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Blerina BEQAJ¹, Entela ÇOBANI²

GROUNDWATER QUALITY AND RISK OF POLLUTION FROM NATURAL, HUMAN AND URBAN TRANSPORT ACTIVITIES IN THE DRINI BASIN

Summary. Groundwater quality study was conducted in the Drini basin situated in the northern part of the Albanian territory. The objective of this study was to identify the quality of groundwater in four different well-defined monitoring sites. Groundwater is vital for the population and is considered to be subject to continuous exploitation with high growth intensity, and permanent risk of pollution from natural and human activities. Contamination of groundwater occurs when synthetic products such as gasoline, oil, road salts and chemicals get into the groundwater and return it unsafe and unfit for human use. Groundwater monitoring was carried out according to a network, which aimed to include mainly the most intensive areas of exploitation and distribution in the aquifer. Samples were collected in two different months of June and October in four monitoring drilling sites and were analysed for those key indicators defined by the rules and procedures for the drafting and implementation of the national programme of environmental monitoring in Albania. The study results reveal that geological formation, human activities as well as environmental conditions affect groundwater quality.

¹ Department of Environmental Engineering, Faculty of Civil Engineering, Polytechnic University of Tirana, Street "Muhamet Gjollesha", Nr: 54, Tirane, Albania. Email: blerina.beqaj@fin.edu.al. ORCID: https://orcid.org/0000-0002-6251-1784

² Department of Environmental Engineering, Faculty of Civil Engineering, Polytechnic University of Tirana, Street "Muhamet Gjollesha" Nr: 54, Tirane, Albania. Email: entela.cobani@fin.edu.al. ORCID: https://orcid.org/0000-0001-6438-6406

Complete chemical analysis revealed that the groundwater in this area results in medium hardness, has good physico-chemical properties, local pollution is encountered, and there is no massive pollution of the basin. They are waters with low mineralisation. Further, they are neutral waters, which meet the allowed norm for drinking water. The pollution displayed is occasional, as the presence of NH₄₊ and NO₂- are isolated cases, manifested mainly by the non-application of areas of strictness and sanitary protection around the drill and the small cover of the subaxillary layer. The analysis performed for microelements shows that the content of some heavy metals is below the maximum allowed amount; this demands serious future attention to the density of the network and the monitoring frequency in this basin. The risk of pollution in the Drini basin is high due to the small protective cover, especially in the source of Dobrac. Intensive exploitation can lead to the mixing of fresh water with water with high mineralisation. The concentration of Cu, Pb, Zn, Cr, Cd, Na+, K+ and Cl- in the water samples known as the major pollutants from the urban transport sector, has shown that the values are within the water quality standard. The low concentration of these pollutants was due to the distance of the drilling sites from the roads in these areas.

Keywords: groundwater quality, pollution, human activity, urban transport

1. INTRODUCTION

Groundwater is vital for the population and is considered to be subject to continuous exploitation with high growth intensity, and a permanent risk of pollution from natural and human activities. The pollution of groundwater is of major concern, first, because of increasing utilisation for human needs, and second, because of the ill effects of increased industrial activity. Groundwater is believed to be comparatively cleaner and free from pollution than surface water. However, prolonged discharge of industrial effluents, domestic sewage and solid waste dump cause it to become polluted, creating health problems [1]. Untreated waste from septic tanks and toxic chemicals from underground storage tanks and leaky landfills may contaminate groundwater. Studies of variations in major ions help to identify the chemical processes and interaction between soil and water that are responsible for the changes in groundwater quality regarding space and time.

Materials situated on the land's surface can move through the soil to reach groundwater. Pesticides and fertilisers frequently used in agriculture can find their way into groundwater supplies over time. Even road salt, toxic substances from mining sites, and used motor oil in the transport sector may also seep into groundwater. Road salts are used during winter on highways to prevent cars from slipping. When the ice melts, the salt washes off the streets and eventually ends up in the nearest water bodies. Since groundwater is a part of the hydrological cycle, contaminants in other parts of the cycle, such as the atmosphere or bodies of surface water, may eventually be transferred into the groundwater supplies.

Earon et al. [2] demonstrated that the metals Fe, Al, Zn, Mn, Pb, Ni, Cr, Cd and the ions Ca^{2+} , SO_4^{2-} , K^+ , Na^+ , Mg^{2+} , NO_3^- , and Cl^- in groundwater are significantly related to road transportation, decreasing exponentially as the distance from the roadside increases. In addition, many monitoring studies have demonstrated that Pb, Cu, Cr, Cd and Zn pollution are severe in diverse roadside environments [3].

The importance of groundwater recharge on seasonal variation in the major-ion concentration of groundwater is reported in previous studies [4]. Anthropogenic activities like population explosion, industrial growth, inputs of fertiliser, pesticides, and irrigation have been crucial factors for determining the quality of groundwater. Numerous publications have reported that urban development and agricultural activities directly or indirectly affect groundwater quality [5-14].

Groundwater chemistry, in turn, depends some factors, such as general geology, degree of chemical weathering of various rock types, quality of recharge water and inputs from sources other than water-rock interaction. Such factors and their interactions result in a complex groundwater quality [15-18].

Groundwater regime is characterised by the change in time and space of their quantity and quality and is expressed through the set of indicators of quantitative and qualitative changes such as temperature, flows, hydraulic slope, flow velocity and chemical composition.

The determination of the groundwater quality was done in the aquifer of the Drini basin both for its water reserves and for its practical importance, that is, for the supply of drinking and technological water. The purpose of monitoring is to preserve the reserves from exploitation, protection of existing water sources, as well as to assess the causes of groundwater pollution. Groundwater monitoring was carried out according to a network aimed to include mainly the most intensive areas of exploitation and distribution in the aquifer. Complete chemical analysis were conducted in four monitoring drilling sites and the measurement was done with a quantum probe of some indicators such as pH, oxygen content, etc.

2. MATERIALS AND METHODS

Groundwater samples were collected in four monitoring drilling sites in selected stations of the Drini Basin. The monitoring key indicators defined by the rules and procedures for the drafting and implementation of the national programme of environmental monitoring in Albania are hardness (german degree), pH, alkalinity, acidity, content of nitrates, electrical conductivity (ECw), heavy metal content, areas with high salinity, areas sensitive to pollution in volume, degree of exposure of the population to polluted groundwater, total salinity (TDS), exceedances of the quality norms of indicators.

Monitoring drilling network, sampling frequency, types and number of analysis are presented in Table 1 below.

Tab. 1.

	Monitoring	Sampling	Type of analysis	Number of	Sampling
	drilling network	frequency	obtained	analysis	period
Drini Basin	4	2	Chemical	8, 2	June -
			microelements		October

Monitoring drilling network, sampling frequency, types and number of analysis

In four monitoring sites, groundwater samples were taken in two different months, starting from June until October. Sampling and analytical determinations of the above parameters were performed according to the Albanian standard (STASH 3904-88) methods, at the analytical laboratory of the Albanian geological service. Interpretation of the data obtained from the laboratory is performed based on the criteria of Albanian standards given as follows (Table 2).

Tab. 2.

Indicators	Method of determining	Unit measure	STASH 3904-88
pН	Quanta probe	$-\log(H^{+})$	6.5-8.5
Potassium (K ⁺)	Atomic absorption spectroscopy	mg/l	10-12
Sodium (Na ⁺)	Method with atomic absorber	mg/l	20-100
Calcium (Ca ²⁺)	EDTA titration method	mg/l	75-200
Magnesium (Mg ²⁺)	Complexonometry method with EDTA titration	mg/l	20-50
Fe ²⁺³	Spectrophotometric determination	mg/l	0.05-0.3
$\mathrm{NH_4}^+$	DEVARDA alloy with distillation method	mg/l	nl-0.05
Bicarbonate(HCO ₃ ⁻)	Volumetric method	mg/l	
Carbonate (CO ₃ ²⁻)	Volumetric method	mg/l	
Chloride (cl)	Volumetric method with Mohri salt	mg/l	25-200
Sulphate (SO ₄)	Gravimetric method with barium chloride	mg/l	25-250
NO ₃ -	Method with DEVARDA alloy with distillation	mg/l	25-50
NO ₂ -	Method with DEVARDA alloy with distillation	mg/l	nl-0.05
Dry residue	Gravimetric method by drying at 105°C	mg/l	500-1000
Total Hardness	Defined as the sum of the Ca ²⁺ and Mg ²⁺ concentrations	°german	10-25 (30)
Temperature	Quanta probe	°C	8-15 (20)
Dissolved oxygen	Quanta probe		> 8
ECw	Quanta probe	μS/cm	400-2500

Indicators for water quality and their determining method (according to Albanian Standards-STASH 3904-88)

3. RESULTS AND DISCUSSION

Mineralisation values range from 221.465-341.885 mg/l (freshwater classified according to mineralisation), however, acceptable deviations from the minimum general mineralisation values of 0.17-0.2 g/l (drilling in the old bed of the Kir River) have also been observed. This is due to the presence of strong groundwater activity in the river.

The waters of the Drini basin are carbonate waters.

Overall strength ranges from 7.73-11.76 german degrees. Water is within the norm (STASH norm 10-20 german degrees, maximum allowed content 25 german degrees). Groundwater results in medium hardness.

The general mineralisation is in the range of 221.465-341.885 mg/l and within the norm of the Albanian standard (up to 1 gr/l).

 NH_4^+ content is not met (STASH rate is not allowed, maximum allowed content is 0.05 mg/l, EU norm [19] maximum allowed content is 0.1 mg / l).

Nitrate content (NO₃⁻) is 1.285-10.585 mg/l, which is within the allowed norm (STASH rate 25-50 mg/l, EU 25-50 mg/l).

		ECw	384. 7	360	252. 5	393	400- 2500	
		2O2	5.22	8.94	9.32	8.84	8<	
		(D ⁰) T	17.6 0	17.6 5	15.9 5	17.5 5	8-15, 20	
		Hardness ° gj	11.33	10.64	7.73	11.76	10-25 (30)	
		mg/l Dry residue	208. 2	197. 4	139. 1	139. 1 219. 1		
		Total mineralisatio n	315.84	313.36	221.47	341.89	1200	
	IS	- ^z ON	0.00	0	0	0.00	nl - 0.05	
g/l) 1 analyse	I analys	- ^ɛ ON	3.18	8.41	1.29	10.6	25- 50	
sults (m	chemica	-z⁺OS	23.4 1	16.8 1	15.0 2	16.8 7	25- 250	
Analysis results (mg/1) Complete chemical analysis	nplete (CI-	11.2 4	6.21	5.33	7.1	25- 200	
	5	CO ³ 5-	12	3 0		0		
		HCO ₃	195.2	211.97 144.87		225.7		
		+ [†] HN	0.05	0.00 5	0.05	0.1	nl - 0.05	
		$E^{\varepsilon_{5+3}}$	0.01 3	0.01	0.02	0.01	0.05-0.3	
		Mg^{2+}	33.4 2	12.4 6	12.4 6 9.85 11.2		20- 50	
		$C^{g}{}_{5^{+}}$	26.0 5	58.1 2	39.0 8	65.6 3	75- 200	
		+ ^{\$} N	9.8	4.1 5	2.4 8	4.3 1	20- 100	
		Κ+	1.2 9	0.3 4	0.4 3	0.3	10- 12	
		Hď	7.9 4	7.4 4	7.6 8	7.4 5	6.5- 8.5	
	Monitorin g site		Site 1.St. Velipoië	Site 2. Kisha e Madhe	Site 3. Hot i Ri	Site 4. Dobrac	STASH 3904-88	

Complete chemical analysis results for the collected underground water samples

Tab. 3.

Tab. 4.

Monitoring		Ni	Mn	Zn	Pb	Cu	Со	Cr	Cd
site									
Site 4:	June	0.001	0.002	0.007	0.003	0.002	0	0	0
Dobrac									
Site 4:	October	0	0.003	0.001	0.001	0.001	0	0	0
Dobrac									
STASH		nl-	0.02-	0.1-5	nl-	0.1-		nl-	nl-
3904-88		0.05	0.05		0.05	1.5		0.05	0.005

Results of analysis for microelements

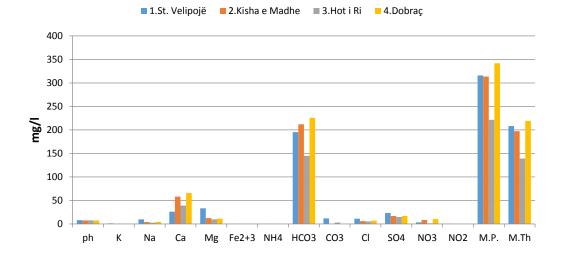


Fig. 1. Graphical representation of the Drini basin chemistry analysis

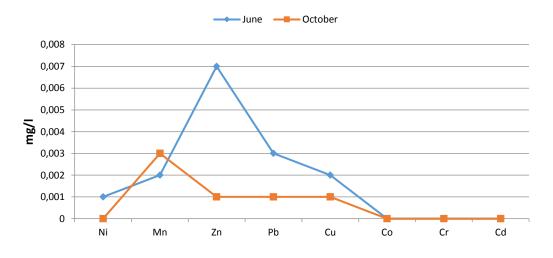


Fig. 2. Graphical representation of the Drini Basin microelements analysis for two monitoring periods

The pH of the waters varies in the values 7.44-7.94, these values are within the norm (6.5-8.5, maximum allowed 5 and 9.5, EU 6.5-8.5). Thus, groundwater is weakly alkaline.

The risk of pollution in this basin is high due to the small protective cover, especially in the source area of Dobrac. Intensive exploitation can lead to the mixing of fresh water with water with high mineralisation. NH_4^+ content reaching the amount of 0.1 mg/l in Dobrac monitoring site (STASH rate is not allowed, maximum allowed content is 0.05 mg/l, EU norm, maximum allowed content is 0.1 mg/l).

Chemical analysis shows the nitrite content, around the values 0-0.05 mg/l, and in some cases, these values exceed the norm. The content of nitrites in drinking water is not allowed while the maximum allowed content according to the Albanian standard is 0.05 mg/l (EU rate is 0.1 mg/l). The waters of the Drini basin are carbonate waters.

The total mineralisation is in the range of 221.465-341.885 mg/l within the norm of the Albanian standard (up to 1 gr/l). They are fresh water with total mineralisation < 1 gr/l.

Many studies have demonstrated that Cu, Pb, Zn, Cr, Cd, Na⁺, K⁺ and Cl⁻ are indicators of roadside contaminated environments. Physical and chemical parameters such as Cu, Pb, Zn, Cd, Cr, Ni, pH, TDS, Ca²⁺, Mg²⁺, Na⁺, K⁺, SO4²⁻, Cl⁻, HCO3⁻, and NO3⁻ were equally tested in groundwater samples to evaluate the impact of the transportation sector on groundwater environments. Only the drilling site of Dobrac contains Pb, Cu, Zn, Mn, Ni microelements. The concentration of such elements in the groundwater samples shows that the values were within the norm of the Albanian quality standards, thus they are within the water quality standard. The low concentration of these pollutants was due to the distance of the drilling from the roads in these areas.

4. CONCLUSIONS AND RECOMMENDATIONS

Summarily, the Drini basin groundwater has good physico-chemical properties. Although local pollution was encountered, there was no massive pollution of it. They are waters with low mineralisation-sweet. They are neutral waters, which meet the allowed norm for drinking water.

The pollution displayed is occasional, as the presence of NH_4^+ and NO_2^- are isolated cases, manifested mainly by the non-application of areas of strictness and sanitary protection around the drill and the small cover of the subaxillary layer. The risk of pollution in the Drini basin is high due to the small protective cover, especially in the source of Dobrac. Intensive exploitation can lead to the mixing of fresh water with water with high mineralisation.

The analysis performed for microelements shows that the content of some heavy metals is below the maximum allowed amount, thus, demands for crucial future attention to the density of the network and the monitoring frequency in this basin.

Furthermore, it is recommended to implement areas of strictness and sanitary protection around the drilling sites for the protection of groundwater from surface pollution.

In some of the pumping stations used for the supply of drinking water to the population in the monitored ponds, the areas of strictness and sanitary protection are not applied; therefore, attention should be given to the protection of the groundwater from possible massive pollution from local ones encountered during monitoring.

The concentration of Cu, Pb, Zn, Cr, Cd, Na⁺, K⁺ and Cl⁻ in the groundwater samples has shown that the values were within the norm of the Albanian quality standards, thus, they are within the water quality standard. The low concentration of these pollutants was due to the distance of the drilling sites from the roads in these areas.

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