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Water Quality Parameters Evaluation of Sipna Stream, Duhok area, Kurdistan Region-Iraq

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ABSTRACT

Due to the security situation surrounding the Sipna area, there has been a rapid migration of the population to the Sipna area over the past fifteen years, which has increased agricultural activities as well as some small and medium factories. This has necessitated the evaluation of the water quality and its appropriateness for various uses in the Sipna area. The Sipna stream, which is part of the Greater Zab River, is located in the Sheladize area, 60 km to the northeast of Duhok City in the Iraqi Kurdistan Region. Between the low-flow season (12-October/2021) and the high-flow season (18-April/2022), forty surface water samples were taken by polyethylene bottle from both seasons. The study aims to assess the quality of surface water and the extent of the impact of human activities on the Sipna stream and the possibility of using it as a database for comparison in the future. The findings indicate that Ca-bicarbonate and TDS values range from 219-606 ppm with an average of 321 ppm for the dry season and 188-685 ppm with an average of 251 ppm for the wet season, it is the dominant water type in the study area. According to to mean values, the main ion concentrations for cations were Ca^{2+}> Mg^{2+}> Na^{+}> K^{+}, and HCO_3^-> SO_4^{2-}> Cl^-> NO_3^- anions. The most prevalent hydrochemical natural processes are rock weathering and its mainly responsible for the water quality in the study area. Water indices and comparisons to the WHO standard revealed that the Sipna stream's quality is suitable for use as drinking water and a wide range of other purposes.

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تقييم معايير جودة المياه في نهر سبنة – منطقة دهوك – إقليم كردستان العراق

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الملخص

يعتبر نهر سبنة جزء من نهر الزاب الأعلى الذي يقع في منطقة شيلادزي على بعد 60 كم شمال غرب مدينة دهوك ضمن أقليم كردستان العراق. تم جمع 40 نموذج مائي من نهر سبنة مقسمة على فترتي منسوب الماء المنخفض (تشرين الاول 2021) والماء العالي (نيسان 2022). بسبب الظروف الأمنية التي تحيط بمنطقة سبنة وقربها من الحدود العراقية–التركية مما ادى الى نزوح جماعي اليها وبالتالي زاد من الفعاليات الزراعية وبعض الصناعات المتوسطة في المنطقة وهذا مما تطلب وجود دراسة هيدروكيميائية لتقيم هذه المياه وتبيان مدى أستخداماتها المختلفة. بينت الدراسة بان نوع المياه هي كالسيوم–بايكربونيت ومعدل ملوحة تصل الى 413 جزء بالمليون في موسم المياه المنخفض وبزيادة نسبية طفيفة تصل الى 437 جزء بالمليون في موسم المياه العالي. ونسبتا لمعدل تراكيز الأيونات فيمكن ترتيبها تنازليا كما يلي: الكالسيوم> المغنيسيوم> الصوديوم> البوتاسيوم. كما بينت الدراسة ان أهم العمليات الطبيعية التي أثرت على نوع المياه هي التجوية للصخور المحيطة التي يمر عليها النهر بالأضافة لبعض الفعاليات البشرية مثل الزراعة وتصريف المياه السكنية، ومن مقارنة تركيز المياه للدراسة الحالية مع معدلاتها في الصحة العالمية اوضحت بان مياه منطقة سبنة صالحة للشرب وجميع الاستخدامات الاخرى.

Introduction

Southeast Turkey's mountains are the source of the Greater Zab River. It travels 460 km through sparsely populated parts of Turkish and Iraqi Kurdistan before entering the Tigris River, with the Greater Zab serving as the Tigris' most important tributary in Iraq [1]. Surface water resources are essential for the growth of human settlements, industries, and agriculture in any society on Earth. However, because they are so easily accessible for the disposal of wastewater, they are becoming more and more valuable and under threat. They also play an important role in the provision of potable water to most urban and some rural communities in the Sipna area [2,3]. Additionally, they help with industrial, agricultural, recreational, and drinking water demands [4,5].

Numerous human and natural causes have the potential to have an impact on the quality of surface water [6,7]. However, in recent decades, growing urbanization and population expansion have accelerated the usage of surface and groundwater resources, leading to significant environmental issues including surface water contamination [8]. Human migration usually results from several factors, including social, economic, and political ones that are exacerbated by shifting environmental circumstances, as well as commonly by demographic and developmental trends, the more gradual process of migration may be brought on by slow-onset environmental degradation, whereas forced migration may be the consequence of an environmental calamity like a tsunami or flood, or a government-instigated relocation [9].

People are more likely to migrate illegally, irregularly, unsafely, exploitatively, or unintentionally when their options for safe migration are reduced, merged with the income threats posed by environmental change. Additionally, many populations will be at risk because they lack access to safe migration routes from small island environments and marginal agricultural lands in the world's drylands and mountains [10]. The Sipna stream (locally known as Sipna valley) and addition to Sherank, Banistan, and Seri tributaries produced by a collection of springs that feed the mainstream which is part of the Greater Zab are situated in the Sheladize region, 60 km to the northeast of Duhokn within the Iraqi Kurdistan Region, between (37°03'34.1" to 37° 0' 45.37") N and (43°39'16.8" to 43°49' 48.81.") E and it covers an area of 255km2 and is 41km long (Fig. 1).

The Sipna area, which lies close to the Turkish-Iraqi border, is made up of several districts and villages with a diverse population of people. In addition to having plenty of water and a favorable environment, this area's agricultural and tourist sectors benefited from these features.

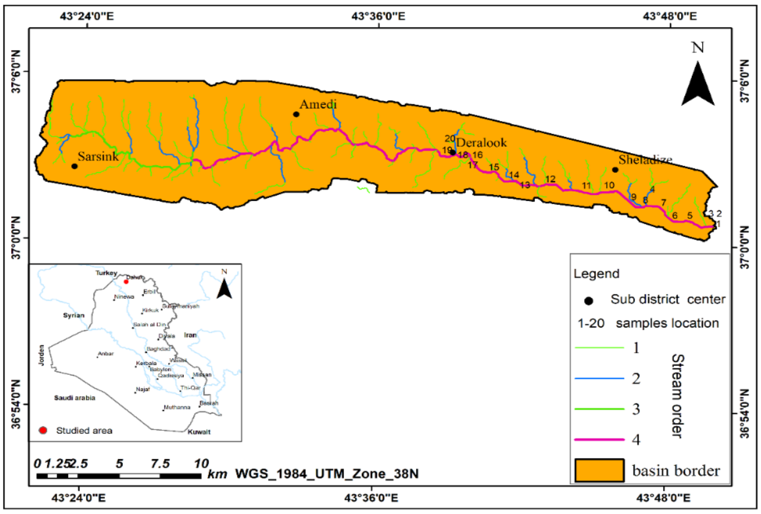

Fig 1. The Location map of the Sipna area.

Because of the security situation surrounding the region and near the Iraqi-Turkish border, there has been a rapid migration of people to the Sipna area over the past fifteen years. As a result, there has been an increase in agricultural activity as well as some small and medium factories.

Tectonically, the study area is located within the high-folded Zone that is part of the Unstable Shelf of the Arabian Platform or is thought to be a part of the Outer Platform [11,12]. The Sipna basin is represented by a synclinal shape that is bordered by the Mateen anticline in the Northern part and the Gara anticline in the South part [13,14]. The sedimentary cover of the Arabian Margin subducting plate is primarily responsible for the fold and thrust system that defines the high folded Zone [15]. The rocks that are exposed in the study area are carbonate, marly limestone, marl, and clastic rocks that extend from the Upper Cretaceous to the Paleogene age associated with the Garagu, Aqra, Gercus, Pila Spi, Fatha, Injana, and Lower and Upper Mukdadiya Formations along the Sipna area (Fig. 2).

The Sipna area has an arid to semi-arid climate with dry summers and cold, rainy winters. Spring and fall have shorter seasons than summer and winter [16]. The goal of the current study is to chemically evaluate the water quality and its suitability for various uses, with the results being used as a database for future comparisons and the effect of population growth (agricultural, domestic, and industrial activities) on the chemical composition of water in the Sipna area.

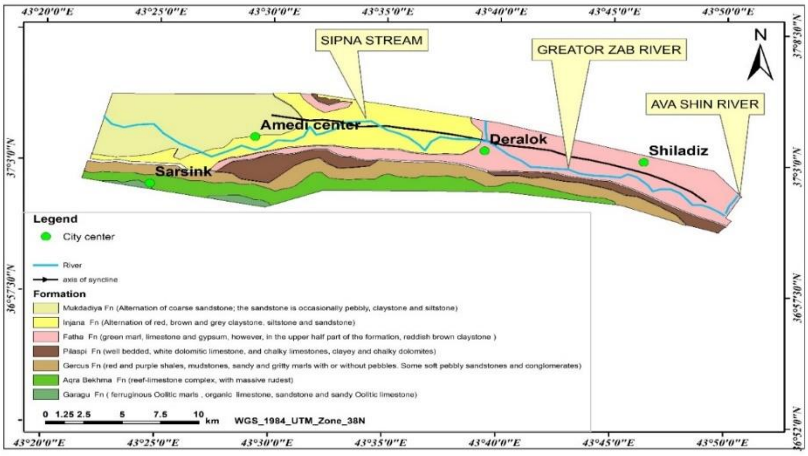

Fig 2. Geological map of Sipna area (Sissakian et al., 2015)

The lack of studies and research dealing with the evaluation of the water quality of the Greater Zab River, most of which include areas far from the study area within Erbil city [17,18], but most of them included the geomorphological, morphometric and hydrological aspects in addition to the impact of climate change on the water resources of the Greater Zab basin [19,20,21].

Sampling

In the study area, surface water was sampled from different 20-sites along Sipna stream from 12-October/2021 (low-flow season) to 18-April/2022 (high-low season), and by 20 samples for each season (Fig.1). A total of 40 samples were filtered with 0.45 µm for chemical analysis [22]. Sampling was collected by 2 polyethylene plastic bottles (1000ml) between 10-20cm depth to reduce impact surface slicks [24] and washed with deionized distal water before the sampling process. After collection, samples were stored refrigerated at 4°C to reduce bacterial growth [25], and they were analyzed within 48hrs of collection.

Methodology

The electrical conductivity (EC), temperature (T°C), and hydrogen ion concentration (pH) of the surface water sampling were measured in the field using portable conductivity-pH meter model number pH-03. They were analyzed for chemical parameters (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, HCO_3^{-}, SO_4^{2-}, Cl^{-}, and NO_3^{-}) and heavy metals (Cd, Cr, Cu, Mn, Ni, Pb, and Zn) by the Laboratory of Duhok Environment Directorate/ Kurdistan Region, Iraq as described by [22].

The total hardness as well as the Ca^{2+} and Mg^{2+} ion concentrations were examined using the EDTA (0.01N) titrimetric technique [25]. The Flame Emission photometric BWB-type was used to assess the amounts of Na^{+} and K^{+} ions [26]. Titration with H_2SO_4- 0.02N was used to determine the concentration of HCO_3^{-} ions [27]. By utilizing a UV Spectrophotometer of the CECIL-9000 technique type, the concentration of SO_4^{2-} and NO_3^{-} ions was determined, and the concentration of Cl^{-} ions was determined using the $AgNO_3$ (0.012N) titration method [28].

Whereas the concentrations of heavy metals (Cd, Cr, Cu, Mn, Ni, Pb, and Zn) were assessed using the Japanese-made Shimadzu AAS-7000 Atomic Absorption Spectrometric technique [29]. The Electroneutrality condition may be used to determine the precision of the main ion lab test. For each set of comprehensive studies of the water surface sample, the difference between the total cations and the anions is calculated [30]. The following equation was then used:

$$\%U = \Delta/S \times 100 \quad \ldots\ldots\ldots (1)$$

$$A = 100\text{-}U \quad \ldots\ldots\ldots (2)$$

$$\Delta = r\sum cations - r\sum anions$$

$$S = r\sum cations + r\sum anions$$

Where: r= epm unit (epm= ppm/equivalent weight of ions)

Δ= Difference absolute value of the sum of cations and anions

U= Relative Difference

A= accuracy

According to [31], the chemical results of the surface water samples in the Sipna area showed within the permissible limit for interpretation when the reaction error (U) or uncertainty is ($U \leq 5\%$), but if ($5\% < U \leq 10\%$) then the result is acceptable with hazard, and it is not acceptable if ($U > 10\%$).

Results

The findings of the analytical chemical analysis of the surface water samples collected in the Sipna area between 12-October/2021 (low-flow season) to 18-April/2022 (high-low season) are shown in Tables (1 and 2). The results of the pH values of the study area samples showed a slight variation in the pH values for both seasons. In the dry season, the pH content ranged from (7.3-8.2) with an average of (7.99 ±0.22), whereas in the wet season, it ranged from (7.0-8.1) with an average of (7.85 ±0.27). TDS levels are higher during the dry season (219–606 mg/l), with an average of (321 ±99.37) mg/l than during the wet season (188–685 mg/l), with an average of (251±131.74 mg/l).

The findings indicate that surface water temperatures are often higher in the wet season (14.5-25.3) C° with an average (21.39) C° compared to the dry season (15.0-20.0) C° with an average (17.94 ±1.51) because spring water is usually warm in the winter and cold in the summer seasons. The research also revealed that Sherank, Banistan, and Seri, three river tributaries produced by a collection of springs that feed the main branch, had greater EC, TDS, and temperature findings than the Sipna stream (Table 3). The findings for the cations (Ca^{2+}, Mg^{2+}, and Na^{+}) in the dry season indicated that their range of concentrations from (50 to 146 mg/l), (10.7 to 43 mg/l), and (1.4 to 29

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mg/l), respectively, were approximately higher than the wet season, which ranged from (37 to 142 mg/l), (7.8 to 48 mg/l), and (2.3 to 33.2 mg/l). A similar pattern is seen with anions (HCO3-, SO42-, and Cl-), which range from (190 to 350 mg/l), (11 to 221 mg/l), and (8 to 66 mg/l), respectively, in the dry season and from (146 to 369 mg/l), (31 to 217 mg/l), and (8 to 42 mg/l) in the wet season. When compared to the dry seasons, NO3- and K+ ions showed a little increase in content, with ranges of (0.8 to 57 mg/l), (0.8 to 2.3 mg/l), and (0.7 to 41 mg/l), (0.5 to 2.5 mg/l), respectively (Table 4).

Except for select locations (Harika bridge area SN.5), where Pb content reached up to 12.61 ppb, the findings of the concentrations of heavy metals throughout the dry season revealed rates lower than the amounts permitted for drinking water (Table 5).

The correlation coefficient analysis is nearly often used to determine the source of ions in the hydrochemical environment [32,33,34].To examine and assess the link between main chemical ions and physical characteristics, the Pearson correlation coefficient has been used [35, 36, 37, 38]. In addition to this, Gibbs (1970) and Scholar (1967) diagrams were applied to investigate variables impacting the kind of water and its chemistry [29]. The results demonstrate a substantial positive correlation (P>0.01) between TDS and cations (Ca2+, Mg2+, Na+), with coefficients of (0.952, 0.916, and 0.797, respectively), as well as a significant negative

correlation (P<0.01) between pH and all ions in the Sipna area were completed by SPSS-19 (Table 6).

Table 1: Chemical analysis of water samples in the dry season of the Sipna area.

S. N	Unit	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Sum	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-	Sum	U%
1	ppm	59.2	24.4	9.5	1.7	95	196	56.9	14	2.7	270	5.77
	epm	2.95	2.01	0.41	0.04	5.41	3.21	1.19	0.39	0.04	4.82	
	epm%	54.53	37.15	7.58	0.74	100	66.46	24.64	8.07	0.93	100	
2	ppm	60.8	36.1	16.2	1.9	115	214	98.3	28	1.0	341	2.9
	epm	3.03	2.97	0.7	0.05	6.75	3.51	2.05	0.79	0.02	6.37	
	epm%	44.89	44	10.37	0.74	100	55.1	32.18	12.4	0.31	100	
3	ppm	65.6	27.3	18.7	1.8	113	196	74.1	30	2.5	303	6.16
	epm	3.27	2.25	0.81	0.05	6.38	3.21	1.54	0.85	0.04	5.64	
	epm%	51.25	35.27	12.7	0.78	100	56.91	27.3	15.07	0.71	100	
4	ppm	113.6	31.2	2.7	0.9	148	214	220.7	12	1.0	448	0.53
	epm	5.67	2.57	0.12	0.02	8.38	3.51	4.6	0.34	0.02	8.47	
	epm%	67.66	30.67	1.43	0.24	100	41.44	54.31	4.01	0.24	100	
5	ppm	49.6	33.2	11.5	1.8	96	190	57.3	16	2.5	266	9.19
	epm	2.48	2.73	0.5	0.05	5.76	3.11	1.19	0.45	0.04	4.79	
	epm%	43.05	47.4	8.68	0.87	100	64.93	24.84	9.39	0.84	100	
6	ppm	57.6	27.3	10.6	1.7	97	192	61.1	18	2.4	274	6.14
	epm	2.87	2.25	0.46	0.04	5.62	3.15	1.27	0.51	0.04	4.97	
	epm%	51.07	40.04	8.18	0.71	100	63.38	25.55	10.26	0.8	100	
7	ppm	57.6	22.4	10.2	1.7	92	192	64.5	16	2.1	275	2.17
	epm	2.87	1.84	0.44	0.04	5.19	3.15	1.34	0.45	0.03	4.97	
	epm%	55.3	35.45	8.48	0.77	100	82.26	9.68	7.83	0.23	100	
8	ppm	72	13.7	1.4	0.5	88	218	20	12	0.7	251	4.93
	epm	3.59	1.13	0.06	0.01	4.79	3.57	0.42	0.34	0.01	4.34	
	epm%	74.95	23.59	1.25	0.21	100	82.26	9.68	7.83	0.23	100	
9	ppm	72	10.7	1.6	0.5	85	216	21.3	8	2.4	248	3.41
	epm	3.59	0.88	0.07	0.01	4.55	3.54	0.44	0.23	0.04	4.25	
	epm%	78.9	19.34	1.54	0.22	100	83.29	10.35	5.41	0.94	100	
10	ppm	60.8	25.4	11.2	1.8	99	219	12.2	27	2.1	260	10.0
	epm	3.03	2.09	0.49	0.05	5.66	3.59	0.25	0.76	0.03	4.63	
	epm%	53.53	36.93	8.66	0.88	100	77.54	5.40	16.41	0.65	100	
11	ppm	60.8	20.5	11.4	1.8	95	192	80	16	2.1	290	0.28
	epm	3.03	1.69	0.5	0.05	5.27	3.15	1.67	0.45	0.03	5.3	
	epm%	57.49	32.07	9.49	0.95	100	59.43	31.51	8.49	0.57	100	
12	ppm	60.8	22.4	12.2	1.9	97	215	11.2	25	2.3	254	9.55
	epm	3.03	1.84	0.53	0.05	5.45	3.52	0.23	0.71	0.04	4.5	
	epm%	55.60	33.76	9.72	0.92	100	78.22	5.11	15.78	0.89	100	
13	ppm	59.2	22.4	12.1	2	96	206	67.1	16	2.5	292	0.94
	epm	2.95	1.84	0.53	0.05	5.37	3.38	1.4	0.45	0.04	5.27	
	epm%	54.93	34.26	9.87	0.93	100	64.14	26.56	8.54	0.76	100	
14	ppm	56	24.4	11.9	1.9	94	190	67.1	16	2.2	275	3.57
	epm	2.79	2.01	0.52	0.05	5.37	3.11	1.4	0.45	0.04	5.0	
	epm%	51.96	37.43	9.68	0.93	100	62.2	28	9.0	0.8	100	
15	ppm	56	23.4	12.2	1.9	94	192	63.6	16	2.2	274	3.12

	epm	2.79	1.92	0.53	0.05	5.29	3.15	1.33	0.45	0.04	4.97	
	epm%	52.74	36.29	10.02	0.94	100	63.38	26.76	9.05	0.80	100	
16	ppm	60.8	20.5	12.2	1.9	95	196	61.9	16	2.2	276	3.41
	epm	3.03	1.69	0.53	0.05	5.3	3.21	1.23	0.45	0.06	4.95	
	epm%	57.17	31.89	10	0.94	100	64.85	24.85	9.09	1.21	100	
17	ppm	128	42.9	25.9	2.5	199	350	122.3	66	40.9	579	1.37
	epm	6.39	3.53	1.13	0.06	11.11	5.74	2.55	1.86	0.66	10.81	
	epm%	57.52	31.77	10.17	0.54	100	53.10	23.59	17.21	6.10	100	
18	ppm	145.6	42.9	29.4	1.2	219	350	147.8	50	35.2	583	5.72
	epm	7.27	3.53	1.28	0.03	12.11	5.74	3.08	1.41	0.57	10.8	
	epm%	60.03	29.15	10.57	0.25	100	53.15	28.52	13.06	5.27	100	
19	ppm	78.4	20.5	3.5	0.8	103	190	106.3	12	1.0	309	0.78
	epm	3.91	1.69	0.15	0.02	5.77	3.11	2.21	0.34	0.02	5.68	
	epm%	67.76	29.29	2.60	0.35	100	54.75	38.91	5.99	0.35	100	
20	ppm	60.8	21.5	12.7	2	97	200	67.1	16	2.1	285	2.27
	epm	3.03	1.77	0.55	0.05	5.4	3.28	1.4	0.45	0.03	5.16	
	epm%	56.11	32.78	10.18	0.93	100	63.57	27.13	8.72	0.58	100	

Table 2: Chemical analysis of water samples in the wet season of the Sipna area.

S.N	Unit	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	Sum	HCO_3^-	$SO4^{2-}$	Cl^-	NO_3^-	Sum	U%
1	ppm	48	7.8	3.6	1.8	61.2	152	30.7	10.8	3.9	197	3.71
	epm	2.39	0.64	0.16	0.05	3.24	2.49	0.64	0.3	0.06	3.49	
	epm%	73.77	19.75	4.94	1.54	100	71.35	18.34	8.59	1.72	100	
2	ppm	68.8	30.3	14.5	1.8	115	236	98.7	18	2.7	355	0.92
	epm	3.43	2.49	0.63	0.05	6.6	3.87	2.06	0.51	0.04	6.48	
	epm%	51.97	37.73	9.54	0.76	100	59.72	31.79	7.87	0.62	100	
3	ppm	43.2	17.6	4.2	1.9	67	154	31.4	10.8	4.5	201	3.93
	epm	2.15	1.45	0.18	0.05	3.83	2.52	0.65	0.3	0.07	3.54	
	epm%	56.14	37.86	4.7	1.3	100	71.19	18.36	8.47	1.98	100	
4	ppm	108.8	39	2.7	0.8	151	228	216.6	8	0.8	453	1.74
	epm	5.43	3.21	0.12	0.02	8.78	3.74	4.51	0.22	0.01	8.48	
	epm%	61.84	36.56	1.37	0.23	100	44.1	53.18	2.6	0.12	100	
5	ppm	42.4	19	4.2	1.9	62	157.2	44.4	10	3.9	216	0.77
	epm	2.11	1.56	0.18	0.05	3.9	2.58	0.92	0.28	0.06	3.84	
	epm%	54.1	40	4.62	1.28	100	67.19	23.96	7.29	1.56	100	
6	ppm	41.6	14.6	4.3	1.9	62	152	35.6	9	3.9	201	0.28
	epm	2.08	1.2	0.19	0.05	3.52	2.49	0.74	0.25	0.06	3.54	
	epm%	59.09	34.09	5.4	1.42	100	70.34	20.9	7.06	1.7	100	
7	ppm	40	19.5	4.3	1.9	66	150	35.3	10	3.9	199	4.06
	epm	2	1.6	0.19	0.05	3.84	2.46	0.74	0.28	0.06	3.54	
	epm%	52.08	41.67	4.95	1.3	100	69.49	20.9	7.91	1.7	100	
8	ppm	36.8	16.6	4.3	1.9	60	152	37.1	10	3.9	203	2.13
	epm	1.84	1.37	0.19	0.05	3.45	2.49	0.77	0.28	0.06	3.6	
	epm%	53.33	39.71	5.51	1.45	100	69.16	21.39	7.78	1.67	100	
9	ppm	41.6	16.1	4.4	2.1	64	160	36.2	10	4	210	1.09
	epm	2.07	1.32	0.19	0.05	3.63	2.62	0.75	0.28	0.06	3.71	
	epm%	57.02	36.36	5.23	1.38	100	70.62	20.22	7.54	1.62	100	
10	ppm	38.4	15.6	4.7	2.2	61	152	44.1	12	4.2	212	5.22
	epm	1.92	1.28	0.2	0.06	3.46	2.49	0.92	0.34	0.07	3.82	
	epm%	55.5	36.99	5.78	1.73	100	65.18	24.08	8.9	1.83	100	
11	ppm	44.8	16.1	4.5	2	66	155	37.1	10	4	206	2.14
	epm	2.24	1.32	0.2	0.05	3.81	2.54	0.77	0.28	0.06	3.65	
	epm%	58.79	34.65	5.25	1.31	100	69.59	21.1	7.67	1.64	100	
12	ppm	44.8	14.6	4.5	2	66	157	37.4	9	4	207	0.27
	epm	2.24	1.2	0.19	0.05	3.68	2.57	0.78	0.25	0.06	3.66	
	epm%	60.87	32.61	5.16	1.36	100	70.22	21.31	6.83	1.64	100	
13	ppm	48	10.7	4.5	2.1	65	154	43.1	9	4.1	210	3.03
	epm	2.4	0.88	0.19	0.05	3.52	2.52	0.9	0.25	0.07	3.74	
	epm%	67.99	24.92	5.67	1.42	100	67.38	24.06	6.68	1.87	100	
14	ppm	44.8	12.7	4.5	2	64	154	38.2	11	4.5	208	2.35
	epm	2.24	1.04	0.2	0.05	3.53	2.52	0.8	0.31	0.07	3.7	
	epm%	63.45	29.46	5.67	1.42	100	68.11	21.62	8.38	1.89	100	
15	ppm	48	12.7	4.6	2	67	146	40.5	10	4.2	201	1.51
	epm	2.4	1.04	0.2	0.05	3.69	2.39	0.84	0.28	0.07	3.58	
	epm%	65.04	28.18	5.42	1.36	100	66.76	23.46	7.82	1.96	100	
16	ppm	41.6	14.6	4.6	2	63	155	39.1	10	3.8	208	2.78
	epm	2.04	1.2	0.2	0.05	3.49	2.54	0.81	0.28	0.06	3.69	
	epm%	58.45	34.38	5.73	1.43	100	68.83	21.95	7.59	1.63	100	
17	ppm	142.4	48.3	33.2	2.3	226	369	208.6	42	57.1	677	0.36

	epm	7.11	3.97	1.44	0.06	12.58	6.05	4.34	1.18	0.92	12.49	
	epm%	56.52	31.56	11.44	0.48	100	48.44	34.75	9.45	7.36	100	
18	ppm	104.8	24.9	11.9	1.1	143	286	86	18	29.8	420	2.35
	epm	5.23	2.05	0.52	0.03	7.83	4.69	1.79	0.51	0.48	7.47	
	epm%	66.8	26.18	6.64	0.38	100	62.78	23.96	6.83	6.43	100	
19	ppm	48	15.6	2.3	0.8	67	153	45.1	9	3.5	211	0.53
	epm	2.4	1.28	0.1	0.02	3.8	2.51	0.94	0.25	0.06	3.76	
	epm%	63.16	33.68	2.63	0.53	100	66.76	25	6.65	1.59	100	
20	ppm	48	13.2	4.5	2	68	154	56.7	9	4.7	224	3.86
	epm	2.4	1.09	0.19	0.05	3.73	2.52	1.18	0.25	0.08	4.03	
	epm%	64.34	29.22	5.1	1.34	100	62.53	29.28	6.2	1.99	100	

Table 3: Comparison of physical variables of the water samples from the studied area.

	Dry season (October 2021)					Wet season (April 2022)				
S.N	TC°	Ph	EC (us/cm)	TDS (ppm)	TH (ppm)	TC°	pH	EC (us/cm)	TDS (ppm)	TH (ppm)
1	18	7.7	453	290	248	14.1	7.7	294	188	152
2	18	8.1	580	371	300	18.1	8.1	537	344	296
3	19	8.2	528	338	276	18.2	8	304	195	180
4	15.5	8	687	440	412	21.5	7.8	722	462	432
5	16.5	8.2	464	297	260	17.6	8	313	200	184
6	17.5	8.1	453	290	256	20.7	7.9	299	192	164
7	18	7.8	431	276	236	22.1	8	300	192	180
8	16	7.8	361	231	236	23.5	7.95	299	191	160
9	15	7.9	342	219	224	19	7.95	298	191	170
10	19	8.1	434	278	256	22	7.95	313	200	160
11	19	8.1	424	272	236	22.7	7.93	301	193	178
12	18	8.1	436	279	244	25	7.96	300	192	172
13	18.5	8.1	432	276	240	23.1	7.95	299	192	164
14	19	8.1	416	266	240	20.6	7.94	305	195	164
15	18.75	8.1	421	270	236	22.5	7.96	304	195	172
16	20	8.1	430	275	236	23.6	7.97	302	193	164
17	20	7.8	847	542	496	25.3	7.2	1070	685	554
18	20	7.3	947	606	540	24.6	7	686	439	364
19	16	8	518	332	280	22	7.9	299	192	184
20	17	8.2	442	283	240	21.5	7.97	304	195	174
Range	15-20	7.3 -8.2	342 -947	219 -606	224 -540	14.1 - 25.3	7 – 8.1	294. – 1070	188– 685	152 – 554
Mean	17.94	7.99	502	321	285	21.39	7.85	393	251	218
CV%	8.42	2.75	30.91	30.91	31.55	13.14	3.44	52.44	52.43	49.73

Table 4: Mean and range of chemical variables of the water samples from the studied area.

	Dry season (October 2021)								Wet season (April 2022)							
	Cations				Anions				cations				Anions			
	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^-	$SO4^{2-}$	Cl^-	NO_3^-
Range	49.6-145.6	10.7-42.9	1.4-29.4	0.5-2.5	190-350	11.2-220.7	8- 66	0.7-40.9	36.8-142.4	7.8-48.3	2.3-33.2	0.8-2.3	146-369	30.7-216.6	8-42	0.8-57.1
Mean	72	26	12	2	216	74	22	6	56	19	7	2	179	62	12	8
CV%	36.27	32.24	59.66	33.54	21.68	66.21	65.02	199.11	50.60	51.82	106.14	22.95	32.38	87.44	60.91	167.44

***Table 5: Trace elements (ppb) values of water samples in the Sipna area*.**

S.N	Parameters						
	Cd	Pb	Zn	Cu	Mn	Cr	Ni
1	0.25	15	43.9	130	77	6	B.D
2	0.21	B.D	B.D	119	74	1	B.D
3	0.19	10	7.5	111	74	6	B.D
4	0.18	B.D	5.3	99	69	3	B.D
5	0.15	25	19.3	111	78	12	B.D
6	0.17	21	25.1	99	73	10	B.D
7	0.17	7	B.D	97	68	4	B.D
8	0.16	B.D	B.D	95	71	1	B.D
9	0.15	B.D	B.D	95	68	4	B.D
10	0.17	5	B.D	99	73	4	B.D
11	0.18	9	B.D	95	73	3	B.D
12	0.15	8	3.2	105	71	3	B.D
13	0.16	7.5	B.D	97	74	5	B.D
14	0.18	6	4.8	111	78	6	B.D
15	0.17	2	4.8	103	70	2	B.D
16	0.18	14	10.7	99	71	2	B.D
17	0.17	B.D	B.D	111	66	3	B.D
18	0.15	B.D	B.D	99	68	3	B.D
19	0.17	B.D	2.1	107	68	2	B.D
20	0.16	7	5.3	105	73	3	B.D
Max	0.25	25	25.1	130	78	12	B.D
Min	0.15	B.D	B.D	95	66	1	B.D
Mean	0.169	10.5	12	105	72	4.15	B.D
WHO 2008	3	10	3000	2000	400	50	70
IQS 2009	3	10	3000	1000	100	50	20

Note: Blow detection limit of Cd (<0.1), Cr (<0.2), Cu (<0.4), Mn (<0.1), Ni (<0.5), Pb (<0.05), Zn (<0.02).

Table 6: Pearson's Correlation Coefficient (r) of the chemical components in the Sipna area.

Ions	Ca	Mg	Na	K	HCO_3	SO_4	Cl	NO_3	T	PH	EC	TDS	TH
Ca	1												
Mg	0.787	1											
Na	0.660	0.797	1										
K			0.317	1									
HCO_3	0.926	0.822	0.828		1								
SO_4	0.815	0.777	0.461		0.637	1							
Cl	0.704	0.756	0.894		0.840	0.409	1						
NO_3	.0750	0.606	0.747		0.824	0.486	0.750	1					
T				0.343				.395	1				
PH	-0.616		-0.337		-0.591	-0.365	-0.319	-0.756	-0.370	1			
EC	0.952	0.916	0.797		0.935	0.841	0.771	0.767		-0.548	1		
TDS	0.952	0.916	0.797		0.935	0.841	0.771	0.767		-0.548	1.000	1	.
TH	0.972	0.909	0.746		0.936	0.844	0.761	0.735		-0.525	0.989	0.989	1

Note: Correlation is significant at the $P< 0.001$ ($r= 0.534$); and $P<0.01$ ($r= 0.464$). The $r< \pm0.30$ is omitted

According to the chemical analysis's coefficient of variation (CV%) values which is a reflection of the measures of dispersion for these results [39]. the majority of cations and anions from both seasons in the Sipna area varied from 21.68% to 199% (Table 4). According to the results of the hypothetical salt combination rates for the surface water samples in the Sipna area, HCO3- salts dominate (Table 7), and their levels are the same in the dry and wet seasons, reaching 67.26% and 68.58%, respectively. While there is a minor relative rise in the SO42- and Cl- salts during the dry season (34.81% and 11.76%) compared to the wet season (30.75% and 7.67%).

Table 7: The mean of hypothetical salts combination of water samples in the studied area.

Hypothetical salts	$Ca(HCO_3)_2$	$CaSO_4$	$Mg(HCO_3)_2$	$MgSO_4$	$MgCl_2$	Na_2SO_4	NaCl	$NaNO_3$	KCl	KNO_3
Dry season	54.79	12.63	12.47	21.29	4.48	0.99	7.05	1.68	0.23	0.55
Wet season	58.28	5.78	10.30	23.16	3.07	1.81	4.48	1.07	0.12	1.16

Discussion

Due to geogenic and human activities, stream water hydrogen potential is often alkaline or slightly acidic [40]. Since the pH ranges from (7.1 to 8.2) for surface water samples in the Sipna area, all samples taken into consideration are slightly alkaline and fall below WHO standard drinking water consumption guidelines (Table 8). When the chemical composition of the Sipna stream's surface water and its tributaries was compared to the WHO's [41] and IQS [42] requirements for drinking water, it was discovered that the Sipna stream's surface waters are acceptable for human consumption and meet all relevant Iraqi and international standards (Table 8).

Sherank, Banistan, and Seri tributaries within the studied area produced by a collection of springs that feed the mainstream had relatively increased EC, TDS, and T°C findings than the Sipna stream (Table 3). which has helped to raise the salinity content in the surface water. This increase in ions is attributed to the processes that dissolve carbonate rocks and gypsum as well as agricultural and domestic activities (Table 4).

The weathering of carbonate rocks is the primary source of bicarbonate in rivers because of its interaction with carbonic acid, which is formed when carbon dioxide is dissolved in the water [43]. In general, the Sipna stream and its tributaries (Sherank, Banistan, and Seri) throughout

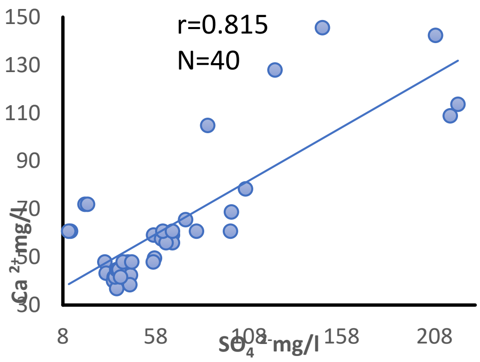
Table 8: comparing the parameters for studied samples with the standards of drinking water [41,42].

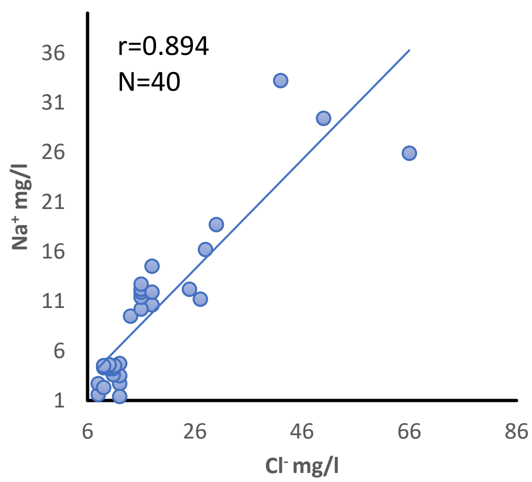
Parameter	Dry Season (Oct.2021)		Wet Season (Apr.2022)		IQS 2009	WHO 2008
	Range	Mean	Range	Mean		
pH	7.30-8.20	7.99	7 – 8.1	7.85	6.5-8.5	6.5-8.5
TDS	219-606	321	188 - 685	251	1000	1000
EC	342-947	502	294–1070	393	1500	1500
TH	224-540	285	152-554	218	500	500
Ca_2^+	49.6-145.6	72	36.8-142.4	56	150	100
Mg_2^+	10.7-42.9	26	7.8- 48.3	19	100	125
Na^+	1.4-29.4	12	2.3 – 33.2	7	200	200
K^+	0.5-2.5	2	0.8- 2.3	2	12	12
HCO_3^-	190-350	216	146- 369	179	600	300
SO_4^{2-}	11.2-220.7	74	31.4- 216.6	62	400	250
Cl^-	8-66	22	8 - 42	12	350	250
NO_3^-	0.7-40.9	6	0.8-57.1	8	50	50

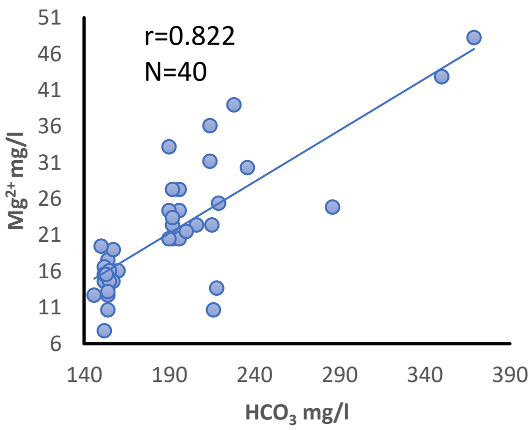
the dry and wet seasons had the following mean cation concentrations in all surface water samples: In terms of cations, Ca2+> Mg2+> Na+ >K+, as well as anions, HCO3- >SO42-> Cl- >NO3-.

The surface water samples from the Sipna area show a positive significant correlation (P<0.01) between TDS and chemical analyses (cations and anions), showing that (Ca2+, Mg2+, Na+, and K+) and (HCO3-, SO42-, Cl-, and NO3-) are the primary factors of the change in salinity. The weathering and dissolving of salts connected to the Fatha Formation and exposed in the Sipna area also contribute to the positive significant correlation between Na+ and Cl- (P<0.01), reflecting their origins. The significant correlation (P<0.01) revealed that the limestone, dolomite, and gypsum rocks that predominate in the Sipna area are the major sources of the Ca2+, Mg2+, and SO42+ ions (Fig. 3). While the NO3-, Cl-, Na+, and to some degree, SO42- strong correlations (P<0.01) indicate the contributions of the sources from agricultural activities and domestic in the Sipna area.

Piper diagram [44] was used to analyze the hydrochemical characteristics of water quality and type shown that the Ca- and Mg- types inside alkaline earth that dominate alkalies facies (Fig. 4), which is Ca-Mg-HCO3 solutions enter the surface water as a result of the weathering and dissolving of carbonate rocks within various formations that are exposed at the surface in







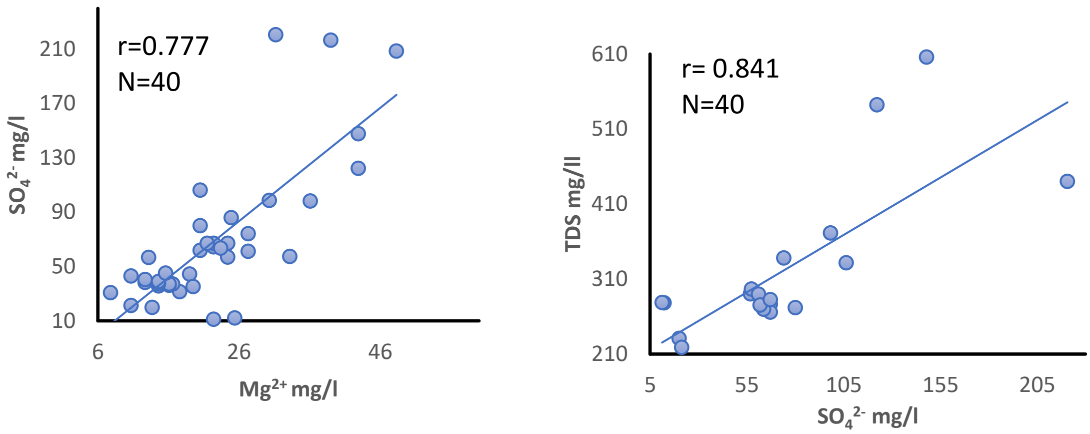
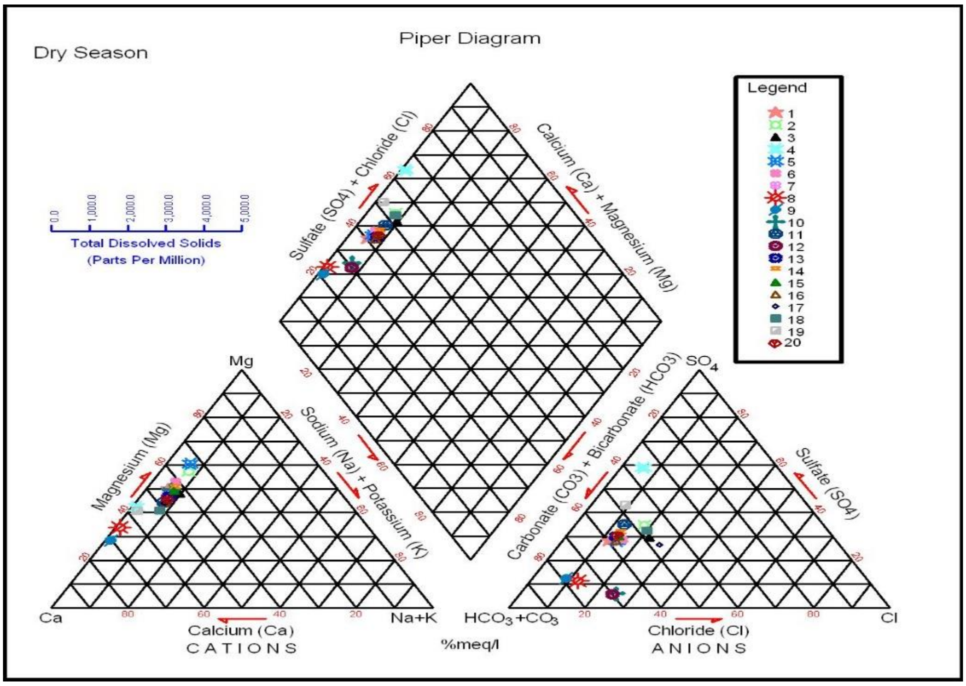


Fig.3 Variation diagrams of some ions in water samples of the Sipna area for both seasons.



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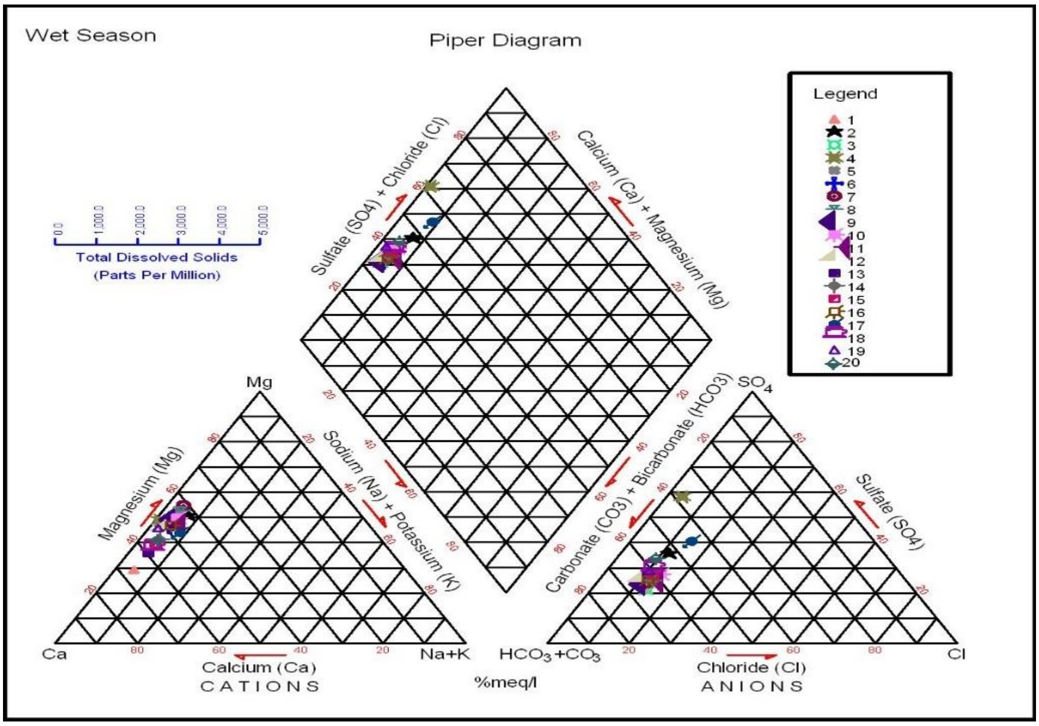


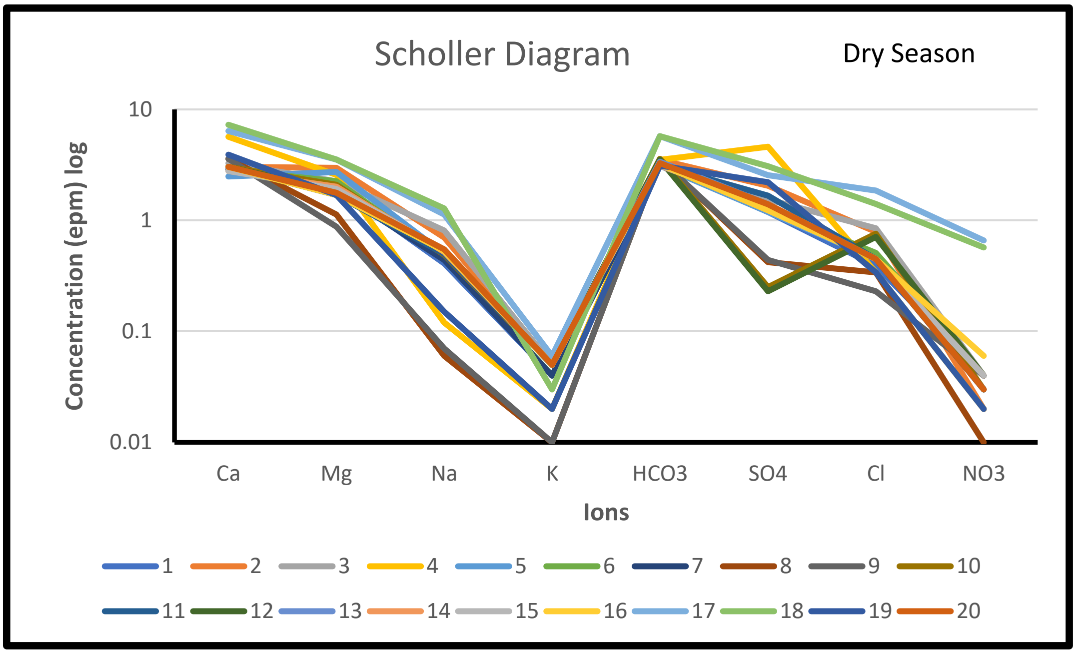
Fig. 4: Piper diagrams for water samples in the Sipna area from both seasons (dry and wet).

the studied area. By projecting these ions on a semi-logarithmic framework, Schuler's categorization (1972) illustrates the link between the concentrations of cations and anions in water and identifies their chemical type [45].

When this categorization was applied to the samples from the Sipna region, it revealed that the chemical composition of the surface water samples had both parallel and non-parallel associations (Fig. 5). While the non-parallel relationships reflect their impact on pollution processes, as is the case with sulfate and nitrogen ions, because of domestic and agricultural activities, especially during the summer season, the parallel relationships of the hydrochemical composition of surface waters in the Sipna area show the influence of weathering and thawing processes through the flow of these waters on exposed rocky layers of geological formations. The majority of the surface water samples taken during the two research periods are classified by Schuler as being of the Ca-HCO3 type, with a relative enrichment in Mg and SO42- concentration. Throughout the various phases of the investigation, Sipna water's hydrochemical properties were discovered.

One of the important tools for analyzing hydrochemical processes is the Gibbs diagram [46, 47, 48]. According to the findings, all forty surface water samples from dry and wet seasons fall into the Na+/(Na++Ca2+) or Cl-/(Cl-+HCO3-) value <0.5, and TDS values are low to moderate, ranging from 251 to 412 mg/l. Also, most of the Sipna area had water of Ca-bicarbonate, in addition, SO42- is the second most prevalent ion in the surface stream water after cations (Ca2+ and Mg2+) and anions (HCO3-), showing that the majority of cations and anions in the Sipna stream are generated from the rock weathering (Table 4). Generally, the trace elements (Cd, Cr, Cu, Mn, Ni, Pb, and Zn) during the dry season had shown rates lower than the concentrations permitted for drinking water that reflect the normal background in the Sipna area (Table 5).

The study demonstrates the degree to which urbanization impacts and helps to increase the level of concentrations of some ions, particularly SO42-, Cl-, and NO3-, or in other words, salinity in surface waters during the study period, as well as the importance of weathering and dissolution processes for the rocks that the river runs on. The majority of the surface water samples collected during the study periods, according to Schuler's classification, are of the Ca-HCO3 type with relative enrichment in Mg and SO42- content.



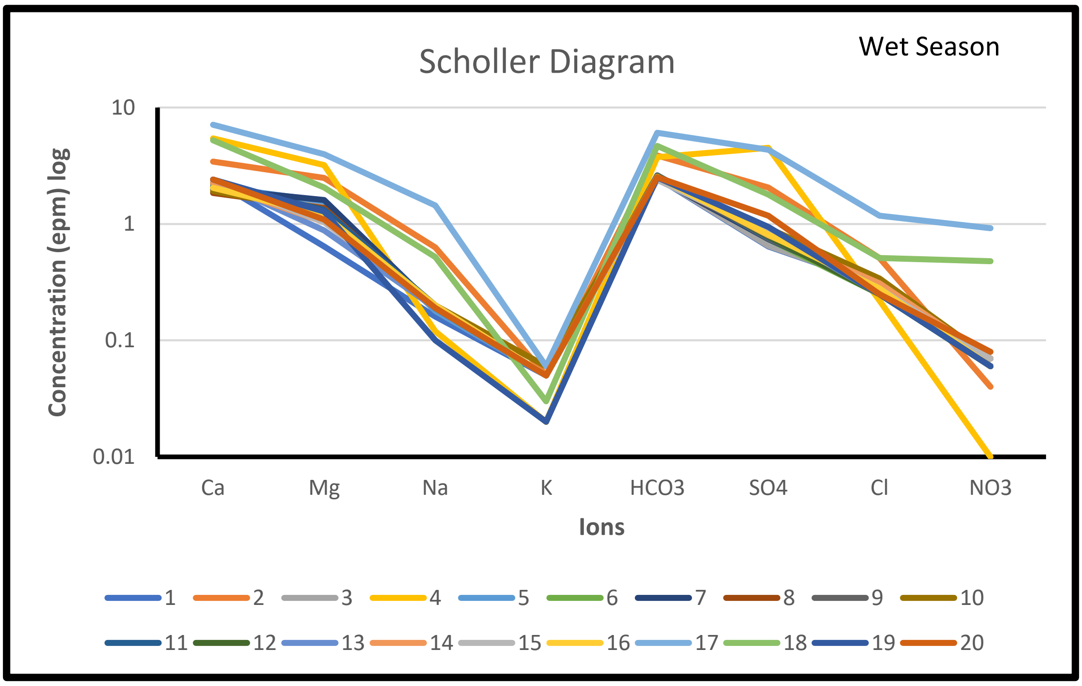


Fig.5: Scholler diagrams (1972) for major ions in Sipna area for dry and wet seasons.

Conclusions

Due to the surrounding region's security situation and the consequent rise in domestic and agricultural activity, the Sipna area suffered rapid population movement throughout the prior time. The samples taken from the Sipna stream and its branches have high concentrations of Ca2+, Mg2+, HCO3-, and SO42-, with the Ca-Mg-bicarbonate type predominating and sometimes the Ca-sulfate type as well. The limestone, dolomite, and gypsum that are exposed in the area suggest that water-rock weathering is the main hydrochemical process. The unparallel relationships of Schuler's diagram represent their influence on pollution processes (natural or anthropogenic), as is the case with SO42- and NO3- ions during low levels of water. All of the samples taken into consideration are slightly alkaline and within the WHO [41] and IQS [42] recommended drinking limits.

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