surface water infiltration; multi-factor processes; geogenic enrichment; rainfall and contamination from agricultural fertilizer. In addition, land management practices have a significant impact on groundwater chemistry. Many statistical methods such as multivariate statistical techniques are also used to evaluate and interpret large data sets with a view to obtaining better information about water quality and in identifying variations and sources of groundwater contamination (Devic et al., 2014).

When assessing water quality, a differentiated approach is usually applied based on individual physico-chemical indicators, which are compared with standard values, but in this way a comprehensive overall view of the state of groundwater cannot be created. The complex or integrated approach allows the obtained data to be integrated into a whole, and the final assessment to be expressed in the form of a number, taking into account the suitability of groundwater for drinking and domestic water supply (Vasileva, 2019). It uses the Groundwater Quality Index method. This is a mathematical model for calculation, through which a more complete integrated view of the quality status of the groundwater is obtained and groups the waters into certain quality classes. It was first developed by (Horton, 1965) for surface water estimation. The history of the application of the index is described in the works of Saeedi et al. (2009); Bharti and Katyal (2011) etc. In the studies of Vasileva (2019); Ram et al. (2021), it is reported that a number of researchers (Brown et al., 1972; Boah et al., 2015; Jareda et al., 2016; Shankar and Kawo, 2019; Bawoke et al., 2020) have developed different WQI or GWQI models based on weighting and evaluation of different water quality parameters. As a result, a numerical evaluation expression with values from 0 to 100 was obtained, which expresses the combined impact of the investigated parameters for the overall state of water quality.

The aim of the study was to assess the quality of water sources from a mixed urbanized area using the Water quality index model.

Materials and Methods

The study was carried out in a model catchment – the village of Lozen, Sofia (N42°37.519, E23°27.533) with an altitude of 700–900 m, which falls in the area of the high fields of Western Central Bulgaria, located in the foothills on the Lozen Mountain (Figure 1). The climate is moderately continental, subhumid, with negative winter temperatures, the average summer temperatures are above 20 °C, in July they reach 30 °C. The annual amount of precipitation is about 590–600 mm, with a predominance of autumn-winter precipitation. (Levicharska, 1991).



Fig. 1. Lozen village, Sofia region
Source: Authors' own elaboration

Monitoring of the waters was carried out during the spring-summer period of 2022. The soil was defined as Leached Cinnamon Forest Soil (Chromic Luvisols), (WRBSR, 2006). The soil has a heavy sandy-clay soil texture containing particles < 0.01 mm – 66.1% on average for the layer 0–90 cm (Table 1), weakly acidic to neutral reaction, with values of humus (2.48%) in 0–30 cm soil layer, organic C (1.24%) and total nitrogen (0.132%), the cation exchange capacity (CEC) is high in the range of 39.8–41.0 cmol/kg soil. The degree of saturation with bases is low, in which calcium predominates (Simeonova et al., 2016a). The relative weight of this soil is 1.28 g/cm^3 for the surface layer and increases in depth -1.44, in the case of total porosity the dependence is opposite, it decreases in depth 51.8–46.7%. The field capacity of the soil varies between 28.9 and 27.1%. The soil has a good water holding capacity, low filtration rate – 0.0003 cm/s, this soil is characterized by poor hydraulic conductivity between layers and deeper groundwater (Stoichev et al., 1980; Mateva et al., 1982). The depth of some of the investigated groundwater varied from 10 to 36 m.

Twelve water sources were included in the monitoring studies (catchments, domestic wells and fountains), located only in the urbanized area. The areas adjacent to the wells were used to grow home vegetable gardens, which were intensively fertilized and irrigated. The waters were analyzed for the values of pH, electrical conductivity (EC), major cations and anions (K^+, Na^+, Ca^{2+}, Mg^{2+}, NO_3^-, HCO_3^-, Cl^-, SO_4^{2-}) by the following methods: pH – potentiometrically, EC electroconductivity (Arinushkina, 1970); nitrates, sulfates and chlorine were measured by "Spectroquant Pharo 100"; Merck Millipore (PHARO 100). Potassium and sodium were determined by flame photometer, calcium and magnesium – by atomic absorption spectrometry – AAS (Page et al., 1982), hydrocarbonate by titration with $0.02nH_2SO_4$ to pH 4.4 (Arinushkina, 1970).

The following physico-chemical characteristics were determined: TDS – Total dissolved solids is a total quantitative indicator of dissolved substances contained in the water, which are found in the form of inorganic salts and a small amount of soluble organic substances. It was found that the relationship between this parameter TDS and EC for groundwater is linear and can be calculated by the formula: TDS (mg/l) = A x EC in mS/m (Weaver et al., 2007), where A is a coefficient that can take different values between 5.5 and 9. Total hardness $TH_{(CaCO_3)}$ is the concentration of Ca^{2+} and Mg^{2+} ions expressed as $CaCO_3$ equivalent (Pal et al., 2018). In the material, the results are presented in mgeqv/l.

Calculation of the Water Quality Index (WQI)

The groundwater quality index was calculated according to equations presented in the works of Brown et al. (1970); Boah et al. (2015); Jareda et al. (2016); Jeyakumar et al. (2017). Calculations pass through several stages:

1) Calculation of q_i, this is a measure of the quality rating for each parameter (i,) involved in the model;

$$q_i = 100\ [v_i - v_{i0} / S_i - v_{i0}],\ q_i = 100[v_i / S_i],$$

where v_i – is value of the i^{th} parameter, S_i is standard permissible value of the i^{th} parameter, v_{i0} is the ideal value for each parameter, which is assumed to be 0 for drinking water. With the exception of the pH parameter, for which a value of 7.0 is assumed, for naturally pure waters, and for dissolved oxygen, for which a value of 14.6 mg/l is assumed (Boah et al., 2015).

2) Calculation of W_i weight coefficient (normalized weight) of each parameter. The weights for the water quality parameters were assumed to be inversely proportional to the recommended standards for the corresponding parameters by the following equation:

$$W_i = K / S_{i,},$$

where W_i is unit weight for the i^{th} parameter S_i is standard value of the i^{th} parameter, K is constant of proportionality and is given by the following equation:

$$K = 1 / [1/vs_1 + 1/vs_2 + ... + 1/vs_n].$$

The overall water quality index is estimated by linearly aggregating the quality score with a weight unit $WQI = \Sigma\ q_i W_i / \Sigma\ W_i$

The calculated WQI values are categorized into five classes or five types of water (Table 2), with the highest class being water of excellent quality to water not suitable for drinking.

Table 1. Physico-chemical characteristics of the studied soil

Dept, cm	pH /H_2O/	Humus, %	Total N %	$CaCO_3$ %	C/N	CEC cmol/kg	Particle size, %		
							0.05–0.001	< 0.001	< 0.01
0–30	6.80	2.48	0.132	0.00	10.0	39.8	36.1	37.7	65.1
30–60	6.40	1.29	0.110	0.00	8.50	40.8	36.3	39.5	67.3
60–90	6.60	1.40	0.100	0.00	7.50	41.0	44.5	38.0	65.8

Source: Authors' own elaboration

Table 2. WQI range and status of the water

WQI*	Groundwater quality status
0–25	Excellent
26–50	Good
51–75	Poor
76–100	Very poor
> 100	Unsuitable for drinking

*Brown et al. (1972), Chatterjee and Raziuddin (2002)
Source: Authors' own elaboration

According to Bora and Goswami (2016), water of excellent and good quality can be used for drinking purposes, irrigation and industry, with poor – for irrigation and industrial purposes, with very poor for irrigation, and when it falls into the latter group it must be treatment before use.

Results and Discussion

To understand the processes of water formation, the content of chemical elements in them and their quality, it needs to be considered in the context of the natural factors on which their formation depends on, but also to be connected with the ways of land use, which reflect different degrees of anthropogenic load as a result of applied agricultural practices in the adjacent territories. In the studied catchment, as it has been mentioned above, there is no direct hydraulic connection between the individual aquifers. This fact of one is a precondition that there is no direct connection between the anthropogenic load and pollution with nitrates, and on the other hand, the possibility of refreshing the underground water, through the inflow of fresh water is limited. This requires a specific approach when assessing water pollution in this area depending on the specific conditions of land use, the hydrogeological characteristics of the terrain and the water balance in the area of the given water source. Here, rather, the relief (the territory is on a weakly pronounced sloping terrain in the highest commercially exploited part of the mountain), and the hydrogeological features of the terrain, which determine the territories of aquifers, have a significant influence on the pollution of the groundwater in the area (Simeonova et al., 2016b).

Results obtained for the chemical composition of groundwater in the spring-summer period of 2022 showed that that they had pH values between 7.5 and 8.7 (average 7.9) (Table 3), which indicates the alkaline nature of the groundwater (ideal pH range is between 6.5–8.5; Regulation № 9/2001). Electrical conductivity provides information about the water composition, because the higher the electrical conductivity, the more unavailable it is to plants, regardless of the applied irrigation. It was established that higher electrical conductivity is characteristic of waters with a higher amount of dissolved substances and, accordingly, a higher concentration of ions in them (Jeyakumar et al., 2017). From the results obtained it can be seen that the lowest electrical conductivity was registered in sample 1 – 136 µS/cm (Table 3), while the highest is in sample 9 – 1100 µS/cm. However, the MPCL for drinking water of 2000 µS/cm was not exceeded (Regula-

Table 3. Chemical composition of groundwater, Lozen village, 2022

№	pH	EC µS/cm	TDS mg/l	$TH_{(CaCO3)}$ meqv/l	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-
					mg/l							
S1	7.5	136	85.7	9.1	14.4	3.9	7.4	1.3	42.9	18.0	50.0	13.4
S2	8.2	1070	674.1	14.7	209.6	41.8	36.9	9.7	376.0	89.0	155.0	96.2
S3	7.7	1190	749.7	11.6	162.4	34.2	40.8	2.0	375.1	124.0	112.0	85.9
S4	7.8	474	298.6	5.7	64.0	27.1	25.	0.3	231.3	79.0	9.2	18.6
S5	7.8	444	279.7	3.5	42.4	14.6	27.8	1.7	138.4	70.0	5.6	13.3
S6	8.2	825	519.8	7.1	72.8	38.7	38.7	0.6	112.5	172.0	87.0	109.6
S7	8.3	481	303.0	5.5	65.6	24.0	62.1	2.9	217.9	93.0	10.1	15.3
S8	8.7	335	211.1	4.4	53.6	17.9	20.9	0.4	176.8	100.0	15.3	66.8
S9	7.6	1100	693.0	11.0	134.5	45.2	31.1	0.7	245.6	169.0	101.0	70.7
S10	7.7	1050	661.5	10.5	133.6	40.2	14.2	1.9	138.4	217	107. 0	116.4
S11	8.4	816	514.1	6.5	76.0	29.5	29.0	25.1	133.9	199.0	106.0	106.8
S12	7.5	1050	661.5	16.4	216.8	56.7	43.4	5.6	230.3	144.0	20.7	174.0
min	7.5	136	85.7	3.5	14.4	3.9	7.4	0.3	42.9	18.0	5.6	13.3
max	8.7	1070	749.7	16.4	216.8	56.7	62.1	25.1	376.0	199.0	155.0	174.0
mean	7.9	748	471.0	8.8	103.8	31.4	31.4	4.4	201.6	122.8	64.9	73.9
SDV	0.4	357	224.7	4.1	66.3	14.7	14.4	7.1	100.3	58.72	52.1	51.1
CV%	5	48	47	46	64	47	45	160	50	48	80	69

Source: Authors' own elaboration

tion № 9/2001). According to Ram et al. (2021), in densely urbanized areas high EC in some places suggests mixing of wastewater with groundwater.

As can be seen from the Table 3, there is a significant variation in the studied parameters. According to Qin et al. (2013), the significant variation in groundwater hydrochemical parameters is due to both natural and anthropogenic processes. The total mineralization of waters or total dissolved solids (TDS) is highly dependent on point sources of pollution such as agricultural practices, domestic runoff, which cause contamination and discharge of waters. Industrial or wastewater treatment also significantly affect the concentration of ions in waters. In the present study, TDS ranged from 85.7 to 749.7 mg/l, (mean 471.0 mg/l) (Table 3). In many water quality standards (TDS) ranges between 500–1000 mg/l, although according to this indicator the studied water sources fit within these limits, significant loading of some of them was also taken into account (№ 2, 3, 9 and 12). The rest of the groundwater can be classified as excellent and good quality according to TDS indicator. Total hardness TH (as $CaCO_3$) is the amount of dissolved calcium and magnesium in the water. It can be expressed in different measurement units, in our research it was given as mgeqv/l (Regulation 9, MPCL – 12 mgeqv/l). From the researched samples it was found that total hardness varied between 3.5 and 16.4 mgeqv/l, on average of 8.8 mgeqv/l. A certain part of the samples, about 50%, had a high total hardness that was at the limit or exceeded the MPCL. It should be noted that the illuvial horizon of this soil gradually passes into carbonate-enriched soil forming materials. It is known, that water is a good solvent for such type of minerals.

Content of major ions in groundwater

Potassium and sodium content in the groundwater

In general, potassium is present in many minerals and rocks that are relatively soluble. In addition, vegetable crops were grown in the area, which were treated with fertilizers, crop protection chemicals and also irrigated. The potassium content in the wells varied within very wide limits between 0.3–25.1 mg/l. Large differences in absolute values and a significant coefficient of variation were found (Table 3). However, 92% of the wells contained potassium between 0–10 mg/l, and 8% between 25–50 mg/l. The sodium content along both profile lines of the studied area varied between 7.4–62.1 mg/l. It was found that in 67% of the water sources the values of this element were in the range between 25–50 mg/l, and in 8% between 0–10 mg/l. The trend was opposite to that for potassium.

Calcium and magnesium content in the groundwater

The concentrations of Ca^{2+} in the studied wells ranged between 14.4 and 216.8 mg/l, on average of 103.8 mg/l, with the highest reported content fully corresponding to the highest nitrate content (Table 3). The data obtained showed that 58% of the wells contained calcium between 0–100 mg/l, while 25% of them fell into the range 100–200 mg/l, and 17% were between 200–250 mg/l. Some of the examined wells contained calcium above the MPCL of 150 mg/l for drinking water (Regulation 9/2001). From the results for magnesium content, it was found that 92% of the examined wells contained magnesium from 0–50 mg/l and none exceeded the MPCL for this element – 80 mg/l (Regulation 9). A similar distribution of calcium in the same area was observed in a study by (Simeonova et al., 2016c), while magnesium showed a slight decrease in its concentrations compared to the monitoring conducted 15 years ago.

Nitrate content in the groundwater

Nitrate concentrations in the studied groundwater varied in a wide range – 13.3–174.0 mg/l, average 73.9 mg/l. The mechanisms of the entry of nitrates into the groundwater are different and are determined by many factors: soil, topography and ways of land use, the hydrogeological features of the terrain, which determine the movement of water in the aquifers, the use and storage of mineral and organic fertilizers, climatic (the amount of precipitation), type and number of irrigations.

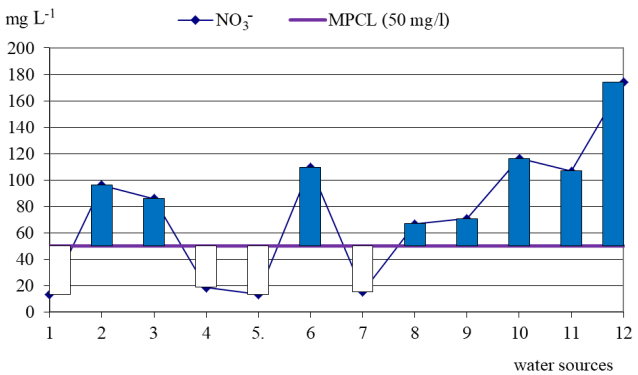


Fig. 2. Nitrate content in groundwater, Lozen village, 2022

Source: Authors' own elaboration

The shallower wells generally have higher nitrate nitrogen content, as do those at lower points on the hydraulic gradient (Fig. 2). The areas adjacent to all wells where nitrate content was above 100 mg/l were used for intensive vegetable production, and together with the livestock reared in

the past, as well as the illegal storage of manure, continued to play a role as a point source of pollution. In a study by Simeonova et al. (2016b), conducted in the same watershed where groundwater monitoring had been ongoing for about 15 years, it was found that loadings with elements persisted but did not deteriorate. Interest represents the fact that the wells were almost equally distributed regarding nitrate content. The summarized data showed that 34% of the surveyed wells contained nitrates in the groundwater of 10–25 mg/l, the same percentage was calculated for the surveyed water sources in the range of 50–100 mg/l and above 100 mg/l, i.e. in more than 60% of the wells the nitrate content was around and above the MPCL for drinking water (50 mg/l NO_3^-). Those wells whose adjacent territories were not used for intensive vegetable production, as well as those located in the upper part of the watershed, contained lower concentrations of nitrates.

Hydrocarbonates, chlorides and sulfates content in the groundwater

It was observed that 17% of the investigated water sources contained hydrocarbonates between 300–400 mg/l, while 8% exceeded 400 mg/l. The most were the wells containing HCO_3^- below 150 mg/l – 42%. The chlorine content varied widely from 5.6 to 155.0 mg/l. According to Stoicheva et al. (2013), it is possible that the anthropogenic load increases the dynamics of chlorine, because there is no mechanism in the soil to absorb chlorine from the waters. Chlorine, like sodium, has high mobility and transitional status in the biological turnover of nutrients. At this site, 50% of the wells contained chlorine between 0–50 mg/l and no well exceeded the MPCL (250 mg./l) for drinking water for chlorine (Regulation № 9/2001). From Table 3 it can be seen that 42% of the water sources contained sulfates between 50 and 100 mg/l, and 17% of them fell within the limits between 150–250 mg/l. It was established that the monitoring wells did not exceed the MPCL (250 mg/l) for sulfate content in drinking water.

According to results of the study, the cations in the investigated water sources were arranged in the following order $Ca^{2+} > Na^+ > Mg^{2+} > K^+$, while the anions were in the following sequence – $HCO_3^- > SO_4^{2-} > NO_3^- > Cl^-$. This arrangement showed that calcium, hydrocarbonates, and sulfates dominated the ion concentration in groundwater, which can be related to anthropogenic loading, weathering processes, and ion exchange processes.

Table 4 showed the results of the calculated water quality index (WQI), which ranged from 20.13 to 137.56. According to the data obtained 33% of the water sources were of excellent and good quality, the remaining 67% fell into the category of poor and very poor quality. As can be seen from the results, water loading is also reported for soils with a heavier soil texture and deeper groundwater. This confirms the fact that water pollution is due to complex causes. As a precondition for ground water pollution are both the physico-chemical and hydpavric characteristics of the soil, as well

Table 4. Water Quality Index (WQI)

	Parameter	Standards Si	1/Si	Unit weight (Wi)	№ Sample	WQI
1	pH	6.5–8.5*	0.153	0.407	S1	20.13
2	EC, µS/cm	2000*	0.0005	0.001	S2	77.37
3	TDS mg/l	1000 ***	0.001	0.003	S3	56.82
4	$TH_{(CaCO_3)}$ mgeqv/l	12*	0.083	0.221	S4	37.36
5	Ca^{2+}	150*	0.006	0.018	S5	33.08
6	Mg^{2+}	80*	0.012	0.033	S6	62.08
7	Na^+	200*	0.005	0.013	S7	55.20
8	K^+	12 **	0.083	0.221	S8	61.67
9	HCO_3^-	300*	0.003	0.009	S9	50.48
10	SO_4^{2-}	250*	0.004	0.011	S10	59.58
11	Cl^-	250*	0.004	0.011	S11	137.56
12	NO_3^-	50*	0.02	0.053	S12	77.03
K			2.65			
ΣWi				1.01		

Regulation 9/2001*, WHO (2004); **WHO (2017) ***

Source: Authors' own elaboration

as the land use in the area. Obviously, the heavier mechanical composition, weak hydraulic conductivity and hydraulic connection between the aquifers reduces the possibility of fresh water inflow and groundwater refreshing. The mechanisms of entry of chemical elements are different, which should not be considered unilaterally, but should cover the wide variety of natural and anthropogenic factors acting simultaneously.

Conclusion

An investigation of the groundwater in urbanized area was carried out, mainly on domestic wells. It was established that the waters have an alkaline reaction and a calcium-hydrocarbonate composition. A significant variation of the chemical elements and a high content of some of them, which exceed the MPC for drinking water, were observed. Regarding the content of elements, they were arranged in the following orders: $Ca^{2+} > Na^{+} > Mg^{2+} > K+$ and $HCO_3^{-} > SO_2^{4-} > NO_3^{-} > Cl^{-}$. According to the results of the WQI model, the groundwater quality status could be classified into following categories: excellent and good quality (33% of the investigated wells), poor (42% of the domestic wells), while the remaining samples were categorized as very poor quality and unsuitable. When assessing the quality of water in the area, it is necessary to take into account the characteristics of the territory of the region – sloping relief, slow movement of water along the soil profile, and weak hydraulic connection between aquifers, the land use in the recent past and at the present time. Carrying out periodic monitoring of the chemical composition of the waters will allow to update the information on their condition.

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