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HYDROCHEMICAL ANALYSIS AND EVALUATION OF GROUNDWATER QUALITY FOR IRRIGATION IN MASIS REGION, ARMENIA

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The aim of the study was to assess the groundwater quality for agricultural irrigation in Masis Region, which is one of the traditional agricultural areas of Armenia. In order to evaluate the quality of groundwater in the study area, 27 groundwater samples were collected and analyzed to obtain various parameters such as electrical conductivity (EC), pH, as well as Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^-, CO_3^{2-} and Cl^- contents. The detected concentrations were interpreted and compared with different international irrigation standards. Study results led us to the conclusion that to control the process of soil salinization in the Masis Region (especially in the eastern and southern parts) the groundwater from great depths should be used for irrigation of agricultural areas, and an alternative source of irrigation water should be found in Ranchpar Village due to unsuitability of groundwater for these purposes.

Keywords: groundwater, irrigation, water quality, physicochemical indices, soil salinization, Masis Region.

Introduction. Groundwater is the main source of water used for agricultural and industrial human activities in the countries where surface water is in short supply [1]. Groundwater is used as irrigation water in the Ararat plain, which is a traditional agricultural region. However, it is important not only the availability of groundwater, but also its sufficient quality for use in irrigation purposes. Groundwater quality has an important role for sustainable development of human society. Generally, the quality and quantity of groundwater mainly depends on the geochemistry of soils and rocks through which water flows before reaching the aquifers, on the balance of precipitation and evaporation, the quality of recharged water, etc. [2–6]. Salts found in groundwater used for irrigation purpose may affect soil structure and crop productivity [7], and the presence of toxic elements may adversely affect vegetation and reduce the suitability of soil for agricultural use [8].

In recent decades, many scientists from different countries have focused attention on the negative effects of poor irrigation water quality on soil properties

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and crop yields [9–12]. The results of the various investigations have shown that the evaluation of groundwater quality is needful for the protection and proper management of agricultural land [13–15]. Therefore, the assessment of groundwater quality and its sustainable use are of paramount importance in arid and semi-arid agricultural regions, where irrigation water is of critical social and economic importance. Masis Region is one of the traditional agricultural areas of Armenia. There is not enough surface water in the region, and therefore groundwater plays a significant role as a resource for irrigation of agricultural land. In consideration of the mentioned, the aim of our study was the assessment of the groundwater quality used for irrigation, and its suitability for agricultural purposes from various points of view.

Materials and Methods.

Studied Area. The Masis Region is situated in the central part of the Ararat plain, stretching from East to West, in the basin of the Hrazdan River downstream, and has an area of 182.2 km^2. It has a flat surface and a mean height of 800 *m*. The semi-desert landscape prevails in the study area. The climate is dry continental, the average temperature in January is –5°*C* to –6°*C*, in July – 22–26°*C*, annual precipitation is 200–300 *mm*, and the length of vegetation period is 210 days [16].

Irrigated meadow-brown soils, irrigated residual-meadow-brown soils, wet meadow-brown-soils, and saline-alkali soils are the main soil types prevailing in the Masis Region [17].

Groundwater Sampling. Groundwater for the study was taken in April 2019. When choosing sampling points, three main indicators were taken into account: the uniform spatial distribution, the depths of groundwater, and the capacities of pumping stations. During the water sampling the coordinates of sampling sites, the depth of the wells, and the altitude of sites above sea level were recorded by GPS and described in registration book. The type of soils irrigated by this water and the major crops grown there were also determined and described.

The sampling was performed in one-liter containers, immediately after the sampling the water was sealed and stored under the cool conditions. Samples were labeled in the field during the sampling.

Groundwater Sample Analysis. In the laboratory the samples were stored in a refrigerator. The contents of Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^-, CO_3^{2-} and Cl^- ions and pH were determined by means of laboratory ionometer (I-160 M), the electrical conductivity (EC) was measured using the conductometer MARK 603.

Assessment of Groundwater Irrigating Properties. To assess the suitability of groundwater for irrigation purposes we used sodium percentage (Na%) and residual sodium carbonate (RSC) indices and some physicochemical parameters of groundwater, such as pH, EC and Cl^-. According to these parameters, irrigation water was classified for compliance with international standards (Tab. 1).

Sodium Percentage (Na%). The sodium content in irrigation water is usually expressed in Na%. It affects the soil structure by exchange process of sodium in water for Ca^{2+} and Mg^{2+} in soil, which reduces the permeability. To assess the suitability of water quality for irrigation, the percentage of sodium in water is calculated by the following equation:

$$\mathrm{Na} = \frac{(\mathrm{Na}^+ + \mathrm{K}^+)}{(\mathrm{Ca}^{2+} + \mathrm{Mg}^{2+} + \mathrm{Na}^+ + \mathrm{K}^+)} 100\%,$$

where ions concentrations are expressed in *meq/L*.

Residual Sodium Carbonate (RSC). The quantity of bicarbonate and carbonate in excess of alkaline earth metals (Ca+Mg) also influences the suitability of water for irrigation purposes. For the determination of the hazardous effect of carbonate and bicarbonate of irrigation water the RSC is calculated by the following equation:

$$RSC = (CO_3^{2-} + HCO_3^{-}) - (Ca^{2+} + Mg^{2+}),$$

where ions concentrations are also expressed in *meq/L*.

Table 1

Groundwater classification for irrigation purposes according to physicochemical and statistical parameters

Parameter	Categories	Ranges	Description
EC, $\mu S \cdot cm^{-1}$ [18]	Excellent	< 250	Low salinity water
	Good	250–750	Medium salinity water
	Permissible	750–2250	High salinity water
	Doubtful	2250–5000	Doubtful for irrigation
	Unsuitable	> 5000	Unsuitable for irrigation
Cl^{-}, *mg/L* [19]	Class-I	<177.5	Very good – good for irrigation
	Class-II	177.5–355	Good – hazardous for irrigation
	Class-III	>355	Hazardous – very hazardous for irrigation
pH [20]	Class-I	7–8	No restriction on use
	Class-II	6.5–7 or 8–8.5	Moderate restriction on use
	Class-III	< 6.5 or > 8.5	Severe restriction on use
Na% [18]	Excellent	0–20	Excellent for irrigation
	Good	20–40	Good for irrigation
	Permissible	40–60	Permissible for irrigation
	Doubtful	60–80	Doubtful for irrigation
	Unsuitable	> 80	Unsuitable for irrigation
RSC, *meq/L* [21]	Good	< 1.25	Generally safe for irrigation
	Medium	1.25–2.5	Marginal as an irrigation source
	Bad	> 2.5	Generally not suitable for irrigation without improvement

Results and Discussion. Considering the natural-climatic conditions of the site, the depths of the wells used for irrigation, and the spatial distribution, in the Masis Region the sampling was performed from 27 observation posts. The data concerning the coordinates of wells as well as their depths are given in Tab. 2. The deepest underground well was registered in the observation post 15-N-2 with the depth of 200 *m* and the well with the smallest depth of 6 *m* was found in the post 04-Ha. The pumps of deep wells had high capacity and their water irrigated large agricultural areas, while the pumps of small wells were of low capacity and their groundwater was used only for the irrigation of individual homestead lands.

The accordant values of groundwater quality parameters resumed in Tab. 2 show that the values of pH of groundwater in the investigated wells were in the range of 6.4–7.1 indicating the type of groundwater as weak acid to weak alkaline. As per pH values, four groundwater samples belong to Class-I, and according to the evaluation scale of Ayers and Westcot [20] (Tab. 1), the groundwater with such pH values can be used for irrigation without any restriction, while twenty-one groundwater samples belong to Class-II and can be used for irrigation with moderate restriction. Groundwater of only two wells belongs to Class-III and can be used for irrigation with severe restriction. It should be pointed out that both of these wells are located in the Ranchpar community. The values of EC in different investigated wells ranged from 618 to 4635 $\mu S{\cdot}cm^{-1}$. In concordance with the Wilcox classification of irrigation water [18], based on the EC (Tab. 1), the studied groundwater samples belong to the following categories: 2 groundwater samples to good category, 16 groundwater samples to permissible category, 9 groundwater samples to doubtful category. The wide range in EC is essentially specified by hydrogeochemical processes and anthropogenic activities dominating in this area.

The contents of Na^+, K^+, Ca^{2+}, Mg^{2+}, HCO_3^- and Cl^-, as the main ions, were studied in groundwater. These ions are also important from the standpoint of salinity hazard for soils and are used, when calculating indices for the assessment of water irrigation properties.

Table 2

Coordinates, depths of sampled wells and some physicochemical characteristics of groundwater *

Sample number	Coordinates	Depth of wells	pH	EC	Na^+	K^+	Ca^{2+}	Mg^{2+}	HCO_3^-	Cl^-
01-H-1	N 40°06,422' E 044°19,975'	96	6.7	1219	85.7	6.36	88.5	100.8	256.2	93.8
02-H-2	N 40°06,369' E 44°19,339'	18	6.86	1958	95	3.02	170	188.4	378.2	122
03-H-3	N 40°06,359' E 44°19,916'	148	6.68	1385	97	6.24	88	125.9	325.7	86.8
04-Ha	N 40°07,162 E 44°22,479'	6	7.1	1398	126	10.13	66	73.5	341.4	107.4
05-Da	N 40°06,373' E 44°25,046'	10.5	6.59	1832	133	18.1	121	126.9	366	115.5
07-Dash	N 40°05,977' E 44°23,544'	10	7.07	1152	113.5	24.7	71.2	58.3	302.1	91
08-Z	N 40°05,451' E 44°23,619'	12	7.0	1693	163	24.6	85.4	94.9	438.9	131
09-M-1	N 40°04,393' E 44°25,873'	15	6.89	2034	215	9.61	130	117.7	471	207
10-R-1	N 40°01,737' E 44°21,785'	100	6.56	2682	312	13.5	138	160.7	534.4	522
11-R-2	N 40°01,551' E 44°22,308'	95	6.47	2784	232	13.3	149	182.2	549	530
12-R-3	N 40°01,470' E 44°22,274'	160	6.4	3246	277	12.3	189	205.7	622.2	583
14-N-1	N 40°01,988' E 44°24,666'	100	6.81	1137	83.6	8.54	62.7	75.1	292.8	142
15-N-2	N 40°01,429' E 44°25,432'	200	6.7	877	78.2	5.47	47.4	50.2	248.4	94.4
16-Kh	N 40°05,306' E 44°28,492'	16	6.9	1144	92.2	2.68	120	126.9	317.2	94.1
17-Mar-1	N 40°03,785' E 44°28,171'	13	6.9	2652	316	10.01	174	213.6	451.4	260
18-Mar-2	N 40°03,544' E 44°28,159'	8	6.7	3710	386	6.32	178	238.5	488	351
19-Mar-3	N 40°03,257' E 44°27,941'	18	6.9	2806	292	14.7	145	167.8	427	194
20-Dz-1	N 40°02,740' E 44°28,257'	54	6.91	2004	208	10.47	93.2	110.7	414.8	157
21-Dz-2	N 40°02,761' E 44°28,532'	16	6.81	3416	291	14.1	173	204.4	427	227
22-A-1	N 40°02,140' E 44°28,003'	100	6.97	1708	175	10.33	77.2	105.8	353.8	149
23-A-2	N 40°02,183' E 44°28,392'	20	6.94	4635	400	17.3	258	283.5	646.6	625
24-M-2	N 40°04,242' E 44°23,555'	8	7.0	3487	328	32.1	106.7	128.9	646.6	428
25-Sip-1	N 40°04,919' E 44°21,096'	150	6.6	1284	84.5	7.44	107.1	83.7	366	124
28-Sis-1	N 40°03,792' E 44°22,788'	100	6.6	618	59.7	4.94	38.4	42.7	155.2	74.3
29-Sis-2	N 40°03,364' E 44°23,248'	150	6.7	672	69.6	5.9	40.8	38	184	74.5
30-SN-1	N 40°04,604' E 44°24,415'	150	6.78	992	113.4	6.85	53	59.4	290.4	96.3
31-SN-2	N 40°04,596' E 44°23,914'	10	6.8	1179	126	8.28	64.7	67.2	341.6	100.2

* Concentrations of all ions (except the pH values) are reported in *mg/L*, EC in $\mu S\ cm^{-1}$, depth of wells in meters; CO_3^{2-} ion was not detected in any groundwater sample.

As follows from Tab. 2, the lowest contents of Na^+, Ca^{2+}, HCO_3^- and Cl^- ions were observed in groundwater of sampling point 28-Sis-1, and the lowest contents of K^+ and Mg^{2+} were found in groundwater of sampling points 16-Kh and 29-Sis-2, respectively. The highest contents of all ions were observed in groundwater of sampling point 23-A-2, except for K^+, the maximal content of which was registered in groundwater of sampling point 24-M-2. CO_3^{2-} ion was not found in any groundwater sample, which is logical because it could be detected in groundwater with higher alkalinity values.

Study results revealed higher contents of the investigated ions in the groundwater of shallow horizons (with the exception of groundwater from the sampling points 10-R-1, 11-R-2 and 12-R-3) as compared with groundwater from deeper levels. Depending on the concentration of Cl^- in irrigation water, as well as on the sensitivity of agricultural crops, this ion can have toxicity effect on the plants. The amount of Cl^- in the investigated groundwater varied in the range of 74.3–625 *mg/L*. According to the Doneen's classification [19] (Tab. 1), the groundwater from 17 wells belong to the Class-I (very good – good for irrigation), the groundwater from 5 wells belong to the Class-II (good – hazardous for irrigation), and the groundwater from the remaining 5 wells belong to the Class-III (hazardous – very hazardous for irrigation). On the whole, the distribution pattern of all studied ions was as follows: $HCO_3^- > Cl^- > Na^+ > Mg^{2+} > Ca^{2+} > K^+ > CO_3^{2-}$.

Table 3

Descriptive statistics of hydrochemical parameters characterizing the irrigation properties of the groundwater

Sample number	Na%	RSC, *meq/L*	Sample number	Na%	RSC, *meq/L*
01-H	23.27	–8.63	17-Mar-1	34.56	–19.10
02-H	14.81	–18.00	18-Mar-2	37.06	–20.78
03-H	22.72	–9.55	19-Mar-3	38.11	–14.23
04-Ha	37.84	–3.83	20-Dz-1	40.14	–7.09
05-Da	27.31	–10.63	21-Dz-2	33.63	–18.68
07-Dash	39.81	–3.47	22-A-1	38.31	–6.88
08-Z	38.79	–4.98	23-A-2	32.81	–25.93
09-M-1	37.04	–8.59	24-M-2	48.41	–5.48
10-R-1	40.67	–11.53	25-Sip-1	23.86	–6.33
11-R-2	31.54	–13.63	28-Sis-1	33.20	–2.93
12-R-3-1	31.73	–16.39	29-Sis-2	37.90	–2.19
14-N-1	29.09	–4.59	30-SN-1	40.19	–2.84
15-N-2	35.07	–2.48	31-SN-2	39.18	–3.24
16-Kh	19.74	–11.38			

The sodium percentage is a significant parameter in the study of the sodium hazard, as well as for the assessment of groundwater quality for agricultural use. Groundwater with high Na%, used for irrigation purposes, raises the exchangeable sodium content in the soil, affecting the texture and permeability of soil. The use of such groundwater for irrigation inhibits the growth of plants as well. The groundwater classification by Na% is given in Tab. 1. The sodium percentage values of groundwater from different wells of Masis Region varied from 14.81 to 48.41% with a medium value of 33.59% (Tab. 3). Only two groundwater samples quality corresponds to the excellent category for irrigation purposes (02-H and 16-Kh), four groundwater samples quality corresponds to the permissible category

(10-R-1, 20-Dz-1, 24-M-2 and 30-SN-1) and the remaining twenty-one groundwater samples quality is in the good category. The research results revealed that only the groundwater from four wells may have some negative influence on the texture and permeability of the soil.

Therefore, some agromelioration actions, such as deep plowing, good drainage, high leaching and the use of compost, farm manure, and crop residues, are necessary to control the quality of soil in the agricultural areas irrigated from these four wells.

Richards [21] has defined the hazardous effect of carbonate and bicarbonate ions on groundwater quality, and if the concentration of these ions is higher than that of calcium and magnesium, this affects the suitability of groundwater used for irrigation purpose. Groundwater with a high value of RSC has a high pH, and the agricultural lands irrigated with such a kind of groundwater turn to barren due to deposition of sodium carbonate. The classification of groundwater based on the RSC values is shown in Tab. 1. The RSC values of groundwater from all studied wells were below the 1.25 *meq/L* (Tab. 3). So, the groundwater of Masis Region by this point of view was safe for irrigation.

Conclusion. According to EC values almost all groundwater we have studied in the Masis Region was at risk and could lead to salinization of agricultural lands. In this respect, the groundwater in the eastern part of the study area, namely in the eastern part of Masis Town, and in the villages of Marmarashen, Jrahovit and Arevabuyr, as well as in southern part of the study area, notably in the Ranchpar Village, were at higher risk.

The groundwater content of these areas was also high in chloride ions, which could have toxicity effect on crops, and the groundwater of the Ranchpar Village also had a relatively low pH, which can result in detrimental effect on the physico-chemical properties of the soil.

In terms of horizontal distribution, the groundwater of shallower horizons are at the highest risk, while the groundwater of the deeper levels passing through different rock layers change their salt composition and the content of salts decreases (except for the deeper groundwater of the Ranchpar Village, which is of high salinity). Described processes, in turn, reduce the groundwater risk toward soil salinization. As concerns the sodium, carbonate and bicarbonate hazard, the studied groundwater was generally of sufficient quality.

Given all of the above, in order to prosper in preventing the process of soil salinization, groundwater from great depths should be used for irrigation of agricultural areas in the Masis region (especially in the eastern and southern parts), and in Ranchpar Village an alternative source of irrigation water should be found.

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