

Hydrochemical Characterisation of Groundwaters in the Sana'a Basin, Yemen

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Abstract: In the present study, the physico-chemical parameters were applied to characterize and classified ground- and spring water samples collected from the Sana'a basin. Twenty four groundwater from deep wells and 13 spring water samples were. Selected anions (Cl^- , HCO_3^- , NO_3^-) and cations (Ca^{2+} , Mg^{2+} and Na^+) were measured in the collected samples. Additionally, the heavy metals Pb, Ni and Cd were measured in the groundwater samples. The physico-chemical parameters, which include water temperature, electrical conductivity, pH-value and bicarbonate, were measured in the field during the water sampling. The water samples were classified in groups according to their major ions content. The classification was based on several hydrochemical methods such as Ca^{2+} and Mg^{2+} hardness, Sodium Absorption Ratio (SAR), Magnesium hazard (MH), saturation indices (SI) and Piper diagram. To ensure the suitability of ground- and spring water in the Sana'a basin for drinking purposes, the hydrochemical parameters were compared with the guidelines recommended by the World Health Organisation (WHO) and the Yemen National Water Resources Authority (NWRA) standards. In order to check the suitability of ground- and spring water for irrigation purposes the samples were classified based on MH and calculated SAR. The calculated values were plotted on the diagram recommended by the United State Salinity Laboratory (U.S.S.L).

Key words: Deep wells and spring water • Heavy metals • Groundwater classification in the Sana'a basin
• Groundwater in Yemen and hydrogeochemistry of the Sana'a basin

INTRODUCTION

The Sana'a basin was subjected to accelerated anthropogenic, economic and social developments during the last two decades. As a result of a high rate of population growth (7% per annum) [1], uncontrolled immigration to this area and the expansion of the agricultural activities, the demand for water has increased tremendously in the last 20 years. The increasing demands meet limited resources. To satisfy the increased need for water, new groundwater wells have been drilled at various locations in the basin and the abstraction from all groundwater sources has increased beyond the perennial yield of the Sana'a basin which led to rapid drop of the groundwater level. An annual average of the dropdown in the water levels ranges between 4 and 5 m/year [2]. This problem seems even more serious when taking into account the gradual degradation of the water quality and marked drought events recorded in the country within the last few years. The overexploitation of

the groundwater in the basin bears the risk of wells falling dry, a degradation of the water quality due to the infiltration of the sewage water, particularly in the alluvium aquifer below the urban area and in the sandstone aquifer in the northern part of the basin and increasing salinities due to intensive groundwater pumping. Furthermore the groundwater in the agricultural area could be contaminated by the increased and uncontrolled application of the fertilizers and pesticides.

In a rather recent evaluation study of water resources in the country, Foppen [3] assumed that the Sana'a basin would not only enter a phase of water deficit in the near future. However, he also attested that, if no remedial and immediate solution actions were undertaken to correct the deficit, water shortage in the basin could become a critical problem.

In the present study the water samples were divided into different groups or classes according to their chemical composition. For classification purpose, four categories were used; the total water hardness (TH),

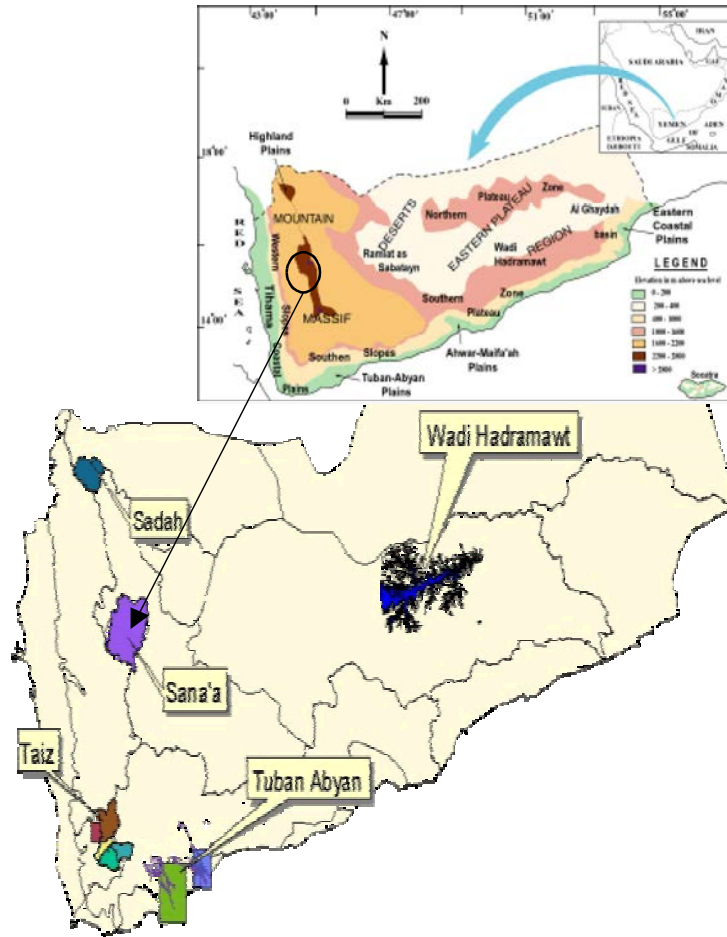


Fig. 1: Location map of the study area (after NWRA, 2007)

Sodium Absorption Ratio (SAR), Saturation Index (SI) and Piper diagram. The classification associated with evaluation of the water quality in the Sana'a basin according to its use for the various proposes, e.g. the water hardness is an important parameter for the assessment of the water quality for domestic purposes. For further evaluation of the water quality for domestic purposes, the guideline values recommended by WHO and NWRA were used. About 80% of water in Sana'a basin is used for irrigation purposes, so the evaluation of the water quality for this purpose is an important goal of this work. For this evaluation, the SAR and salinity hazard diagram used by United State Salinity Laboratory (USSL) is used.

General Characteristics of the Study Area

Regional Setting, Topography, Climate: The Sana'a basin is one of the most important highland groundwater basins in Yemen. The basin is located in the central Yemen highlands at an elevation of about 2200 meter above sea

level (m.a.s.l.) between 15° 21' N and 44° 12' E covering an area of about 3.200 km². (WEC, 2002) (Figure 1).

The climate in the Sana'a basin is semi-arid. The hottest season in Sana'a is from June to August and the coldest season is between December and February, with maximum and minimum monthly temperatures in June 31°C and December 4°C, respectively. The average maximum annual temperature in Sana'a from 1983 to 2002 was recorded in June at 31°C. The minimum temperature is 24°C in December. The average minimum annual temperature is 4°C in December-January and maximum 15°C in July. The average monthly temperature ranges between 15 and 25°C. The average monthly humidity in Sana'a ranges between 35 % in June and 52 % in April [4].

Hydrogeological Conditions

Geology: The oldest sedimentary Formation in the region of Sana'a is the Amran Series (Middle to Upper Jurassic) which comprises of limestones, marls and shaly limestones some 350 to 1000 m thick.

The Amran outcrops in the north of the basin, covering about 15% of the Basin area. It occurs at depth beneath the Sana'a plain. At the airport, the top of the Amran is approximately 350 m deep, at Ar Rawdah it is 500 m deep and further south near Sana'a it is 900 m deep or more. The Amran is overlain by a sequence of lagoonal shales, marls and fine grained sandstones interbedded with lignite probably of Upper Jurassic or Lower Cretaceous age which outcrop in a narrow band in the north-eastern part of the basin.

The Tawilah Sandstone (Cretaceous to Tertiary) comprises a series of continental cross bedded sandstones generally medium to coarse grained with interbedded mudstones, siltstones and occasional silty-sandstones.

The overlying Medj Zir Formation is finer grained sandstone with a higher proportion of siltstones and clays. It also contains decomposed volcanic tuffs and "soapy clay beds" associated with the start of regional volcanic activity. It has proved difficult to distinguish the Tawilah and Medj Zir both in aerial photographs and drill cuttings. They are therefore mapped as one formation and referred to as the Tawilah Sandstone or "Cretaceous Sandstone". The Cretaceous Sandstone outcrops over about 15% of the Basin area in the northern part of the Basin. It is thought to reach a thickness of 400 to 500 m where it has been protected from erosion by the overlying Tertiary Volcanics. The Tertiary Volcanics (formerly called the Trap Series) outcrop over some 35% of the area of the Sana'a Basin. They form high plateaus to the south, west and east of the Sana'a plain and underlie the Quaternary deposits in the south of the Basin. The sequence is divided into two groups. The lowest group is the "Stratoid Volcanics" which include the Basal Basalt (a dense homogenous basalt flow with columnar jointing), basalts, tuffs and pyroclastics interbedded with fluvio-lacustrine deposits. The upper "Chaotic Volcanics" comprise mixed basalt flows and rhyolite lavas. The total thickness is variable, reaching an estimated maximum of 700 to 900 m.

Basic intrusive rocks of Tertiary age are present throughout the area in the form of volcanic plugs, dykes and sills. The alignment of the volcanic necks is oriented NNW-SSE. Dykes are well fractured and oriented NNW-SSE and NNE-SSW.

Volcanic activity continued into the Quaternary forming a plateau of extensive basalt cones in the north west of the Basin interlayered with tuffs and alluvial sediments. The Quaternary Basalts have a total thickness

of about 100 to 300 m and cover about 20% of the area of the Basin. They overlie the Amran Limestone, Cretaceous Sandstone and Tertiary Volcanics.

Unconsolidated deposits of the Quaternary cover approximately 15% of the Basin area. They are confined to wadi beds and low areas that form the Sana'a plain. Deposition appears to have been of fluvio-lacustrine nature which led to the accumulation of clays and silts in basins 100 to 300 m deep. Coarse grained colluvium and alluvium occurs in the wadi beds at the foot of hills.

The sedimentary sequence is block faulted and gently folded. The regional dip is southwards under cover of the Tertiary Volcanics.

The unconsolidated Quaternary deposits provide a poorly permeable aquifer which has been heavily exploited in the Sana'a Basin due to its proximity to the urban area. The aquifer is regionally unconfined but locally semi-confined. Due to the fine grained nature of the deposits in the plain, recharge is expected to be mainly indirect, into coarse grained material along wadis and at the base of the hills.

Hydrogeology: The Amran limestone is generally considered to be a poor aquifer although supplies can be obtained from zones of secondary permeability. Karst features however are poorly developed. The depth to water is over 100 m in the plateau area in the northwest of the basin. In the northeast in valleys leading to the Wadi al Kharid the depth to water is less than 35 m and groundwater is abstracted mainly by means of dug wells.

The Cretaceous sandstone forms the main aquifer in the region. It has low regional permeability but locally higher permeabilities are found in weathered and fractured zones. It is heavily exploited to the northeast and northwest of Sana'a where it either outcrops or occurs beneath an unconsolidated cover of up to 50 m thickness. Depths to water in the main area of abstraction were about 30 to 40 m in the early 1970's but have declined by 2 to 4 m/yr since. In the south of the basin the sandstone is confined beneath several hundreds of meters of Tertiary volcanics.

The basalt flows and stratoid sequences of the Tertiary volcanics act as aquicludes, except where fractured or where primary permeability occurs in sediments between flows. The mixed basalt and rhyolite flows at the top of the sequence are more highly fractured and contain perched aquifers which supply dug wells and feed high level springs. The upper layers of the volcanics are highly weathered and relatively permeable where they

underlie the unconsolidated Quaternary deposits in the south of the basin. Here they are exploited together with the unconsolidated aquifer by dug and drilled wells.

The Quaternary basalts are highly permeable due to fracturing and to the presence of clastic deposits between flows. Where the formation is saturated it provides an unconfined aquifer. Water levels are deep ranging from 60 to 130 m depending on the elevation. Wells are generally limited to the southern edge of the outcrop where water levels are less than 100 m deep. In the rest of the area, surface water is stored in cisterns to provide water for domestic purposes.

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MATERIALS AND METHODS

Sampling Campaigns: Sampling campaign in the Sana'a basin, which includes groundwater and spring water samples, was carried out in September/October 2009 by the author accompanied by a representative of the cooperation partners Water and Environment Centre (WEC).

A total of 24 wells for groundwater sampling and 13 springs were chosen. Two samples were taken from each site, one sample for analysis of selected cations (Na^+ , Mg^{2+} and Ca^{2+}) and selected heavy metals (Pb, Ni and Cd) and one for major anions (Cl^- and NO_3^-). The heavy metals were analysed in all of the 24 groundwater samples.

Polyethylene bottles (50 ml) with watertight caps were used for the sampling. The bottles were pre washed with the water sample and filled up entirely and stored in cool-box and later stored in a refrigerator by 4 °C until the transport to the Hydrogeology Laboratory at FUB for the analyses. The samples for determination of the major cation and heavy metals were acidified with two drops of ultra pure HNO_3 to prevent the oxidation.

Groundwater samples were collected mostly from deep boreholes (drill wells); only three samples were collected from dug wells. All the wells (drill and dug) are equipped with pumps. Total depth of the drill wells ranges between 56 m and 450 m. The dug wells are 60, 70 and 80 m depth.

Analysis

On-Site Analysis: The physicochemical parameters such as temperature, pH and electrical conductivity (EC) of the ground- and spring water samples were measured in the field with WTW Microprocessor Conductivity Meter LF 196 device provided by FUB. Because of the time consuming, the determination of bicarbonate was carried out means a quick test in the laboratory of WEC in Sana'a within few hours after sampling.

Laboratory Analysis: Selected ions were analyzed in all 24 groundwater and 13 spring water samples. The heavy metals were measured only in the groundwater samples. The analyses were performed at the hydrogeology laboratory of FUB by labor assistant Mrs. E. Heyde. Measurement of Na^+ , Mg^{2+} , Ca^{2+} , Pb, Ni and Cd were conducted by inductively coupled plasma optical emission spectrometry (ICP-OES), " Cl^- and NO_3^- " by Ion-chromatography (IC), DX 500 DIONEX.

RESULTS AND DISCUSSION

Charge Balance: The analytical results for the groundwater and spring water samples can be assessed for reliability by determining whether the equivalents of the major cations and anions are approximately equal [5]. All water samples are electrically neutral, meaning that the sum of the positively charged cations must be exactly to the sum of the negatively charged anions [6].

A charge balance error can be calculated by the following relationship [6]:

$$balance(\%) = \frac{\sum cations - \sum anions}{(\sum cations + \sum anions)/2} * 100 \quad (1)$$

The hydrochemical analysis is given in mg/l and was transformed to mmol/l to calculate the balance in % according to equation 1. Water analyses are normally considered acceptable if the charge balance error is within $\pm 5\%$ using the equation 1. The charge balance error for the analyses associated with this study varied from -5.84 to +4.91 % for groundwater samples and -5 to +0.10 % for spring water samples. Because of the minor error occurs in one sample (-5.84%), the sample was considered in the evolution.

Physicochemical Parameters

Water Temperature: Generally, the temperature of groundwater increases with depth because of the hydrothermal gradient in the area, which, in turn, is influenced by the volcanic activity among other tectonic factors. It is therefore expected that the deeper the well the higher its water temperature, especially if it lies within the vicinity of areas subjected to recent volcanic activity or along fault zones [2]. Water temperature in the shallow dug wells located in the alluvium aquifer (samples: GW-2, GW-16 and GW-17) could be influenced by the radiation of the sun.

Thirty-three per cent of the total samples, mainly from dug and shallow wells, show low temperatures ranging between 20 to 25°C while 37% shows temperatures ranging between 26-30°C. Temperatures more than 31°C were recorded in 29% of the total samples; most of them located in the northern part of the basin in the limestone aquifer. The temperature range between 31-36°C is interpreted as reflecting geothermal effects throughout the whole area.

The springs generally have lower water temperatures ranging between 18 to 23°C due to the contact with the cold atmosphere.

pH-Values: The lowest pH value of the groundwater was observed in the sandstone aquifer in north-eastern part of the basin with pH value 5.6 and the highest values with 9.4 in the volcanic aquifer in southern part of the basin. It is observed that 54% of the water samples have pH-values in the range of 7.0 and 8.0. The volcanic and alluvium aquifers have the highest pH-values of the groundwater in the Sana'a basin with pH-values range from 7.5 to 9.4 (alkaline water). The samples from sandstone and limestone aquifers have lower pH-values ranging from 5.6 to 7.6. The groundwater in these aquifers is mainly influenced by the hydrothermal activity [7].

Six of the groundwater samples show pH-values outside of the range recommended by WHO (6.5-8.5). The values are above the recommended value in the samples GW18, GW19 and GW20 in volcanic aquifer with pH 9.4, 8.9, 9.0 respectively; and below the recommended value in the samples GW-5, GW-6 in the limestone aquifer and in GW-7 in the sandstone aquifer in the northern part of the Sana'a city with 6.3, 6.3 and 5.6 respectively. The ground-water in this part is affected by the infiltration of domestic sewage via cesspits [7].

In the study area, 11 water samples from springs (85%) show pH values above 7 and only two samples recorded pH values below 7 (SW-3 and SW-8 with

pH-values 6 and 6.7, respectively. This deviation could be due to the long path flow in the underground, consequently the contact with the bearing rocks. Some of the springs were contaminated. The values in SW-3 and SW-10 exceeded the WHO value with values of 6 and 9.4, respectively.

TDS and Electrical Conductivity (EC): The EC was measured in $\mu\text{S}/\text{cm}$ in the field during water sampling at 24 groundwater points and 13 springs. TDS was calculated in mg/l using the equation:

$$\text{TDS} = 0.65 * \text{EC} \quad (2)$$

The EC and TDS of the water is a function of temperature. The higher in temperature gives higher in dissolved minerals, consequently higher EC; this is the reason why the groundwater has higher EC than the spring water.

The TDS of the groundwater in the Sana'a basin is affected mainly by the concentration of the major cations Mg and Ca and HCO_3 . The TDS of the spring water samples is affected by the cations Mg, Ca and Na and the anions HCO_3 and Cl. The concentration of these ions shows systematic increases with TDS. The TDS increases with the increase of the contents of the water from these minerals.

The concentration of total dissolved solids in the groundwater samples and spring water ranges from 1319.5 to 182 mg/l and from 403 to 149.5 mg/l respectively. The low TDS values in the groundwater samples, particularly in the sandstone aquifer, indicate fresh recharge water. The measured electrical conductivity values are found to be within the range of 2030-280 $\mu\text{S}/\text{cm}$ at 25°C in the groundwater samples, while the springs show lower values ranging between 620 and 230 $\mu\text{S}/\text{cm}$. The large variation in EC is mainly attributed to lithologic composition and anthropogenic activities prevailing in the region.

It is common that calcium bicarbonate and calcium sulfate water-type generally have the lowest EC-values [8]. This was observed in the southern part of the basin in the volcanic aquifer where the lowest EC-values were found and ranging between 470 and 280 $\mu\text{S}/\text{cm}$. The dominant water-type in this aquifer is $\text{Ca-HCO}_3\text{-SO}_4$ and Ca-HCO_3 . As a result of the dissolution of the minerals calcite, dolomite and gypsum which are presented in Amran limestone, the highest EC-values were recorded in north-eastern part of the basin in the limestone aquifer with values ranging between 2030 and 560 $\mu\text{S}/\text{cm}$.

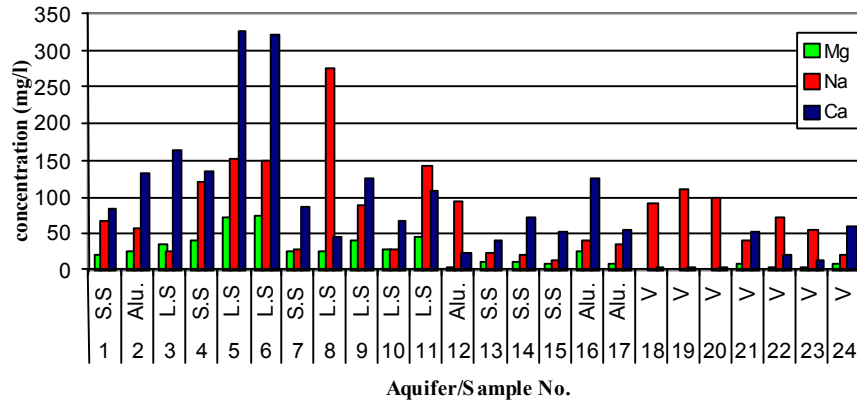


Fig. 2: Concentration of selected cations in the groundwater samples

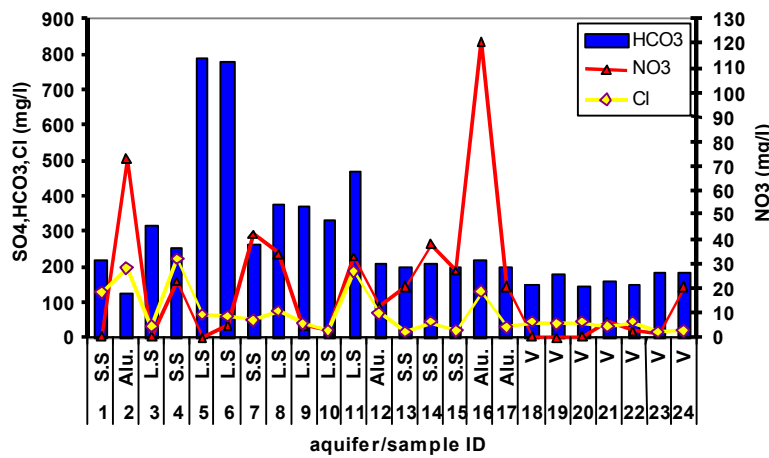


Fig. 3: Concentration of selected anions in the groundwater samples

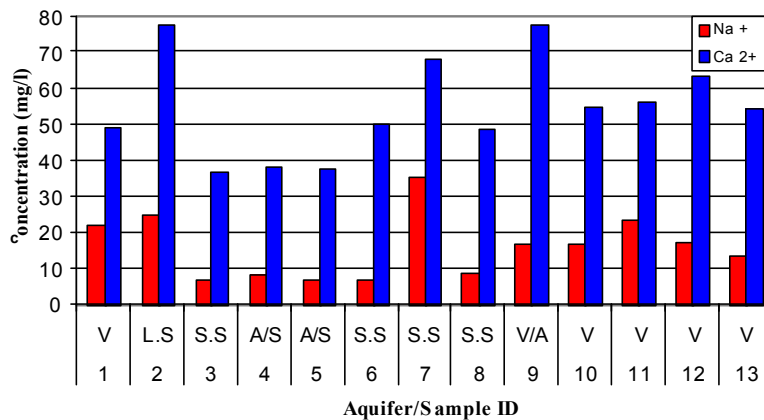


Fig. 4: Concentration of selected cations in the spring water samples

The measured EC-values result indicate that almost all the ground- and spring water samples are within the permissible limits of 1500 $\mu\text{S}/\text{cm}$ recommended by WHO, with the exception of GW-6 in the limestone aquifer where EC was found to be 2030 $\mu\text{S}/\text{cm}$. However, this value is within the permissible limits of 2500 $\mu\text{S}/\text{cm}$ recommended by NWRA.

The calculated TDS values for both groundwater and spring water samples are within the WHO and NWRA standards (1000 mg/l and 1500 mg/l, respectively). Only two of the groundwater samples, namely GW-5 and GW6 in the limestone aquifer, exceeded the calculated TDS values the permissible limits recommended by WHO with 1280.5 and 1319.5 mg/l, respectively.

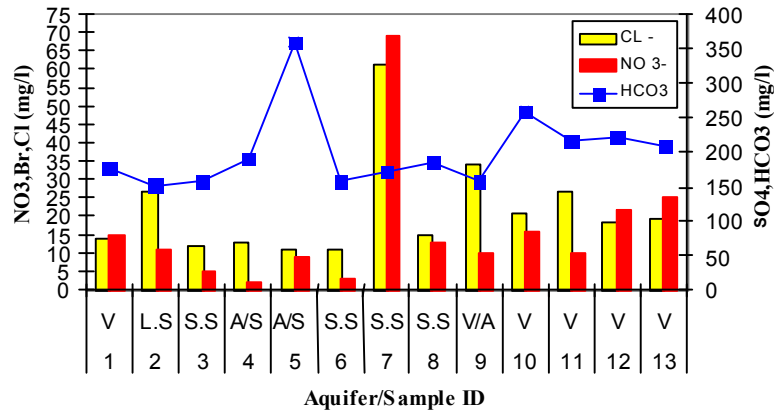


Fig. 5: Concentration of selected anions in the spring water samples

Chemical Composition

Concentration of Selected Ions: Concentration of selected cations and anions in 37 groundwater and 13 spring water samples will be illustrated in Figures 2 to 5.

It is clear from these figures that the concentration of Ca, HCO₃ and Na are higher in the northern part of the basin in the limestone aquifer. The highest concentration of Mg and Ca was found in sample GW-6 and GW-5, whereas the lowest values were found in samples GW-20 and GW-18 in southern part in the volcanic aquifer, respectively. The concentration of Ca ranges from 2.9 to 326 mg/l. The anion HCO₃ shows the highest concentrations in sample GW-5 with 126 mg/l in the sample GW-2 southern part in the alluvium aquifer.

The high concentration of Ca, Mg and HCO₃ ions in the groundwater can be explained by the solution of calcite, dolomite and gypsum which are all present in the Amran limestone group.

Generally Na, unlike Mg and Ca, is not found as an essential constituent of many of the common rock-forming minerals. Na content of the groundwater in the study area ranges from 274 to 11.1 mg/l. The highest value was found in sample GW-8 in the northern part in limestone aquifer and the lowest in GW-15 in western in the sandstone aquifer.

As shown in Figure 5, nitrate was presents in all of the spring and groundwater samples. This might originate from human activity or from minor NH₄ gas emissions from volcanic activity into the groundwater system where it is oxidized to NO₃ [3]. The highest nitrate and chloride concentrations were measured in samples GW-16 with 121 mg/l in the central part of the Sana'a city near the new campus of Sana'a University and in sample GW-4 with 252 mg/l, which comes from the eastern part of the basin in the alluvium aquifer. Groundwater in these parts of the basin is affected by the infiltration of domestic sewage via

cesspits and the subsequent oxidation of NH₄ to NO₃ [7]. This area is dominated by a high population density and lacks a sewer system.

The spring water generally shows a low mineral content. TDS of the spring water samples ranges between 402 to 149.5 mg/l. The springs are located in high elevation ranges between 2103 to 3022 m.a.s.l.; therefore the spring water is cold with temperature ranges between 23 to 18°C. The low solubility associated with these temperatures, in combination with short flow paths and residence times affects the concentrations in this area.

Concentration of Selected Heavy Metals: Selected heavy metals Pb, Ni and Cd were analyzed in the groundwater samples taken from the Sana'a basin. No analyses were conducted in the spring water samples. The measured values show that the concentration of the heavy metals Pb, Ni and Cd in all 24 groundwater samples is below the detection limit. This is probably due to the absence of heavy industry in Sana'a region, since industrial activity is the main responsibility for the presence of the heavy metals in wastewater and later in the groundwater [9].

Water Classification: The classical use of water analyses in groundwater hydrogeology is to produce information concerning the water quality. The water quality may yield information about the environments through which the water has circulated. The main objective following the hydrogeochemical assessment is to determine groundwater suitability to different uses based on different chemical indices. In this study, assessment of the suitability for drinking and domestic consumption was evaluated by comparing the hydrochemical parameters of groundwater in the study area with the prescribed specification of World Health Organization (WHO), [10] and NWRA, [11]. The calculated SAR was used to assessment the suitability for the irrigation purpose.

Water Classification Based on Total Hardness (Ca⁺² and Mg⁺²) for Domestic Purpose: Calcium and magnesium hardness is the concentration of calcium and magnesium ions. The degree of hardness of drinking water has been classified in terms of its equivalent CaCO₃ concentration in four categories [10]: soft water, hard water, medium hard water and very hard water (Table 1). Very hard water is not desirable for many domestic uses; it will leave a scaly deposit on the inside of pipes, boilers and tanks. Hard water is mainly an aesthetic concern because of the unpleasant taste that a high concentration of calcium and other ions give to water. It also reduces the ability of soap to produce lather and causes scale formation in pipes and on plumbing fixtures. Soft water can cause pipe corrosion and may increase the solubility of heavy metals such as copper, zinc, lead and cadmium in water. In some agricultural areas where the fertilizers are applied to the land, excessive hardness may indicate the presence of other chemicals such as nitrate [10]. Hardness in water is the most common water quality problem especially when the main water sources are deep wells as in the Sana'a basin.

Water hardness in most groundwater is naturally occurring from weathering of limestone, sedimentary rock and calcium bearing minerals. Waters that filtrate through limestone are prone to hard water. This is because of rainfall, which is naturally acidic containing carbon dioxide gas, continually dissolves the rock and carries the dissolved minerals into the groundwater system.

The guideline value for drinking water recommended by WHO for water hardness is 500 mg/l [10], this value was also recommended by NWRA, 2000. The optimum range of hardness in drinking water is from 80 to 100 mg/L [10].

The calculated total hardness of ground- and spring water samples in the Sana'a basin presented in Table 2 and 3, respectively. In comparison the results of this study with the classification values given in Table 1, ground- and spring water in the Sana'a basin could be classified in four groups:

Group 1: Very Hard Water: Most of the 37 measured water samples are very hard (49% of the total samples).

Table 1: Classification of drinking-water based on total hardness [10]

Concentration as CaCO ₃ (mg/l)	Classification
0-60	Soft water
60-120	Medium hard water
120-180	Hard water
> 180	Very hard water

Table 2: Calculated Ca⁺² and Mg⁺² hardness, SAR and SI in the groundwater samples collected from Sana'a basin

Sample ID	Aquifer type	SAR (meq/l)	Total hardness (mg/l)	MH(%)	SI-Calcit	SI-Dolomite	SI-Anhydrite	SI-Gypsum
GW-1	S.S	1.17	289.73	19.7	-0.35	-1.03	-1.74	-1.5
GW-2	Alu.	0.84	430.08	15.2	-0.41	-1.29	-1.61	-1.4
GW-3	L.S	0.34	549.32	17.8	0.03	-0.33	-1.16	-0.9
GW-4	S.S	1.63	503.14	23.0	-0.15	-0.54	-1.38	-1.2
GW-5	L.S	1.40	1110.20	18.1	0.57	0.77	-0.7	-0.5
GW-6	L.S	1.38	1107.95	18.8	0.57	0.78	-0.72	-0.5
GW-7	S.S	0.48	310.99	21.9	-0.25	-0.8	-1.83	-1.6
GW-8	L.S	5.68	220.15	37.3	-0.48	-0.91	-1.7	-1.46
GW-9	L.S	1.22	477.36	23.9	-0.01	-0.25	-1.31	-1.07
GW-10	L.S	0.51	271.11	29.7	-0.23	-0.55	-2.3	-2.09
GW-11	L.S	2.07	445.40	29.3	0.03	-0.04	-1.7	-1.51
GW-12	Alu.	3.44	70.58	14.7	-0.89	-2.36	-2.43	-2.2
GW-13	S.S	0.60	138.51	17.2	-0.60	-1.64	-2.8	-2.51
GW-14	S.S	0.43	212.86	12.2	-0.39	-1.38	-2.31	-2.07
GW-15	S.S	0.27	160.71	13.7	-0.50	-1.53	-2.8	-2.52
GW-16	Alu.	0.59	413.36	16.4	-0.19	-0.81	-2	-1.8
GW-17	Alu.	0.80	165.21	13.3	-0.52	-1.56	-2.51	-2.3
GW-18	V	9.69	8.07	6.5	-2.02	-	-3.57	-3.3
GW-19	V	10.44	10.78	6.0	-1.78	-	-3.45	-3.2
GW-20	V	9.24	10.99	4.2	-1.74	-	-3.23	-3.03
GW-21	V	0.98	163.64	13.1	-0.63	-1.82	-2.04	-1.8
GW-22	V	2.84	58.36	9.5	-1.05	-2.79	-2.67	-2.43
GW-23	V	2.59	41.13	11.8	-1.1	-3.04	-3.14	-2.9
GW-24	V	0.45	178.68	10.9	-0.5	-1.61	-2.62	-2.3
WHO-Standard			500.00					
NWRA-standard*			500.00					

Table 3: Calculated Ca⁺² and Mg⁺² hardness, SAR and SI in the spring water samples collected from Sana'a basin

Sample ID	Lithology	SAR meq/l	Total hardness mg/l	MH %	SI-Calcite	SI-Dolomite	SI-Anhydrite	SI-Gypsum
SW-1	V	0.54	152	13.0	-0.55	-1.64	-2.83	-2.59
SW-2	L.S	0.47	268	19.0	-0.13	-0.6	-2.18	-1.94
SW-3	S.S	0.19	112	12.0	-0.74	-2.05	-2.98	-2.74
SW-4	A contact with S.S	0.23	116	11.9	-0.71	-2	-2.93	-2.7
SW-5	A contact with S.S	0.18	120	14.5	-0.72	-1.99	-2.94	-2.7
SW-6	S.S	0.16	152	11.6	-0.57	-1.78	-2.47	-2.23
SW-7	S.S	0.75	213	13.4	-0.48	-1.5	-2.15	-1.91
SW-8	S.S	0.21	153	13.9	-0.59	-1.73	-2.32	-2.08
SW-9	Vcontact with A	0.33	256	16.2	-0.26	-0.94	-2.05	-1.82
SW-10	V	0.38	181	16.5	-0.46	-1.36	-2.61	-2.37
SW-11	V	0.53	179	14.3	-0.44	-1.39	-2.32	-2.08
SW-12	V	0.38	193	12.0	-0.41	-1.42	-2.6	-2.36
SW-13	V	0.31	166	12.0	-0.58	-1.76	-2.616	-2.38

Water of this group has hardness concentrations range between 181 and 1.110 mg/l. The highest values were found in the limestone groundwater aquifer in the northern part of the basin. The minerals calcite and magnesium are thought to derive naturally from rocks of the Amran limestone group which comprises dolomite and gypsum.

Group 2: Hard Water: About 30% of the total water samples represent this water type. This type is to be found mostly in the volcanic and sandstone aquifer in the southern and western part. Water samples have hardness concentrations range between 139 and 179 mg/l.

Group 3: Medium Hard Water: Only four samples represent this water type. It is common in spring water in the alluvium aquifer which is located in contact with sandstone. Hardness concentrations in water sample this type range between 71 and 120 mg/l.

Group 4: Soft Water: About 14% of the water samples are soft water with a low hardness ranging between 8 and 58 mg/l. This water type was observed in volcanic groundwater aquifer in southern part. Water passing through igneous rocks is thought to dissolve only small quantities of minerals.

Water Classification Based on Salinity and (SAR) for Irrigation Purpose: About 80% of groundwater in the Sana'a basin is used for irrigation. The water quality evaluation in the study area is carried out to determine their suitability for agricultural purposes. The suitability of groundwater for irrigation is contingent on the effects on the mineral constituents of the water on both the plant and the soil. In the fact, salts can be highly harmful. They can limit growth of plants physically, by restricting the taking up of water through modification of osmotic processes. Also salts may damage plant growth

chemically by the effects of toxic substances upon metabolic processes. Salinity and toxicity generally need to be considered for evaluation of the suitable quality of the groundwater for irrigation [12]. Parameters such as EC and sodium adsorption ratio (SAR) and the standard diagrams were used to assess the suitability of water for irrigation purposes. The method published by the US SALINITY LABORATORY, STAFF [13] was used for the classification of our samples. The calculated values were plotted in a Wilcox diagram using the software program AquaChem 4.0. The plot can be used to quickly determine the viability of water for irrigation purposes. The Wilcox plot is also known as the U.S. Department of Agriculture diagram. The SAR is plotted as Sodium Hazard on the Y-axis in the Wilcox plot; and the measured EC (Cond.) is plotted on the X-axis as Salinity Hazard. The Conductivity (EC) is by default plotted using a log scale. The calculated values are presented in tables 2 and 3.

Salinity Hazard: Excess salt increases the osmotic pressure of the soil solution that can result in a physiological drought condition. Even though the field appears to have plenty of moisture, the plants wilt because insufficient water is absorbed by the roots to replace that lost from transpiration. The total soluble salt content of irrigation water generally is measured either by determining its EC (as in this study) or by determining the actual salt content in parts per million (ppm). The conductivity values ranged from 280 to 2030 $\mu\text{S}/\text{cm}$. Irrigation water with an EC of $< 700 \mu\text{S}/\text{cm}$ causes little or no threat to most crops while $\text{EC} > 3000 \mu\text{S}/\text{cm}$ may limit their growth [14]. Based on the US Salinity Laboratory classification [13] the salinity hazard for water samples in the Sana'a basin is classified as medium to high. All of the spring water samples and most of the groundwater samples belong to medium salinity hazard as per the salinity hazard classification in the basin. Fourteen groundwater samples fall in the medium salinity hazard

category (C2) while a few of the samples belong to the high salinity hazard category (C3). None of ground- and spring water samples show low salinity contamination (C1). Groundwater that falls in the medium salinity hazard class (C2) can be used in most cases without any special practices for salinity control. However, water samples fall in the high salinity hazard class (C3) may detrimental effects on sensitive crops and adverse effects on many plants. Such areas require careful management practices. As it can be seen only small parts in north of studied area (in the limestone aquifer) have high salinity hazard while the samples from south, east and west of the studied area had medium salinity and are suitable for irrigation. The high salinity hazard samples were found mostly in the limestone aquifer in the northern part of the basin as a result of the dissolution of calcite, dolomite and gypsum, which are presented in the Amran limestone.

Sodium (Alkali) Hazard (SAR): Although sodium contributes directly to the total salinity the main problem with a high sodium concentration is its effect on the physical properties of soil. While a high salt content (high EC) in water leads to formation of saline soil, high sodium content (SAR) leads to development of an alkaline Groundwater Quality Assessment for Different Purposes in Sana'a basin. Irrigation with Na-enriched water results in ion exchange reactions: uptake of Na⁺ and release of Ca²⁺ and Mg²⁺. This causes soil aggregates to disperse, reducing its permeability [14]. The sodium or alkali hazard in the use of water for irrigation is determined by the absolute and relative concentration of cations and is expressed as the sodium adsorption ratio (SAR).

Ions in the equation are expressed in milliequivalent per litre. There is a significant relationship between SAR values of irrigation water and the extent to which sodium is absorbed by the soils. Continued use of water with a high SAR value leads to a breakdown in the physical structure of the soil caused by excessive amounts of colloidal absorbed sodium. This breakdown results in the dispersion of soil clay that causes the soil to become hard and compact when dry and increasingly impervious to water penetration due to dispersion and swelling when wet. Fine-textured soils, those high in clay, are especially subject to this action.

The calculated value of SAR in the study area ranges from 0.27 to 10.44 meq/l in ground waters and from 0.16 to 0.75 meq/l in the spring water samples. The SAR values plotted on the US salinity diagram as alkalinity hazard shows that alkali or sodium hazard for water samples (ground- and spring water samples) in the Sana'a basin

are classified as low (89%), medium (8%) and high (3%). As per the Richard [12] classification based on SAR values (Table 3), most of the samples are excellent category. Thirty-three (out of 37) samples fall in the low sodium hazard category (S1), four groundwater samples belong to the medium sodium hazard category (S2) and one groundwater sample falls in the high sodium hazard category (S1). The source of sodium is most likely natural and could be result of dissolution of the volcanic rocks.

Classification Based on Magnesium Hazard: Calcium and magnesium ions are essential for plant growth but they may associate with soil aggregation and friability. Water contains calcium and magnesium concentration higher than 10 meq/l (200 mg/l) can not be used in agriculture. In the study area the concentrations of calcium and magnesium were found to be below 200 mg/l, only in two of the groundwater samples GW5 and GW-6 exceed the calcium the values 200 mg/l with 326 and 321 mg/l, respectively.

Another indicator can be used to specify the magnesium hazard (MH) is proposed by Szabolcs and Darab (1964) for irrigation water as in the equation 3:

$$\text{MagnesiumHazard (MH)} = \frac{\text{Mg}}{\text{Mg} + \text{Ca}} * 100 \quad (3)$$

If this percentage hazard was less than 50, then the water was safe and suitable for irrigation.

From the calculated value, the magnesium hazard values range between 4.2-37.3% and can be classified as suitable for irrigation use.

Classification Based on Saturation Index (SI): The SI gives information about how much a certain mineral phase (e.g. calcite, Gypsum) has dissolved in the solution relative to the amount it can potentially solve. If the calculated SI= 0, there is equilibrium between the mineral and the solution, while the negative values (SI< 0) indicates an undersaturation and positive values (SI>0) oversaturation [16].

The saturation indices for a total of 37 spring and groundwater samples collected from Sana'a basin were calculated and modeled with the software Aquachem 4.0 for calcite, dolomite, anhydrite and gypsum. The calculated values are presented in the Table 2 and 3.

According to the calculated SI values, the groundwater samples are classified in three categories; most of the samples are classified to be unsaturated in calcite, dolomite, anhydrite and gypsum; tow samples collected from limestone aquifer (GW-5 and GW-6) are

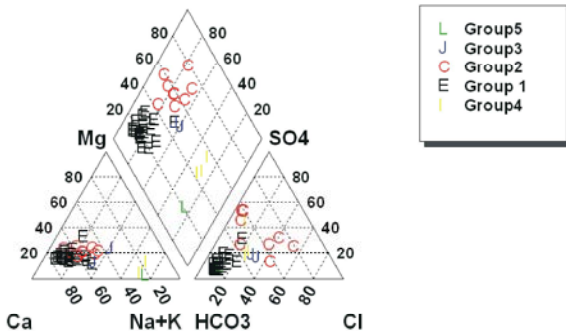


Fig. 6: Piper plots of the ground- and spring water samples

oversaturated in calcite and dolomite with SI-values 0.6 and 0.8, respectively, but under saturated in anhydrite and gypsum; two other samples (GW-3 and GW-11) are in equilibrium with calcite, but under saturated with respect to the other three minerals.

All the spring water samples are classified to be under saturated ($SI < 0$) with the minerals calcite, dolomite, anhydrite and gypsum.

Classification Based on Piper Diagram: The chemical analyses data were plotted in PIPER diagram with the software AquaChem 4.0 to visualize the general chemical characteristics and to classify the ground- and spring water samples in groups of similar geochemical properties.

The Piper diagram in AquaChem plots the major ions as percentages of milli-equivalents in two base triangles. The total cations and the total anions are set equal to 100% and the data points in the two triangles are projected onto an adjacent grid. This plot reveals useful properties and relationships for large sample groups. The main purpose of the Piper diagram is to show clustering of data points to indicate samples that have similar compositions.

In the Piper diagram four major groups of ground- and spring water and a single group can be distinguished. Most samples were classified as earth alkaline waters with prevailing hydrogen bicarbonate (group 1) or sulphate as in group 2 (Figure 6).

Group 1: Water Type Ca-HCO_3 (Low Mineralized): This type of water represents the major water type in the study area and dominates the western part of the Sana'a basin. 12 out of 13 spring water samples and 6 of the groundwater samples. Generally, this water type is characterized by predominant hydrogencarbonate and low electrical conductivities ranging from 230 to 560 $\mu\text{S/cm}$. The low mineralization and the low content in alkalis and earth alkalis are due to the low temperatures of spring and

groundwater, affecting the solubility. In sample GW-14 in the sandstone aquifer an increase in chloride concentration was observed, indicating that this sample is influenced by the infiltration of sewage water. A high concentration in NO_3 was found in this sample. An increase in Mg concentration in samples (GW-10) and (SW-2) in the limestone aquifer is thought to result from the dissolution of limestone from the Amran group.

Group 2: Water of $\text{Ca-Na-Mg-HCO}_3(\text{SO}_4\text{-CL})$: This type of water includes samples GW-3, GW-5, GW-6, GW-9 in the limestone aquifer, GW-1, GW4, GW-7 in the sandstone aquifer and GW-2 and GW-16 in the alluvium aquifer, about a quarter of the total samples. The water is characterized by medium to high electrical conductivities ranging from 680 to 2030 $\mu\text{S/cm}$, an increase of sulphate concentrations compared to group 1 and elevated chloride concentrations accompanied by high concentrations of NO_3 which refers to the infiltration of sewage water around Sana'a city. High concentrations of SO_4 , Mg and HCO_3 in this group are thought to result from the dissolution of calcite, dolomite and gypsum, or combination of these minerals, which are all present in the Amran limestone [7]. This water type occurs commonly in the north-east part of the basin and in the central of Sana'a city.

Group 3: Water of $\text{Ca-Na-HCO}_3(\text{CL})$: This group is represented by three samples, GW-11, GW21 and SW-7. The samples GW-21 and SW-7 plot are of similar background composition. Electrical conductivity is moderate in GW-21 and SW-7 with 450 and 620 $\mu\text{S/cm}$, respectively. The limestone sample GW-11 is characterized by a higher EC value with 1340 $\mu\text{S/cm}$ and an increase in the concentration of SO_4 (125 mg/l), Na (142 mg/l), HCO_3 (466.2 mg/l) and Mg (44 mg/l).

Group 4: Water of $\text{Na-HCO}_3(\text{SO}_4\text{-CL})$: Six samples belong to this water type which is characterized by high Na and low Ca and Mg. This water occurs mainly in the volcanic aquifer in the southern part of the basin (samples GW-18, GW-19, GW-20 and GW-22); however, also sample (GW-8) in the limestone aquifer and (GW-12) in the alluvium aquifer north of Sana'a City belong to this group. Waters with high Na^+ and low Ca^{2+} and Mg^{2+} are often derived either from thermal sources or from groundwaters that are localized in the acidic volcanics. The volcanic and alluvium groundwater samples are characterized by moderate EC ranging between 380 to 520 $\mu\text{S/cm}$ and moderate concentration in SO_4 and HCO_3 (between 41 to

70 and 144.9 to 207.9 mg/l respectively). The limestone sample shows increased EC (1300 μ S/cm) as well as an increase in SO_4 , Ca, HCO_3 and Mg concentrations with 330, 44.6, 378 and 26.5 mg/l, respectively. Chloride was found in all samples of this group in moderate concentrations ranging between 42 to 75 mg/l.

Group 5 (single sample): water of Na-K- HCO_3 : The sample GW-23 comes from the volcanic aquifer in the south-west part of the basin. It was collected from a deep well with total depth of 450 m; the depth to the water table is 255 m. According to the owner, the well was recently deepened. The water is used for irrigation purposes. This sample can be classified as alkaline water which is dominated by Na, K and HCO_3 . The high concentration of alkaline minerals is natural and results from the dissolution of these minerals in the volcanic host rocks.

Water Quality In The Sana'a Basin: To ascertain the suitability of ground- and spring water of the Sana'a basin for drinking as well as irrigation purpose, physicochemical parameters of the water samples taken from the Sana'a basin are compared with the guideline recommended by WHO and NWRA drinking water standard. The standards of NWRA generally apply to two limits, the Optimal Limit (OL) and Maximum Permissible Limit (MPL). Because there are no guidelines for Bromate (Br) recommended by NWRA and WHO, the concentration was compared with Europe Unions standards (EU-standard).

Generally, it can be said that the ground- and spring water in the Sana'a basin is considered to be good for drinking purposes. Some of ground- and spring water samples exceeded the concentrations of HCO_3 , SO_4 and NO_3 in the WHO-standard, but do not exceeded the standard values recommended by NWRA in 2000.

The calculated values of the total hardness (Ca^{+2} and Mg^{+2} hardness) exceeded the WHO and NWRA recommendations in four out of 24 groundwater samples, three of them collected from the limestone aquifer and one from sandstone aquifer.

A classification of water based on SAR was carried out to ascertain the suitability of water for irrigation purposes. The calculated TDS and SAR indicate that the water of the Sana'a basin is suitable for irrigation purposes.

Although the water quality in the Sana'a basin is still good, but it is contaminated mostly by the infiltration of sewage water and salinization due to high ground water abstraction (high EC values were found).

The nitrate and chloride reach the groundwater in deep wells in the different aquifer systems. The highest concentration of NO_3 and Cl at the maximum total well depth 450 m was found to be 33 and 190 mg/l, respectively. The source of the both anions in the groundwater is the infiltration of the wastewater through the cesspits [7, 8].

CONCLUSION

Elevated chloride concentrations accompanied by high concentrations of NO_3 in groundwater can be observed in the central and northern part of Sana'a, particularly in the alluvium and sandstone aquifer, resulting from the infiltration of wastewater.

High EC values are found in the samples collected from the limestone aquifer in the north-eastern part of the basin due to dissolution of calcite, dolomite and gypsum in the Amran limestone.

The groundwater quality in the Sana'a basin is considered to be suitable for irrigation and drinking purposes but it is threaded by the infiltration of wastewater.

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