REGIONAL STABLE ISOTOPE AND HYDROCHEMISTRY INVESTIGATION IN YEMEN AND IN THE REPRESENTATIVE AREA ‘’SANA’A BASIN’’

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SUMMARY

Within this physico-chemical and isotopes study, major ions, temperature, electrical conductivity (EC), pH and environmental stable isotope deuterium (^{2}H) and oxygen-18 (^{18}O) data were used to characterize the ground- and spring water of the complex multi aquifers system of the Sana’a basin in the central Yemen highlands. A total of 24 groundwater samples from deep wells (boreholes and dug) and 13 springs were collected from the Sana’a basin between September and October 2009. Major anions (Cl^-, HCO_3^-, NO_3^- SO_4^{2-} and Br^-) and major cations (Ca^{2+}, Mg^{2+}, Na^+ and K^+) were measured. Additionally, the concentration of selected heavy metals (As, Pb, Cu, Ni, Co, Cd, Fe, Mn, Al and Zn) in groundwater samples was determined. The physical parameters, which include water temperature, electrical conductivity and pH, and determination of hydrogen-carbonate, were measured on site.

The ground- and spring water samples collected from the Sana’a basin were classified in groups according to their major ions (anions and cations) contents. The classical use of the groundwater in hydrology is to produce information concerning the water quality. The classification was based on several hydrochemical methods, such as Ca^{+2} and Mg^{+2} hardness, Sodium Absorption Ration (SAR),Magnesium hazard, saturation indices (SI) and Piper and Schoeller diagram. To ensure the suitability of ground- and spring water in Sana’a basin for drinking purposes, the hydrochemical parameters were compared with the guidelines recommended by World Health Organization (WHO) and National Water Resources Authority (NWRA) standards. In order to check the suitability of ground- and spring water for irrigation purposes the data were plotted on the U.S. SALINITY LABORATORY (U.S.S.L) diagram.

The physicochemical investigation of the ground- and spring water samples collected from Sana’a basin reflects the following results:

The hydrochemical characteristic of ground- and spring water in the Sana’a basin differs from one aquifer to another according to the lithology of the aquifer. Based on Piper- and Schoeller-diagram, five hydrochemical water facies (groups) were recognized as following:

Group 1: Low mineralized water-type of Ca-HCO3 in the western parts of the basin

Group 2: Water-type of Ca-Na-Mg-HCO_3 (SO_4 -Cl) occurs in the north-east part of the basin and central of the city of Sana’a.

Group 3: Water-type of Ca-Na-HCO_3 (Cl)- characterized by moderate to high electrical conductivities.

Group 4: Water-type of Na-HCO_3 (SO_4 -Cl) is mainly present in the volcanic aquifer in the southern part.

Group 5 (single sample): Water-type of Na-K-HCO_3 is characterized by low EC (280µS/cm) and high concentration of alkaline minerals.

Based on Ca^{+2} and Mg^{+2}hardness, the samples were classified into four categories; **very hard** with values range from 181 to 1108mg/l, **hard** (139-179mg/l)**, medium hard** (112-120mg/l) **and soft water** (8-58mg/l).

The calculated saturation shows that the groundwater water of Sana'a is under-saturated (SI<0) with respect to the minerals calcite, dolomite, anhydrite and gypsum.

Generally, the measured EC values, the calculated SAR and Magnesium hazard values indicate that the water in Sana'a basin is suitable for irrigation purposes. The calculated SAR values fall in the 'excellent' category. Based on USSL diagram, most of the samples fall in the categories S1 and C2-C3 indicating a low to medium sodium hazard and medium to high salinity hazard.

The final dataset of the stable isotopes oxygen-18 and D in 248 rainwater samples collected from different geographic regions in Yemen derives two regression lines considered as local meteoric water lines. One line constructed for the highland region with slope **7.1** (n=127) differs slightly from the global slope 8.0 and named as **Yemen Highland's meteoric water line (YHMWL)** defined by the equation:

$$\delta D = 7.1 * \delta^{18}O + 8.2‰$$

and one other derived for the coastal regions named **Coastal meteoric water line (Coastal MWL)** for Yemen with slope to be 4.9 (n=88) which typical for evaporated water and defined by the equation:

$$\delta D = 4.9 * \delta^{18}O + 7.2‰$$

For Sana'a region a regression line was derived with slope 7.4 which plots between 7.1 given for YHMWL and the global slope of 8.0. The regression line, named **Sana'a meteoric water line (SMWL)**, defined by the equation:

$$\boldsymbol{\delta^{2}H = 7.4*\delta 18O + 8.6}$$

The most important factors affecting the isotopic composition in Yemen's rainwater are the altitude, temperature, rainfall amount and the humidity. The rainfall events falling on coastal plain are characterized by their content to the heavier isotope composition $\delta^{18}O$ and δD. The slope of the line 4.9 indicates that these samples are strongly affected by evaporation due to the higher temperature in this region. In contrast, the rainwater in Yemen highland is depleted in the heavier isotopes composition and the samples are little affected by the evaporation due to the low temperature associated with the increase in the altitude and rainfall amount.

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III LIST OF ABBREVIATIONS

°C	degree centigrade (Celsius scale)
‰	per thousand
Alu.	alluvium
AREA	Agricultural Research& Extension Authority, Yemen
AWI	Alfred-Wegener Institute , Potsdam, Germany
D	^{2}H or Deuterium
EC	electrical conductivity
FUB	Freie Universitaet Berlin, German
GMWL	Global Meteoric Water Line
GNIP	Global Network of Isotopes in Precipitation
GW	Groundwater
HWC	High Water Council
IAEA	International Atomic Energy Agency
IAP	Ion Activity Product
ITCZ	Intertropical Convergence Zone
L.S	limestone
LMWL	Local Meteoric Water Line
m.a.s.l.	meters above sea level
m.b.g.l	meter below ground level
m.b.s.l	meters below surface level
MAF	Ministry of Agriculture and Fisheries, Yemen
MCM	Million Cubic Meter
MH	Magnesium Hazard
MPL	Maximum Permissible Limit
NWR	National Water Resources Authority
NWSA	National Water Sources Authority
OL	Optimal Limit
RSCZ	Red Sea Convergence Zone
RW	Rainwater
SAR	Sodium Absorption Ratio
SAWAS	Sources for Sana'a Water Supply
SI	Saturation Index
SMWL	Sana'a Meteoric Water Line

S.S	Sandstone
SW	Spring water
SWSLC	Sana’a Water and Sanitation Local Corporation
TDA	Tihama Development Authority
TDS	Total Dissolved Solids
TH	total hardness
U.S.S.L	United States Salinity Laboratory
V.	Volcanic
VSMOW	Vienna Standard Mean Ocean Water
WEC	Water and Environment Centre
WHO	World Health Organization
YHMWL	Yemen Highland’s Meteoric Water Line
YTS	Yemen Traps Series

1 Introduction

1.1 Introduction and objectives

The Sana'a basin is one of the most important morphological basins located in the central Yemeni highlands at an elevation of about 2200 meter above sea level (m.a.s.l). It covers an area of some 3,200 km² and is populated by 1.8 million. The 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, WEC, 2006), uncontrolled immigration to this area and the expansion of agricultural and industrial 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 ranges between 4 and 5 m/year (WEC, 2001). 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 (observed in many cases), a degradation of the water quality due to infiltration of 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 groundwater in the agricultural area could be contaminated by the increased and uncontrolled application of fertilizers and pesticides.

In a rather recent evaluation study of water resources in Yemen, FOPPEN (2002) assumed that the Sana'a basin would enter a phase of water deficit in the near future. FOPPEN 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.

The strategic importance of this basin motivated this new evaluation and assessment of water resources in the Sana'a basin. The present study consists of two parts: **hydrochemical** investigation within Sana'a basin and **environmental stable isotope** studies in different regions in Yemen including Sana'a Basin. Using the two parts of the investigations, the following objectives were achieved:

Hyrochemical investigations

In this part of the study the chemical composition (major cation and anion) and the most important physical parameters (pH, Temperature and EC) of the ground- and spring water samples from Sana'a basin were determined. Then 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)**, Sodium Absorption Ration (**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 various purposes, e.g. the water hardness is an important parameter for the assessment of water quality for domestic purposes. The water hardness is one of the most common problems of the water quality (WHO, 2004). For further evaluation of the water quality for domestic purposes the guideline-values recommended by the WHO and the NWRA were used.

About 80% of water in Sana'a basin is used for irrigation purposes, so the evaluation of the water quality for irrigation is an important goal of this work. For this evaluation, the **SAR** and **salinity hazard** diagram provided by United State Salinity Laboratory (USSL) was used.

The relationships between pH and HCO_3 and between the electrical conductivity (EC) and the major ions were illustrated in order to obtain how these parameters affect each other in the different aquifer systems.

This part contains also a comparison between the data obtained from this study and data obtained from studies carried out by FOPPEN (2002), SHAMSAN (2004 and 2008) and by FORSTER (2003). The main objective of the comparison is to get information about the change in the water properties in Sana'a basin through the infiltration of sewerage water, particularly below the urban area, and rapid increasing in groundwater abstraction in the last time (2002 to 2009).

Stable isotopes investigation

The aim of the present study is to investigate the stable isotope ($\delta^{18}O$ and δD) composition in groundwater, rainfall, and spring water samples in the Sana’a basin. The stable isotope oxygen and hydrogen data of ground- and spring water samples are used to investigate the recharge mechanism within the Sana'a basin and the stable isotope data of rainwater samples collected from Sana'a basin and other regions in Yemen which used to define the LMWL. Information about the stable hydrogen and oxygen isotope ratios of local precipitation allow to identify recharge areas in the basin and processes related to surface- and groundwater interaction as well as geochemical and hydrologic problems. The results of this work provide some insights into the dynamics of groundwater recharge. Additionally, the establishment of a LMWL for Yemen and Sana'a basin provides a baseline for comparison in future stable isotope studies for this region.

Because of the gaps/lack on the basic information and data which are necessary to carry out such investigations, e.g. isotopic composition of Yemen rainwater and climatic data, particularly rainfall data, this part consider to be more difficult. For the Republic of Yemen few regional or local studies of the signature of the stable isotopes Deuterium and Oxygen-18 in rain water and groundwater exist. In some restricted areas like the western coastal region and small parts of Sana'a basin are isotope Data from surface and shallow groundwater are only available (ABULOHOM, 2002). These isotope data were used for comparison purpose.

Comparisons between the measured $\delta\ ^{18}O$ and δ D values and the other parameters, e.g. the elevation and the air temperature, controlling the ration of the δ-values in the water were made in order to determine the most important parameters affecting the isotopes composition in Yemen's rainwater.

1.2 Regional setting and topography

Yemen, with a total area of about 527.970 km^2, is located in the Middle East at the south-south-western edge of the Arabian Peninsula between 12^0 and 19^0 north of the Equator and 42^0 and 55^0 east of Greenwich. The country is bordered by Saudi Arabia in the north, Oman in the east, the Arabian Sea and the Gulf of Aden in the south, and the Red Sea in the west.

The topography of Yemen varies widely. The country's mountainous interior is surrounded by narrow coastal plains to the west, south, and east and by upland desert to the north along the border with Saudi Arabia. The country can be divided according to altitude and geomorphology into five main regions (NWRA, 1995); **the coastal plains, the Yemen mountain massif, the eastern plateau region, the Yemen Island and the desert** (Fig. 1.1).

The Sana’a basin is one of the most important highland groundwater basins in Yemen (Fig. 1.1). The basin is located in the central Yemen highlands at an elevation of about 2200 m.a.s.l. between 15° 21' N and 44° 12' E covering an area of about 3,200 km^2. It forms the upper part of the catchment area of the Wadi al Kharid and comprises the sub-catchment of the Wadi al Jawf, divided into 22 sub-basins, (WEC, 2001) (Fig. 1.2).

The basin consists of two parts, the 'inner' and the 'outer' part. The inner part is the Sana’a plain where the Sana’a City is located. The outer part is the mountains area surrounding the plain to the west, south and east rising to more than 3.000 m.a.s.l. It reaches the highest point of the Arabian Peninsula with an elevation of about 3760 m.a.s.l in the southwestern part of the basin named Jabal An Nabi Shuayb. The Capital city Sana’a and the seven districts of Sana’a province are situated in the Sana’a basin.

1.3 Population

According to the final results of the general census for the year 2004, the population of Yemen is estimated to be about 19.7 million. According to the world factbook, the total population in 2010 was estimated to be 23.5 million with an annual growth rate of 2.7%. About 74.4 % of the population lives in rural areas.

The population of Sana’a city has grown rapidly in the last 30 years. The average annual population growth was estimated to be around 6.1% in 1997. In 1970 the City had 80,000 inhabitants, a number that rose to 1,935.451 in 2005, about 18.6 % from the total population of the country (NWRA, 1995).

The population density of Sana’a is very high (1665 inhabitants/km^2). According to the results of a population forecast carried out by DAR AL-HANDASH in 2000, the population of Sana’a City for 2020, assuming a moderate growth rate, is going to be 3.4 million inhabitants (JICA, 2007). About 75 % of the population of Sana'a depends wholly on agricultural activity, which mainly comprises Qat and fruit cultivation and livestock (FOSTER, 2003).

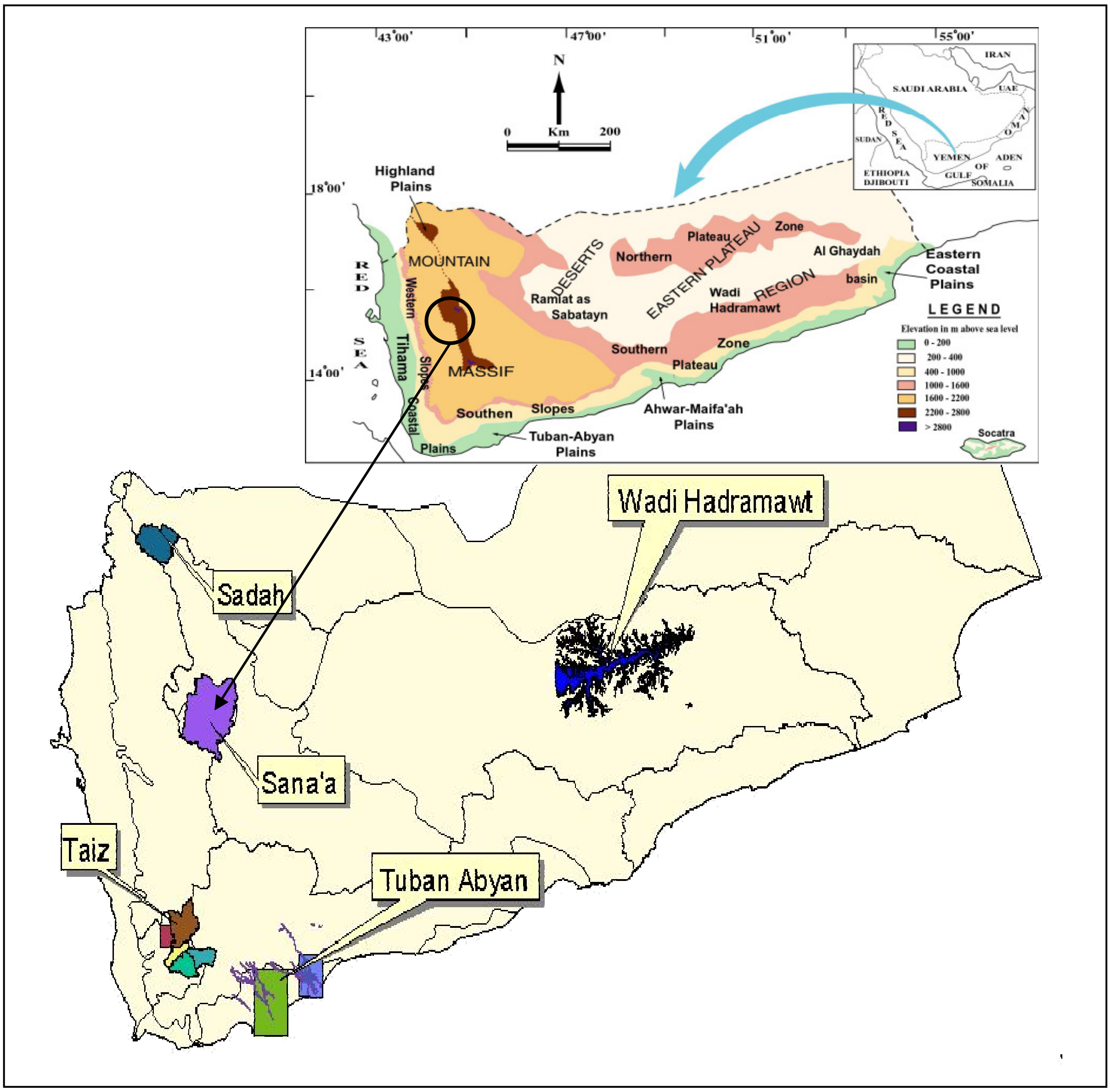

Figure1.1: Geographical regions and Yemen highlands Basins (adapted after NWRA, 2003)

1.4 Climate and meteorology

Topographical variations of Yemen give rise to a wide range of climatic conditions. In general, the climate of Yemen could be classified as semi-arid to arid.

The climate data provided by the Agricultural Research& Extension Authority (AREA, 2005) for the Sana’a basin include temperature, humidity, rainfall amount and evapotranspiration in the period from 1983 to 2002. The data are shown in figure 1.3 and summarized in table 1.1.

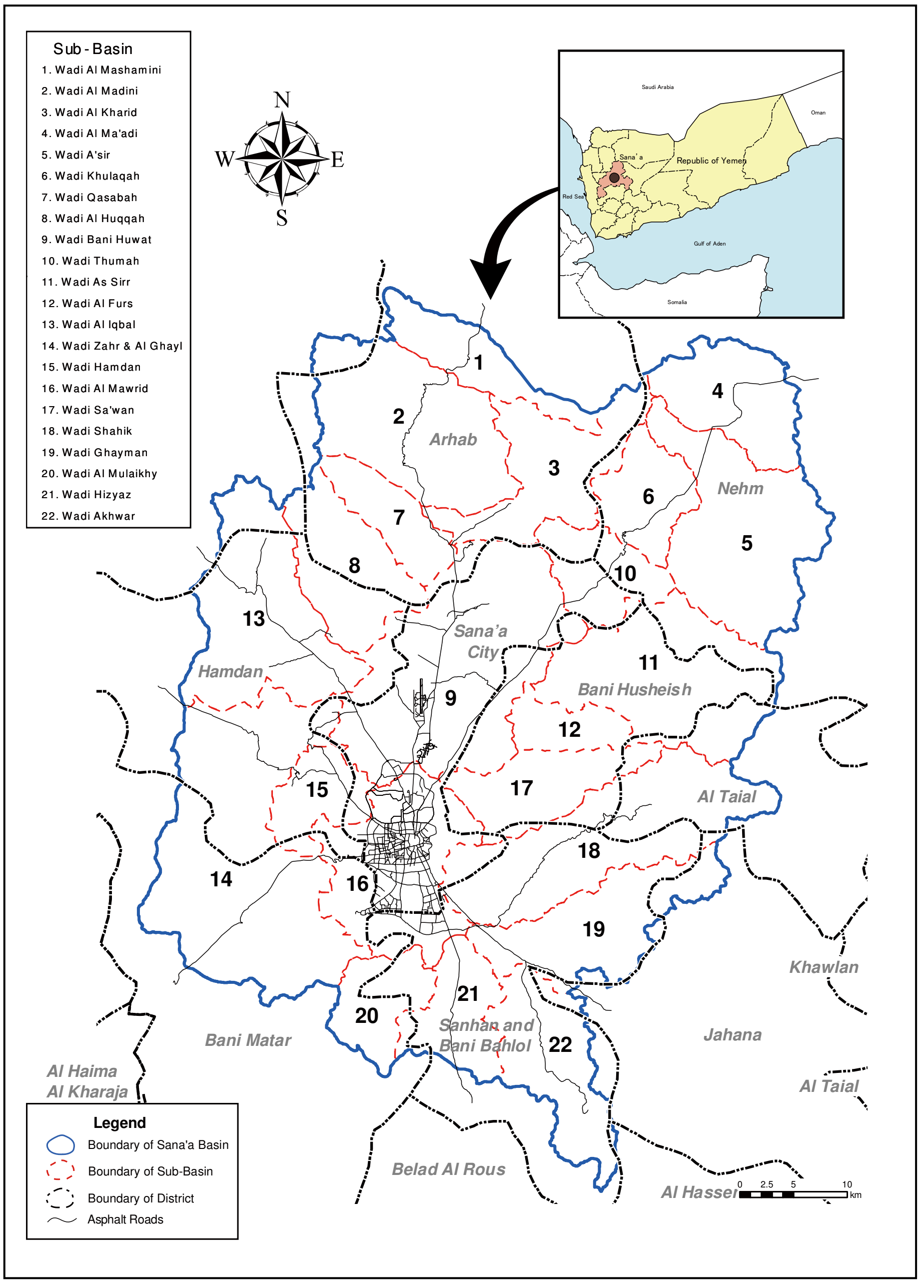

Figure 1.2: Location of the study area (from JICA, 2007)

1.4.1 Temperature and humidity

Temperatures are generally very high in Yemen (particularly in the coastal regions). The eastern and southern coastal plains are characterized by high temperature that reaches 42 °C and drops down to 25 °C. Temperature in Yemen drops down gradually toward higher elevations with an average gradient of 0.6 °C per 100 m differences in elevation to reach 33 °C as a maximum and 20 °C as a minimum. In winter drops the temperature in Yemen highland to be closer to 0 °C. The humidity is very high on the coastal plains (up to more than

80%) whereas it goes down toward the internal parts where it reaches its minimum rate in the desert areas to be around 15%.

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.

Table 1.1: Monthly average climate data in Sana’a from 1983- 2002 (after AREA, 2005)

Month	Max.temp. (°C)	Min. temp. (°C)	Rainfall (mm)	Evapotranspiration (mm)	Humidity (%)
1	24,7	4,4	1,9	88	46
2	26,3	6,8	3,9	104	46
3	27,4	9,5	24,6	113,4	50
4	27,7	10,9	38,6	118,3	52
5	29,4	12,6	15,5	146,1	42
6	31	13,8	8,7	169,5	35
7	30,9	15	26	157,6	43
8	30,3	14,6	38,2	144,9	49
9	29	12,1	3,2	149,4	36
10	25,9	7,8	2,9	120,2	37
11	24,5	4,8	1,3	91,8	42
12	24,3	3,9	2,4	81,3	46

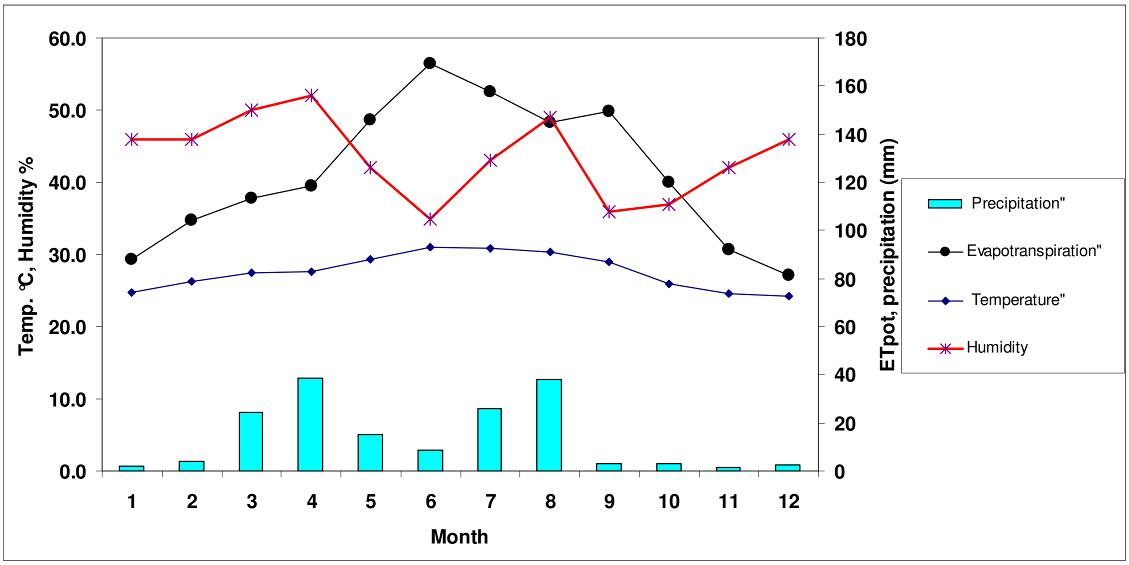

Figure 1.3: Monthly average climate data of Sana'a basin from 1983 to 2002 (Data: AREA, 2005)

1.4.2 Precipitation and runoff

The rainfall of Yemen depends on two main mechanisms, the Red Sea Convergence Zone (RSCZ) and the monsoonal Intertropical Convergence Zone (ITCZ). The RSCZ, whose influence is most noticeable in the west of the country, is active from March to May and to some extent in the autumn, while the ITCZ reaches Yemen in July-September, moving north and then south again so that its influence lasts longer in the south. Both the RSCZ and the ITCZ produce precipitation in convective storms of high intensity and limited duration and extent, but the ITCZ storms have a larger areal extent than those of the RSCZ (Farquharson et al, 1996). The averages annual rainfall is 130 millimeters in the western coastal plain (Tihamah) and 127 millimeters in the southern coastal plain (Aden). The highest mountainous areas of southern Yemen receive from 520 to 760 millimeters of rain a year (Fig. 1.4). It is common that the desert regions in the northern and eastern sections of the country receive no rain for five years or more. The Wadi Hadhramaut in the eastern part of Yemen is arid and hot, and the humidity ranges from 35 percent in June to 64 % in January (country profile, 2006).

The measurement data obtained from AREA indicate there are two rainy seasons in the Sana'a basin. The first rainy period is March-May and the second begins in July and lasts until August. The two wet periods are separated by a distinctly dry period in June. The months of September through February are generally dry, although occasional thunderstorms may bring some rain during these months.

The annual rainfall which is recorded at four rain gauges (Fig.1.5) by the 'Water and Environment Center' of Sana'a University (WEC) for 2007 and 2008 ranges from 117,6 mm at station ***8987*** northern Sana'a city to 281,8 mm at station ***8986*** in the south in 2007, with monthly average ranges from 9,8 mm to 24 mm at the same stations and years as shown in table 1.2 and presented in figure 1.6.

The total runoff in the Sana'a basin was estimated to be about 40.9 MCM/year with the assumptions of 230 mm of annual rainfall, 3,240 km^2 of the area of the Sana'a basin (NWRA, 2007)

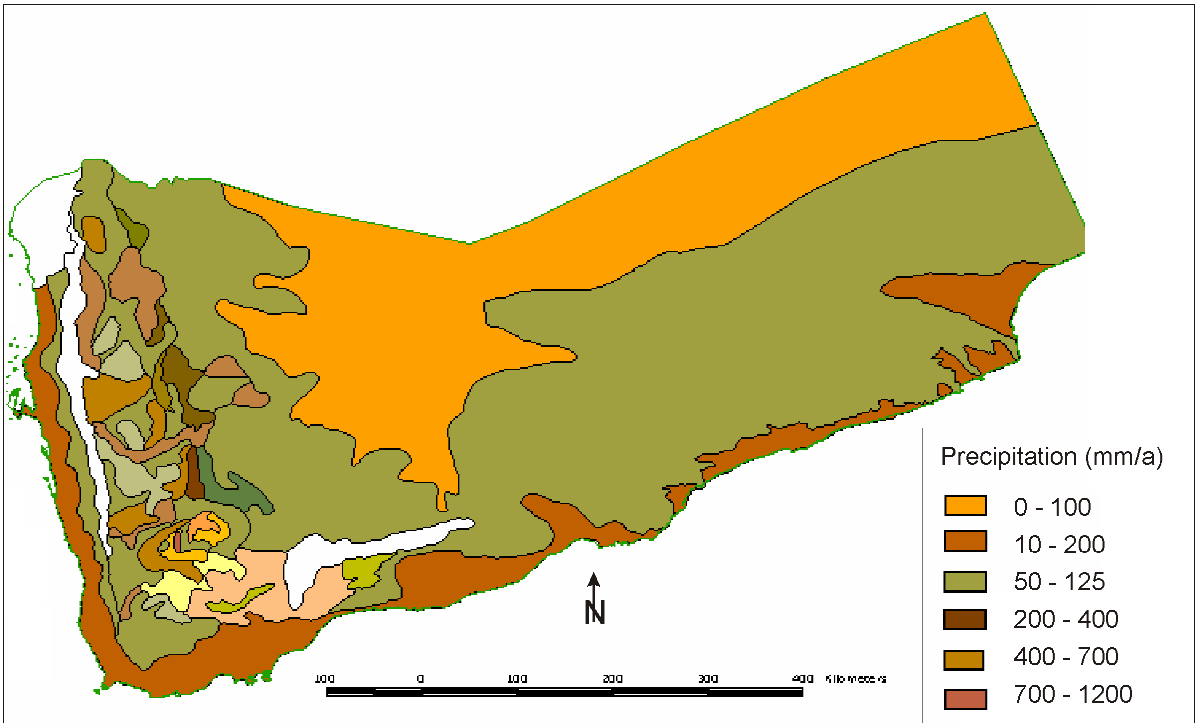

Figure 1.4: Annual rainfall distribution in Yemen (modified from: AREA, 1999)

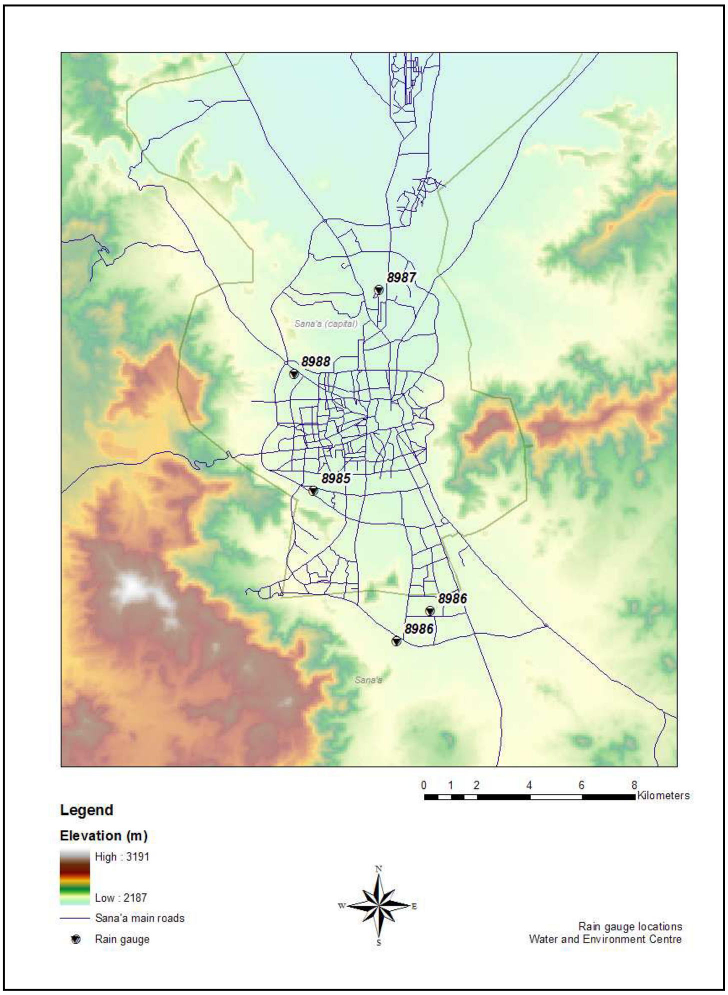

Figure 1.5: Location of rain gauges in Sana'a city (from WEC, June 2009)

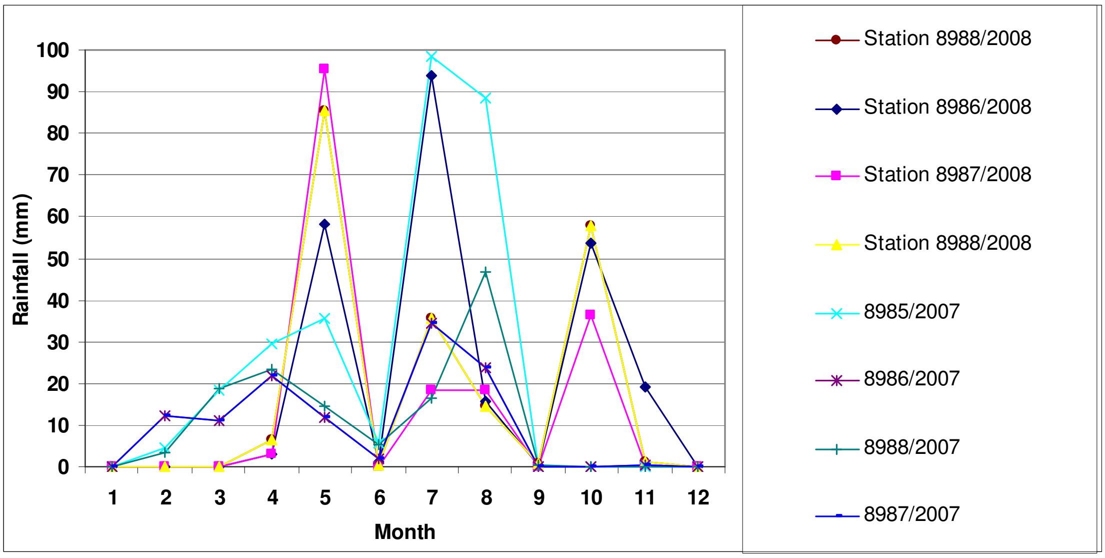

Figure 1.6: Rainfall in Sana'a basin in 2007 and 2008 (after WEC, June 2009)

Table 1.2: Rainfall (in mm) in Sana'a basin in 2007 and 2008 (after WEC, June 2009)

Station	**8985**		**8986**		**8987**		**8988**	
Year **Month**	**2007**	**2008**	**2007**	**2008**	**2007**	**2008**	**2007**	**2008**
1	0	0.2	0,0	0	0	0	0	0
2	4,6	0	9,8	0	12,4	0	3,60	0
3	18,2	0	19,4	0	11,2	0	18,60	0.6
4	29,4	11,8	25,2	3	21,8	3,2	23,20	6,4
5	35,6	85,2	58,6	58,2	11,8	95,4	14,60	85,4
6	5,8	1,2	14,6	1,2	2	0	5,20	0,2
7	98,4	20	93,0	93,8	34,4	18,2	16,40	35,6
8	88,6	13,4	61,2	15,6	23,80	18,4	46,8	14,4
9	0	3,4	0,0	0,4	0	0.6	0,2	0,8
10	0	31,6	0,0	53,6	0	36,4	0	57,8
11	0	4,6	0,0	19,2	0,2	0,4	0	1,2
12	0	0	0,0	0	0	0	0	0
Total/Year	280,6	*171,4*	*281,8*	*245*	*117,6*	*172,6*	*125*	*202,4*
Max	98,4	85,2	93	93,8	34,4	95,4	46,8	85,4
Min	0	0	0	0	0	0	0	0
Average	23,4	15,6	23,5	20,4	9,8	15,6	10,7	18,3

1.4.3 Evaporation and evapotranspiration

The total annual potential evapotranspiration in Yemen were estimated to be 1579 mm in the central part of the country (Dhamar) and 3427 mm in Al-Jawf in the north-eastern part (NWRA, 1995).

In the Sana'a basin, the annual potential evaporation for the year 1990 was estimated to be about 2000 mm using the Penman method and the annual potential evapotranspiration by 2475 mm/year (JICA, 2007).

SAWAS (1996) estimated the annual potential evapotranspiration in Sana'a basin to be 2475 mm, based on a meteorological statistics with a maximum in June with average of 9.4 mm/day and a minimum in February with average 4.8 mm/day (SAWAS, 1996). Between 1983 and 2002 the average annual evapotranspiration was estimated to be about 1485 mm/year with a maximum monthly average of 170 mm in June and minimum monthly average of about 81 mm in December (AREA, 2005).

2 The Sana'a basin

2.1 Geology and Hydrogeology

The general geology of the Sana'a basin is shown in figure 2.1. North-South and West-East cross sections are presented in figures 2.2 and 2.3, respectively.

The geology of Sana'a basin complex and comprises four geological formations which form the main aquifers systems of the basin (figure 2.1). The Sana'a basin consists of two parts; the plain with an elevation up to 2200 m which is surrounded to the west, south and east by mountains rising to 3000bm. The plain is situated on thick succession of **quaternary alluvium** which comprises silts, clays, sands, gravels and volcanic detritus. The surrounding mountain comprises **volcanic rocks of Tertiary to Quaternary** age, and the **Cretaceous Tawilah sandstone** which outcrops in the north-west and north-east of Sana'a. In the north-east of the basin outcrops the **Jurassic limestone** of Amran group which is considered to be the oldest sedimentary formation in the region of Sana'a (SAWAS, 1996).

The important groundwater aquifers in Sana'a Basin are described in the following:

2.1.1 Amran limestone

The underlying Amran group consists mainly of fossiliferous carbonate (shallow-water limestone and marls) of upper Jurassic with total thickness between 410 and 520 m (Al-THOUR, 1997) but exceeding 800 m in the Wadi Attaf (RYBAKOV, 1999). The rocks of Amran limestone can be found in the vicinity of Taiz in the south and near to Bajel City in the northwest of Yemen. In the northern and central part of Yemen the Amran group covers disconformably the Sandstone of the Kohlan Formation. The Tawilah Formation lie unconformably Sana'a basin on the basement rocks as in Sada'h basin in north Yemen (J. DOWGIALLO, 1986).

In Sana'a basin, Amran limestone outcrops in the northern part of the basin, covering about 15% of the basin area (Fig. 2.4) and consisting mainly of limestone and gypsum and locally with intercalated shales. It occurs at depth range between 350 m in northern and 900 m in southern beneath the Sana'a plain (WEC, 2004).

The Amran Limestone is generally considered to be a poor and semi-confined aquifer. Well yields range from 3 to 6 l/s (RYBAKOV, 2004). Groundwater can be obtained from zones of secondary permeability. Transmissivities were measured and recorded values range from 75 to 860 m^2/d, and storage coefficients ranging from $5x10^{-4}$ to 0.002 (TIBBITS & AUBEL, 1980). The depths to water levels were measured in 7 wells in the northeast of the basin range between 39 m and 342 m. The groundwater quality in the limestone is reported to be generally good (RYBAKOV, 2004).

2.1.2 Cretaceous sandstone (Tawilah sandstone formation)

The Tawilah group unconformably overlies the Amran group and consists mainly of fluvial to continental clastics - predominantly sandstones interbedded with siltstone, marl and shale. The rocks of Tawilah group outcrop cover a large part of northern and central Yemen, north to Sana'a City, south-west of Taiz City, along the road between Rada'a-Al-Bayda and around the Qataba'a area (AL-KHERBASH and Al-ANBAAWY, 1996). The exposed thickness of this group varies from 150 to 400 m and reaches a maximum to the south of Sana'a.

Hydrogeologically, the Tawilah sandstone formation forms the most important aquifer in the Sana'a basin and covers about 15 % in the northern part of the basin. The formation is composed of sandstone with intercalated conglomerates, siltstones, and clays. The thickness of the sandstone in the Sana'a plain is variable (SAWAS, 1996). In the northern area it is about l00m thick, in the central and the southern areas the thickness increases to about 400 m. Cross bedding can be observed in this formation.

The aquifer is partly confined and partly unconfined. In the south, this formation is dipping under a complex of tertiary volcanic rocks and alluvial sediments (Fig. 2.2 and 2.3). There, it is hydraulically connected with the other formations. It has low regional permeability (less than 0.05m/d) but this has been enhanced locally by fracturing to give values of about l m/d or more (WEC, 2004). Figure 2.6 shows the fracturing in the Tawilah sandstone.

Transmissivity values are very wide and range from 50-100 m^2/d in undisturbed zones to 400-2000m^2/d in fault zones. The hydraulic conductivity varies from 0.5 to 3m/d and 0.01 to 0.22 specific yields (FOPPEN, 2002). Groundwater is so heavily extracted from this aquifer that many wells have gone dry and the relative importance of this resource has decreased.

Depths to groundwater levels in the main area of extraction were recorded in the early 1970s around 30 to 40 m, but a decline in the groundwater level since the early 1970s range from 1.5 to 4 m/yr was recorded (SAWAS, 1996). At the present time the depth to the water levels range from 200-400 meter below ground level (m.b.g.l) (WEC, 2004).

2.1.3 Tertiary volcanic

This volcanic unit is part of the Yemen Traps Series (YTS). They are developed in the west of Yemen and form the major part of the western highland between Sana'a and Taiz covering an area of about 45,000 km^2. The thickness ranges between a few hundred metres and 3000 m. The Tertiary volcanics consists of basalt-rhyolite lavas, ignimbrites and volcanic clastic rocks. The YTS is associated with alkaline or peralkaline granites and numerous basic and acidic dykes (AL-KHERBASH and Al-ANBAAWY, 1996).

In the Sana'a basin the Tertiary volcanic rocks cover around 35% of the basin, comprises rhyolites, Andesites, Trachyts and basalts interbeded with fluviatile and lacustrine sands, clays and shales. They outcrop in the plateau surrounding the Sana'a plain but were also overlained by the Sana'a plain alluvial and quaternary basalts. The basalt has a thickness of some 800 m in southern Sana'a, but thins out north of Sana'a. The mixed basalt and rhyolite flows at the top of the sequence are more highly fractured (Fig. 2.7) 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 (SAWAS, 1996).

Tertiary volcanic is considered as poor, unconfined aquifer. The transmissivity was obtained from pumping test carried out by SAWAS in 1996 and recorded values ranging from less than 1 m^2/d to 200 m^2/d. The hydraulic conductivity ranges from 0.5 to 2 m/d. The specific yield was estimated by 0.01 (SAWAS, 1996).

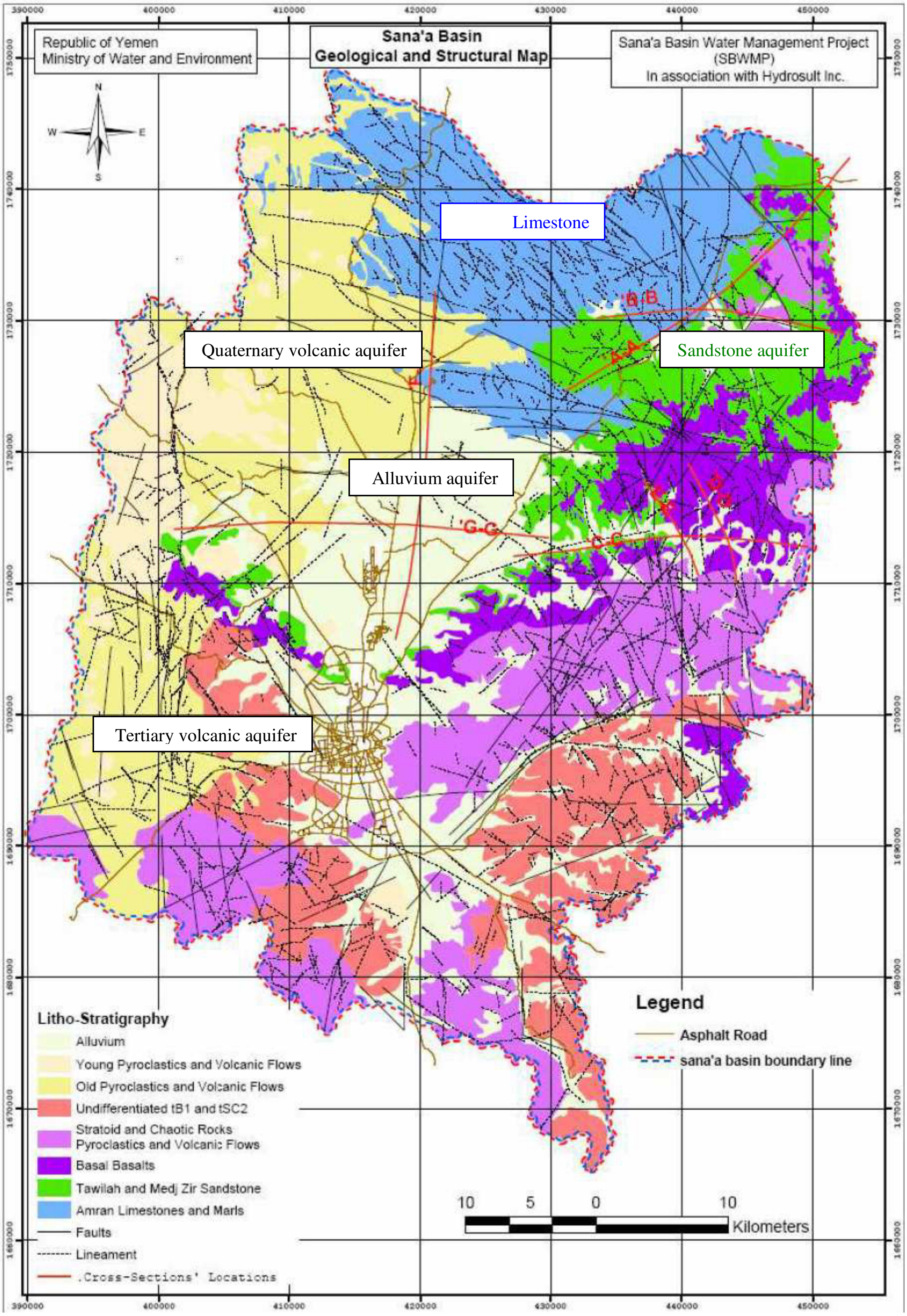

Figure 2.1: Geological map of Sana'a basin (after HYDROSULT, 2009)

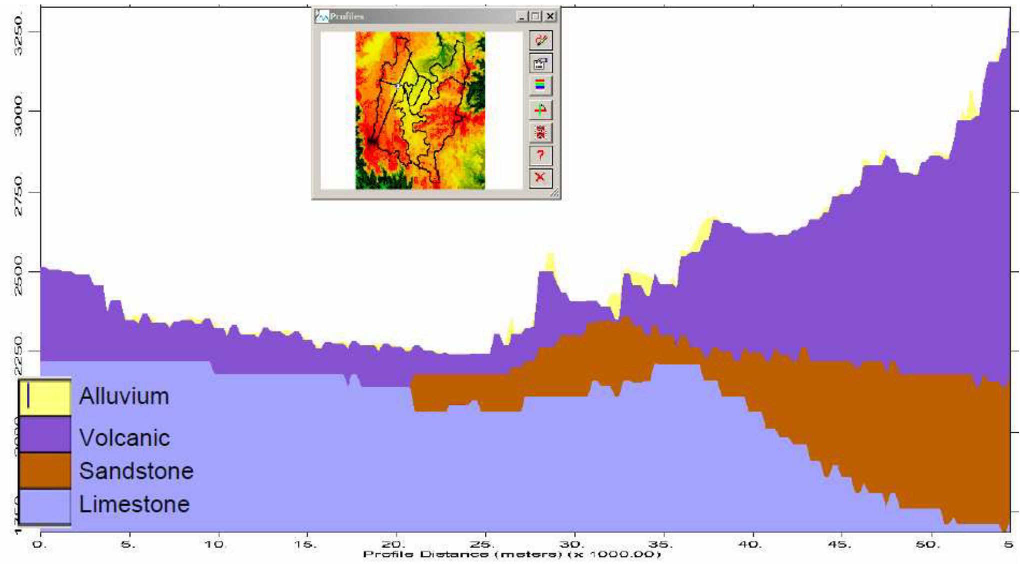

Figure 2.2: North-South geological cross-section of the Sana'a basin (from HYDROSULT, 2009).

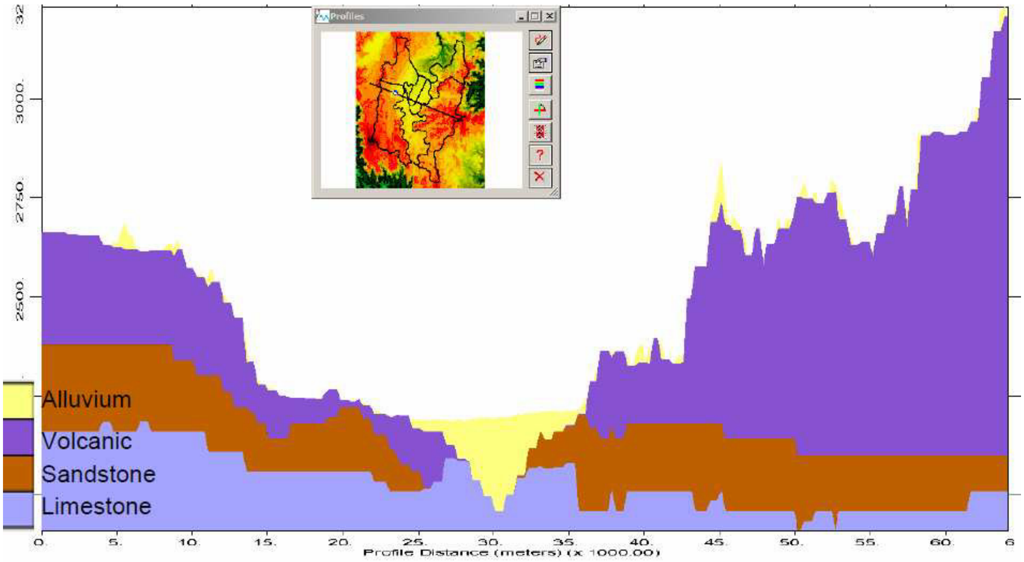

Figure2.3: West-East geological cross-section of the Sana'a basin (from HYDROSULT, 2009)

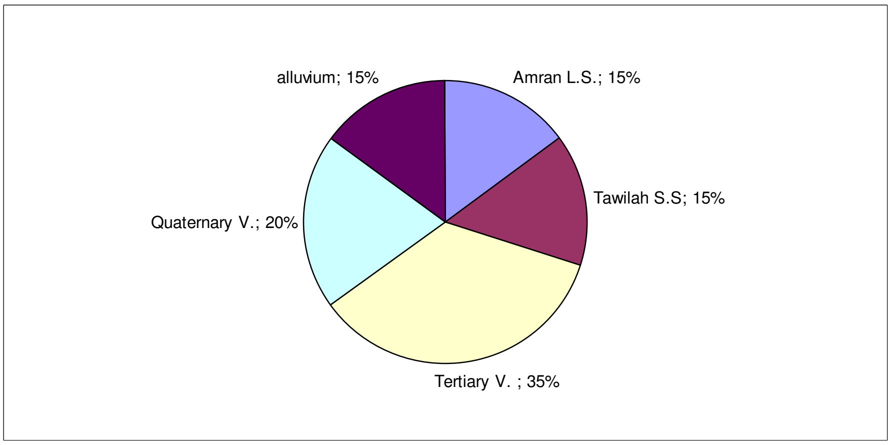

Figure 2.4: Distribution of the aquifers in Sana'a basin

2.1.4 Quaternary volcanic (basalt cones)

Quaternary volcanic activity is concentrated in three regions in the north of Yemen: Sana’a, Marib and Dharma, with the areas covering a combined area of about 17,000 km^2. They are covered by numerous volcanic cones or lava streams. The volcanics are mostly alkali olivine basalts (AL-KHERBASH and Al-ANBAAWY, 1996).

In the north west of Sana’a basin the Quaternary volcanics form a plateau of extensive basalt (has coning forms) interlayered with tuffs and alluvial sediments (HYDROSULT, 2009). The basalt layers are highly permeable due to fracturing and to the presence of clastic deposits in between flows. The formation is saturated with groundwater which provides an unconfined aquifer confined aquifer. The total thickness of the formation is unknown.

In this study, water levels were measured in a total of 7 wells ranging from 84 to 255 m.b.g.l. The wells are generally limited to the southern edge of the outcrop where water levels are less than 100 m deep (SAWAS, 1996).

The transmissivity value was estimated to be 51 m^2/d (SAWAS, 1996). Table 2.1 presents the main hydraulic parameters of the aquifer.

2.1.5 Quaternary alluvial aquifer

This aquifer covers about 15% of the basin area and is considered as very important source of groundwater for irrigation and private potable supply in the agricultural areas. The aquifer has been heavily exploited in the Sana’a Basin because of its relatively shallow water table (about 40m.b.g.l) and due to its proximity to the urban area. Due to overexploitation serious decline in water level has been recorded (HYDROSULT, 2009).

The alluvium sediments with a maximum thickness of 200 m are located in the centre of the Sana’a plain, and mainly composed of sands, clays, and silts. The unconsolidated Quaternary deposits are very poorly sorted and provide a poorly permeable aquifer. The aquifer is regionally unconfined but locally semi-confined (HYDROSULT, 2009). Due to the fine grained nature of the deposits in the plain, recharge is expected to be mainly into coarse grained material along wadis and at the base of the hills (WEC, 2004).

Figure 2.5: Layers of Amran limestone

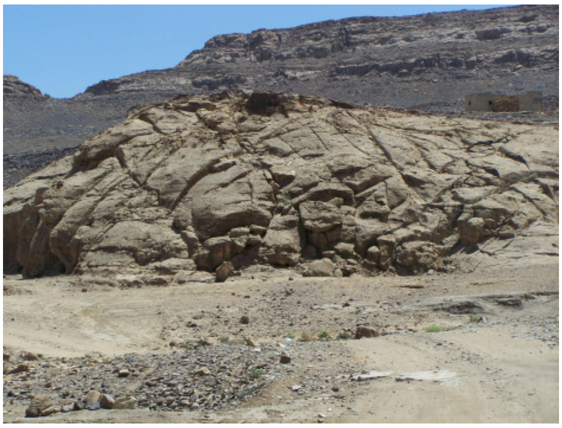

Figure 2.6: Fracturing in Tawilah sandstone

Figure 2.7: Tertiary fractured basalt

Table 2.1: Aquifers properties

Aquifer name	**Alluvium**	**Quaternary volcanics**	**Tertiary volcanics**	**Cretaceous Tawilah Sandstone**	**Jurassic Amran Limestone**
Aquifer type	Regionally unconfined, locally semi-confined	unconfined	mainly unconfined, but confined in some locations	Party confined and partly unconfined	semi-confined aquifer
Lithology	Sands, clays and silt	basalts cones interlayered with tuffs and alluvial sediments	rhyolites, Andesites, Trachyts and basalts interbeded with fluvitile and Lacustrine sand, clay and shale	sandstone with intercalation of conglomerates, siltstones, and clays	limestone and gypsum with intercalated shales
Permeability [m/day]	3.5	highly permeable	3	2	2.2
Transmissivity [m^2/day]	27.9	51	45.8	280.3	25.6
Saturated thickness [m]	53.9	Unknown	80.5	163.3	40.3

2.2 Groundwater in the Sana'a basin

2.2.1 Groundwater recharge

Infiltration of surface flows in ephemeral wadis is believed to be the most important and least predictable component of recharge from precipitation in the Sana'a basin (ALDERWISH 1995). The percentage of recharge from precipitation was estimated to be 3 to 4% (NWSA, 1996). Foppen (2005) estimated the mean recharge in the Sana'a basin to be 4-8% of the precipitation measured at Sana'a.

In previous studies the total recharge amount was estimated with two methods, one is based on the Darcy Law which based on the transmissivity and assumed simplified aquifer, while the other based on the recharge coefficient (precipitation data).

The estimation of the recharge based on Darcy Law was applied by the National Water Sources Authority (NWSA) in 1973, 1982 and 1996 and recorded three values with 59, 45-28 and 35x10^6 m^3/yr respectively. In general, the Darcy equation can only be applied for steady flow in isotropic confined aquifers, but these conditions do not exist in the Sana'a basin.

Nevertheless, the estimations based on the recharge coefficient method came to more or less the same amount. The method was used by the Ministry of Agriculture and Fisheries (MAF) in 1986, by the High Water Council (HWC) in 1988-1992 and the NWRA in 2001 and gives values from 63, 42, and 46x10^6 m^3/yr respectively. According to JICA (2007) NORMAN & MULAT estimate the total annual recharge amount to be of about 50.7x10^6 m^3/yr, using precipitation data from 1991 to 2003.

SAWAS in 1996 reported from 29x10^6 m^3/yr groundwater recharge from direct infiltration of precipitation (SAWAS, 1996). According to WEC (2002) and HYDROSULT (2007) the total groundwater recharge for the Sana'a basin is about 67.7x10^6 m^3/yr.

Other studies considered the return flow of irrigation and infiltration of domestic sewage in the urban areas of Sana'a into the quaternary alluvium, in addition to the recharge by infiltration of precipitation, as recharge amount. E.g. Al-HAMDI (2000) estimated the total volume of wastewater infiltration in the city in 1995 around 10-20x10^6 m^3/yr.

This amount was not considered as recharge amount in the study from NWRA in 2007 because the improvement of irrigation efficiency makes the recharge amount small and treated wastewater will be used for irrigation purpose in future.

The estimated values are summarized in table 2.2 and shown in figure 2.8.

Table 2.2: Estimated groundwater recharge in the Sana'a basin

Study	Year	Recharge (Mm^3/yr)	Method
NWSA	1973	59	Darcy
NWSA	1983	36.5	Darcy
MAF	1986	63	R.C
HWC	1988-1992	42	R.C
NWSA	1996	35	Darcy
NWSA	1996	29	R.C
NWRA	2001	46	R.C
WEC 2002, HYDROSULT 2007	2002	67.7	R.C
NORMAN& W. Mulat	2007	50.7	R.C

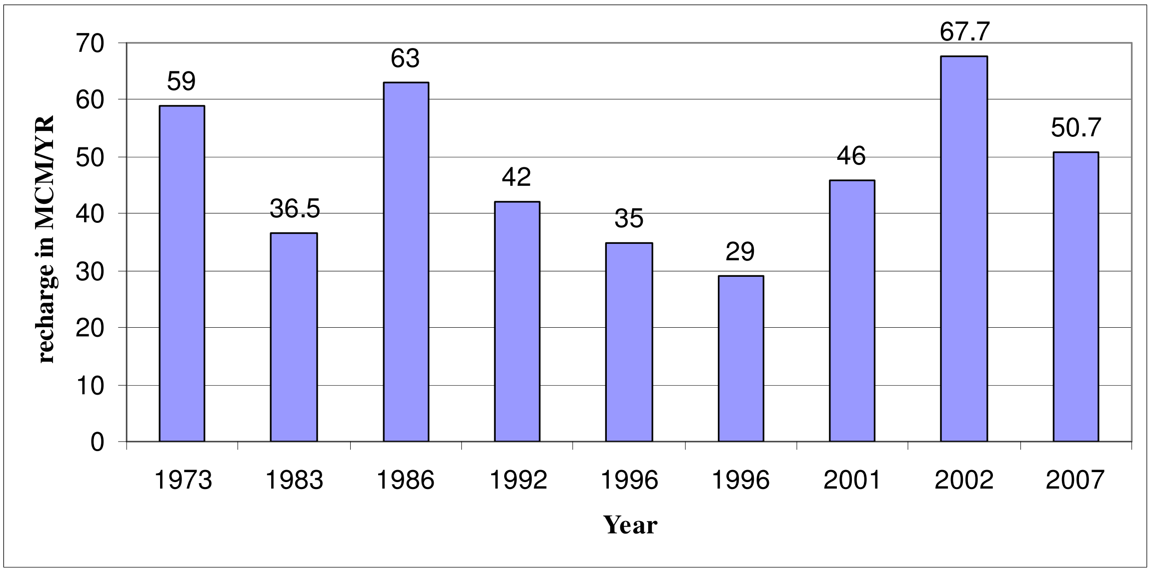

Figure 2.8: Groundwater recharge in the Sana'a basin

2.2.2 Groundwater Abstraction

The volume of groundwater abstracted from the differences aquifers in the Sana'a basin was estimated based on well inventory studies in the Sana'a basin in the period from 1973 to 2001. The calculation is depending on the well yield and the pumping duration which varies from the rain season to the dry season. The average well yield ranges from 6 l/s for boreholes to 3 l/s for dug and dug/bore wells. The springs give average values of about 0.062 l/s. Springs with high yield were observed in the north-eastern part and southern part of the basin, with 9.2 l/s and 6.25 l/s respectively (WEC, 2004).

The total number of wells has grown from about 173 wells in 1973 in central plain areas around Sana'a city to around 4500 wells in 1996 in the same area. In 2004 a total of 13.425 water points were recorded during an inventory program conducted by WEC. As a consequence, the total abstraction of groundwater in Sana'a basin has grown. In 1990 the total abstraction was estimated by TS-HWC to be about 180x10^6 m^3/yr and in 2004 to be about 260x10^6 m^3/yr (WEC). According to JICA (2007) Norman, Mulat and GAF (2005), the total abstraction were estimated in 2007 of about 270 and 253 x10^6 m^3/yr respectively.

The total estimated abstraction in the period from 1973 to 2007 is summarized in table 2.3 and illustrated in figure 2.9.

According to the estimated abstraction and recharge data from NORMAN & MULAT (JICA REPORT, 2007) it can be concluded that the abstraction amount exceed the recharge amount by more than five times.

Figure 2.10 shows the water balance in Sana'a basin according to NORMAN&MULAT (data obtained from JICA, 2007).

Table 2.3: Estimated groundwater abstraction in the Sana'a basin

Study	**Year**	**Abstraction (x10^6 m^3/yr)**	**notice**
Foppen et.al.,2005	1973	60	Well inventory in 1973,1984,1994-1995 and 2001
TS-HWC, 1990	1991	180	hydrogeological survey
WEC, ITC,2001	2000	246.7	hydrogeological survey
Foppen et.al.,2005	2001	370	Well inventory in 1973,1984,1994-1995 and 2001
WEC, 2002	2002	270	Wells inventory
WEC, 2004	2004	260	hydrogeological survey in 2001
WEC, ITC, 2001	2005	293.8	hydrogeological survey
JICA, 2007	2005	269.1	hydrogeological survey
Norman & Mulat, 2007	2007	270	hydrogeological survey
GAF, 2007	2007	253.1	Satellite imagery
Hydrosult, 2009	2007	270	Wells inventory

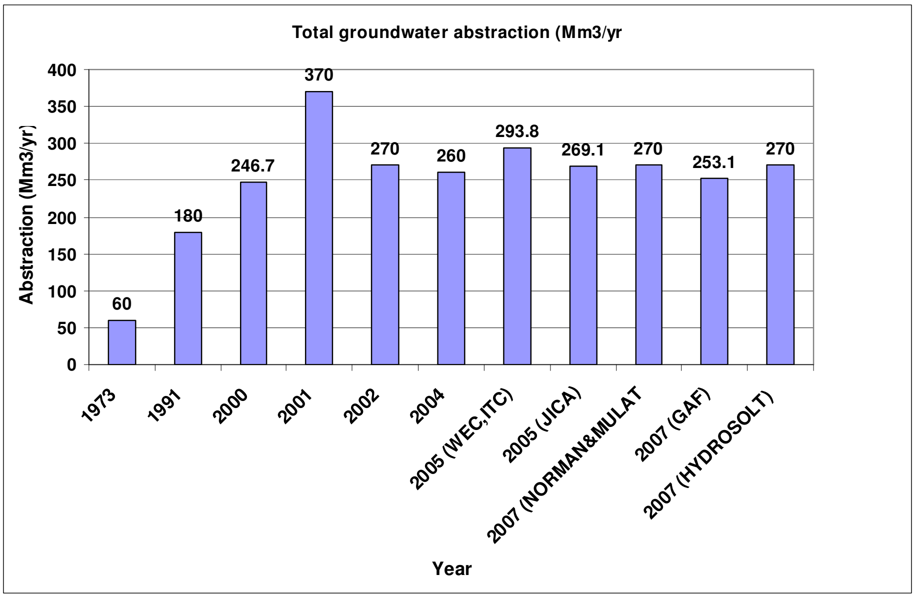

Figure 2.9: Groundwater abstraction in the Sana'a basin

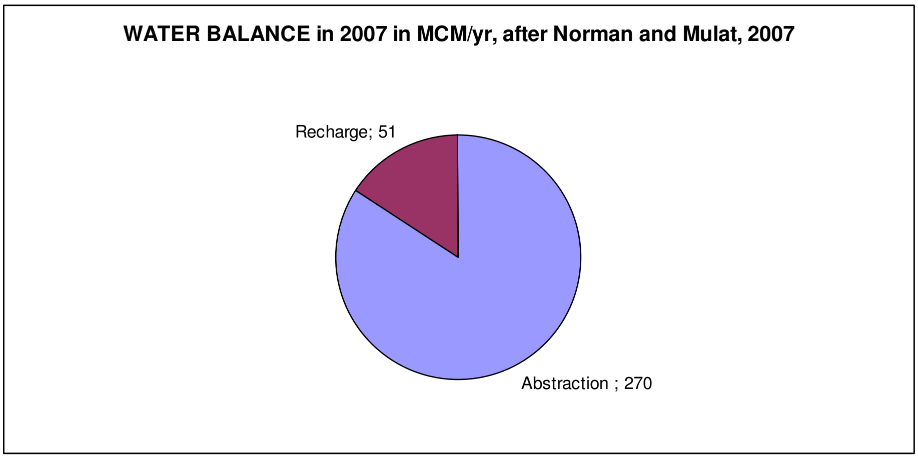

Figure 2.10: Water balance in the Sana'a basin according to NORMAN&MULAT (data: JICA, 2007)

2.2.3 Groundwater use

Groundwater in the Sana'a basin is used exclusively to satisfy the water needs of the different water-using sectors, namely irrigation, domestic and industrial use (Fig. 2.11).

The greatest part of the groundwater abstraction is used for irrigation purposes. According to GAF the total annual groundwater abstraction for irrigation purposes in 2004/2005 was estimated to be about 209.20x10^6 m^3/yr (JICA, 2007). This forms about 80% of the total groundwater abstraction which estimated to be about 260 x10^6 m^3/yr according to WEC, 2004. Moreover, the cash crops (qat and grapes) are estimated to consume around 40 and 25% respectively of the agricultural water demand in the region.

The second groundwater-using sector is the abstraction for domestic purpose, which results from population growth of Sana'a from 80,000 inhabitants in 1970 to about 1,935.451 in 2005. As a result of this population growth the groundwater abstraction increased rapidly, leading to a clear declination in groundwater levels in Sana'a basin from less than 50 m.b.s.l. in the early 1970's to more than 350 m.b.s.l. in 2008 with an average of 4-5 m/year declination.

The abstraction for domestic use is from wells operated by Sana'a Water and Sanitation Local Corporation (SWSLC) and from private wells with a total abstraction estimated to be about 14.7 x10^6m^3/yr and 31.7 x10^6m^3/yr, respectively (sum 46.6 x10^6m^3/yr) in 2006 (NWRA, 2007). This is about 18% of the total groundwater abstraction.

Abstraction for industrial purpose is very low. Demand from water for most industries is satisfied through their own wells, it is unregulated and unrecorded. The total abstraction was estimated in 2005 to be 4.8 x10^6 m^3/yr (NWRA, 2007). This is only 2 % of the total abstraction.

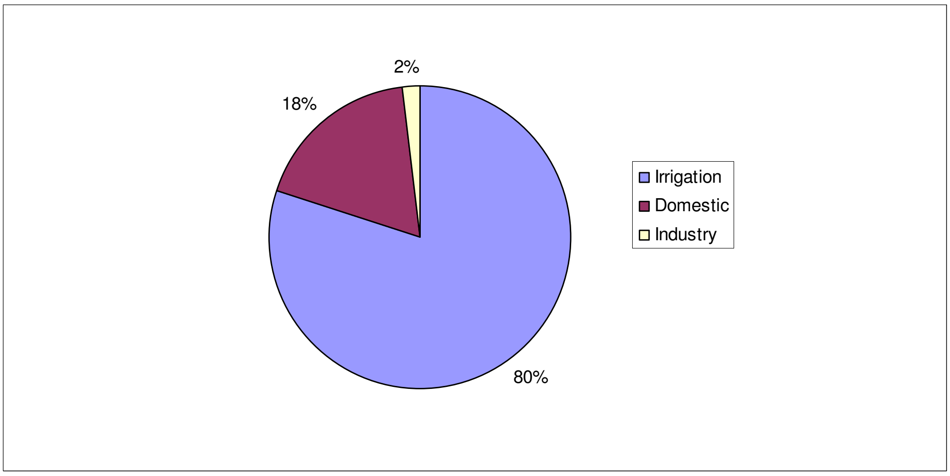

Figure 2.11: Groundwater use in Sana'a basin

2.2.4 Groundwater flow

The direction of the groundwater flow was determined based on measurement of groundwater levels in 1972, 1985 and 1990-1993. Groundwater levels contours for the 1972 situation could be drawn based on data of ITALCONSULT, 1973 and presented in figure 2.12.

According to the contours map the general groundwater flow is to the north. The flow direction in the mountainous areas on the western slopes is towards east and west on the eastern slopes. The same flow pattern was observed for the period between of 1985 and 1990 by SELKHOZPROMEXPORT and SAWAS.

WEC determined the flow direction based on measurements of the groundwater elevations in meters above sea level, averaging them for every group of wells within one square kilometre, and drawing a well elevation map per km^2. The groundwater flows from the eastern, southern, and western high plateau zones towards the central zone and eventually towards Wadi al Kharid in the Northern where it is known to be discharged naturally through the Al Kharid springs (WEC, 2004).

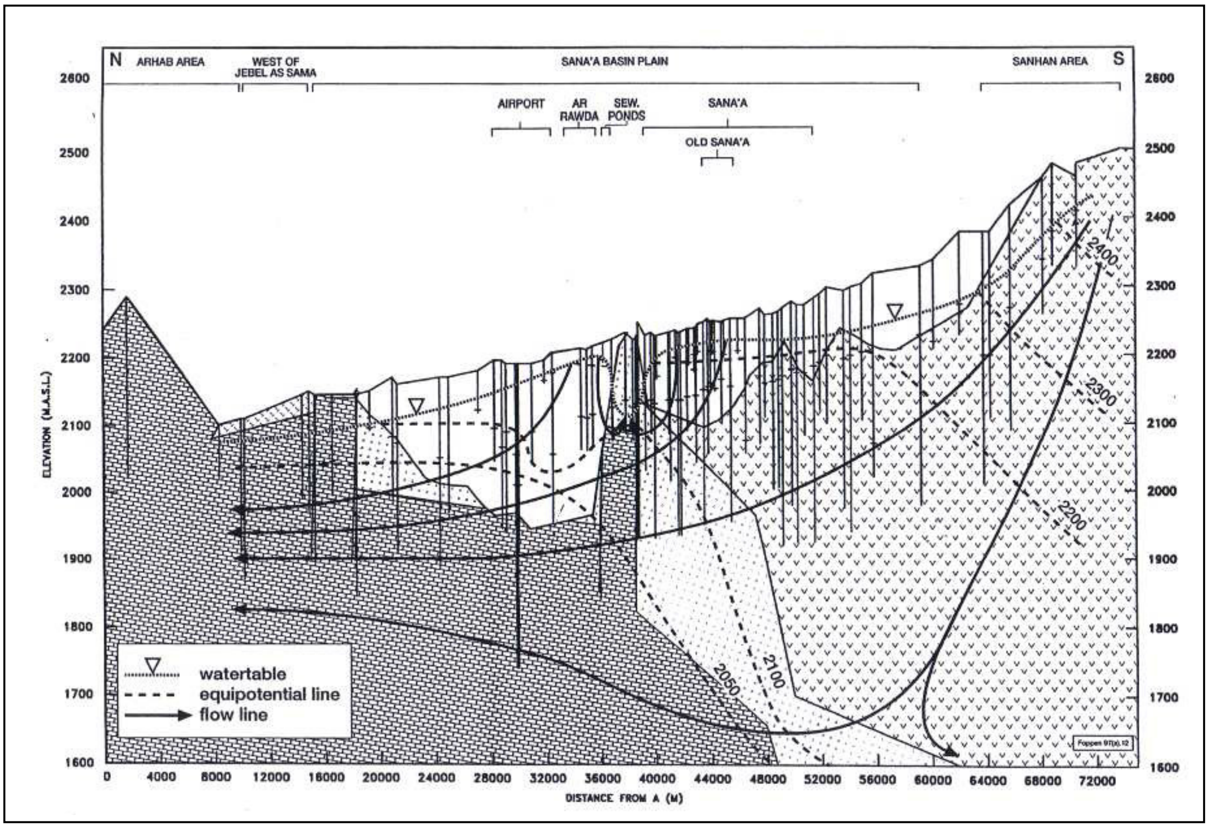

Figure 2.12: Groundwater flow in Sana'a basin (from ITALCONSULT, 1973)

2.3 Previous studies relevant for the study area

A large number of groundwater studies have been undertaken within or adjacent to the Sana'a basin since 1973 (TS-HWC, 1992). A number of groundwater studies have attempted to estimate the groundwater recharge/abstraction amount (see table 2.3 and figure 2.9). Wells inventory studies were carried several times; the most recent one was performed by WEC in 2004.

Other studies investigated the groundwater hydrochemical quality in the basin. Between 1987 and 1996 the Project " Sources for Sana'a Water Supply (SAWAS) conducted a long term study including hydrological measurements, rainfall records, groundwater levels observations, chemical and microbiological analyses of water samples, well inventories, geophysical surveys, and the drilling of exploratory boreholes (SAWAS, 1996).

In 2002 a modeling study was conducted by J.W.A. FOPPEN based on hydrochemical analyses of samples taken in 1995 and 2000 from the alluvium, volcanic and sandstone aquifers below the urban area of Sana'a. Some of the samples were taken from outside the urban area (FOPPEN, 2002).

There are only few studies using isotopes techniques either in the Sana'a basin or in other regions of Yemen. FOSTER (2003) used the stable isotopes deuterium and oxygen-18 and the radioactive isotope Helium (^{3}H) and carbon (^{14}C) to investigate the recharge mechanism and to estimate the groundwater ages in the alluvium and sandstone aquifer in the Sana'a basin. Unfortunately, the data of this study could not found, only one plot ^{18}O vs. ^{3}H exists.

The most relevant studies for the present work are studies carried out in 2005 and in 2008 by SHAMSAN (submitted to NWRA) which includes the analyses of stable isotopes (^{2}H and ^{18}O) and the radioactive isotope (^{3}H) and hydrochemical analyses. The first one (SHAMSAN, 2005) comprises a total of 16 groundwater samples taken from deep wells located in the sandstone and tertiary volcanic aquifer, the second one (SHAMSAN, 2008) comprises a total of 32 groundwater samples taken from shallow- quaternary deposits (less than 100 m), volcanic and sandstone aquifer.

A comparison is made between the data of the current study and data obtained by SHAMSAN. Because the study of 2005 and 2008 comprised only three aquifers (quaternary alluvium, tertiary volcanic and sandstone), other data obtained by SAWAS (1996) and FOPPEN (2002) were included for a better correlation of the entire aquifer system of Sana'a basin. The results of this comparison are discussed in chapter 7.2.

Isotopic composition of the groundwater samples taken from the Sana'a basin were compared with data existing for a total of 12 groundwater samples taken from Sada'h basin (about 224 km north Sana'a). The samples were collected by the author in October 2008 and analyzed at the Geological Institute at the Freie University Berlin (Germany).

3 Stable isotopes in hydrogeology

3.1 Basic principles and objectives

Isotopes are nuclides with the same atomic number (proton number) but with different numbers of neutrons. Hydrogen and oxygen stable isotopes of water (which used in the present study) are widely used as tracers of hydrogeological processes such as precipitation, groundwater recharge, groundwater–surface water interactions, hydrograph separation, basin water hydrology, and evolution of surface or soil waters undergoing evaporation (FONTES, 1980; MAZOR, 1991; GAT, 1996; CLARK and FRITZ, 1997; GIBSON et. al, 2005). The stable isotope ratios of hydrogen and oxygen-18 (δ^2H and $\delta^{18}O$) in world precipitation are forming a linear relationship defined by Craig in 1961 as GMWL (see 3.2). The stable isotope ratios are conventionally reported as parts per thousand (‰) or per mil deviation from a standard using the delta (δ) notation (IAEA 2000). For oxygen and hydrogen isotope ratios, the Vienna Standard Mean Ocean water (VSMOW) is used as the standard (the isotopic ratios of VSMOW are zero):

$$\boldsymbol{\delta_{sample}} (‰) = \left[\frac{R_{sample} - R_{reference}}{R_{reference}}\right] \times 1000 \qquad \text{(eq. 3.1)}$$

where R is the ration of the heavier to the lighter isotope.

Evaporation before or during infiltration increase the oxygen and hydrogen isotope ratios of the residual fraction and this residual water no longer follows the trace of meteoric water line (MWL) (KENDDALL et. al, 1998). So the variations of ^{18}O and ^2H concentrations are controlled by fractionation during evaporation and condensation which take place under equilibrium or non-equilibrium conditions (see 3.2). Other factors affecting the isotope composition are discussed later in this section.

Up to now, no regional studies of the signature of the stable isotopes deuterium and oxygen-18 in rainwater or groundwater were published for any location in Yemen with exception of the Local meteoric water line equation for Sana'a basin published by A. SHAMSAN in 2008 which was defined by the equation (SHAMSAN, 2008):

$$\delta^2H = 8 * \delta^{18}O + 13.14\ ‰ \qquad \text{(eq. 3.2)}$$

The first objective of this section in the present study was to derive a LMWL for Yemen and Sana'a basin, based on direct precipitation sampling. The precise relationship between the **δD**

and $\delta^{18}O$ of precipitation vary from geographic region to region making it advantageous to establish a LMWL for any detailed field investigation using stable isotopes of water samples.

The second objective was to compare the isotopic composition of local meteoric water to that of groundwater and spring water samples taken from Sana'a basin. The stable isotopes (deuterium and oxygen-18) were used in this study- as in many hydogeological studies- in order to investigate groundwater recharge mechanisms, hydraulic interconnection of multiple aquifer systems of Sana'a basin and to determine the content of the deuterium and oxygen-18 in rain water samples taken from Sana'a basin and others geographic units of Yemen. Furthermore, the isotope data obtained from this study can provide useful information on the relationship between rainwater and groundwater in the different aquifers of Sana'a basin.

The third objective was to find out which most parameters affect the stable isotope deuterium and oxygen-18 composition of rainwater samples. A relationship between $\delta^{18}O$, δD and the different parameters was given and discussed later in the presents work (chapter 6.2).

The results obtained from the present study will be a contribution for future studies on groundwater system in Sana'a basin and the whole country of Yemen and could be considered as basis for the establishment of a Local Meteoric Water Line (LMWL) for Sana'a basin and maybe for Yemen.

3.2 Isotope fractionation

During isotopic fractionation, heavy and light isotopes partition differently between two compounds or phases. Isotope fractionation occurs because the bond energy of each isotope is slightly different, with heavier isotopes having stronger bonds and slower reaction rates. The difference in bonding energy and reaction rates is proportional to the mass difference between isotopes. Thus, light elements are more likely to exhibit isotopic fractionation than heavy isotopes (CLARK&FRITZ, 1997).

3.2.1 Equilibrium fractionation

Equilibrium fractionation describes isotopic exchange reactions that occur between two different phases of a compound at a rate that maintains equilibrium, as with the transformation of water vapour to liquid precipitation. The fractionation between two substances A and B can be expressed by use of the isotope fractionation factor alpha (α) (W.G.MOOK, 2006):

$$\boldsymbol{\alpha_{A\text{-}B} = R_A / R_B} \quad \text{(eq. 3.3)}$$

where R = the ratio of the heavier isotope to the lighter isotope (i.e., D/H, $^{18}O/^{16}O$, etc.) in compounds A and B.

The α-values are dependent on many factors, of which temperature is generally the most important. Other factors include chemical composition, crystal structure, and pressure.

A relationship between fractionation factors α and δ–values can be expressed by the following equation (CLARK and FRITZ 1997):

$$\boldsymbol{\alpha_{A\text{-}B} = (\delta_A + 1000) / (\delta_B + 1000)} \qquad \text{(eq. 3.4)}$$

The isotopic difference in these tow compounds can be expressed by the enrichment factor ε in ‰-notation (CLARK and FRITZ 1997):

$$\boldsymbol{\varepsilon_{A\text{-}B} = (\alpha_{A\text{-}B} - 1) \times 1000} \qquad \text{(eq. 3.5)}$$

3.2.2 Kinetic (non- equilibrium) fractionation

Kinetic fractionation is fractionation that is unidirectional, where equilibrium is not attained. In kinetic processes the lighter, i.e. lower atomic mass, of two isotopes of an element will form the weaker and more easily broken bond (GAT, et. al, 2007). The lighter isotope is more reactive; therefore it is concentrated in reaction products, enriching reactants in the heavier isotope.

Kinetic fractionation is affected by several factors such as the temperature, wind speed, salinity, and the humidity which considered as the most important factor (KENDAL et. al, 1998). At lower humidity, water-vapor exchange is minimized, and evaporation becomes an increasingly non-equilibrium process (CLARK and FRITZ 1997).

3.2.3 Rayleigh fractionation

Rayleigh fractionation occurs when a substrate mass is depleted during a physicochemical reaction and a product is removed from system (Fig. 3.1). The Rayleigh equations can be used to describe an isotope fractionation process if: (1) material is continuously removed from a mixed system containing molecules of two or more isotopic species (e.g., water with ^{18}O and ^{16}O), (2) the fractionation accompanying the removal process at any instance is described by the fractionation factor α, and (3) α does not change during the process (KENDALL C. and J. J. MCDONNELL, 1998). Under these conditions, the evolution of the isotopic composition in the residual (reactant) material is described as (KENDALL C. and J. J. MCDONNELL, 1998):

$$(R / R_\circ) = (X_l / X_{l\circ})^{\alpha-1} \qquad \text{(eq. 3.6)}$$

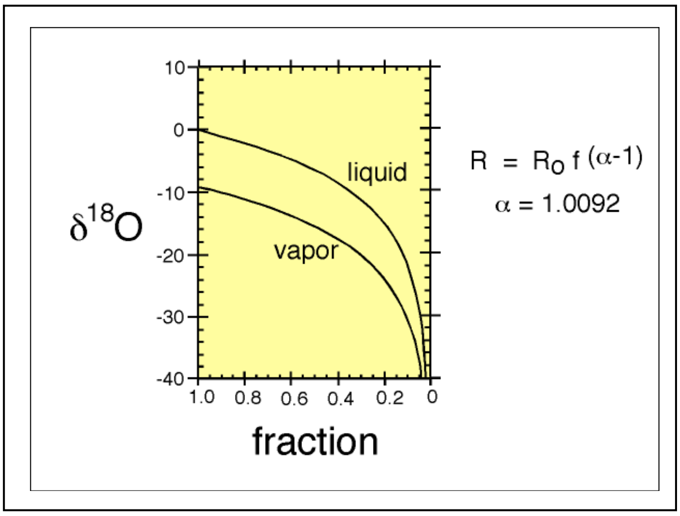

Figure 3.1: Change in the ^{18}O content of rainfall according to a Rayleigh distillation (from GAT and GONFIANTINI, 1981)

where R = ratio of the isotopes (e.g., $^{18}O/^{16}O$) in the reactant, $R_\circ$ = initial ratio, X_l = the concentration or amount of the more abundant (lighter) isotope (e.g.,^{16}O), and $X_{l\circ}$ = initial concentration. Because the concentration of $X_l >> X_h$, X_l is approximately equal to the amount of original material in the phase. Hence, if $f = X_l/X_{l\circ}$ = fraction of material remaining, then:

$$\mathbf{R} = R_\circ\, f^{(\alpha-1)} \qquad \text{(eq. 3.7)}$$

The term Rayleigh fractionation is typically applied to the case of chemically Open-system where the isotopic species removed at every instant were in thermodynamic and isotopic equilibrium with those remaining in the system at the moment of removal (KENDALL C. and J. J. MCDONNELL, 1998).

3.3 Isotope effects and the Meteoric Water Line (MWL)

As a result of kinetic and equilibrium processes during evaporation from the ocean and subsequent condensation, the ratios of the stable isotopes of hydrogen (H and ^2H) and oxygen (^{16}O and ^{18}O) in water within a particular air mass vary with temperature during condensation and with relative humidity during evaporation (CLARK and FRITZ, 1997). The stable isotope ratios of water vapor in an air mass reflect the origin of the air mass, and the ratios in the precipitation that evolves from the air mass reflect both the origin of the air mass and the conditions under which condensation occurs. As an air mass travels away from the ocean (or other source areas for water vapor) and precipitation occurs, precipitation that is enriched in the heavier isotopes leaves the air mass first. The remaining water vapor then is composed of lighter isotopes. Subsequent precipitation has an increasingly lighter stable isotope composition. This depletion effect has been called the "continental effect" and results in lighter stable isotope ratios farther away from the ocean (Fig. 3.2).

Furthermore, a strong linear correlation exists between mean annual isotopic composition of precipitation and mean annual surface air temperature **(temperature effect)**. This relationship corresponds to a 1‰ decrease in mean annual delta oxygen-18 ($\delta^{18}O$) with a 1.1 to 1.7°C decrease in mean annual temperature; $\delta^{2}H$ varies with temperature in a similar manner to $\delta^{18}O$ (CLARK and FRITZ, 1997). As a result, precipitation at higher latitudes has a lighter stable isotope composition than precipitation closer to the equator **(latitude effect)**. This temperature effect also is seen as a result of elevation; cooler temperatures at higher elevations result in $\delta^{18}O$ depletion that varies between -0.15 and -0.5 ‰ per 100m rise in elevation **(altitude effect)** (CLARK and FRITZ, 1997). As a result of seasonal differences in temperature, strong seasonal variability in stable isotopic composition of precipitation occurs that is particularly pronounced in continental locations where seasonal temperature differences are extreme. The relation between $\delta^{2}H$ and $\delta^{18}O$ for meteoric waters is found to be linear (Fig. 3.3) and named as Global Meteoric Water Line (GMWL) defined by the equation presented by Craig in 1961:

$$\boldsymbol{\delta^{2}\mathrm{H} = 8 * \delta^{18}O + 10\ ‰} \qquad \text{(eq.3.8)}$$

This linear relation was developed as an average of many local water lines that differ from the GMWL as a result of climatic and geographic factors. Differential fractionation of $\delta^{2}H$ and $\delta^{18}O$ occurs as a function of **humidity** during primary evaporation of water vapor from the ocean and as a function of **temperature** during secondary evaporation as rain falls from a cloud. These two factors affect the slope and intercept of the Local Meteoric Water Line (LMWL) and produce a different LMWL at different locations. The LMWL can be expressed through the deuterium excess parameter (d-excess) defined by DANSGAARD in 1964:

$$\mathbf{d\text{-}excess = \boldsymbol{\delta}^{2}H - 8 * \boldsymbol{\delta}\ ^{18}O} \qquad \text{(Eq. 3.9)}$$

Greater isotopic fractionation of ^{18}O than ^{2}H with evaporation during rainfall or sublimation during snowfall results in disproportional enrichment of ^{18}O relative to ^{2}H and a lower slope for the LMWL. In particular, the d-excess is generally regarded as the most useful parameter for characterizing the vapour origin of water. It can be used as an indicator of fractionation by evaporation (low d-excess value), whereas the high d-excess reflects fast evaporation at its source region due to low humidity (CLARK and FRITZ, 1997).

With information about the stable hydrogen and oxygen isotope ratios of local precipitation, it may be possible to identify recharge areas in this basin and processes that occur during recharge and to evaluate surface- and groundwater interaction and many other geochemical and hydrologic problems. The establishment of a LMWL for Yemen and Sana'a basin provides a baseline for comparison in future stable isotope studies for this region.

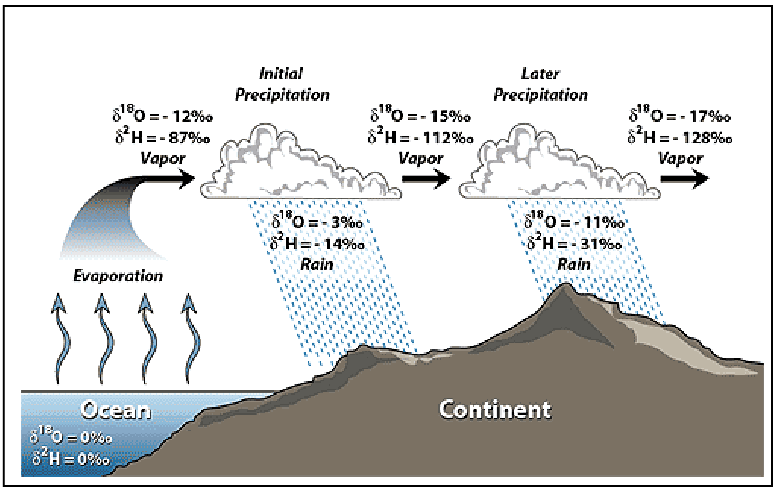

Figure 3.2: Rain-out and continental effect on δ^2H and δ^{18}O values of the precipitation (from HOEFS 1987 and COPLEN et. al 2000)

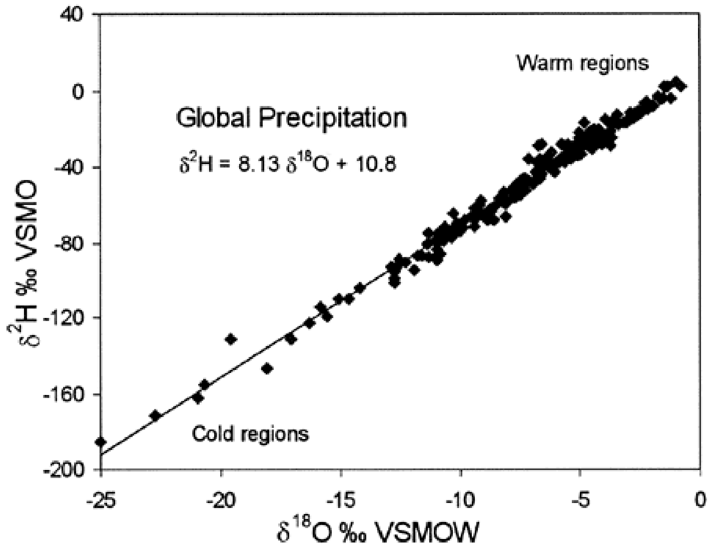

Figure 3.3: Linear relationship between δ^2H and δ^{18}O in global precipitation (from CLARK and FRITZ 1997)

4 Methods

4.1 Selection of the sampling-sites

For this study three types of water samples (groundwater, spring water and rainwater) were collected for physico-chemical and stable isotope analyses. A preselecting of the sampling-sites that includes deep wells (dug and boreholes) and springs was required. This preselecting was done jointly by WEC represented by Dr. N. ABU LOHOM and the author in September 2009. Rainwater sampling-sites were chosen in cooperation with Tihama Development Authority (TDA) in April 2008. The ground- and spring water sampling-sites are shown in figure 4.1. Table 4.1 and 4.2 summarising general information on the sampling wells and springs such as sample ID, coordinates, aquifer type, total depth of the well and the depth to the water table. The location of the samplings sites (latitude, longitude and altitude) which includes the wells and springs, meteorological stations and private home-roofs were located by means of GPS.

By selection of sampling-sites for spring- and groundwater samples, it was considered that the wells and springs should cover the largest part of the basin and be distributed among the various aquifers system in Sana'a basin as shown in figure 4.1 and summarized in table 4.3. Two springs of a total of 13 are located in the contact zone between two different lithological units (sandstone and alluvium) (Fig. 4.5).

The selection of groundwater sampling wells was based on well location, the availability of well information, the ability to contact the current well owner, and accessibility. The wells were not designed for groundwater monitoring, but are currently in use for drinking water supply and irrigation. Well information such as total depth of the wells, depth to water table, lithology and year of construction were also obtained from inventory wells data carried out by WEC in 2002 and occasionally by asking the well owner. According to information obtained from wells owner, dug wells are usually older than 50 years with a diameter of about 3m and an average depth ranging between 25 to 50 m. Drill wells have a diameter of 0.25 -0.35 m and they are usually uncased when they are underlying hard rock. Depth of the drill wells range mostly from 100 to 400 m with an average from 200 to 300 m (FOPPEN, 2002). Groundwater is present near the bottom of the well (table 4.1 and figure 4.8). In some cases there were no data about the total depth of the well or the depth to water table; therefore this information was completed by information supplied by the owners based on the number of the pipes used, which are normally 3 or 6 m long. In some cases it was not possible to take water samples from some wells because the wells were not operated or the owners were either not on site or would not operate the engines. In these cases the nearest wells with the same properties (aquifer type, well elevation, depth to water table, etc…) were chosen to take water samples. In case of dug wells, one sample was taken by hand because the engine was defect (Fig. 4.3).

Where springs were selected for water sampling we made sure that the spring was not dry, that it was accessible and that the spring water was not contaminated. In some cases it was either difficult to reach some of the springs or to locate them. Some springs were contaminated with washings materials, plastic bags or cans because the habitants near the springs use the spring water for washing purposes (Fig. 4.6 and 4.7). Other springs were contaminated through still water or water plants (Fig. 4.8).

Rainwater samples were collected at 16 sites for a regional stable isotope study. The sites are located along an altitudinal gradient from 14 m.a.s.l. in the coastal plain to 2500 m.a.s.l. in the Yemen highland (Fig. 4.9). Most of the sampling-sites are located along the Yemen Mountain Massif. Three sites are located along the coastal plains, two of them along the west coastal plain (Bajel and Al-Hodaidah) and one site is located along the south coastal plain (Sayoon). No samples were taken from the Yemen desert; rainfall events are very rare in this region.

Some of the samplings-sites are meteorological stations for observation the rainfall events. Six of them belong to TDA; three belong to WEC and one to NWRA. The others are private home-roofs. The location of sampling-sites is shown in Figure 4.2 and summarised in table 4.4.

For the isotope study in the Sana'a basin, rainwater samples were collected from two sampling- sites (n=65). One site is private home-roof in the north-east part of Sana'a City and the other site is a station for rainfall observation that belongs to WEC and is located at the roof of the WEC building in the centre of Sana'a city.

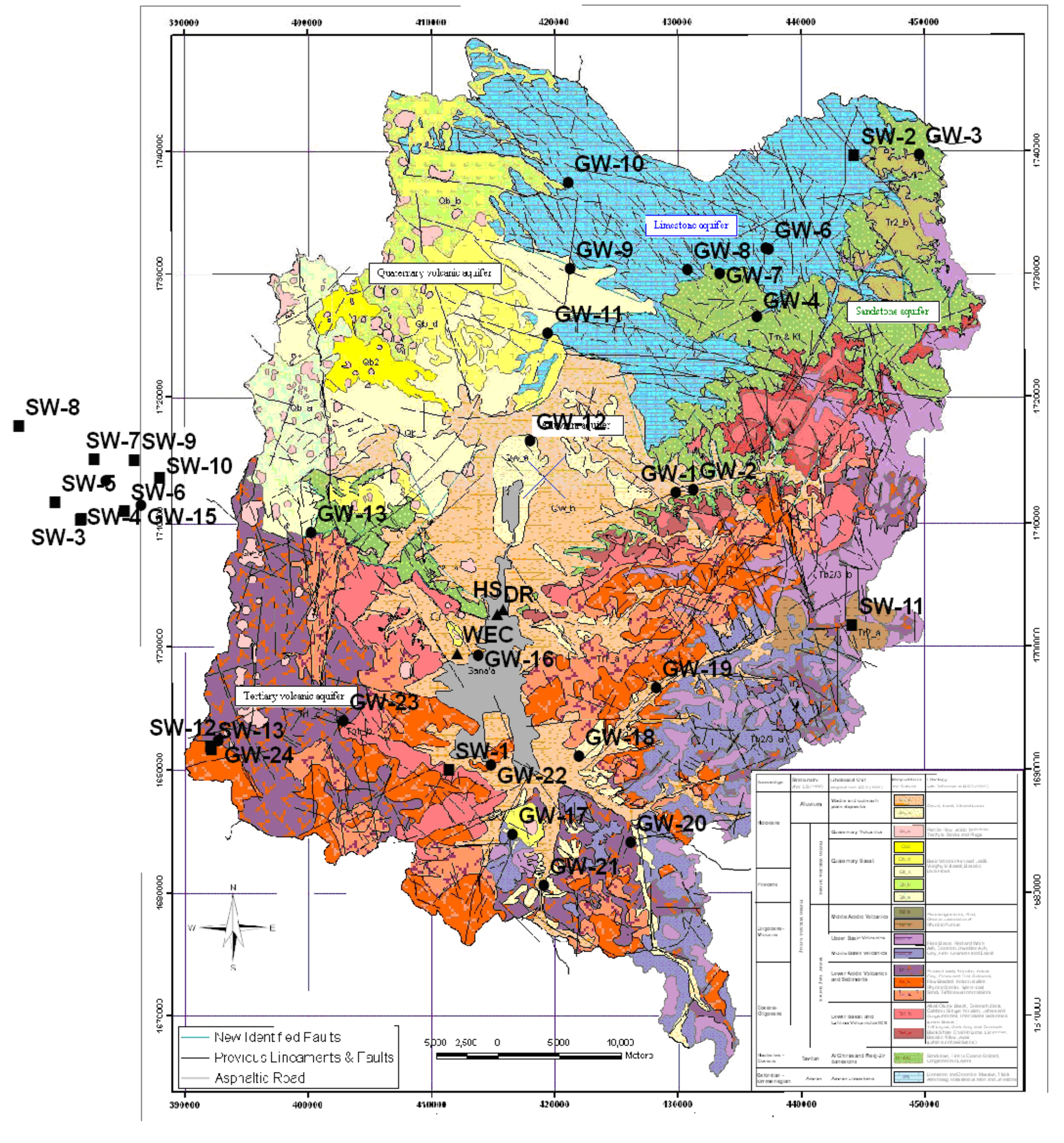

Figure 4.1: Study area and sampling locations (modified from HYDROSULT, 2009)

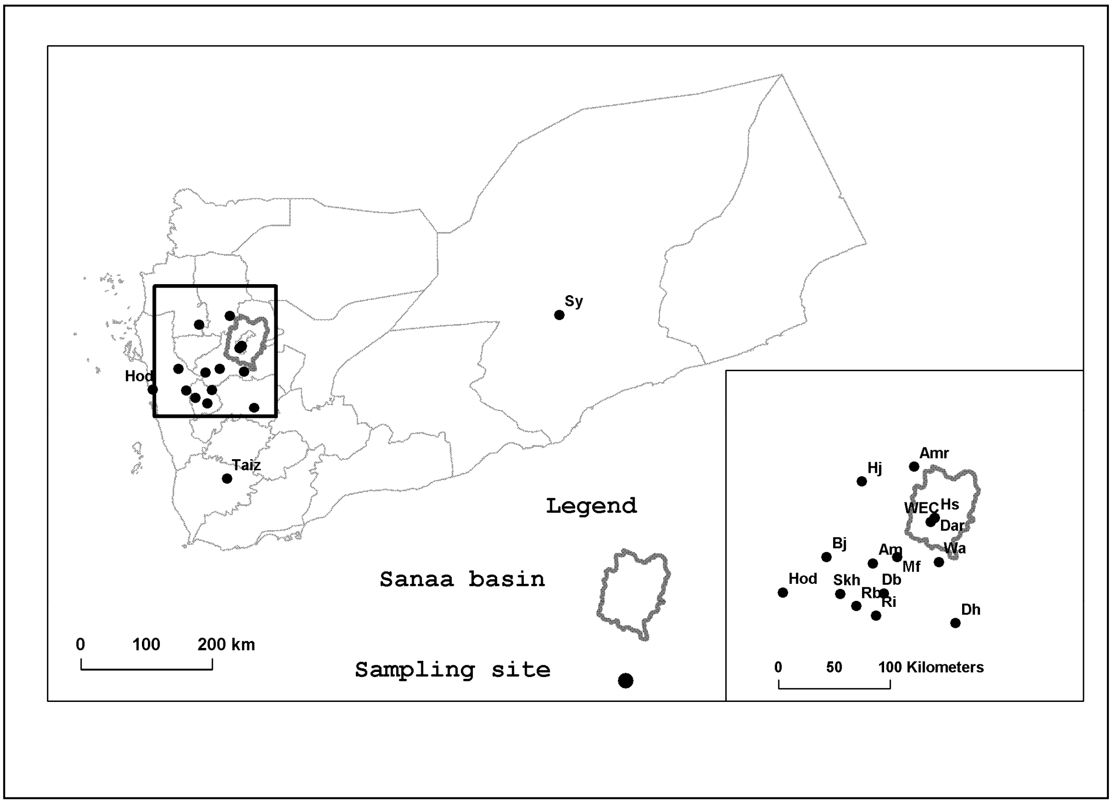

Figure 4.2: Sampling-sites of rainwater

Figure 4.3: Sampling by hand from 50 m depth dug well

Table 4.1: Description of groundwater sampling-sites

/.Samp well ID	Aquifer type	sampling date	depth of		location			notice
			well	WT	elevation (m)	N	E	
GW-1	S.S	01.10.2009	300	140	2233	1712721	428799	
GW-2	.Alu	01.10.2009	70	60	2244	1712635	431132	dug well
GW-3	L.S	01.10.2009	160	55.14	2181	1739793	449455	
GW-4	S.S	01.10.2009	150	120	2093	1726629	436297	
GW-5	L.S	01.10.2009	250	210	2009	1732150	437005	
GW-6	L.S	01.10.2009	250	220	2006	1732115	437265	*
GW-7	S.S	01.10.2009	150	80	2130	1730112	433332	
GW-8	L.S	01.10.2009	56	39	2102	1730439	430697	
GW-9	L.S	01.10.2009	250	210	2130	1730505	421193	*
GW-10	L.S	01.10.2009	350	342	2291	1737494	421046	
GW-11	L.S	01.10.2009	450	320	2152	1725307	419380	*
GW-12	.Alu	01.10.2009	160	32.92	2176	1716588	417906	
GW-13	S.S	02.10.2009	280	180	2546	1709097	400176	
GW-14	S.S	02.10.2009	200	170	2557	1713338	383541	*
GW-15	S.S	02.10.2009	160	130	289	1711358	386433	
GW-16	.Alu	03.10.2009	60	40	2264	1699129	413749	Dug*
GW-17	.Alu	03.10.2009	80	60	2294	1684681	416478	Dug*
GW-18	V	03.10.2009	400	320	2338	1690977	421922	*
GW-19	V	03.10.2009	150	120	2428	1696566	428141	*
GW-20	V	03.10.2009	450	255	2379	1684013	426094	
GW-21	V	03.10.2009	300	250	2384	1680527	419022	
GW-22	V	03.10.2009	450	250	2322	1690303	414763	
GW-23	V	03.10.2009	450	255	2558	1693861	402780	
GW-24	V	03.10.2009	120	84	2927	1692249	392701	

* Depth to water table was estimated

Table 4.2: Description of spring water sampling-sites

Sample ID	Region	Village	location			lithology
			N	E	Elevation ((m	
SW-1	Al-Amanh	Bit Bous	1689925	411332	2455	volcanic
SW-2	Nihm	Al-Ghidah	1739706	444175	2103	limestone
SW-3	Al-Mahwit	Bab Al-Ahjur	1710238	381567	2502	sandstone
SW-4	Al-Mahwit	Bab Al-Ahjur	1710146	381505	2460	alluvium sandstone contact
SW-5	Al-Mahwit	Sha'allal	1711566	379465	2500	alluvium sandstone contact
SW-6	Al-Mahwit	Al-Dafir	1710881	385063	2541	sandstone
SW-7	Al-Mahwit	Al-Awar	1715056	382618	2582	sandstone
SW-8	Al-Mahwit	Nameran	1717753	376514	2752	sandstone
SW-9	Al-Mahwit	Kulaqah	1714999	385890	2522	volcanic alluvium contact
SW-10	Al-Mahwit	Hajar Sa'aed	1713590	387923	2537	volcanic
SW-11	Khawlan	Jabal Al-Loz	1701576	444017	2669	volcanic
SW-12	Bani Matar	Mahal	1691763	392027	2988	volcanic
SW-13	Bani Matar	Shalif	1691588	392109	3022	volcanic

Table 4.3: Spring- and groundwater samples from different aquifer in Sana'a basin

Samples Type	Aquifer/ lithology	Total samples
groundwater	Sandstone	6
	Limestone	7
	Aluvium	4
	Volcanic	7
spring water	Sandstone	4
	Volcanic	5
	Limestone	1
	Aluvium contact Sandstone	2
	Volcanic contact Alluvium	1
Total samples		37

Figure 4.4: Some springs were difficult to locate

Figure 4.5: Spring in S.S. at contact with Alluvium

Figure 4.6: Spring in Volcanic aquifer

Figure 4.7: Spring in Limestone aquifer

Figure 4.8: Spring influenced by still water and water plants

4.2 Sampling campaigns

4.2.1 Ground- and spring water samples

A 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 WEC.

A total of 24 wells for groundwater sampling, and 13 springs were chosen. Three samples were taken from each site, one sample for analysis of major cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}) and selected heavy metals (As, Pb, Cu, Ni, Co, Cd, Fe, Mn, Al, Zn), one for major anions (Cl^- , SO_4^{2-}, NO_3^- , Br^-) and one for stable isotopes oxygen-18 and deuterium. 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 with 4C° until transportation 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 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. Figure 4.9 and table 4.1 show comparisons between the total depth of the well and the depth to water table.

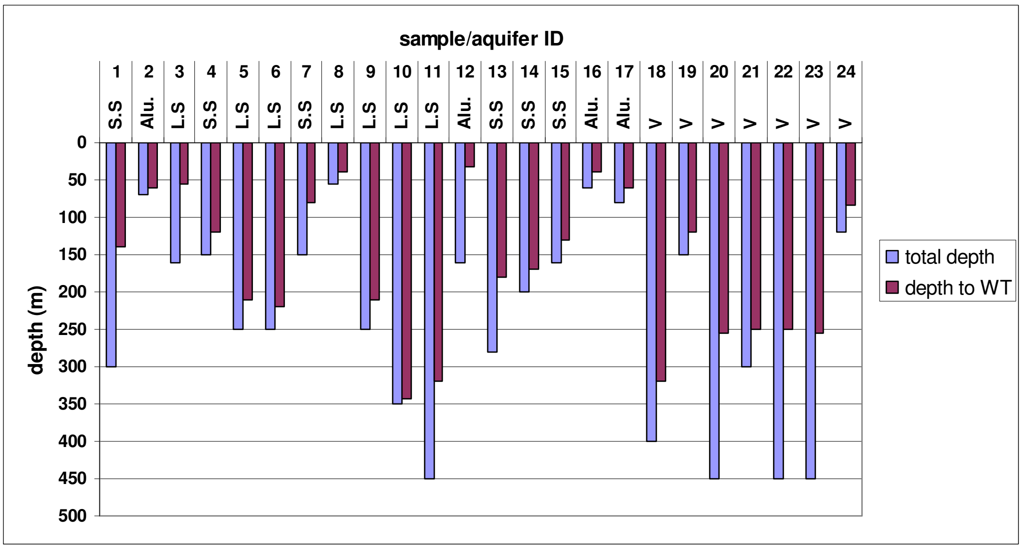

Figure 4.9: Total depth of wells vs. the depth to water table

4.2.2 Rainwater samples

A total of 255 rainwater samples were collected at 17 sites for oxygen and hydrogen stable isotopic analyses (Fig. 4.10 and 4.11). The samples were collected from May 2008 to August 2010 by local meteorological observers or representative in the rainy season. At the end of each event, air temperature, date and the time of sampling were noted on the bottles. More details on rainwater sampling sites and the sampling campaigns are given in table 8 and 9 in the appendix, respectively.

The sample bottles for Isotope analysis were prewashed with sampled water, filled almost completely to the top without bubbles, and capped tightly to protect the samples from evaporation and exchange with atmospheric water vapour. The samples were kept cold until transportation to the laboratory.

Due to the lack on more meteorological stations, rainfall amount in some stations was either estimated according to the information obtained by the contacts with the persons who collected the samples or completed from the data recorded at the nearest meteorological station; e.g. the rainfall amount for the private home-roof stations in Sana’a City (DARES and HASABAH) were completed from the data recorded at the nearest meteorological station from WEC (station: 8987). Unfortunately, no data about the rainfall amount were found for the most rainfall events.

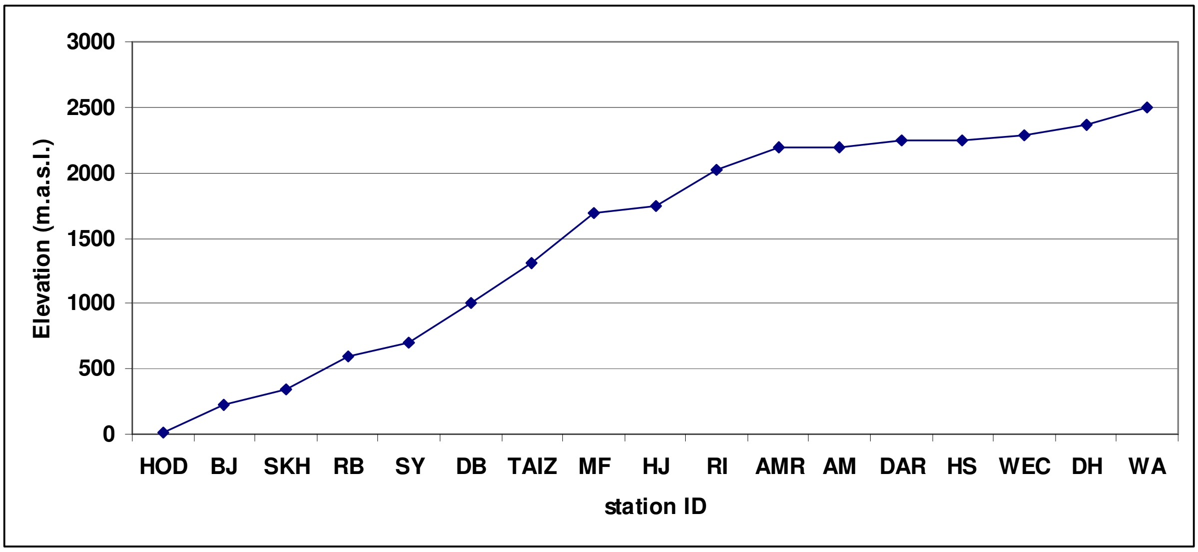

Figure 4.10: Sampling-sites vs. the elevation

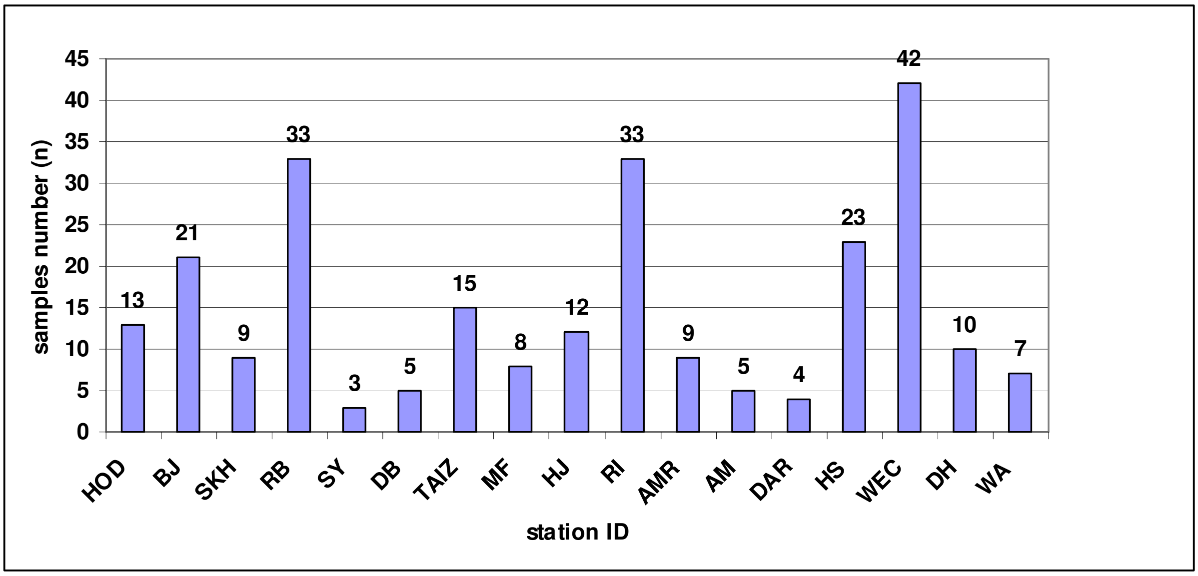

Figure 4.11: Total rainwater samples (n= 284)

4.3 Analysis

All physicochemical parameters measured in the field and laboratory are summarized in figure 4.12

4.3.1 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. Determination of hydrogencarbonate was carried out with a quick test in the laboratory of WEC in Sana'a within few hours after sampling. No physicochemical parameters for rainwater samples were measured in the field.

4-3-2 Laboratory analysis

The laboratory analysis comprises determination of major cations (Na^+ , K^+ , Ca^{2+} , Mg^{2+}), anions (Cl^- , SO_4^{2-}, NO_3^- , Br^-), selected heavy metals (As, Pb, Cu, Ni, Co, Fe, Mn, Al, Zn) and stable isotopes of Oxygen-18 and deuterium. Precision and analytical methods are detailed in table 4.4.

4.3.2.1 Ions

Major ions (cation and anion) were analyzed in a total of 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 **K^+, Na^+ ,Ca^{2+} ,Mg^{2+}, Mn, Pb, Cu, Fe, Cd, Ni, Co, Zn, Al** were conducted by inductively coupled plasma optical emission spectrometry (ICP-OES), **Cl^- ,NO_3^- ,SO_4^{2-} ,Br^-** by Ion-chromatography (IC) and flame atomic absorption spectrometry (FIAS AAS) was used for **As**.

4.3.2.2 Stable isotopes

Oxygen-18 and deuterium isotope ratios δD and $\delta^{18}O$ were measured at the Alfred-Wegener Institute (AWI) isotope laboratory in Potsdam/Germany by Dr. H. Meyer in a Finnigan MAT mass spectrometer using the equilibrium method. Analyses were done on carbon dioxide that has equilibrated with the water sample at a constant temperature (18 ±0.01 C°). 5 ml water were added to reaction vessels, then evacuated by pumping and connected to the mass spectrometer. The precision of measurement is approximately 0.1‰ for $\delta^{18}O$ and 0.8‰ for δD. The precision in isotope measurement ranges between 0.02‰ and 0.09‰ in $\delta^{18}O$ and between 0.1‰ and 0.4‰ in δD. At the AWI laboratory, own standards were used, which were calibrated in reference to the VSMOW standard.

All oxygen and hydrogen isotopic analyses are reported in the conventional d-notation relative to the VSMOW standard in which:

$$\delta \equiv \left[\frac{R}{R_{VSMOW}} - 1\right] * 1000 \qquad \text{(eq. 4.1)}$$

where R and R_{VSMOW} represent either the $\delta^{18}O$ or the δD ratio of the sample and the Standard, respectively.

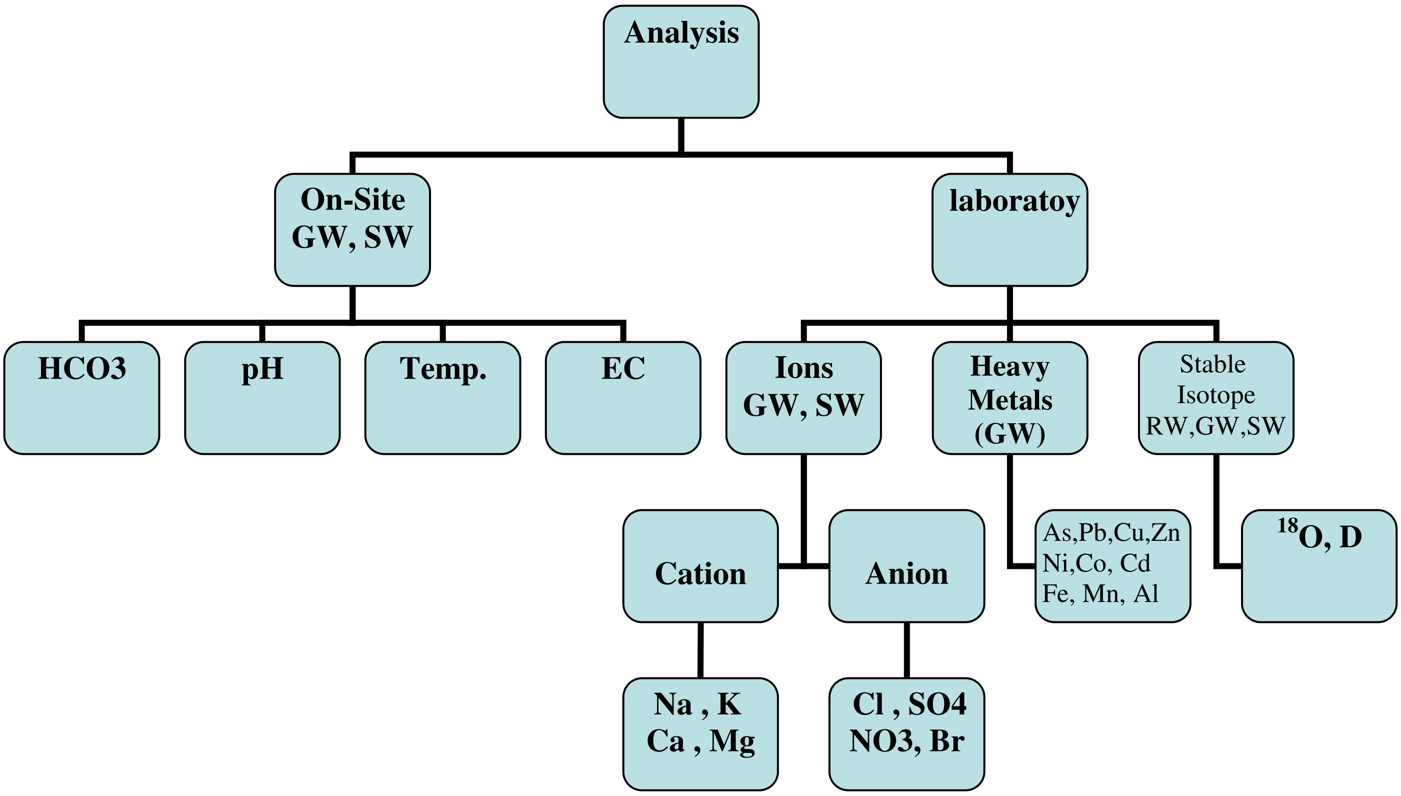

Figure 4.12: On-site and laboratory analysed parameters

Table 4.4: Detection limit and analytical methods

Parameter	Method	Type	Detection limit
K^+	ICP	Optima 2100 PerkinElmer	0,2 mg/l
Na^+	ICP		0,2mg/l
Ca^{2+} ,Mg^{2+} , Mn, Pb, Cu, Fe, Cd, Ni, Co, Zn, Al	ICP		0.02 mg/l
As	FIAS AAS	PerkimElmer	0,005 mg/l
Br^-	IC	DX 500 DIONEX	0,5 mg/l
Cl^- ,NO_3^- ,SO_4^{2-}	IC	DX 500	0,5 mg/l
$\delta^{18}O$	mass spectrometer	Finnigan MAT 253	0.1‰
δD	mass spectrometer	Finnigan MAT 253	0.8‰

5 Results and Discussion

All physicochemical parameters measured in the field and laboratory are presented in table 1 to 3 in the appendix. The results are compared with the WHO and NWRA guidelines for drinking water quality and discussed in chapter 6.1 of this study.

5.1 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 (HEM 1985). 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 (WEIGHT, 2008).

A charge balance error can be calculated by the following relationship (WEIGHT, 2008):

$$balance(\%) = \frac{\sum cations - \sum anions}{\left(\sum cations + \sum aninons\right)/2} * 100 \qquad \textbf{(eq. 5.1)}$$

The hydrochemcial analysis is given in mg/l and was transformed to mmol/l to calculate the balance in % according to equation 5.1. Water analyses are normally considered acceptable if the charge balance error is within ±5% using the equation 5.1. If the charge balance is outside 5%, it can mean one of the several things (WEIGHT, 2008):

- problems with the field measurements (e.g., alkalinity),
- problems with lab analyses,
- incorrect assignment of the charge for one or more of the major solutes,
- The list of compounds that were analysed was incomplete.

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. Only water samples with an error of less than ±5% were considered. According to figure 5.1, only one sample (GW-12) was discarded for these reasons. Because of the minor error of this sample (-5.84%), the sample was considered in evolution.

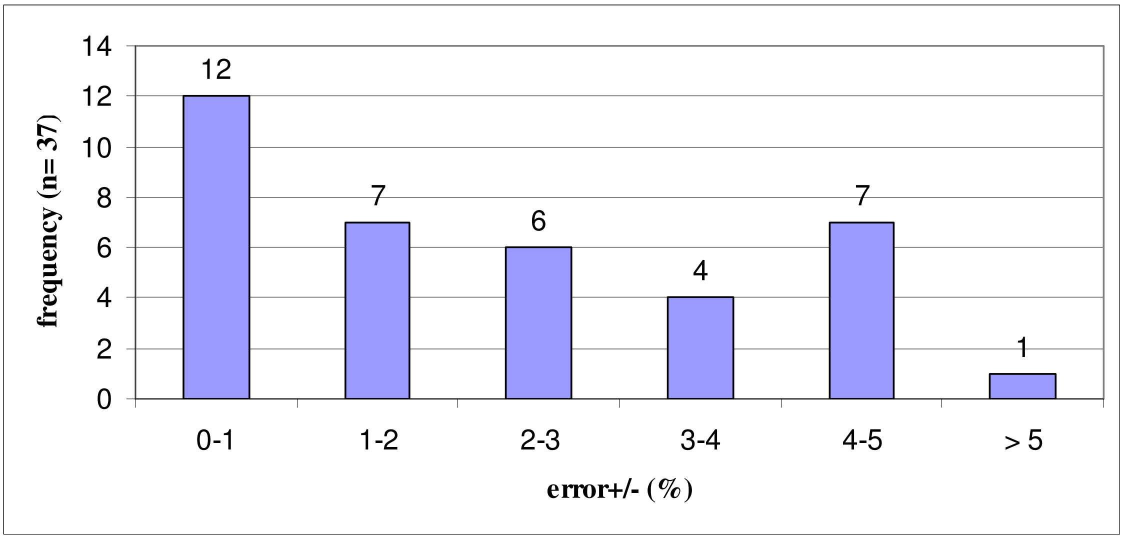

Figure 5.1: Electrical balances vs. frequency of measured samples

5.2 Physicochemical parameters

Physicochemical parameters, which include water temperature, pH and the EC, were measured in ground- and spring water samples taken from Sana'a basin.

5.2.1 Water Temperature

The measurement of water temperature is very important because the most of the physical and chemical properties of the water such as the density, pH and the mass are temperature-dependent, as is the solubility of all substances. The TDS concentration of groundwater increases with temperature. Higher temperatures not only have a negative influence on the palatability of water, but also they increase the solubility of any harmful substances in the water and accelerate the growth of microorganisms, while the oxygen content of the water is lowered (WHO, 2004). Consequently the temperature of drinking water should be low.

In this study, the temperature of the groundwater samples and spring water was measured on site during water pumping/sampling. Spring water temperatures were measured directly in the spring.

In general, 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 (SAWAS, 1996). 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 (WEC, 2004). 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.

Figure 5.2 shows the relationship between the water temperature and the total depth of the wells.

Table 5.1 shows that 33% of the total samples, mainly from dug and shallow wells, shows 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 (WEC, 2004).

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

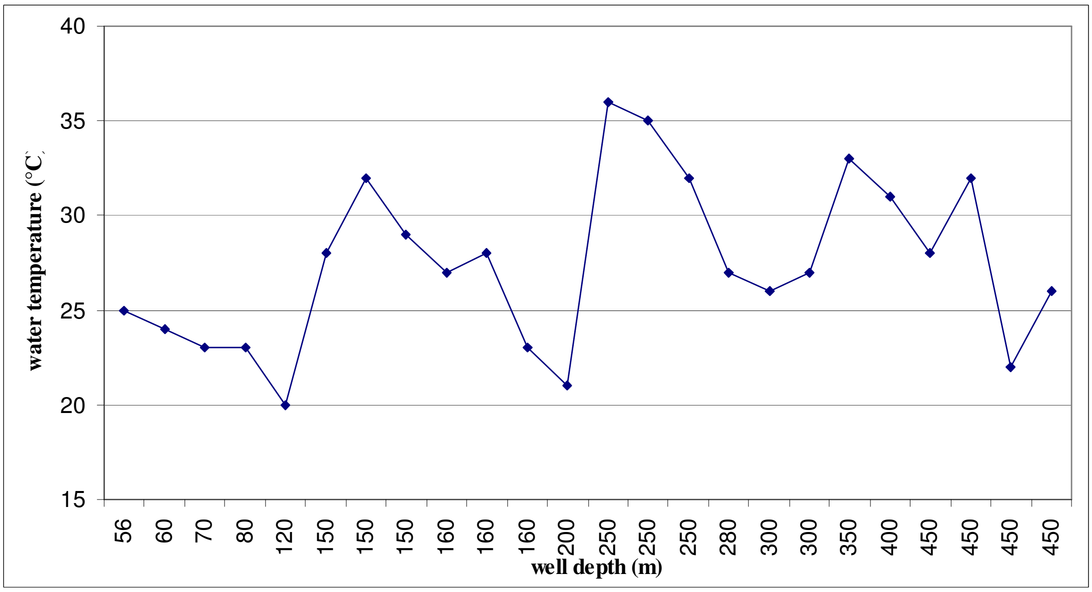

Figure 5.2: Water temperature and total depth of the wells

Table 5.1: Summarized temperature of groundwater samples

Aquifer type	20-25 °C	26-30 °C	31-36 °C	Total
sandstone	2	3	1	6
limestone	1	2	4	7
alluvium	3	1	0	4
volcanic	2	3	2	7
Total samples	8	9	7	24
Total in %	33%	37%	29%	100%

5.2.2 pH-values

The pH of water is a measure of the acidity/alkalinity of the water and is measured as the negative common logarithm of the hydrogen ion activity:

$$\mathbf{pH = -\log (H+)} \qquad \textbf{(eq. 5.2)}$$

The hydrogen ion is very small and is able to enter and disrupt mineral structures so that a low pH contributes to dissolving constituents in water. The greater the H+ availability, i.e., the lower the pH, the more acidic is the water and the higher the TDS in the water. The pH of pure water at 25°C water temperature is 7 and considered neutral. A pH less than 7 is acidic and a pH greater than 7 means the water is alkaline. Natural rainwater is slightly acidic (KRAUSKOPF, 1994) because it is combined with carbon dioxide (CO_2) in the atmosphere, forming carbonic acid (H_2CO_3) according to reaction (1). Most groundwater has pH values between 5.0 and 8.0

$$\mathbf{H_2O + CO_2 \rightarrow H_2CO_3} \qquad \textbf{(1)}$$

Some of the carbonic acid in the rainwater disassociates or breaks down according to reaction (2), producing hydrogenbicarbonate (HCO_3-) and H^+.

$$\mathbf{H_2CO_3 \rightarrow HCO_3^- + H^+} \qquad \textbf{(2)}$$

The hydrogen ion produced by reaction (2) lowers the pH of rainwater. How far it lowers it from the neutral value of 7 depends on how much carbonic acid is in the water, which in turn depends on how much carbon dioxide is in the atmosphere. The more CO_2 present, the more acidic is the water (WEIGHT, 2008).

pH-values above 8.0 are usually associated with sodium-carbonate-bicarbonate waters. Moderately high pH values are commonly associated with waters high in bicarbonate, and the very low pH values (below 4.0) are associated with water containing free acids derived from oxidizing sulfide minerals or from water in contact with volcanic gases containing hydrogen sulfide, hydrochloric acid, and other volatiles (DAVIS S.N., 1966).

In this study 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 (Fig. 5.3). 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 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 (SAWAS, 1996). Figure 5.4 shows that the pH is function of HCO_3.

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 Sana'a City with 6.3, 6.3 and 5.6 respectively.

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, tables 5.2 and 5.3). 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 (see chapter 4.1). The values in SW-3 and SW-10 exceeded the WHO value with values of 6 and 9.4, respectively.

Table 5.2: Summarized pH of groundwater samples

Aquifer type	< 7	7-8	> 8	Total
Sandstone	1	5	0	6
Limestone	2	5	0	7
Alluvium	0	1	3	4
Volcanic	0	2	5	7
Total samples	3	13	8	24
Total in %	13%	54%	33%	100%

Table 5.3: Summarized pH of spring water samples

Aquifer type	< 7	7-8	>8	Total
Volcanic	0	2	3	5
Limestone	0	1	0	1
Sandstone	2	1	1	4
Alluvium contact with Sandstone	0	1	1	2
Volcanic contact with Alluvium	0	1	0	1
Total	2	6	5	13

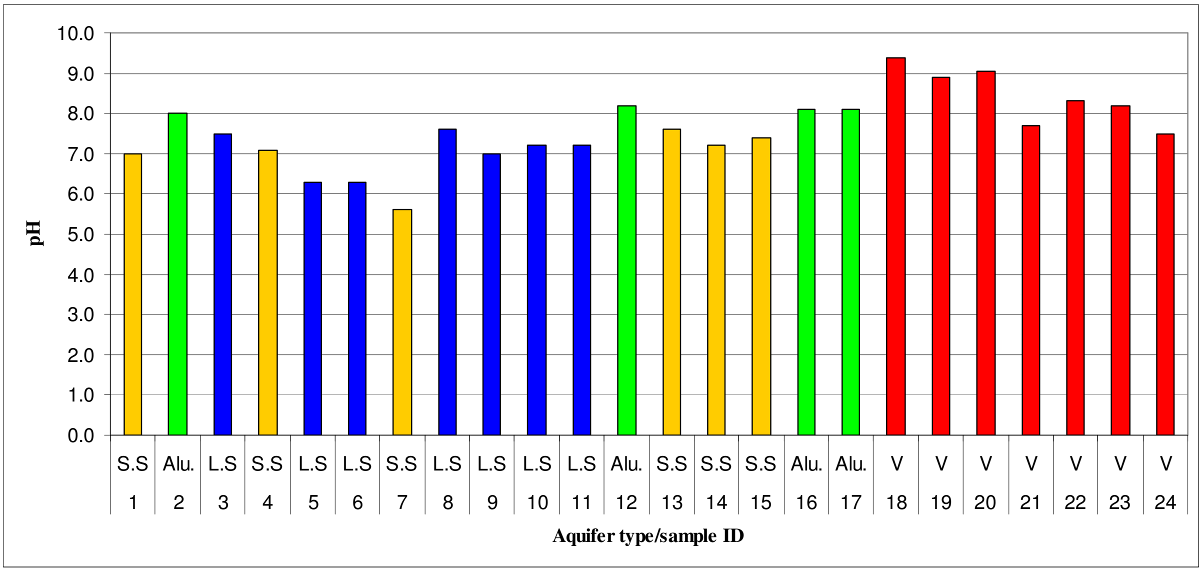

Figure 5.3: pH of groundwater samples

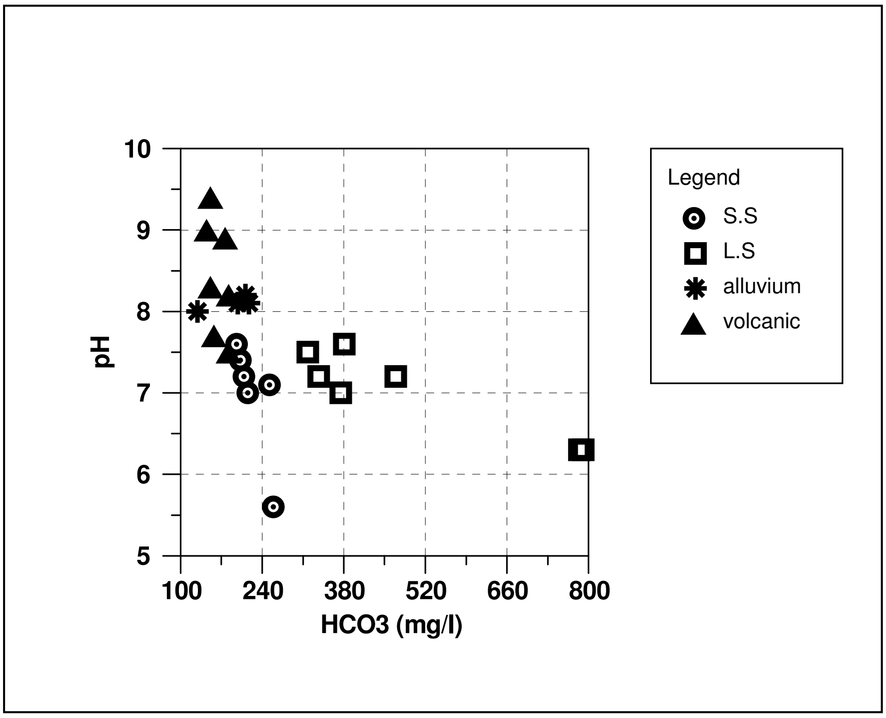

Figure 5.4: Scatter plot pH vs. HCO_3 of the groundwater samples

5.2.3 TDS and electrical conductivity (EC)

Electrical conductivity is a useful tool to evaluate the purity of water. The total mass of dissolved constituents is referred to as the total dissolved solids (TDS) concentration. In water, all dissolved solids are either positively charged ions (cations) or negatively charged ions (anions). In neutral water, the total negative charge of the anions always equals the total positive charge of the cations. A higher TDS means that there are more cations and anions in the water. With more ions in the water, the water's electrical conductivity (EC) increases. By measuring the water's EC, we can therefore indirectly determine its TDS concentration. At a high TDS concentration, water becomes saline. Water with a TDS above 1000 mg/l is not recommended for use as drinking water (WHO, 2004).

In the current study, EC was measured in µS/cm in the field during water sampling at 24 groundwater points and 13 springs. TDS was calculated in mg/l using the equation:

$$\mathbf{TDS = 0.65 * EC} \qquad \textbf{(eq. 5.3)}$$

The EC and TDS of the water is a function of temperature (Fig. 5.5). The higher the temperature the higher the dissolved minerals, consequently higher EC; this is the reason why the groundwater has higher EC than the spring water. Figure 5.6 shows that TDS is a function of EC, the higher EC the higher TDS in the groundwater.

Additional factors controlling the water mineralization in the study area are presented in figures 5.7 to 5.10. It can be observed that the TDS of groundwater in the Sana'a basin is affected mainly by the concentration of the major cations Mg and Ca and major anions HCO_3 and SO_4. The TDS of the spring water samples is affected by the cations Mg, Ca and Na and the anions HCO_3, SO_4 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 µS/cm at 25°C in the groundwater samples, while the springs show lower values ranging between 620 and 230 µS/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 (Davis, 1966). 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 µS/cm. The dominant water-type in this aquifer is Ca-HCO3-SO4 and Ca-HCO3. The highest EC-values were recorded in north-eastern part of the basin in the limestone aquifer with values ranging between 2030 and 560 µS/cm as a result of the dissolution of calcite, dolomite and gypsum, which are presented in Amran limestone (Fig. 5.11). According to SAWAS, 1996 the higher EC- values in the northern part indicate sewage infiltration in this part.

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

The results are summarized in table 5.4

Table 5.4: EC of groundwater samples in µS/cm

Aquifer type	**< 500**	**500-1000**	**1000-2000**	**>2000**	**Total**
Sandstone	3	2	1	0	6
Limestone	0	1	5	1	7
Alluvium	1	2	1	0	4
Volcanic	7	0	0	0	7
Total samples	11	5	7	1	24
Total in %	46%	21%	29%	4%	100%

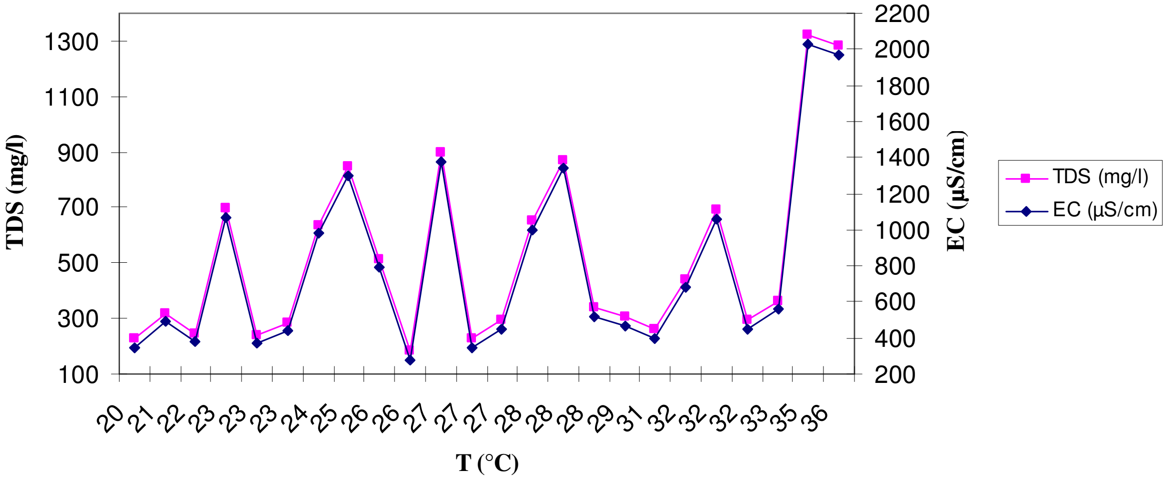

Figure 5.5: Water temperature vs. EC and TDS of the groundwater samples

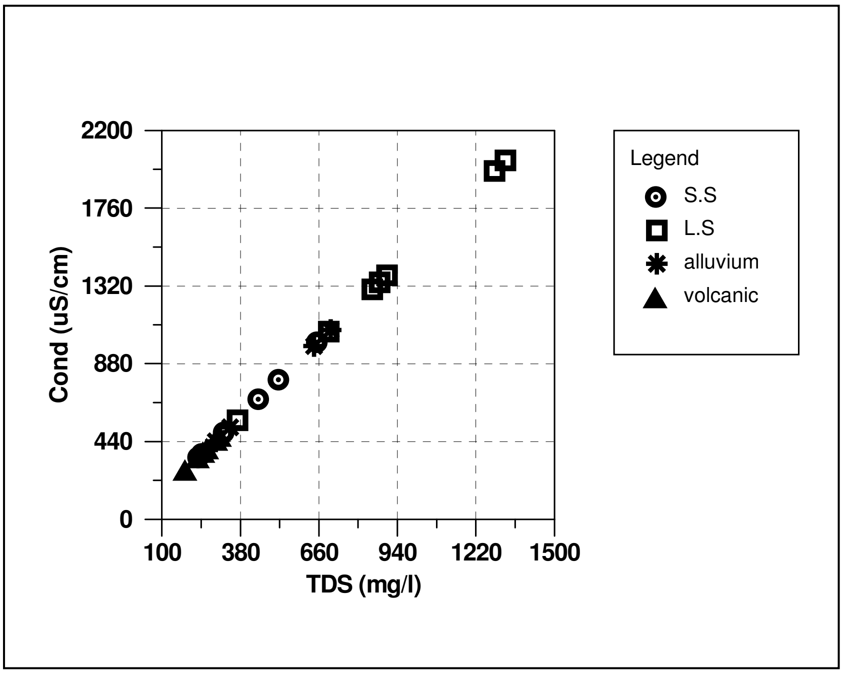

Figure 5.6: Scatter plot EC vs. TDS of the groundwater samples

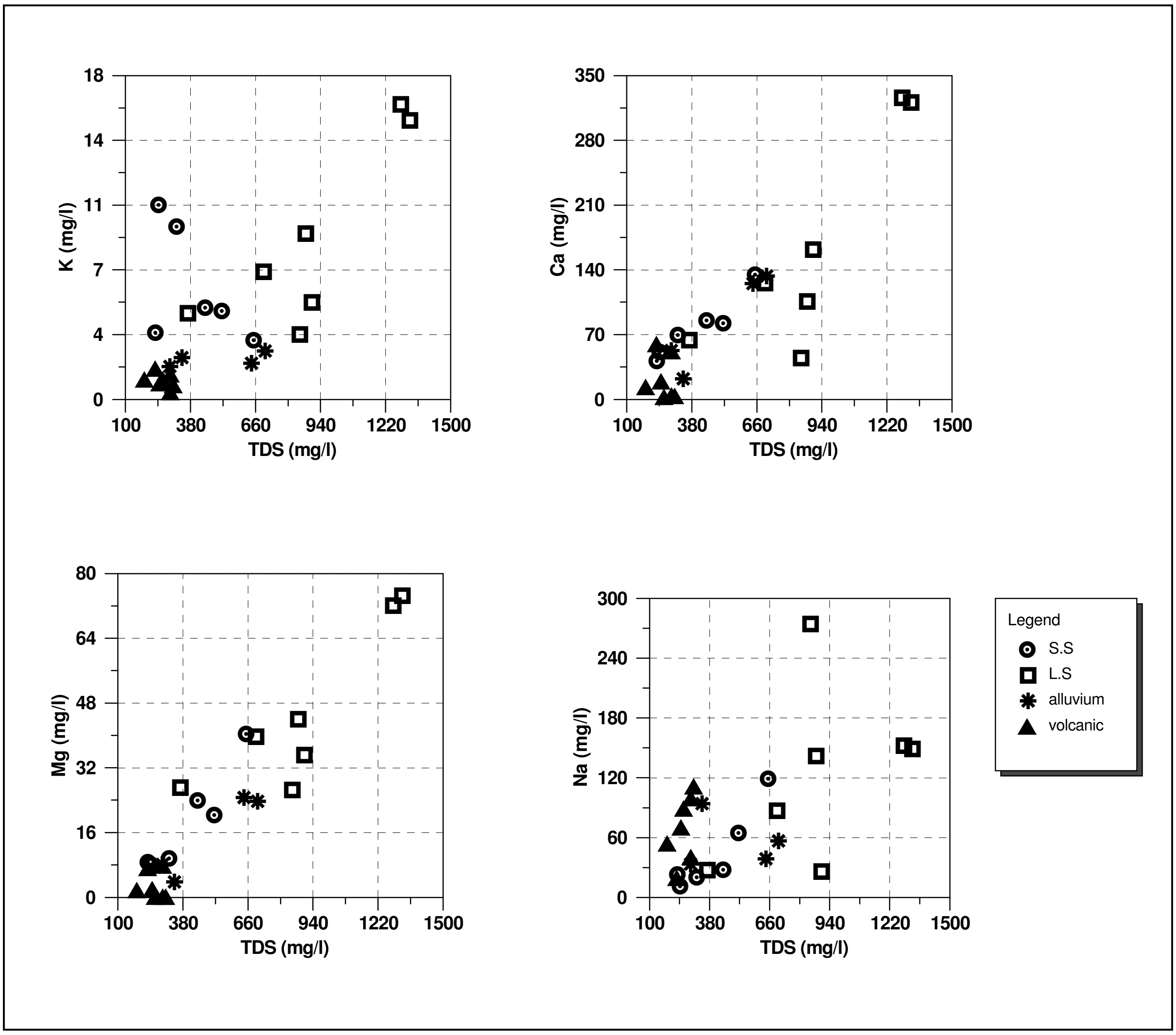

Figure 5.7: Scatter plot TDS vs. major cations in the groundwater samples

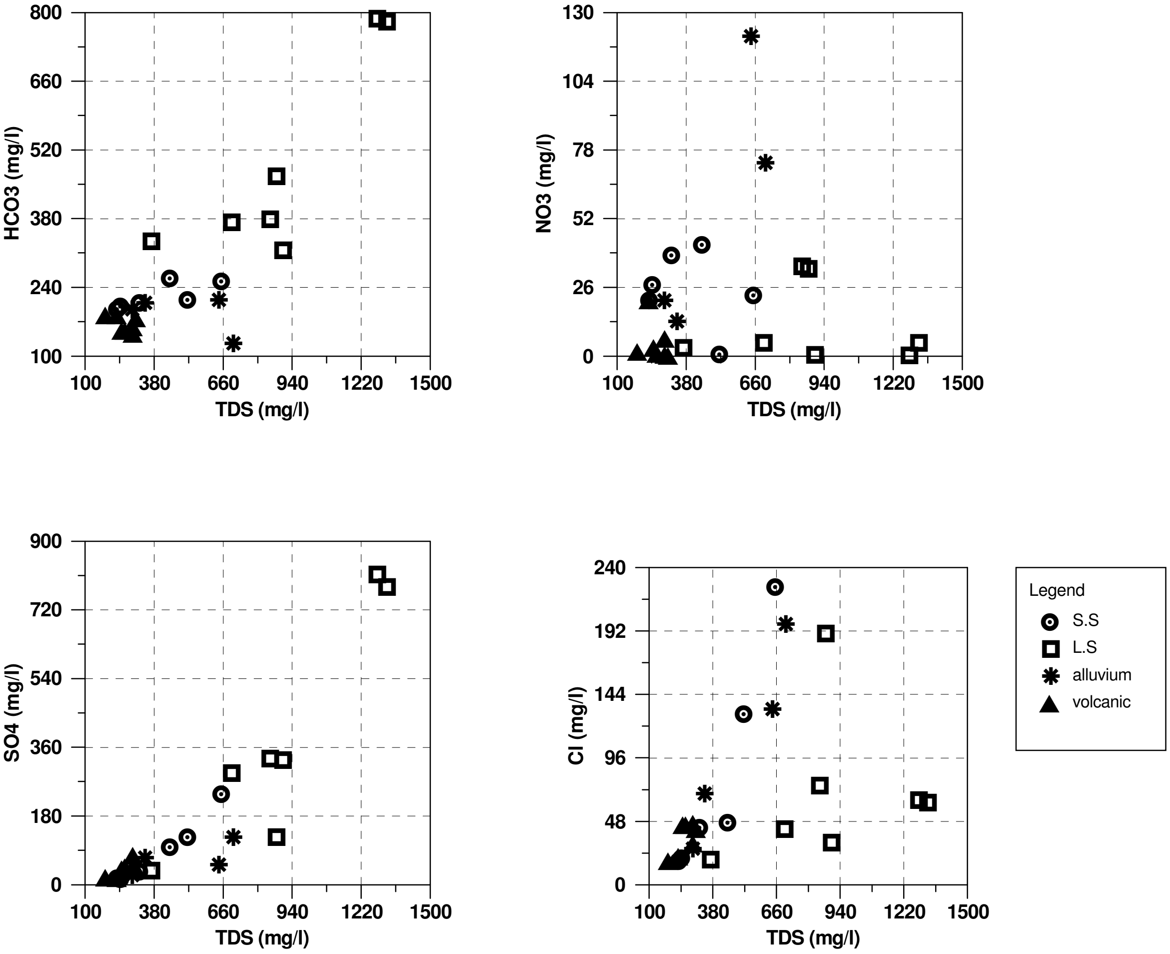

Figure 5.8: Scatter plot TDS vs. major anion in the groundwater samples

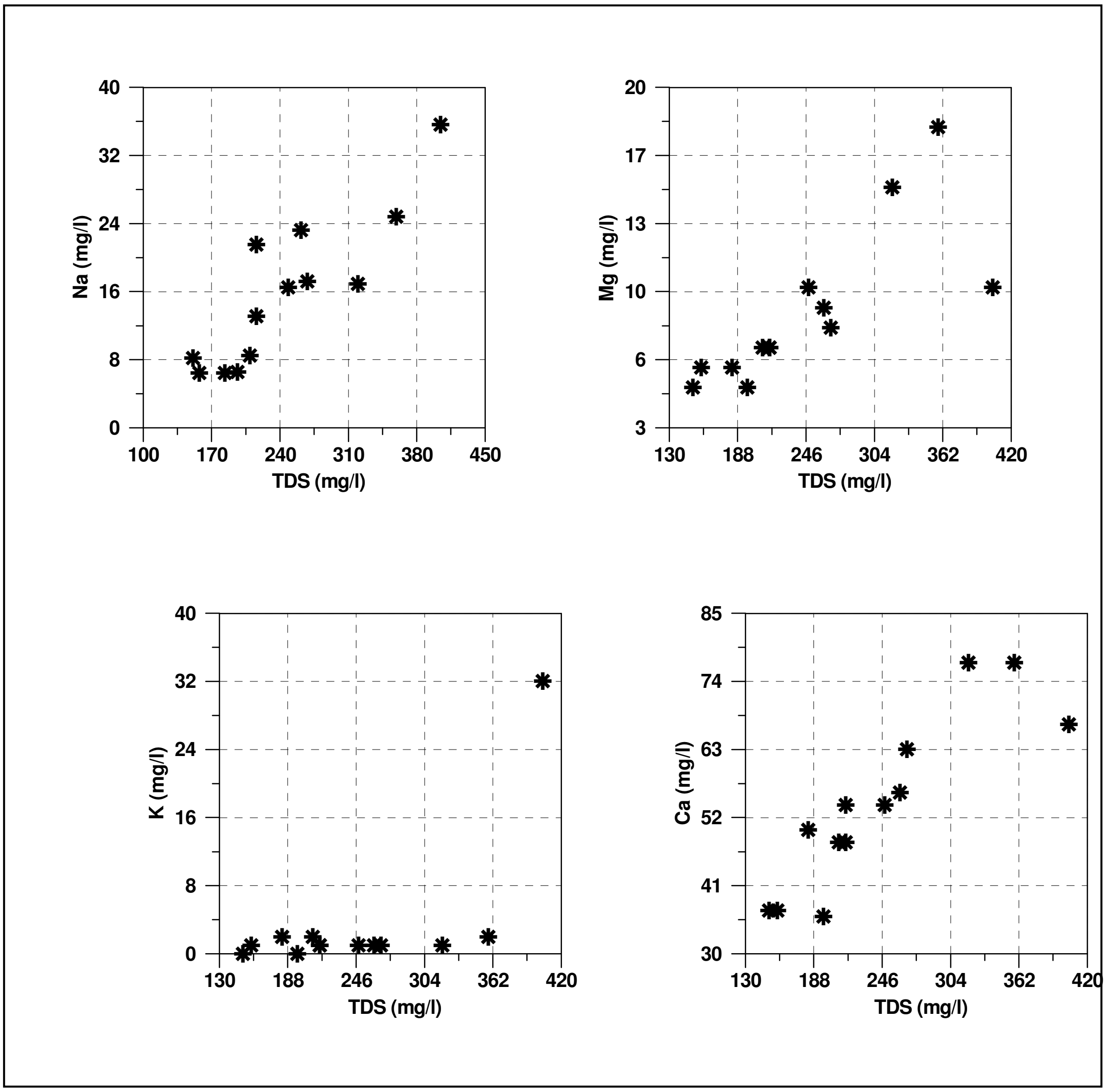

Figure 5.9: Scatter plot TDS vs. major cation in the spring water samples

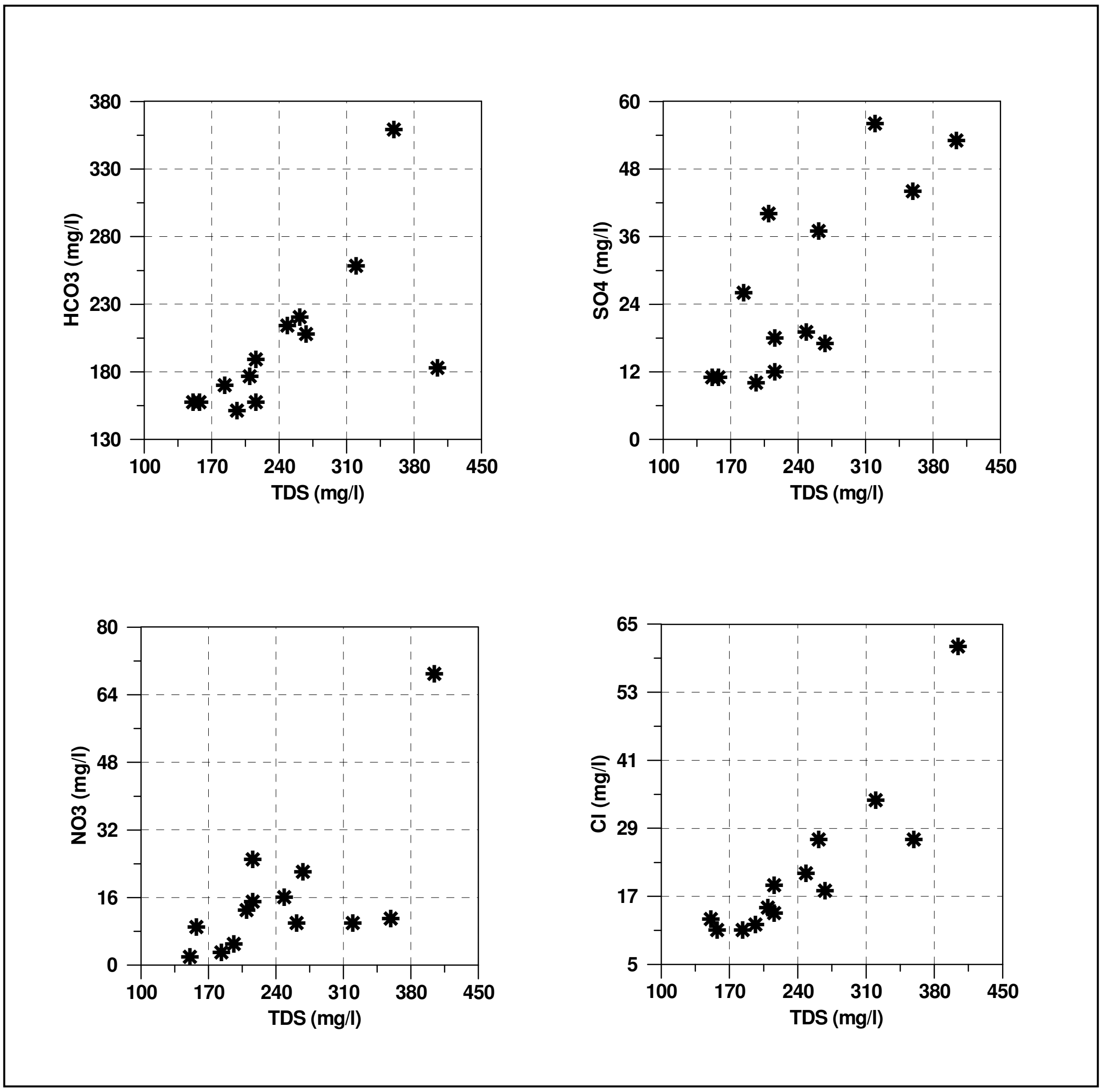

Figure 5.10: TDS vs. major anions in spring water samples

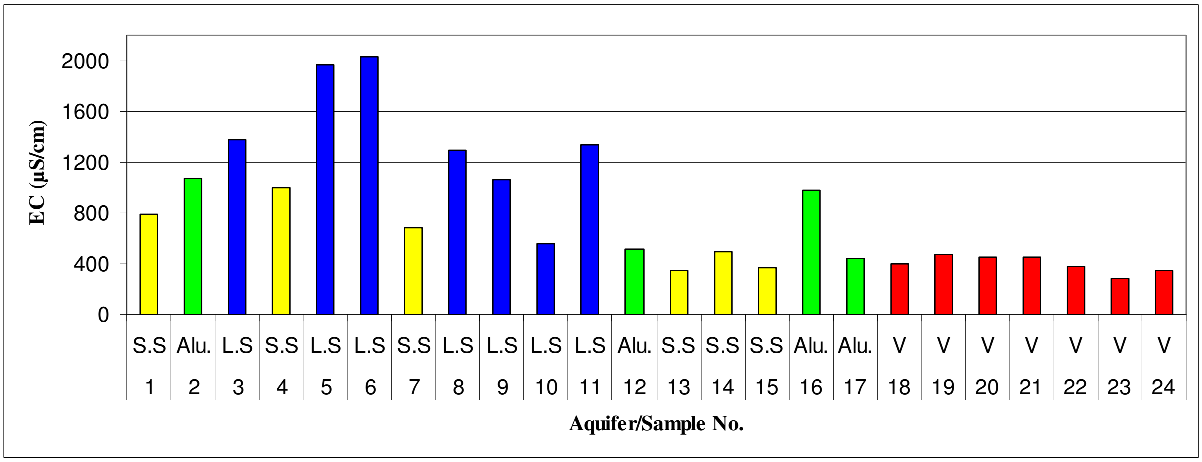

Figure 5.11: EC of groundwater samples

5.3 Chemical composition

5.3.1 Major ions

Concentration of major cations (sodium, potassium, calcium and magnesium) and major anion (chloride, hydrogencarbonate, sulphate, bromate and nitrate) were measured in a total of 37 ground- and spring water samples. The results of the labor analyses are presented in tables 1 and 2 in the appendix.

Calcium, magnesium, sulphate, hydrogencarbonate, potassium and sodium show the highest concentrations 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 Mg and Ca ranges from 0.18 to 75.5 mg/l and 2.9 to 326 mg/l. Sulphate and hydrogencarbonate show the highest concentrations in sample GW-5 with 812 and 787.5 mg/l; the lowest value of SO_4 is 14 mg/l in sample GW-15 in the western part in the sandstone aquifer, and 126 mg/l for HCO_3 in sample GW-2 southern part in the alluvium aquifer.

The high concentration of Mg, Ca and HCO_3 ions in groundwater can be explained by the solution of calcite, dolomite and gypsum which are all present in the Amran limestone group. Sulphate ion concentrations are probably derived from weathering of sulfate and gypsum-bearing sedimentary rocks of the Amran group.

Generally sodium, unlike Mg and Ca, is not found as an essential constituent of many of the common rock-forming minerals. Sodium 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 sandstone aquifer. Potassium concentration of groundwater samples in the study area range between 0.4 mg/l in sample GW-20 southern part in the volcanic aquifer to 16.4 mg/l in the northern part in limestone aquifer. This reflects the natural ratio with sodium of less than one tenth the concentrations (DAVIS, 1966).

Nitrate was presents in all spring and groundwater samples. This might originate from human activity or from minor NH_3 gas emissions from volcanic activity into the groundwater system where it is oxidized to NO_3 (SAWAS, 1996 , FOPPEN, 2002).

The highest nitrate and chloride concentrations were measured in samples GW-16 with 121 mg/l in the central part of 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 NH_4 to NO_3 (FOPPEN, 2002) is dominated by a high population density and lacks a sewer system.

Concentrations of Bromate were compared with EU- guidelines for drink water and were classified as high, exceeding the EU-standard (0.01 mg/l) in all of groundwater and spring water samples. The highest value with 2.5 mg/l was found in sample GW-4 in the northern part and the lowest concentration recorded with 0.3 mg/l in samples GW-13, GW-14 and GW-15 in the sandstone aquifer in the west, and samples GW-23 and GW-24 in the volcanic aquifer in the south.

Figures 5.12 and 5.13 show the distribution of the ions concentration in all of 24 groundwater samples. The averages concentrations of the various ions for each aquifer are shown in figures 5.14 to 5.17.

The spring waters generally show 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 18C°. The low solubility associated with these temperatures, in combination with short flow paths and residence times affects the concentrations in this area.

Figures 5.18 and 5.19 plot the relationship between the aquifer type and the major cations and anions concentrations in spring water; the average concentrations are shown in figures 5.20 to 5.23. The variations in the ion concentrations are not significant. Hydrogencarbonate and calcium are the most dominate ions in all of the spring water samples.

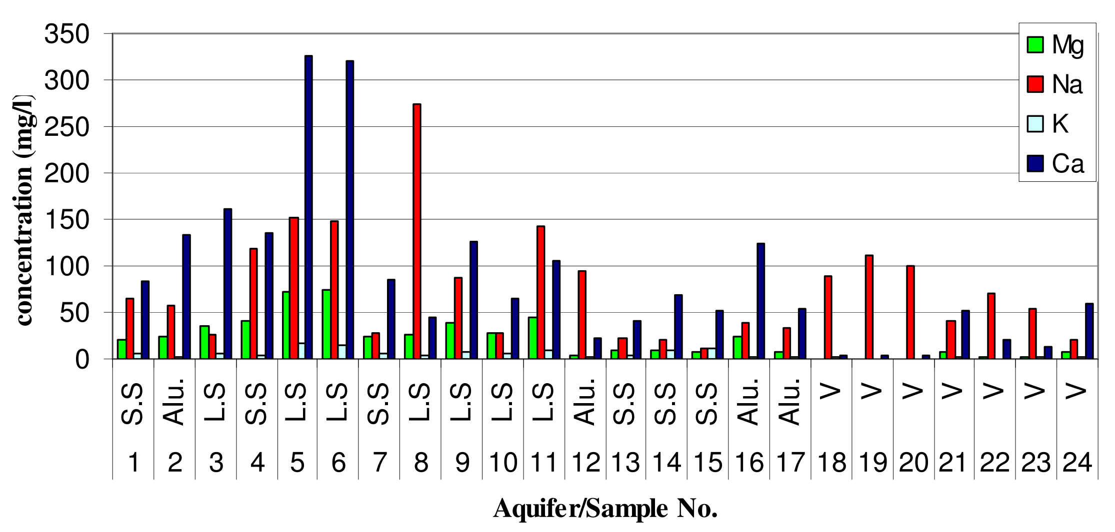

Figure 5.12: Major cations in the groundwater samples

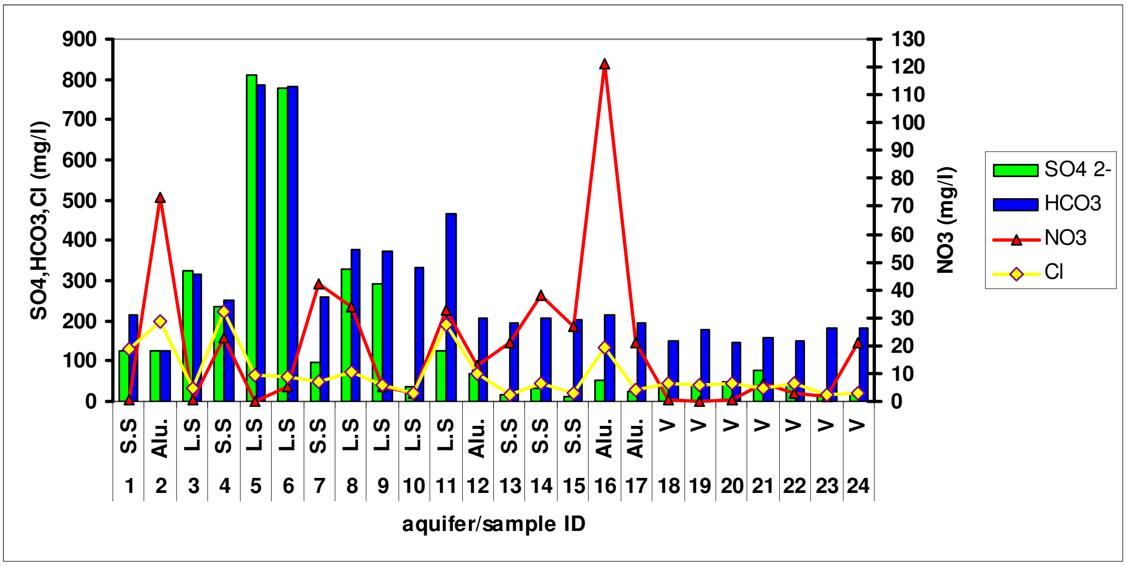

Figure 5.13: Major anions in the groundwater samples

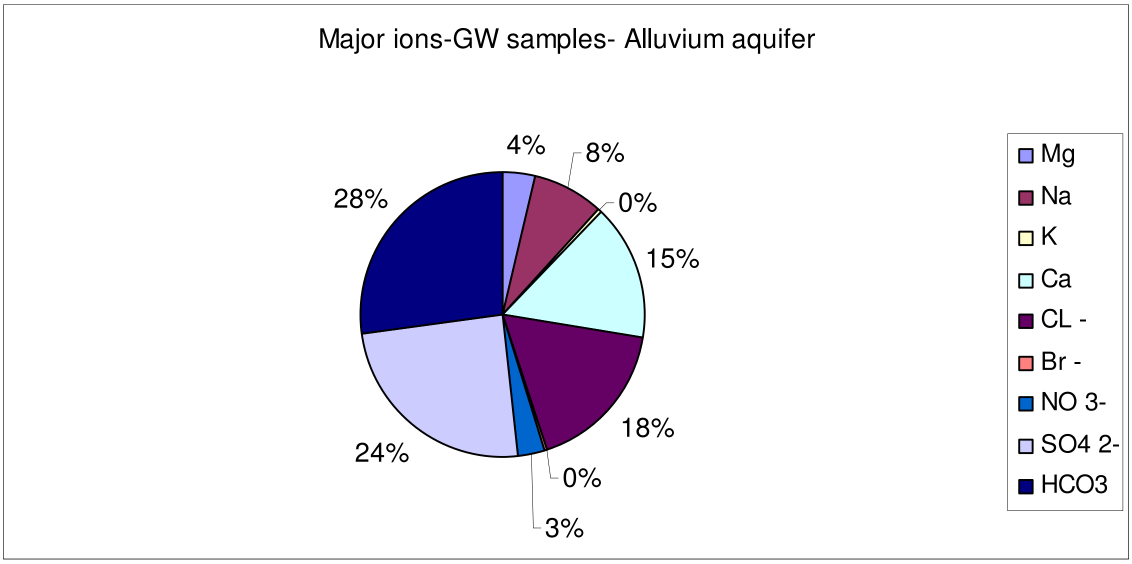

Figure 5.14: Average major ions in groundwater samples in the Alluvium aquifer

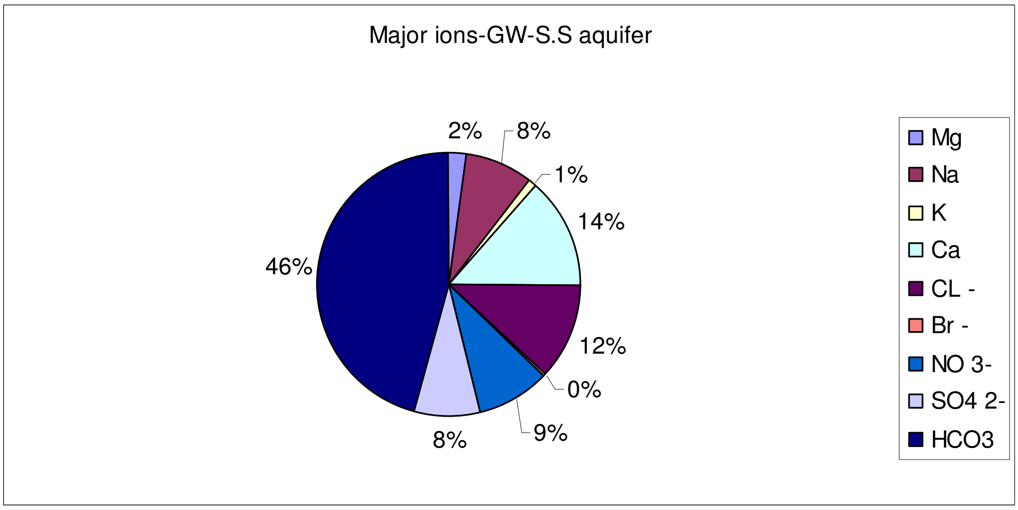

Figure 5.15: Average major ions in groundwater samples in the Sandstone aquifer

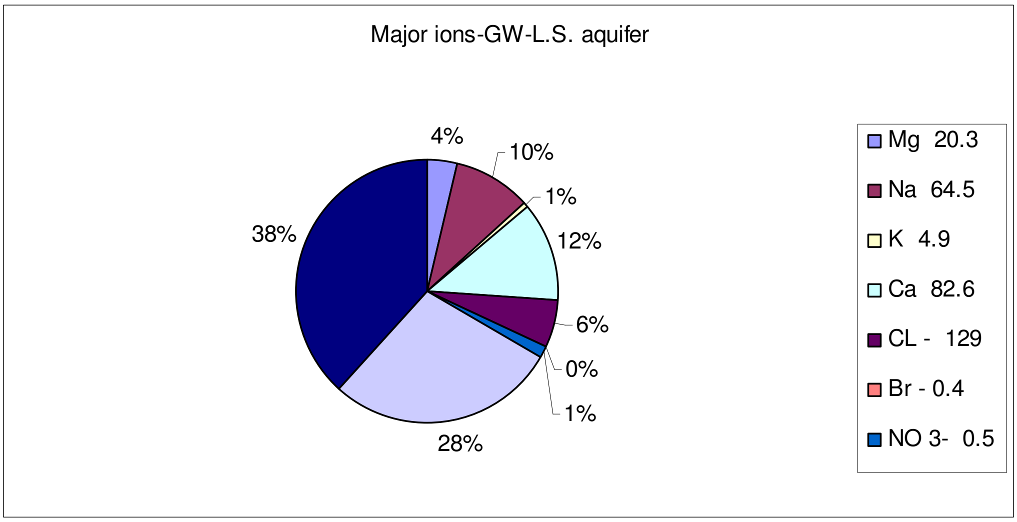

Figure 5.16: Average major ions in groundwater samples in the Limestone aquifer

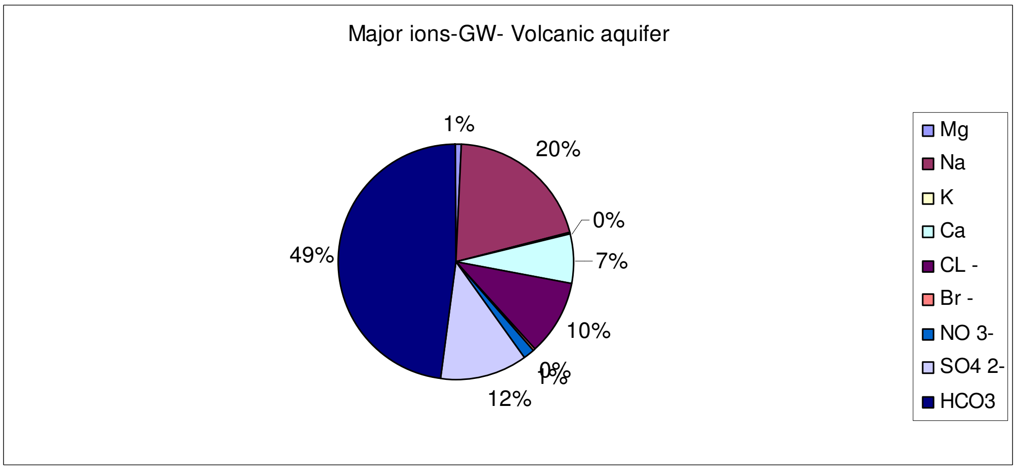

Figure 5.17: Average major ions in the groundwater samples in the Volcanic aquifer

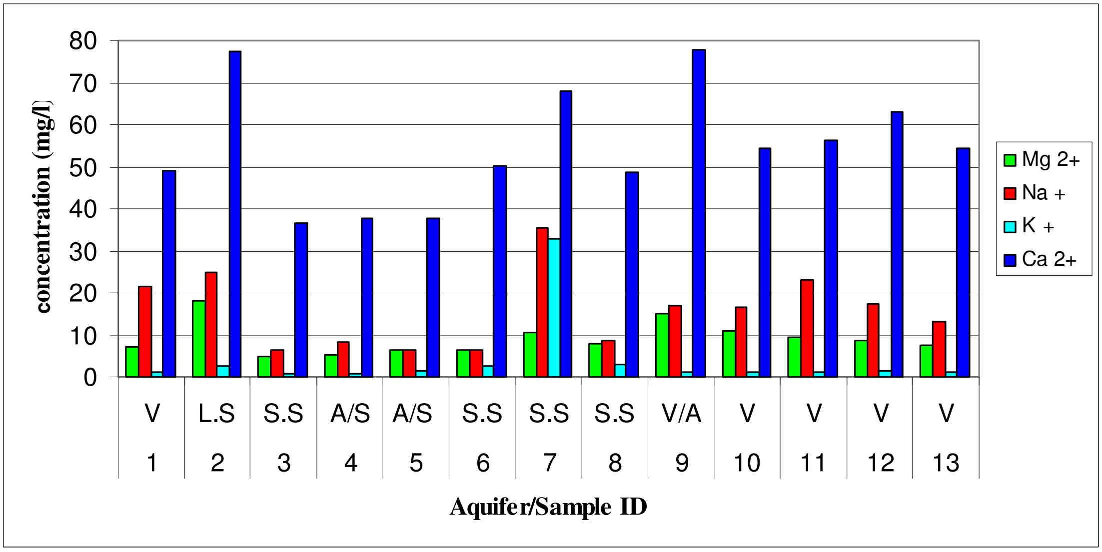

Figure 5.18: Major cations in spring water samples

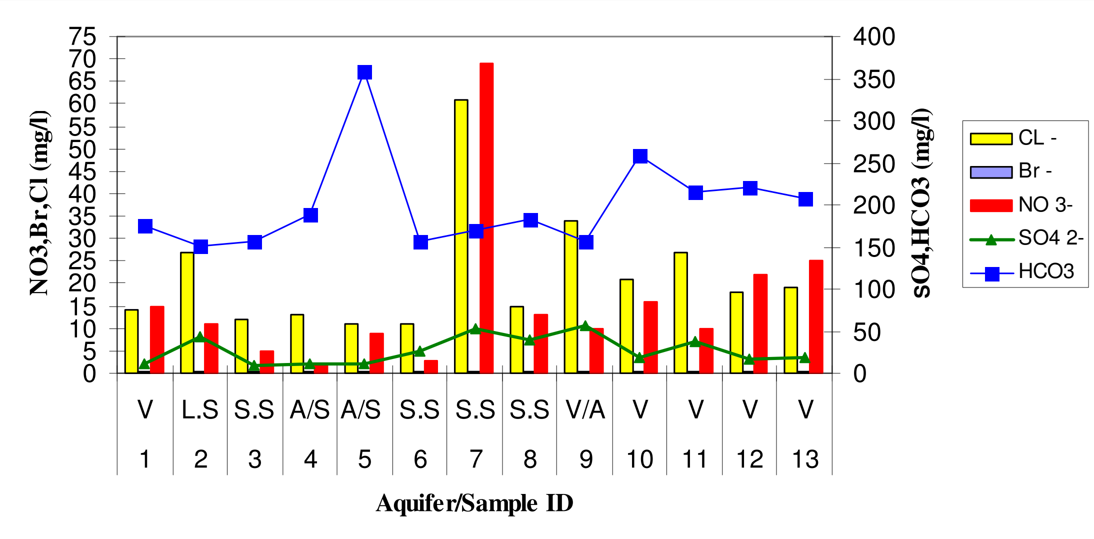

Figure 5.19: Major anions in spring water samples

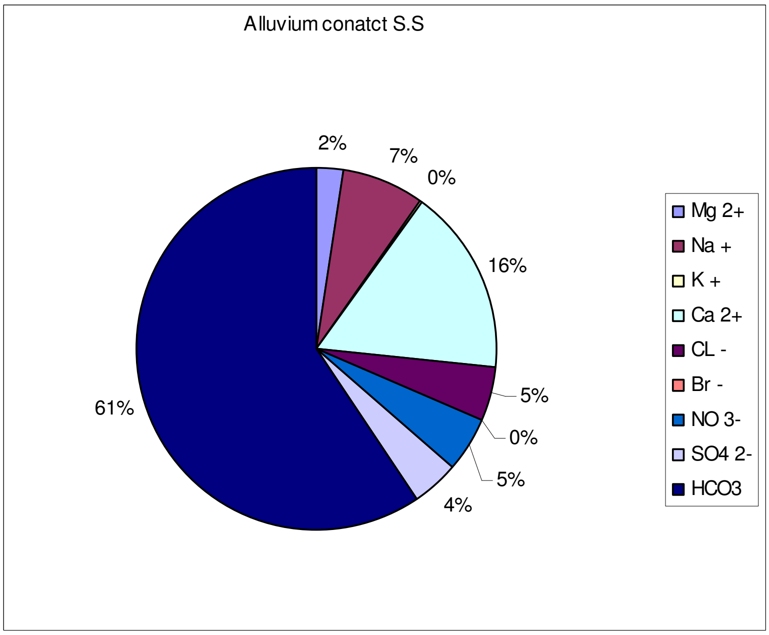

Figure 5.20: Average major ions in the spring water samples (Allu./S.S)

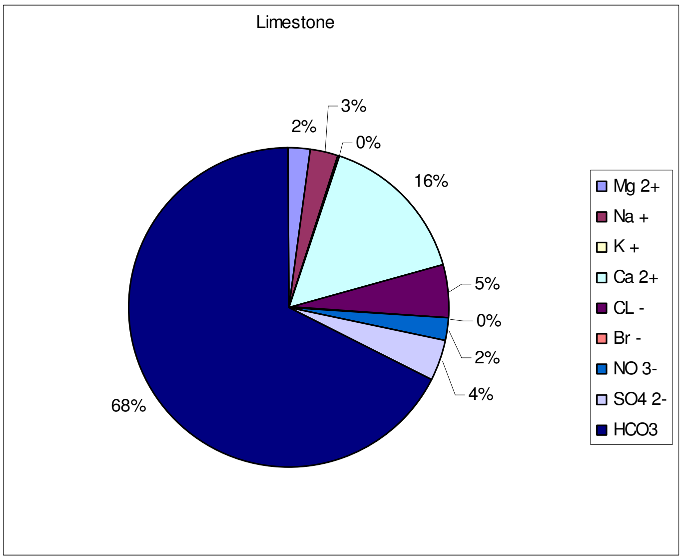

Figure 5.21: Average major ions in the spring water samples in the Limestone aquifer

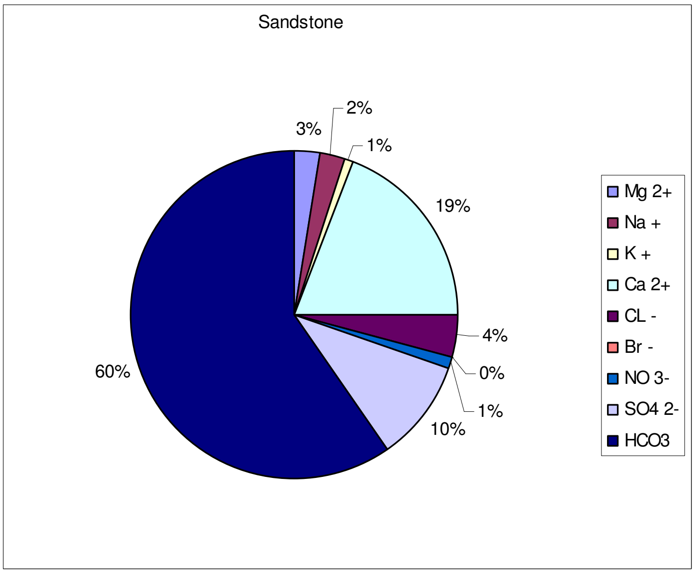

Figure 5.22: Average major ions in the spring water samples in the Sandstone aquifer

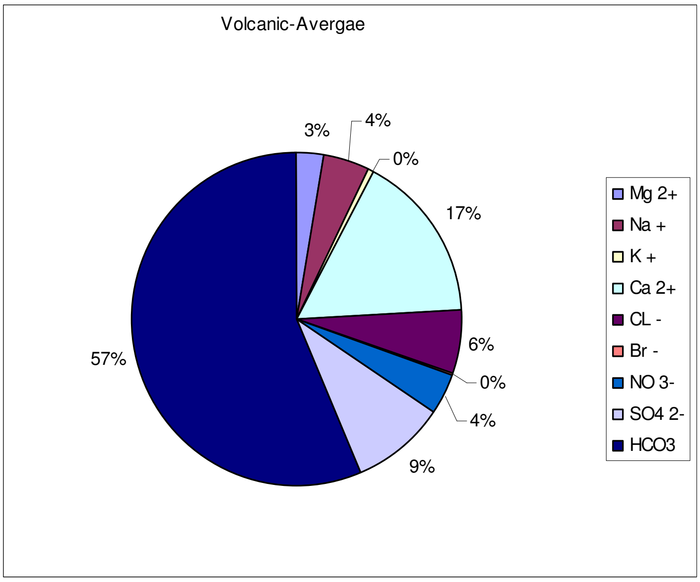

Figure 5.23**:** Average major ions in the spring water samples in the Volcanic aquifer

5.3.2 Heavy metals

Selected heavy metals (As, Pb, Cu, Ni, Co, Cd, Fe, Mn, Al, Zn) were analyzed in groundwater samples taken from Sana'a basin. No analyses were conducted in the spring water samples.

5.3.2.1 What are heavy metals?

Metals with a density higher than 5g/cm^3 are known as heavy metals. Heavy metals occur in waters in dissolved and in chemically-bound form. They come from natural and anthropogenic sources. The weathering and erosion of minerals is one of the major natural sources and occur in the groundwater in different concentrations when the water solved the minerals of the bearing rocks.

Heavy metals reach the groundwater through the infiltration of contaminated surface water or when rainwater washes contaminated soils and infiltrated in the underground. Human activities, which include the industrial and the application of fertilizers and pesticides in agriculture areas (such as in Sana'a basin), are thought to be the major anthropogenic contamination sources.

As trace elements, some heavy metals (e.g. copper and zinc) are essential in low concentration for all living organisms while most of them present toxicity hazard at high concentration to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metal poisoning could result, for instance, from drinking-water contamination, high ambient air concentrations near emission sources, or intake via the food chain (WHO, 2004).

5.3.2.2 Heavy metals in groundwater of Sana'a basin

The main objective of this section is to evaluate the impacts of urbanization on groundwater in terms of heavy metal and trace element contaminations. Groundwater samples are assumed to be free from any anthropogenic contaminations and thus they could be used to evaluate the degree of heavy metal and trace element contaminations in the urbanized areas. The results of our analysis of heavy metal concentrations in groundwater samples collected from Sana'a basin are summarized in table 3 in the appendix and shown in figures 5.24. The measured values show that the concentration of the heavy metals (Pb, Cu, Ni, Co, Cd) in all 24 groundwater samples are below the detection limit (detected limits are presented in table 4.5). 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 (Al-HAMDI, 2000) and later in the groundwater. The heavy metals As, Mn, Al and Zn were found in low concentration in some of the samples with values exceeded neither the values recommended by WHO, 2004 nor by NWRA, 2000 (except for one Al value) (Fig. 5.24).

Iron is the most concentrated heavy metal. It was found in 21 out of 24 samples in high concentration; however, the measured values were not exceed the value recommended by NWRA, 2000 (1 mg/l). The highest concentrations was found in the limestone aquifer in samples GW-5 with 1mg/l, and the lowest measured value in sample GW-7 and GW-9 with 0.03 in the sandstone and limestone aquifer, respectively.

The low concentration of the heavy metals As, Mn, Al, Zn and higher Fe in the groundwater in the study area seems natural, however, the relative high concentration of e.g. zinc and Al in some samples points towards to anthropogenic effects such as the application of fertilizers and pesticides in agriculture areas.

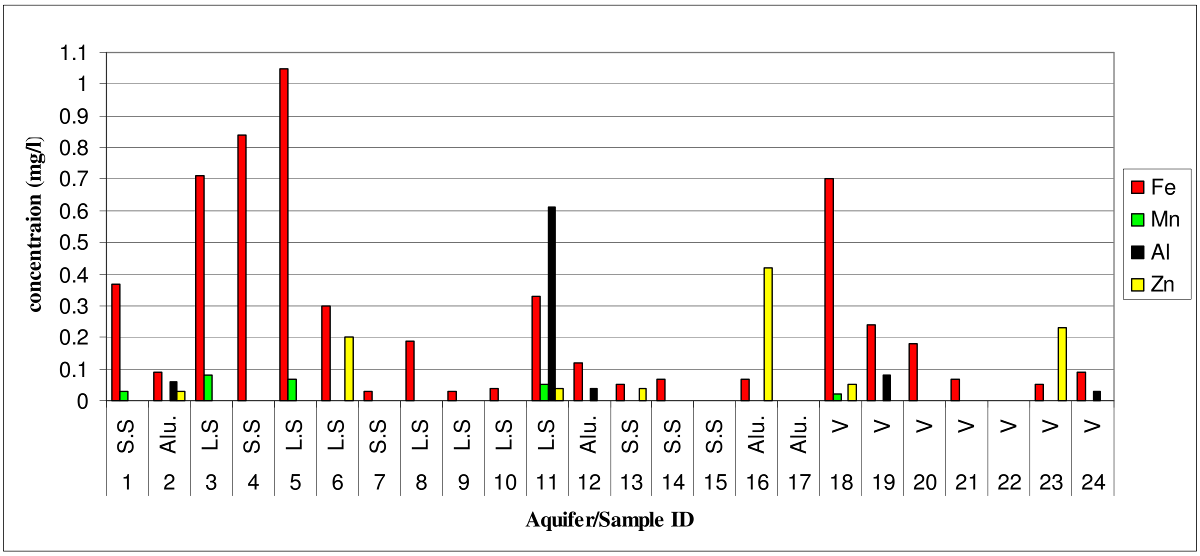

Figure 5.24: Heavy metals in the groundwater samples

5.4 Water classification

The classical use of water analyses in groundwater hydrology 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, 2004) and NWRA, 2000. The SAR was used to assessment the suitability for irrigation purpose.

5.4.1 Classification based on total hardness (Ca^{+2} and Mg^{+2} hardness)

The 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 $CaCO_3$ concentration in four categories (WHO, 2004): soft water, hard water, medium hard water and very hard water (tab. 5.5). 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 (WHO, 2004). 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 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 500mg/l (WHO, 2004); this value was also recommended by NWRA, 2000. The optimum range of hardness in drinking water is from 80 to 100mg/L (WHO, 2004).

The calculated total hardness of ground- and spring water samples in Sana'a basin presented in table 4 and 5 in the appendix. In comparison the results of this study with the classification values given in table 5.5, water in Sana'a basin (spring and groundwater) can be classified in four groups:

Group 1: very hard water

Half of the 37 measured water samples are very hard (Fig. 5.25). Water of this group has hardness concentrations range between 181 and 1.110mg/l. The highest values were found in the limestone groundwater aquifer in the northern part of the basin (Fig. 5.27 and 5.28). The minerals calcite and magnesium are thought to derive naturally from rocks of Amran Limestone group which comprises dolomite and gypsum.

Group 2: hard water

About 30% of total water samples represent this water type (Fig. 5.25). 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 179mg/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 (Fig. 5.28). Hardness concentrations in water sample this type range between 71 and 120mg/l.

Group 4: soft water

About 14% of water samples are soft water with a low hardness ranging between 8 and 58mg/l. This water type was observed in volcanic groundwater aquifer in southern part (figure

5.27). Water passing through igneous rocks is thought to dissolve only small quantities of minerals.

Table 5.5: Classification of drinking-water based on total hardness (WHO, 1994)

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 5.6: Summarized classification of water in the Sana'a basin based on Ca^{+2} and Mg^{+2} hardness

Water type	**Samples**		**Total samples**	**Total in (%)**
	spring water	**groundwater**		
soft	0	5	5	13.5
medium hard	2	1	3	11
hard	6	5	11	27
very hard	5	13	18	48.5
Total samples	13	24	37	100

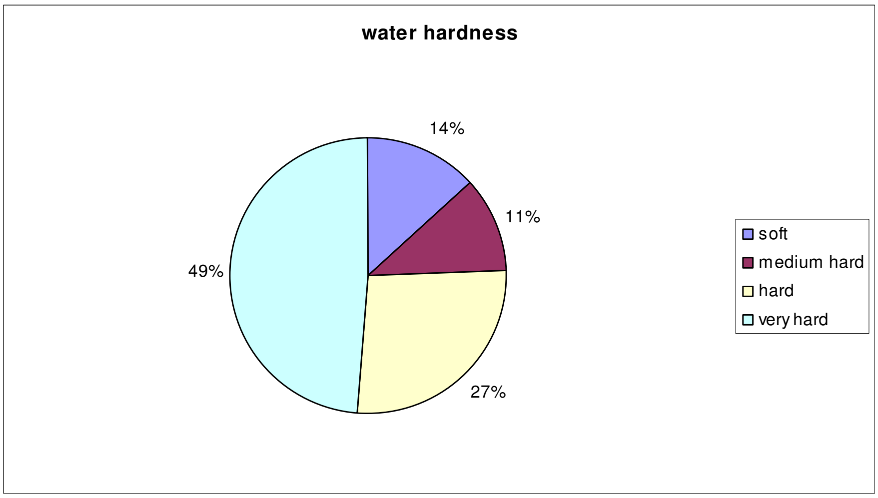

Figure 5.25: Water type in the Sana'a basin based on the total hardness (in %)

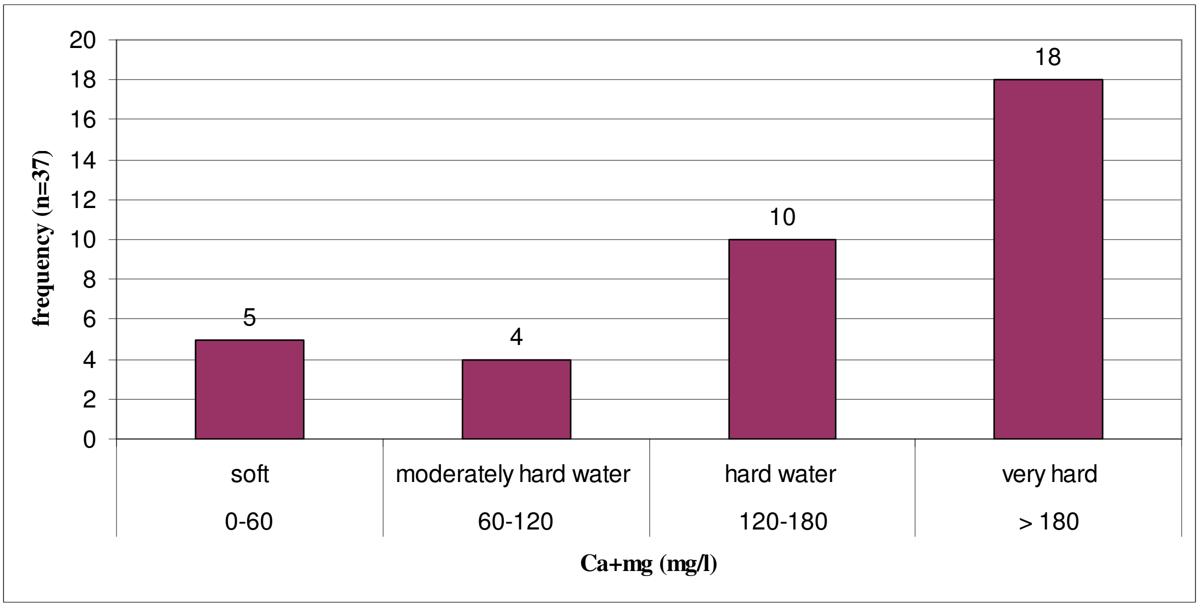

Figure 5.26: Classification of water samples in the Sana'a basin based on the total hardness

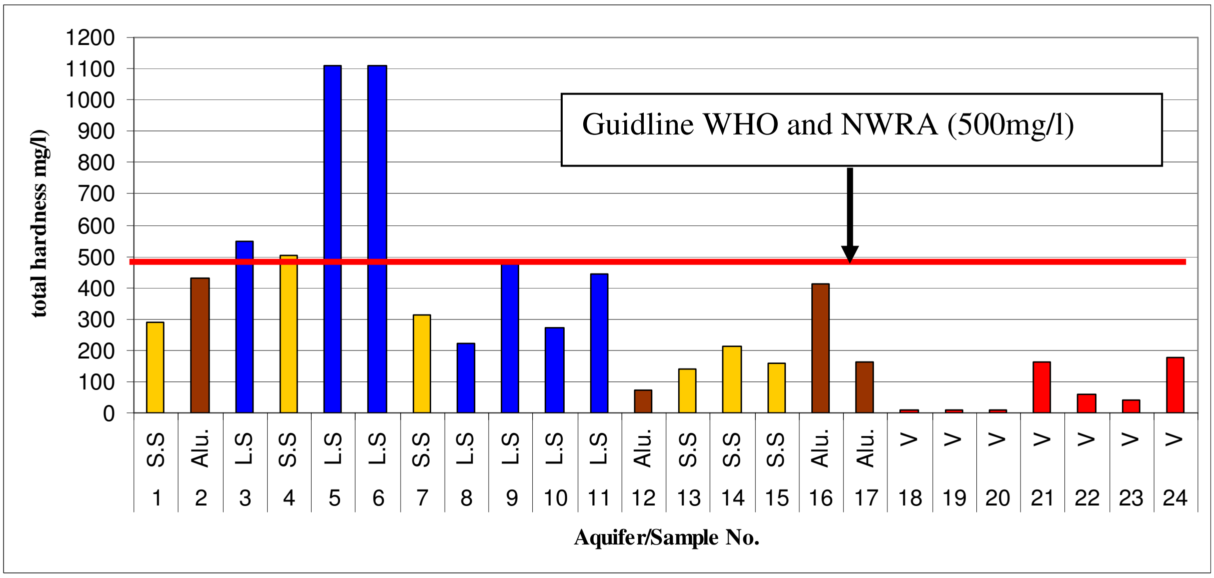

Figure 5.27: Total hardness in groundwater samples-Sana’a basin

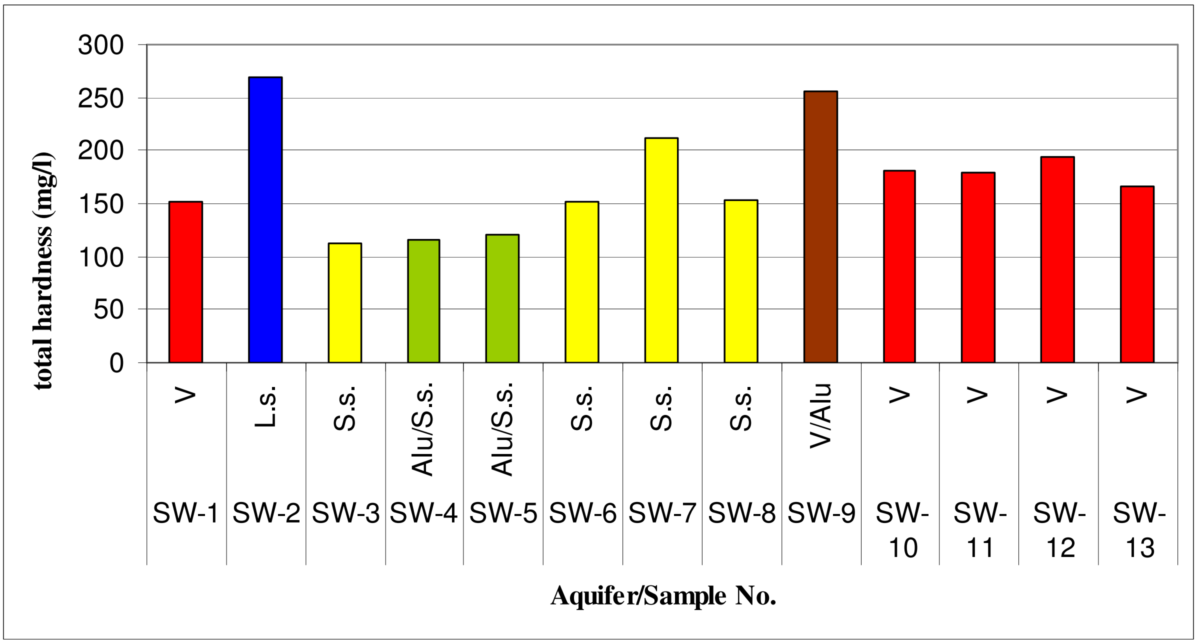

Figure 5.28: Total hardness in spring water samples from Sana’a basin

5.4.2 Classification based on salinity and sodium hazard (SAR)

Table 4 in the appendix shows the calculated values.

About 80% of groundwater in 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 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 groundwater for irrigation (TODD, 1980). Parameters such as EC and sodium adsorption ratio (SAR) and Standard diagrams (figure5.31) were used to assess the suitability of water for irrigation purposes. The method published by the US SALINITY LABORATORY STAFF (1954) 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 (AquaChem v.5.1 User's Manual). 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 Wilcox plot has the following sections (AquaChem v.5.1 User's Manual):

Conductivity (µS/cm)

C1: Low (0-249)

C2: Medium (250-749)

C3: High (750-2249)

C4: Very High (2250-5000)

The SAR values are divided into the following categories:

S1: Low

S2: Medium

S3: High

S4: Very High

5.4.2.1 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 2030µS/cm. Irrigation water with an EC of < 700 µS/cm causes little or no threat to most crops while EC > 3000µS/cm may limit their growth (TIJANI, 1996). Based on the US Salinity Laboratory classification (1954) (Fig. 5.29) the salinity hazard for water samples in Sana'a basin is classified as medium (73%) to high (27%). 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 fall in the category 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 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 Amran Group (see chapter 5.2.3).

5.4.2.2 Sodium (Alkali) Hazard (SAR)

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 water. Irrigation with Na-enriched water results in ion exchange reactions: uptake of Na+ and release of Ca^{2+} and Mg^{2+}. This causes soil aggregates to disperse, reducing its permeability (TIJANI, 1994). 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).The following formula is used to calculate SAR (APPELO and POSTMA, 2007):

$$SAR = \frac{Na}{\sqrt{\frac{Ca + Mg}{2}}} \qquad \text{(eq. 5.4)}$$

Ions in the equation are expressed in milliequivalent per liter. 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 colloidally 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 10.44meq/l in ground waters and from 0.16 to 0.75meq/l in 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 Sana'a basin are classified as low (89%), medium (8%) and high (3%). As per the Richard (1954) classification based on SAR values (Table 5.7), 36 samples are excellent category because none of the samples exceeded the value of SAR = 10 (Fig. 5.30 and 5.31). Thirty-three out of 37 samples fall in the low sodium hazard category (S1) while a few of the samples (four groundwater samples) belong to the medium sodium hazard category (S2) and one groundwater sample fall in the high sodium hazard category (S1) . The major source of sodium is most likely natural and results from the dissolution of silicate minerals (feldspars).

Table 5.7: Salinity and Alkali Hazard Classes (Richard, 1954)

Water class	sodium adsorption ratio (epm)
Excellent	<10
Good	10-18
Doubtful	18-26
Unsuitable	> 26

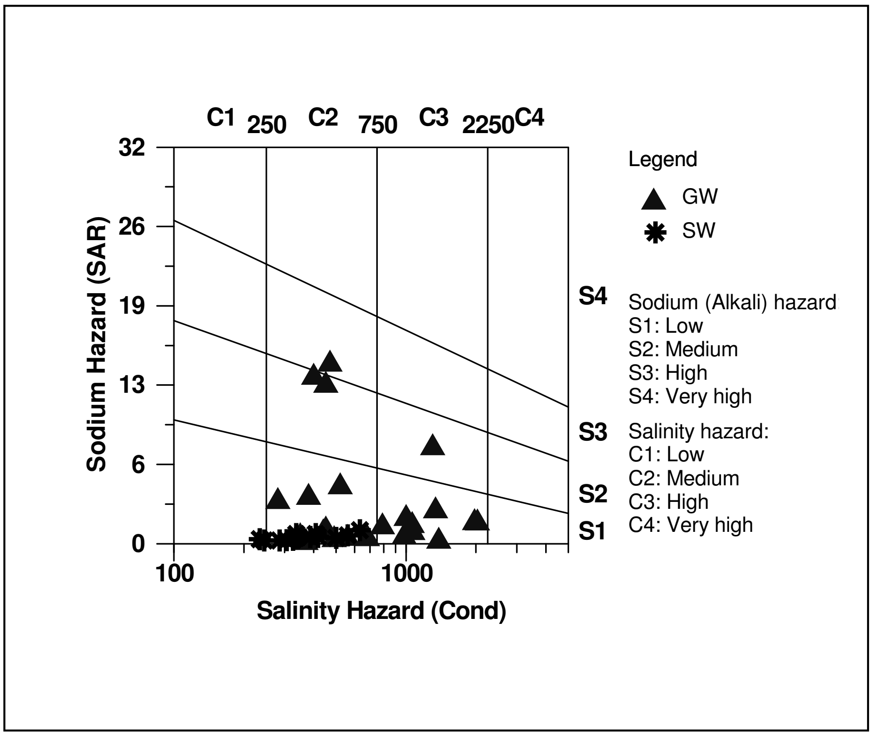

Figure 5.29: Calculated SAR values of ground- and spring water samples

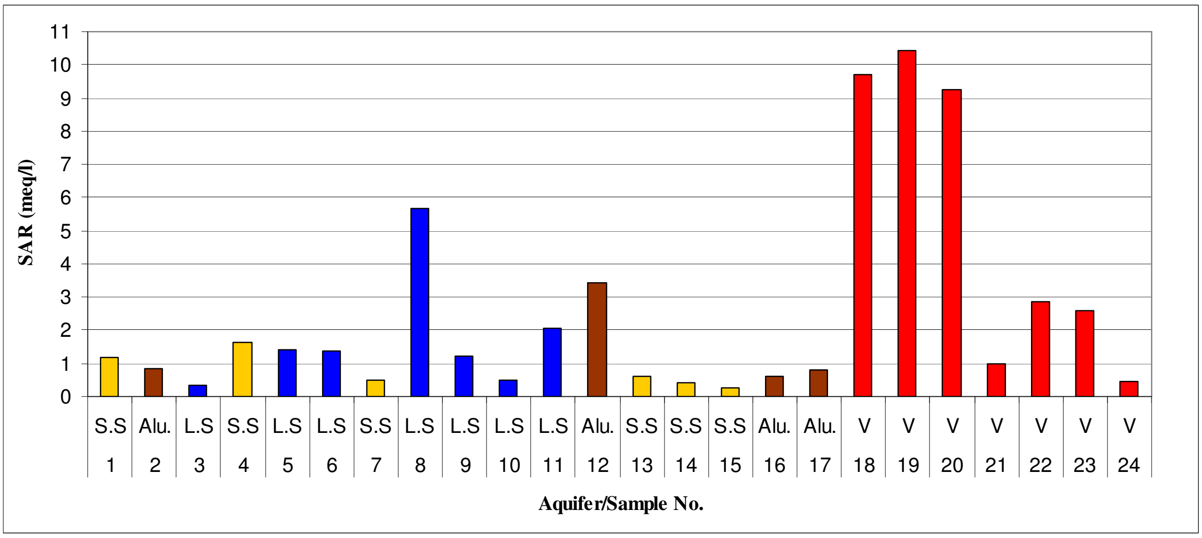

Figure 5.30: Calculated SAR of the groundwater samples

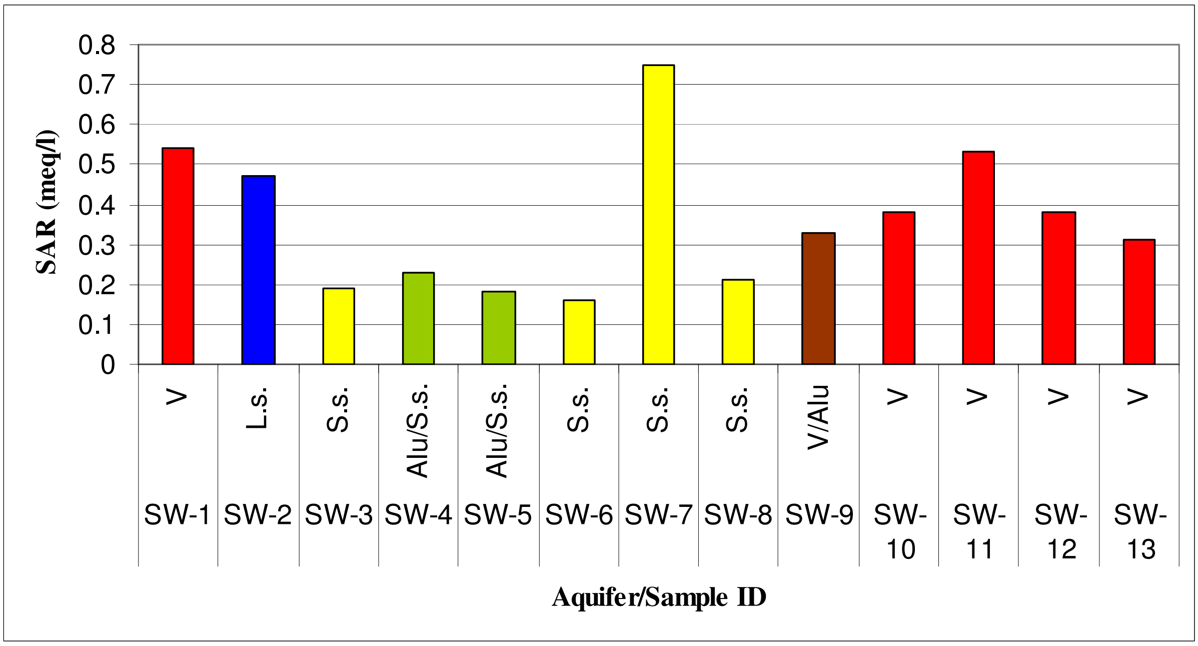

Figure 5.31: Calculated SAR of the spring water samples

5.4.3 Classification based on Magnesium Hazard

Although calcium and magnesium ions are essential for plant growth but they may associated with soil aggregation and friability. Water contains calcium and magnesium concentration higher than 10meq/l (200mg/l) cannot be used in agriculture. In the studied area the concentration of calcium and magnesium were found to be below 200mg/l, only in two groundwater samples GW5 and GW-6 exceed the calcium the values 200mg/l with 326 and 321mg/l, respectively (table 1 and 2 in the appendix).

Another indicator can be used to specify the magnesium hazard (MH) is proposed by SZABOLCS and DARAB (1964) for irrigation water as following formula:

$$MagnesiumHazard(MH) = \frac{Mg}{Mg + Ca} * 100 \qquad \text{(eq.5.5)}$$

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% (table 4 and 5 in the appendix), and can be classified as suitable for irrigation use.

5.4.4 Classification based on saturation index (SI)

Consider the following reaction, where species A and B react to produce species C and D:

$$a.A + b.B \Leftrightarrow c.C + d.D \qquad \text{(eq. 5.6)}$$

Where a, b, c, and d representing the number of moles of these constituents. At chemical equilibrium, the equilibrium distribution of mass between reactants and products can be expressed as:

$$Ks = \frac{[C]^c * [D]^d}{[A]^a * [B]^b} \qquad \text{(eq.5.7)}$$

where Ks is the equilibrium constant, and [A], [B], [C], and [D] are the activities for reactants and products at equilibrium. Depending on the reaction, the equilibrium constant Ks may represent a solubility constant in dissolution reactions, a dissociation constant in acid-based reactions, or a complication constant in complication reactions.

In a groundwater system, some reactions may not be at equilibrium. The departure of a reaction from equilibrium is often described as the ratio of the ion activity product (IAP) to the solubility product (Ks) which named as saturation state (IAP/Ks).

The saturation index (SI) is defined as log of saturation state (IAP/Ks) for a dissolution reaction according to the equation (APPELO and POSTMA, 2007):

$$SI = \log \frac{IAP}{Ks} \qquad \text{(eq. 5.8)}$$

The SI gives information about how much a certain mineral phase (e.g. calcite, Gypsum, etc...) 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 (APPELO and POSTMA, 2007).

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 table 5 and 6 in the appendix. Figure 5.32 shows the SI of the spring and groundwater samples with respect to calcite.

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

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

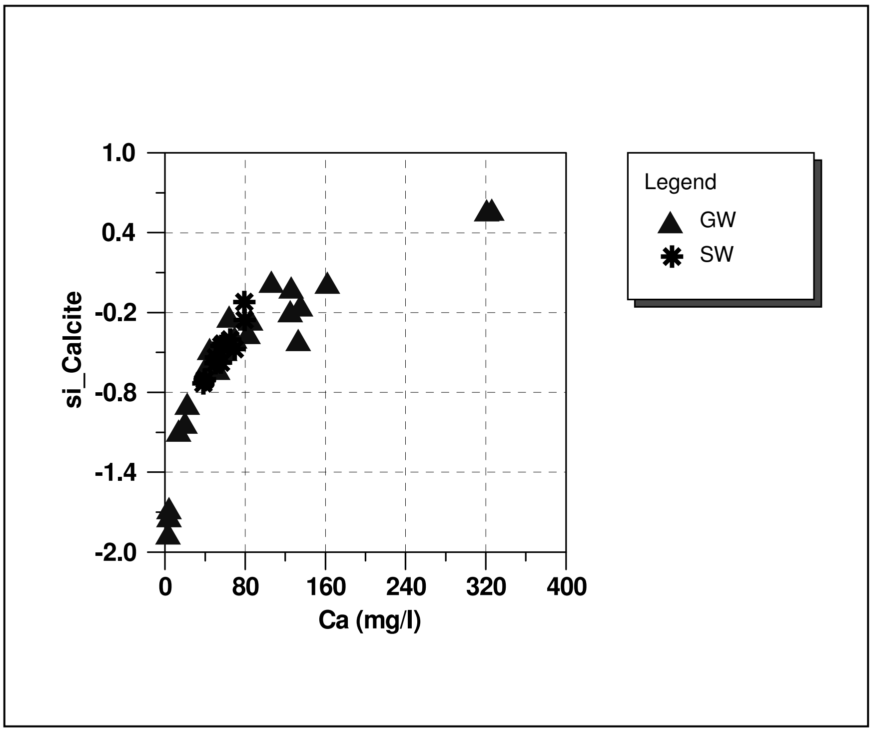

Figure 5.32: SI of spring and groundwater samples with respect to calcite

5.4.5 Classification based on Piper and Schoeller diagrams

The chemical analyses data were plotted in PIPER and SCHOELLER diagrams with the software AQUACHEM 4.0 to visualise the general chemical characteristics and to classify the ground- and spring water samples in groups of similar geochemical properties.

The Piper diagram (Fig. 5.33) 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 (AquaChem v.5.1, User's Manual, 2007).

The Schoeller diagram (Fig. 5.34) is a semi-logarithmic diagram that was developed to represent major ion analyses in meq/l and to plot different hydrochemical water types in the same diagram. In these diagrams the major ions are plotted on the X-axis, and their concentrations are plotted on the Y-axis (AquaChem v.5.1, User's Manual, 2007).

In the Piper and Schoeller diagrams shown in figures 5.33 and 5.34 four major groups of ground- and spring water and a single group (one groundwater sample) can be distinguished. Most samples were classified as earth alkaline waters with prevailing hydrogenbicarbonate (group 1) or sulphate as in group 2.

Group 1: water type Ca-HCO3 (low mineralized)

This type of water, the Ca-HCO3 type (Fig. 5.35), represents the major water type in the study area (about half of all samples) 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 560µS/cm. The low mineralization and the low content in alkalis and earth alkalis is due to the low temperatures of spring and groundwater, affecting the solubility. The temperature ranges between 18 and 23 °C (except for GW-10 with 33°C). 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 dolomite.

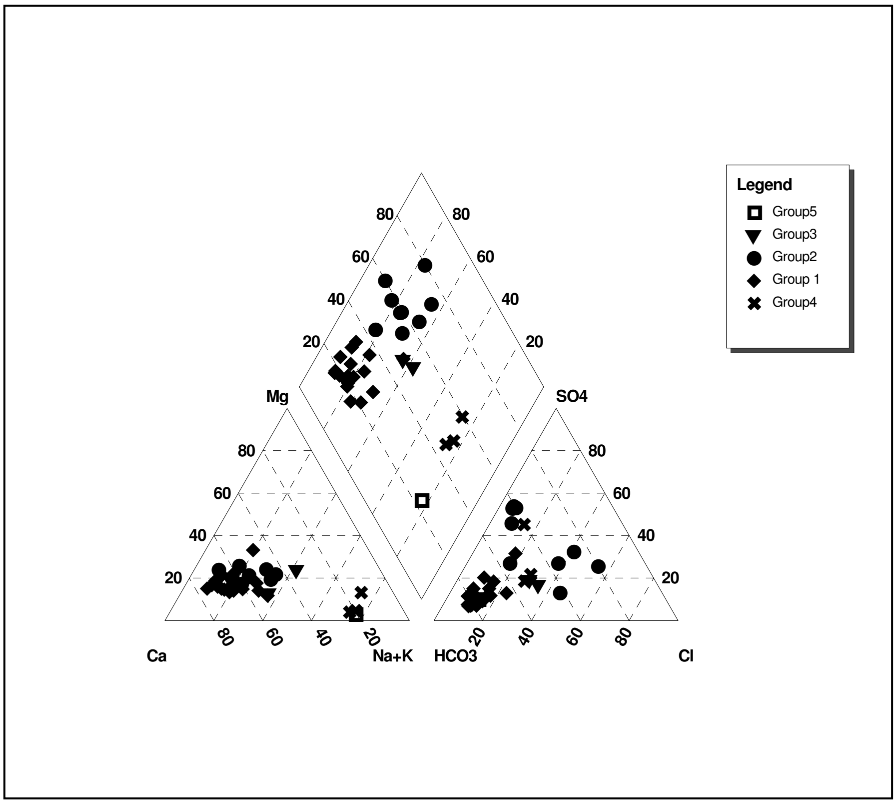

Figure 5.33: Piper plot of the chemical composition of ground- and spring water samples

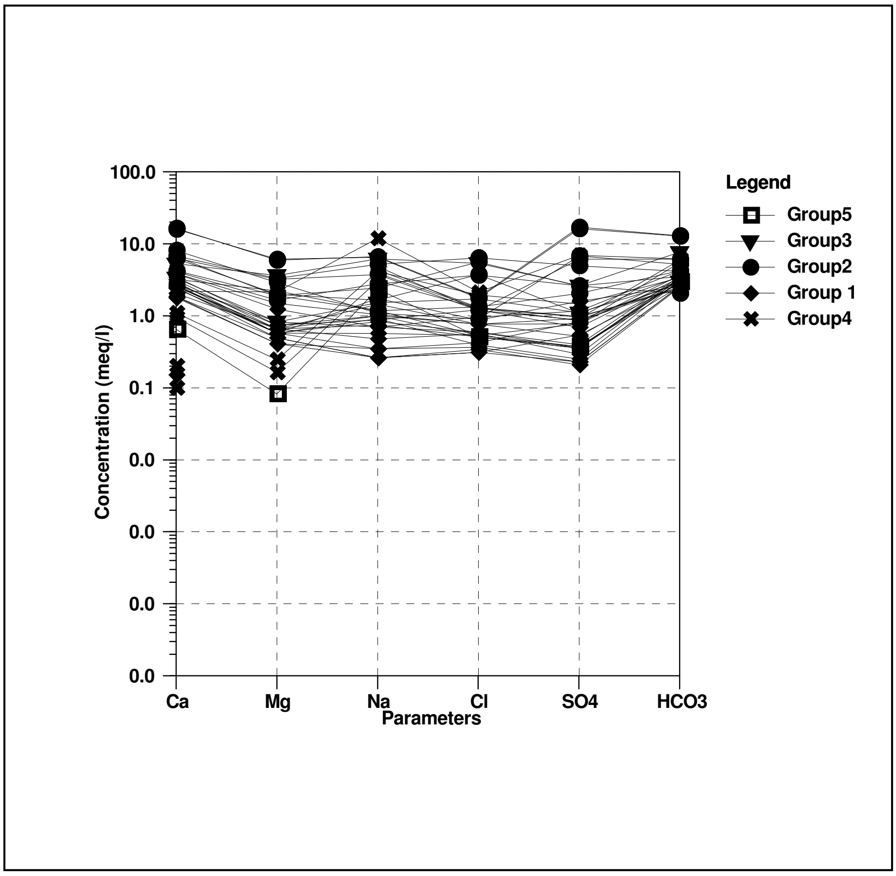

Figure 5.34: Schoeller plot of the chemical composition of the ground- and spring water samples

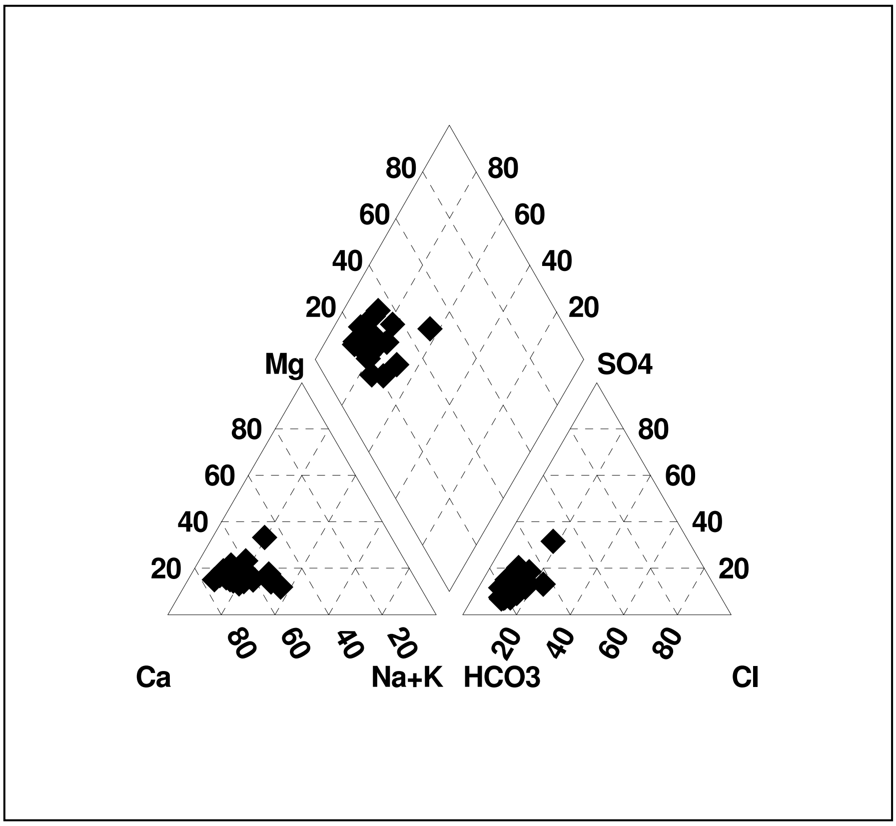

Figure 5.35: Piper plot of group 1

Group 2: water of Ca-Na-Mg-HCO_3 (SO_4 -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 µS/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 (Fig. 5.36).

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 (SAWAS, 1996). This water type occurs commonly in the north-eastern part of the basin and in central Sana'a city.

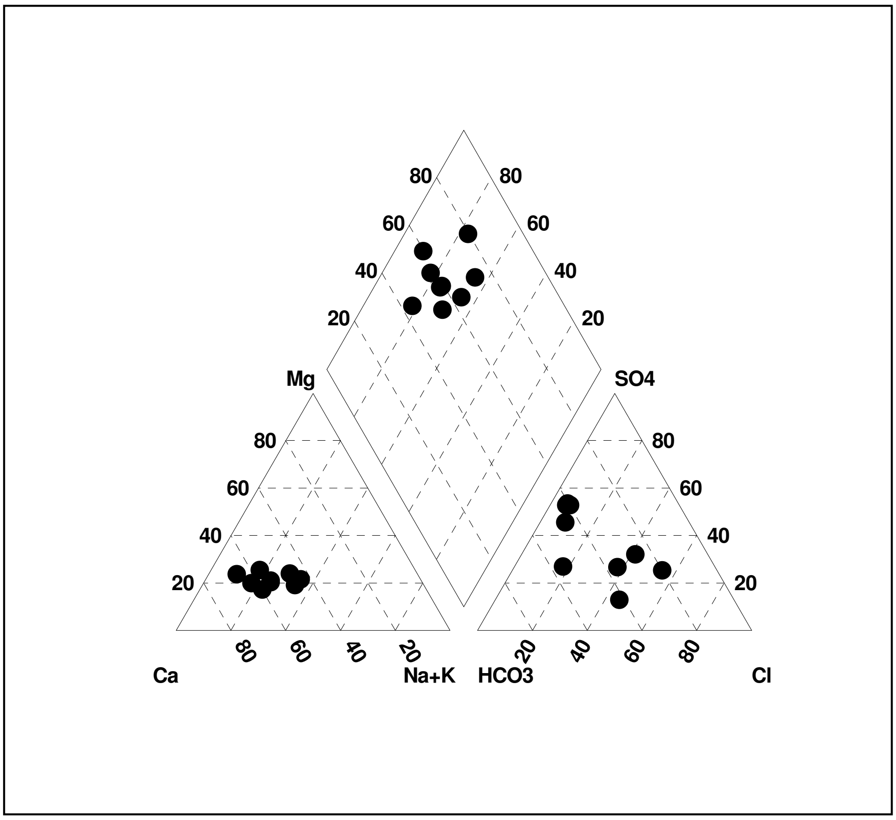

Figure 5.36: Piper plot of group 2

Group 3: water of Ca-Na-HCO_3 (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 µS/cm, respectively. The limestone sample GW-11 is characterized by a higher EC value with 1340 µS/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) (Fig. 5.37).

Group 4: water of Na-HCO_3 (SO_4 -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, sample (GW-8) from the limestone aquifer and (GW-12) from 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 groundwater's that are localized in the acidic volcanics. The volcanic and alluvium groundwater samples are characterized by moderate EC ranging between 380 to 520 µS/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 µS/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.

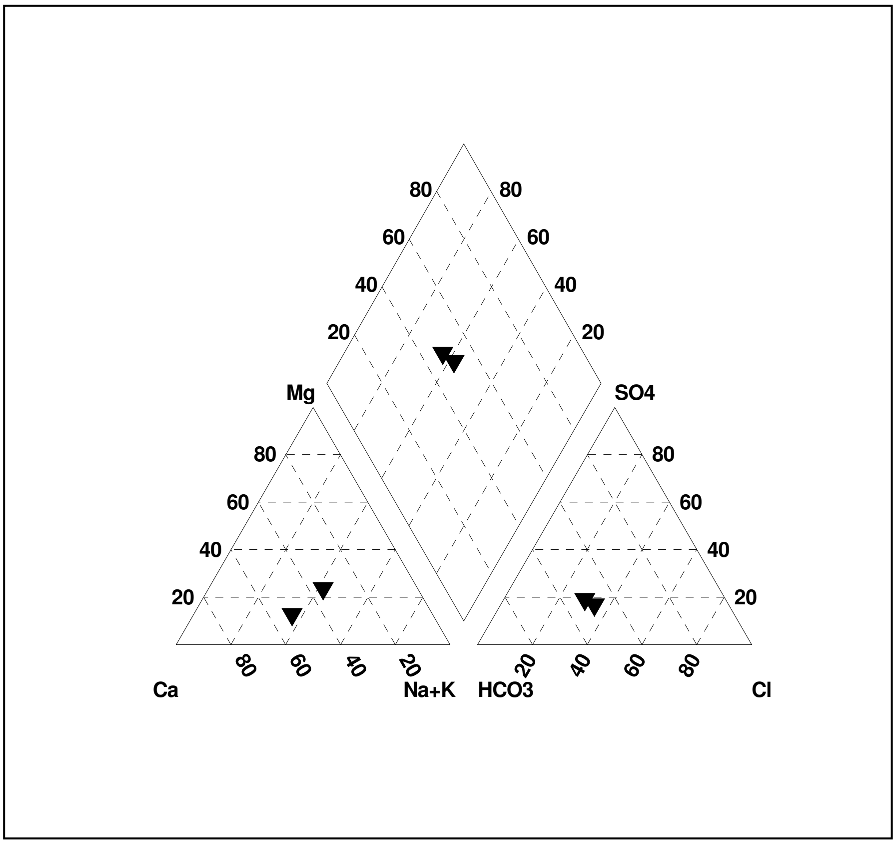

Figure 5.37: Piper plot of group 3

Group 5 (single sample): water of Na-K-HCO_3

The sample GW-23 comes from the volcanic aquifer in the south-western 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 as shown in figure 5.39 (about 80% of the ions). The EC is low (280 µS/cm). The high concentration of alkaline minerals is natural and results from the dissolution of these minerals in the volcanic host rocks.

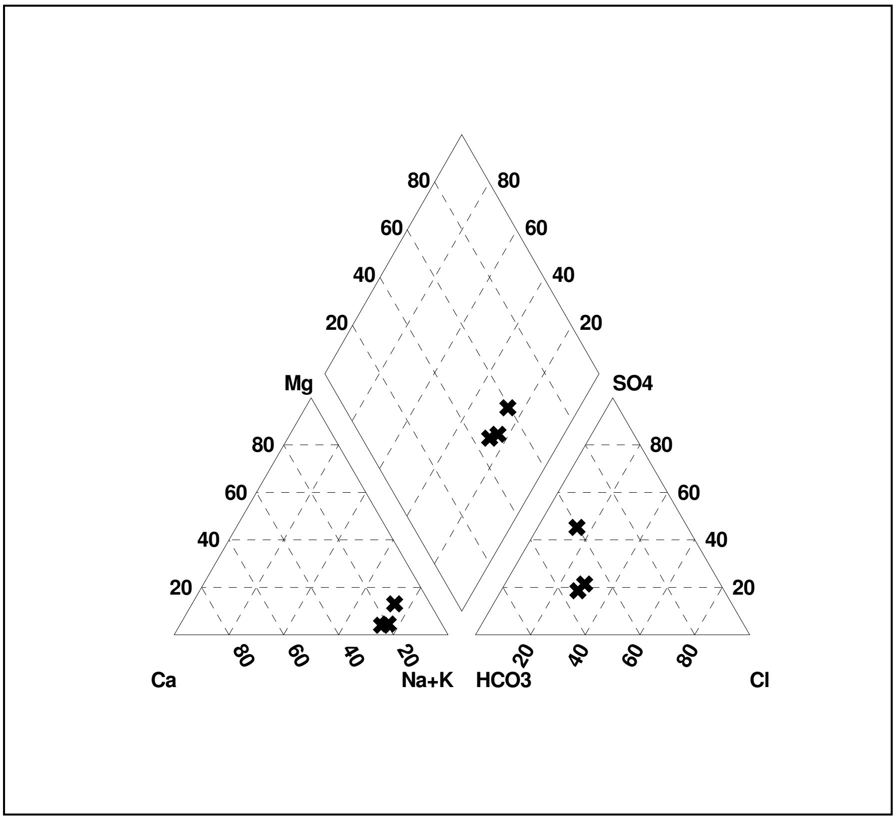

Figure 5.38: Piper plots of group 4

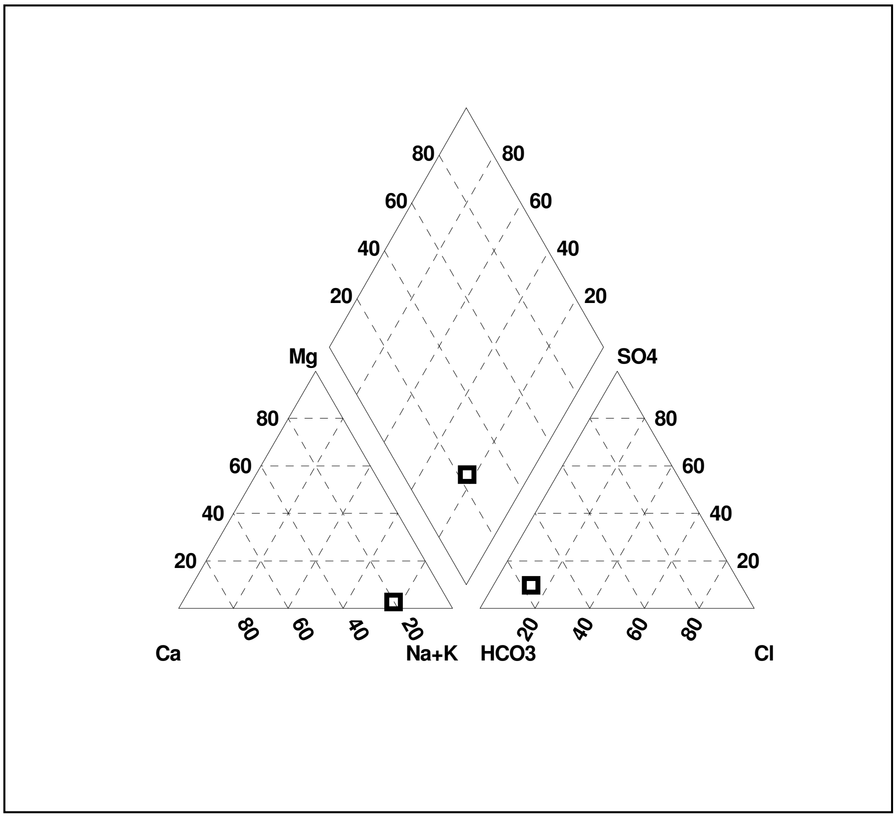

Figure 5.39: Piper plot of group 5

5.5 Hydrochemistry of groundwater of the different aquifers

In general, groundwater in the different aquifers of the Sana'a basin can be considered to be derived from different origins. This conclusion is supported in particular by the scatter plots shown in figure 5.40, which shows the relationship between the concentrations of Na and Cl in all of the groundwater samples taken from Sana'a basin. In this section the hydrochemistry of the groundwater in the differences aquifer systems is discussed separated.

In order to derive a simple classification of the groundwater in the Sana'a basin, alluvium and volcanic aquifers are considered as one aquifer system and the sandstone and limestone as another one. Additionally, this system was implemented in order to make the comparison between the current study and data obtained from previous studies possible (see chapter 6.2, point 3).

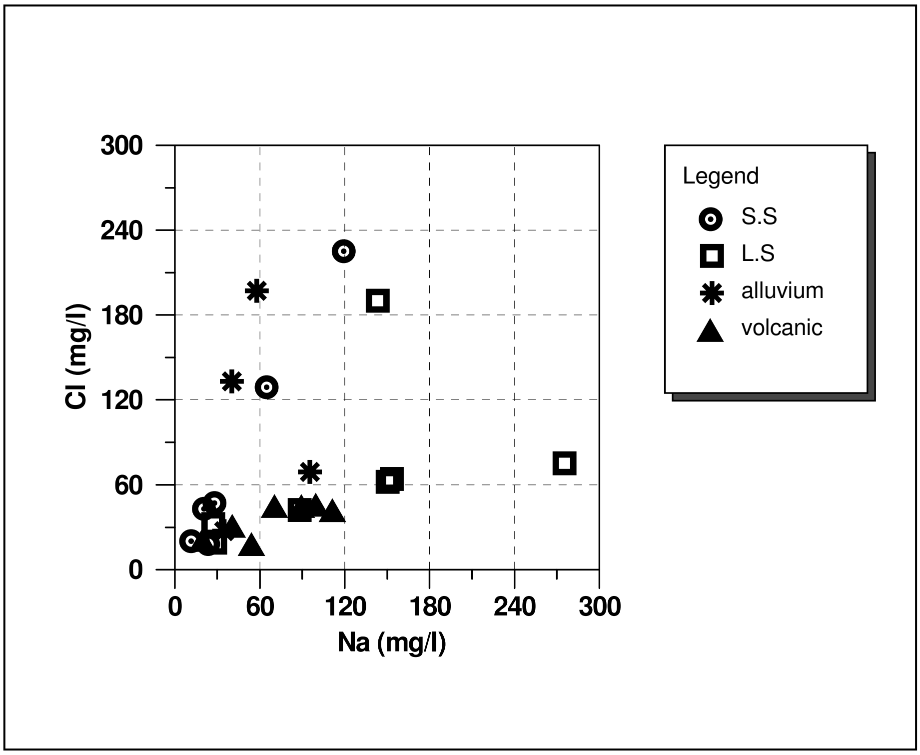

Figure 5.40: Scatter plot Na vs. Cl in the groundwater samples

5.5.1 Hydrogeochemistry of the limestone and sandstone aquifer

In general, the two aquifers show more or less similar water characteristics of Ca-HCO_3 (SO_4-Mg) type with the difference that samples collected from the limestone aquifer show SO_4

anions in high concentrations (Fig. 5.41 and 5.42). Figure 5.42 shows that groundwater in the sandstone aquifer in the northern part of the Sana'a basin contains higher concentration of chloride and nitrite. This is probably due to groundwater contamination through wastewater infiltration from the cesspits in this area (AL-HAMDI, 2000 & SAWAS, 1996). In samples GW-3, GW-5, GW-6 and GW-9 from the limestone aquifer in the northern part of the basin SO_4 exceeded the concentration recommended by WHO in 2008 (250 mg/l) with 326, 812, 780 and 292 mg/l.

Magnesium and sodium occurs as minor ions in all of the samples in concentration ranging from 26.5 to 74.5 mg/l and from 27.1 to 274 mg/l, respectively. Sodium exceeded the WHO guideline value (200 mg/l) in sample GW8 with 274mg/l. The high concentration of SO_4 and Mg could be the reason for the high electrical conductivities in limestone aquifer (Fig. 5.43). The EC ranges from 560 µS/cm in sample GW-10 to 2030 µS/cm in GW-6 in northern and north-eastern part of Sana'a basin.

Three out of six samples (GW-1, GW-4 and GW-7) taken from sandstone aquifer in the eastern and north-eastern part of the basin are of a Ca-SO_4-HCO_3 water type. Sulphate concentrations in these samples reach 125, 237 and 98 mg/l. Other minor ions found are Mg and Na with concentrations ranging from 8.1 to 40.4 and 11.1 and 119 mg/l, respectively. Other characteristics are low to moderate EC values ranges between 350 and 1002 µS/cm and pH of 5.6-7.6.

Nitrite and chloride was found in both aquifers, but the values were higher in samples from the sandstone aquifer, especially in the north-eastern part (sample: GW-1, GW- 4 and GW-7) where the sewage water of Sana'a city could infiltrate to the groundwater.

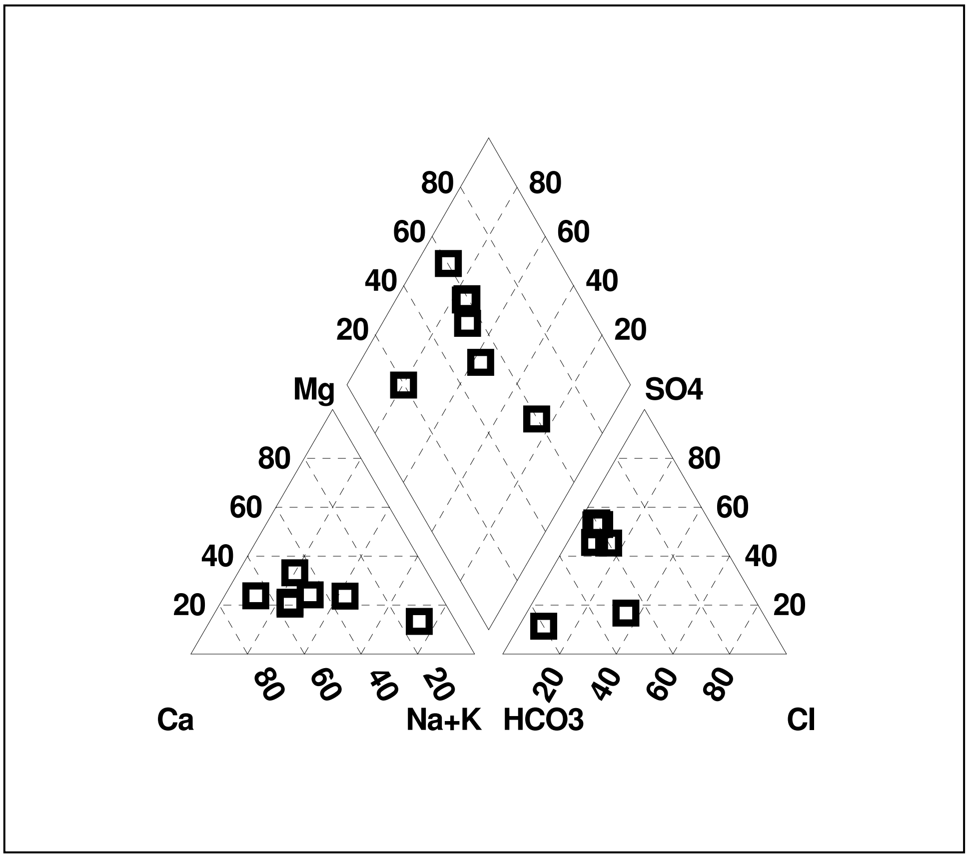

Figure 5.41: Piper plot of Limestone aquifer

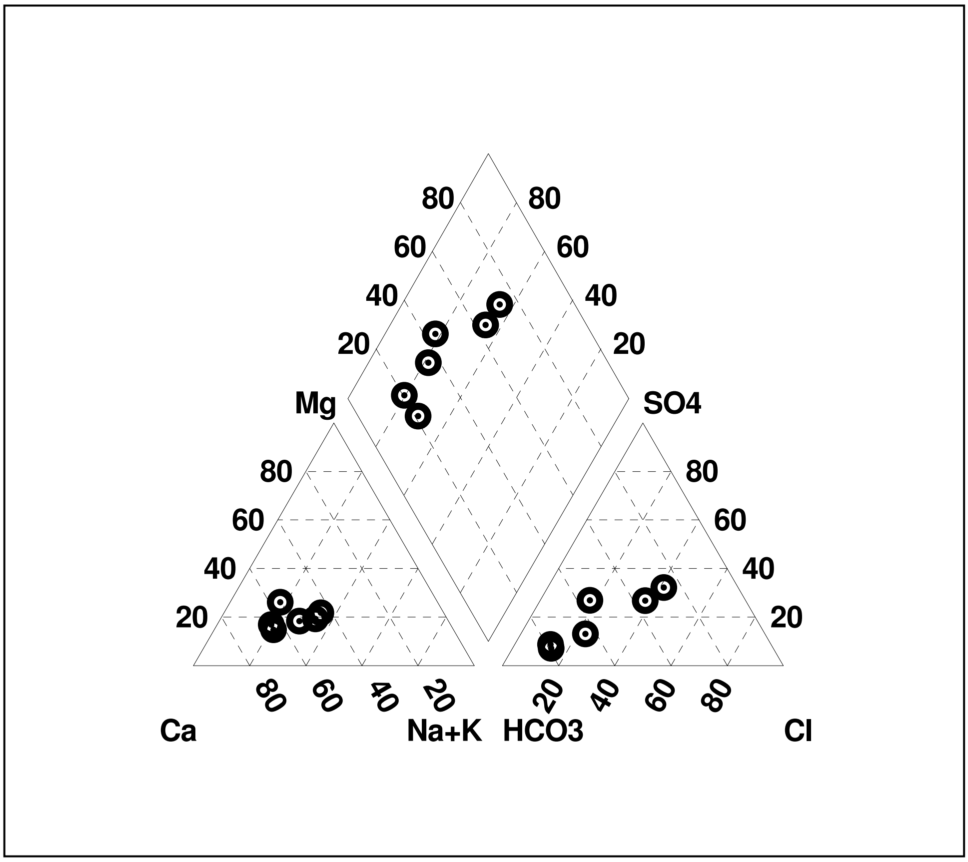

Figure 5.42: Piper plot of Sandstone aquifer

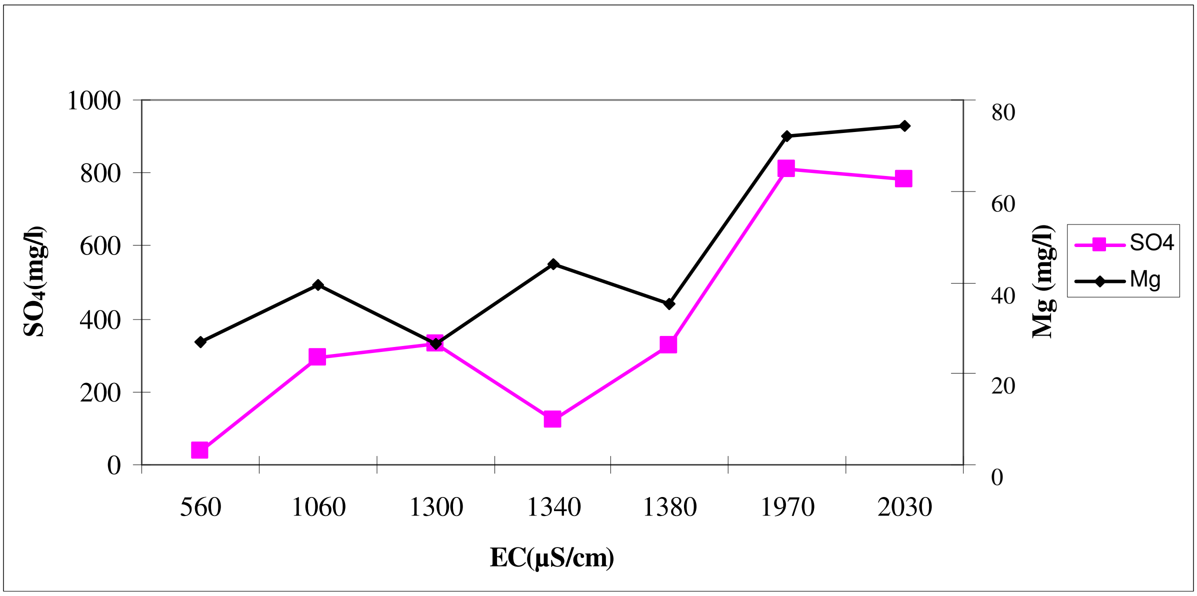

Figure 5.43: EC vs. SO4 and Mg in the Limestone aquifer

5.5.2 Hydrochemistry of volcanic and alluvium aquifer

A total of 11 groundwater samples were taken from both aquifers, analyzed and plotted in Piper diagram (Fig. 5.44). Generally the waters type origin from the both aquifers is Ca-Na-HCO_3. The differences between alluvium water and volcanic water are minor because alluvium sediments mainly consist of volcanic basalt fragments (FOPPEN, 2002). The main difference between the waters types is that the alluvium water is dominated by Ca whereas the dominant cation in the volcanic water is Na. However; the alluvium aquifer shows a higher contamination. Chloride and nitrate were found in high concentrations mainly in the alluvium water with values ranging between 13 to 197 mg/l (Fig. 5.45), indicating that this aquifer is affected by the domestic sewage infiltration, especially in the central part of Sana'a basin where the values exceeded the standard values for drinking water recommended by WHO, 2008 and NWRA, 2000 (50 mg/l) with 73 and 121 mg/l in samples GW-2 and GW-16 respectively.

According to the chemical analyses of the samples collected in this study, it can be concluded that the alluvium aquifer is the aquifer most polluted by the infiltration of sewage water in the urban area of Sana'a city; this becomes exaggerated by the shallow wells in this aquifer (Fig. 5.46). A total depth of the wells in this study ranges between 60 and 160 m and the depth to water table ranges between 32.92 and 60 m. This statement is supported by studies carried out in 1996 by SAWAS and in 2002 by Foppen. The chloride and sulphate values were found in some samples taken from the volcanic aquifer; chloride was found in sample GW-22 and sulphate in GW- 21. These waters are probably influenced by volcanic gasses, surfacing throughout the Sana'a basin (SAWAS, 1996). This section will discuss in details in chapter 6.1.1.

The EC is low to moderate in the volcanic aquifer water, ranging between 280 to 470 µS/cm, and moderate to high in alluvium (440 to 1070 µS/cm) (Fig. 5.11). The pH values are more or less similar and range from 7.5 to 9.4 (Fig. 5.3).

In 2002 the concentration of NH_4 was measured by FOPPEN and was absent in all of groundwater samples taken from alluvium aquifer, while NH_4 in wastewater was found by around 354 mg/l. However, NO_3 in groundwater was found between 35.5 to 106 mg/l, indicating aerobic conditions in the saturated zone (FOPPEN, 2002). In this study NH_4 was not measured.

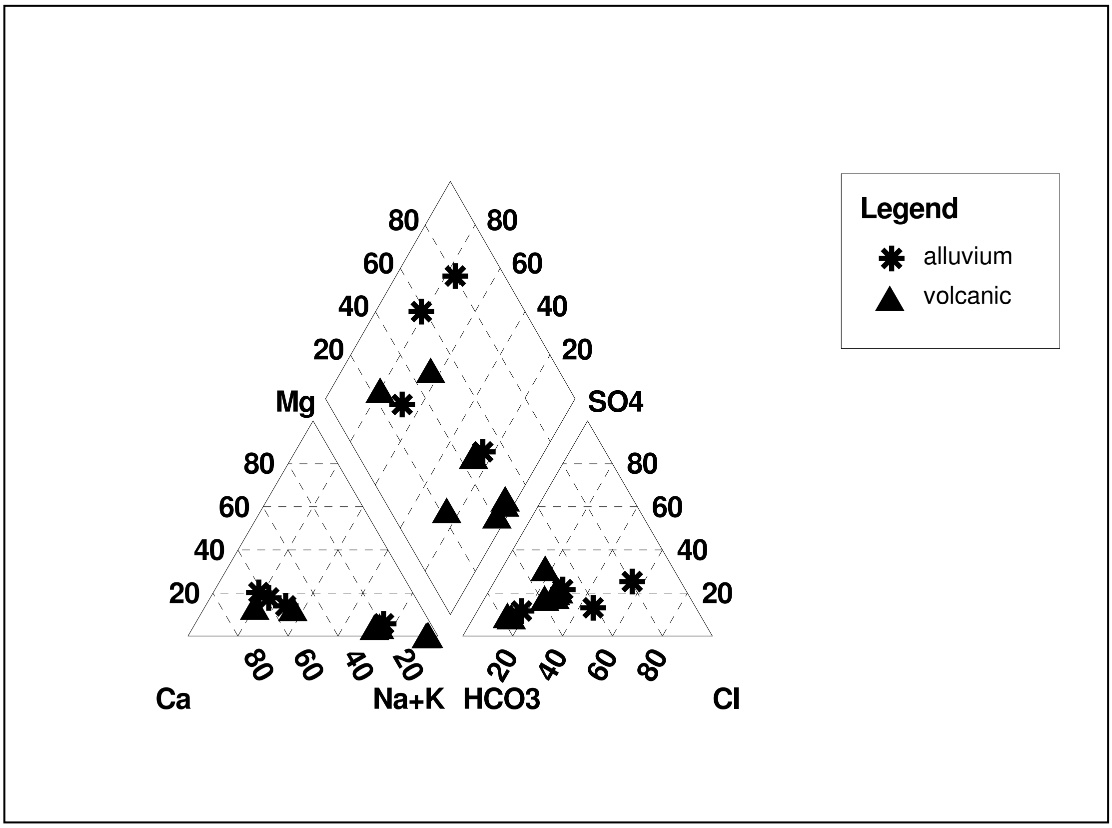

Figure 5.44: Piper plot of the alluvium and Volcanic aquifer

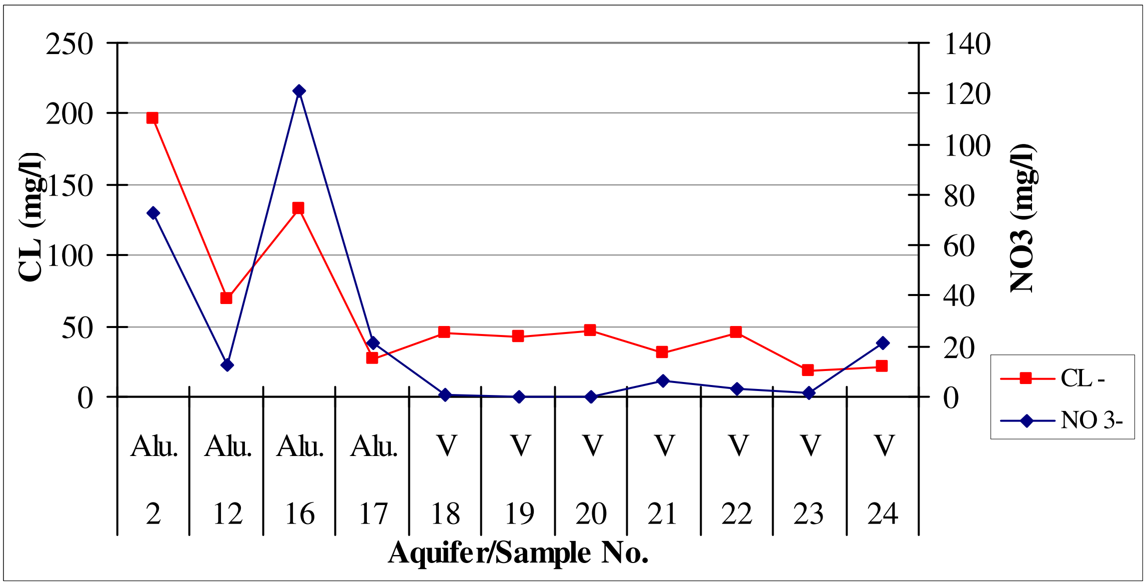

Figure 5.45: Chloride and nitrite concentrations in the groundwater in the alluvium and volcanic aquifer

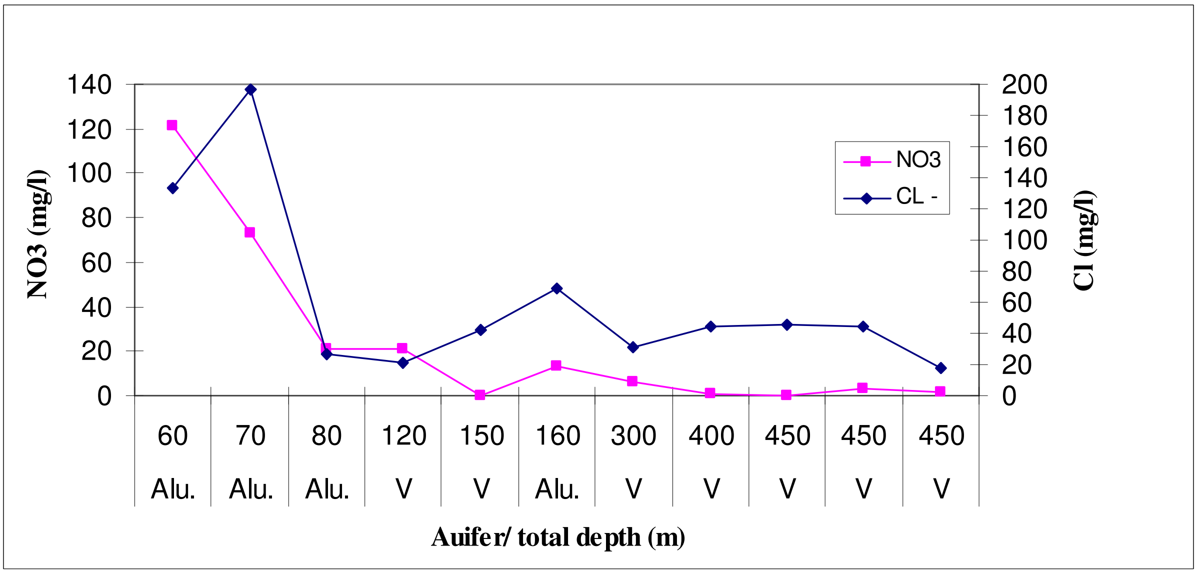

Figure 5.46: Chloride and nitrite concentration in the groundwater in the Alluvium and Volcanic aquifer vs. total depth of the well

5.6 Stable isotopes results

5.6.1 Stable isotopic ($\delta^{18}O$ and δD) composition in rainwater

In the presents study a linear-regression analysis was applied to stable isotope $\delta^{18}O$[1] and δD data measured from 255 rainwater samples collected from 17 sites between 2008 and 2010 to drive the LMWL for Yemen and Sana'a basin. Deuterium-excess was calculated for each of the 248 results and compared with the normally expected global range of d-excess values (10‰). The combination of theses calculations, which includes the linear-regression and calculated d-excess, helped to develop better understanding of the isotopic climate linkages that control oxygen and hydrogen isotope ratios in precipitation falls in the region. Values for $\delta^{18}O$ and δD and d-excess are presented in table 9 and in the appendix plotted in figure 5.6.1.

There are no data exist for isotopes composition in Yemen rainwater, therefore the result of the current study was compared with the isotopic composition data of Ethiopia's precipitation. The data are available at Addis Ababa GNIP (Global Network of Isotopes in Precipitation) stations from the International Atomic Energy Agency (IAEA) database (IAEA/WMO, 2004) at: ***http://isohis.iaea.org.*** The results of the comparison are discussed in details in chapter 7.2.

The oxygen and hydrogen ($\delta^{18}O$ and δD) isotopic composition of the rainwater samples varies in a wide range from +10.54 to -8.03‰ and from +64.12 to –53.57‰ with an average to be +0.32 and +8.61‰, respectively. The d-excess values vary between -23.60 and +22.97‰ with a mean of +5.95‰.

In order to construct a LMWL for Yemen the samples were divided into three groups (Fig. 5.6.1); ***the first group*** comprises the samples collected mostly from regions with higher elevation ranges between 1311 and 2500 m.a.s.l. The rainwater samples of this group are more depleted in the heavier isotopes $\delta^{18}O$ and δD with δ-values range from -4.58 to -0.04‰ and -32.7 to -0.7‰, respectively. The $\delta^{18}O$ and δD data of this group were used to produce a **LMWL for Yemen Highlands**. ***The second group*** contains the samples collected from regions with lower elevation ranges between 14-1000 m.a.s.l. Rainwater samples of this group are more enriched in heavier isotopes $\delta^{18}O$ and δD in comparison to the first group with δ-values range from -4.03 to +6.13‰ and -16.29 to +36.66‰, respectively. The data of this

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[1] Standard δ (delta) notation is used for the stable isotopes $^{18}O/^{16}O$, D/H. The results are reported in per mil (‰) relative to VSMOW and presented in table 8 in the appendix and shown in figure 6.1.

group were use to construct a **LWML for costal regions**. ***The third group*** presented by samples collected mostly from the station WEC which located in Sana'a with an elevation to be 2285m.a.s.l. The δ-values of this group are outside the expected range and enrichment in the heavy isotopes $\delta^{18}O$ and δD with values range between +5.80 to +9.57‰ and +32.3 to +59 ‰, respectively, which might result from errors during the sampling, e.g. the samples were collected from low rainfall events, by rain amount <20mm occurs the amount effect (IAEA, 2004), or the samples were affected by secondary processes such as partial evaporation of the sample during storage in the rain gage. These samples were not considered by constructing the LMWL.

Additionally, a **LMWL for Sana'a basin** was established separately using the isotopes composition data for samples collected from three stations located in Sana'a City.

The three LMWL for Yemen, together with the most important parameters affecting the isotopes composition of Yemen rainwater's are discussed in detail in the following section.

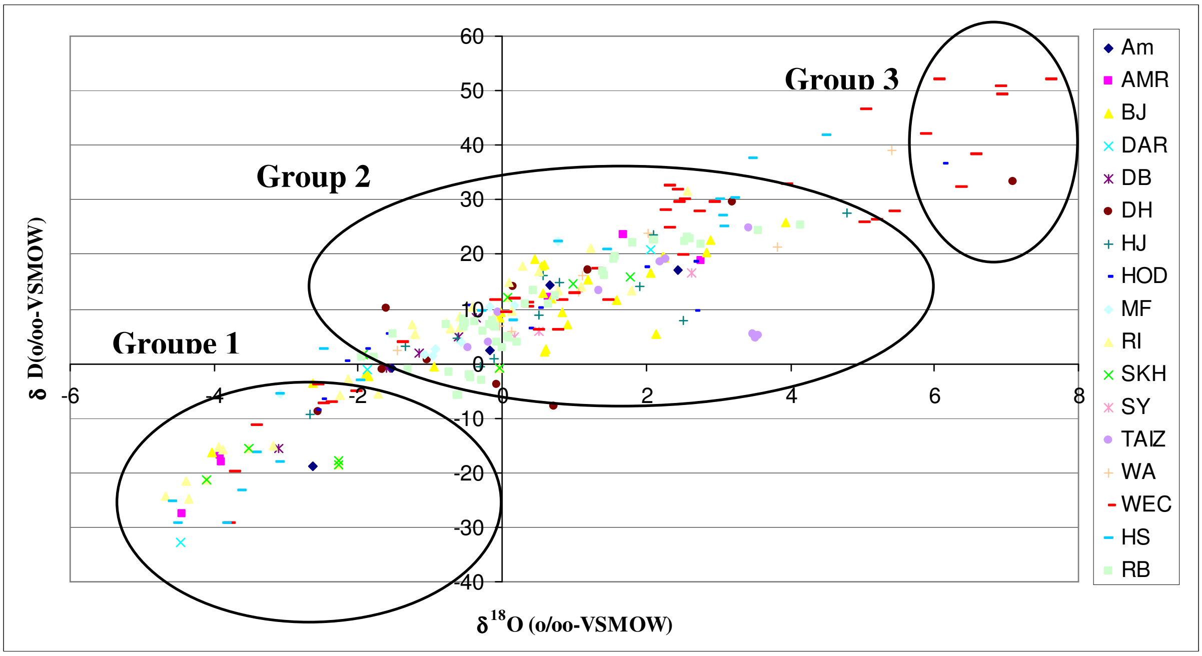

Figure 5.6.1: $\delta^{18}O$ vs. δD in Yemen's rainwater

5.6.1.1 The LMWL

A total of 127 samples collected from high elevation were used to construct a **LMWL for Yemen Highland's**. The samples were collected from the stations AMR-AM-HJ-RI-TAIZ-WA-WEC-HS-DAR-DH-MF located at elevations ranging from 1311 to 2500 m.a.s.l. (Fig. 4.9).The $\delta^{18}O$ and δD values ranging from -4.68 to 4.50‰ and from -32.70 to 41.90‰, respectively. The d-excess values vary between -12.10 and +22.97‰ with a mean of +8.62‰. The final data of these samples produce a regression line plots in figure 5.6.2 and defined by the equation:

$$\boldsymbol{\delta D = 7.1*\delta^{18}O + 8.2‰} \qquad (R^2 = 0.91) \qquad \text{(eq. 5.6.1)}$$

The equation 5.6.1, named as **Yemen Highland's MWL (YHMWL)**, plots slightly below the global water line (i.e. lower d-excess) with a slop of **7.1** near the expected slope of 8.0 for the GMWL. Such deviations result from differences in climatic factors, such as air temperature, secondary evaporation, seasonality of precipitation and moisture source and occur in precipitation globally (CLARK AND FRITZ, 1997, SIMPKINS, 1995; ROZANSKI et. al, 1993; FRITZ et. al, 1987).

The second LMWL in this study is the LMWL for the western costal regions using isotopes composition data for 88 rainwater samples collected from stations located at low elevations ranging from 14 to 1000 m.a.s.l (stations: HOD-BJ-RB-SKH-DB). Three values outside the expected range for samples collected from southern coastal (station SY) were excluded. The values for $\delta^{18}O$ and δD range between -4.03 and +6.13‰ and from -16.29 to 36.66‰, respectively. The d-excess value vary between -12.38 and +18.20‰ with a mean of +5.49‰. The regression for all rainwater samples data yielded a slope of 4.9 ($n = 88$, $r^2 = 0.8$) which characteristic for evaporation under increased equilibrium conditions with higher humidity during evaporation. The d-excess value for the regression is 7.2 between the 8.2 derived for the YHMWL and the d-excess of 10 for the GMWL.

The final dataset used to establish a **LMWL for the Yemen coastal regions** is shown in figure 5.6.3 and defined by the equation 5.6.2:

$$\boldsymbol{\delta D = 4.9*\delta^{18}O + 7.2‰} \qquad (R^2 = 0.8) \qquad \text{(eq. 5.6.2)}$$

An establishing a **MWL for the Sana'a basin** is a one of the most important part of this work. Defining the LMWL for precipitation falls in any region is an important part of groundwater investigations that compare isotopic ratios in groundwater with precipitation at specific locations (more details are given in chapter 5.6.2). Oxygen and hydrogen isotopic composition varies in a wide range; $\delta^{18}O$ changes from -8.02 to +4.50‰ while δD varies from -53.60 to +41.90‰ with an average to be -0.21 and +7.02‰, respectively. The d-excess values range from 0.00 to 22.40‰ with a mean of +8.68‰. The **Sana'a MWL (SMWL)** should be defined by the final set of all 65 data for the samples collected from Sana'a basin excluding 13 values outside the expected range (see chapter 5.6.1). This line is shown in figure 5.6.4 and defined by the equation 5.6.3:

$$\boldsymbol{\delta^2H = 7.4*\delta 18O + 8.6} \qquad (R^2 = 0.95) \qquad \text{(eq. 5.6.3)}$$

This line plots approximately along the GMWL and indicates that the precipitations fall in Sana'a region is probably little affected by evaporation (primary and secondary).

The $\delta^{18}O$ and δD of rainfall at the IAEA station at Addis Ababa vary between -4‰ and 0‰, with the d-excess being in the range between 10 and 20‰. Spatial variation of the isotopic composition of Ethiopian rainfall is relatively small (KEBEDE, et. al, 2005, SCHOELL AND FABER, 1976). The weighted mean isotopic composition of non-evaporated rainfall at Addis Ababa is -2‰ for $\delta^{18}O$ and -1‰ for δD (KEBEDE, et. al, 2009). The local meteoric water line for Addis Ababa is defined by the equation 5.6.4 (DEMLIE et. al, 2008):

$$\boldsymbol{\delta^2H = 7.2*\delta^{18}O + 12} \text{ (eq. 5.6.4)}$$

Comparing the YHMWL with the local meteoric water line for Addis Ababa, the slope of the YHMWL (7.1) is similar to the slop for the Addis Ababa meteoric water line (7.2), but the d-excess 8.2 for YHMWL is different from that for Addis Ababa 12; this may be a reflection of regional differences in the two study areas. The differences in δD and $\delta^{18}O$ values used to develop the lines result from differences in the altitude, amount of evaporation and precipitation that takes place in the two study areas. The city Addis Ababa is located at an elevation of about 2400 m.a.s.l with a mean annual temperature of 17 C° and an average rainfall of about 1200 mm/a (KEBEDE, et. al, 2009). Another reason for the difference is probably that the LMWL for Addis Ababa was derived based on the calculated ***weighted***

mean values which based on data of the rainfall amount. In this study the rainfall amount during the storm event is not considered for the construction of the LMWL.

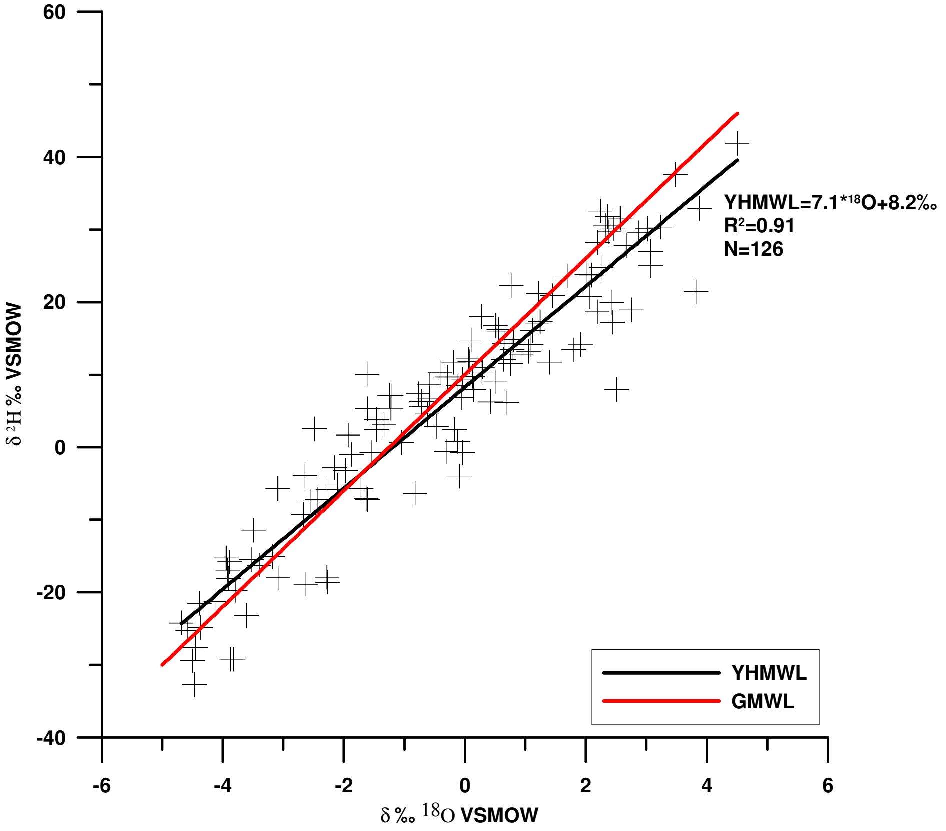

Figure 5.6.2: δ^{18}O vs. δD of rainwater samples collected from Yemen's highland

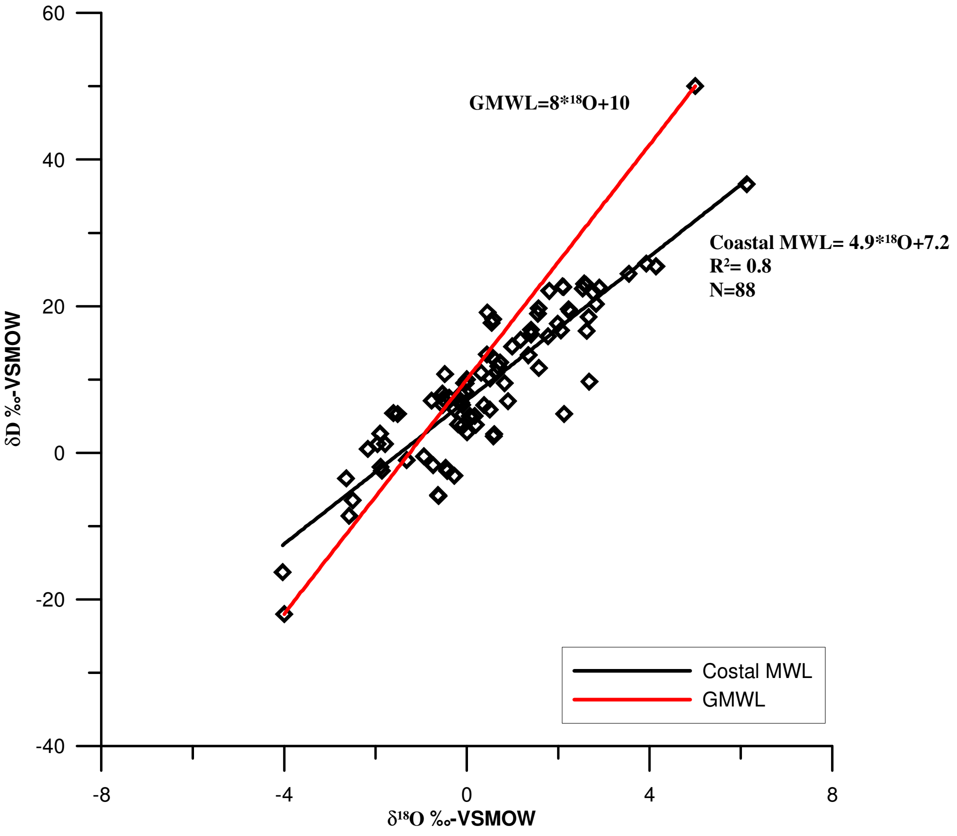

Figure 5.6.3: δ^{18}O vs. δD of rainwater samples collected from coastal regions

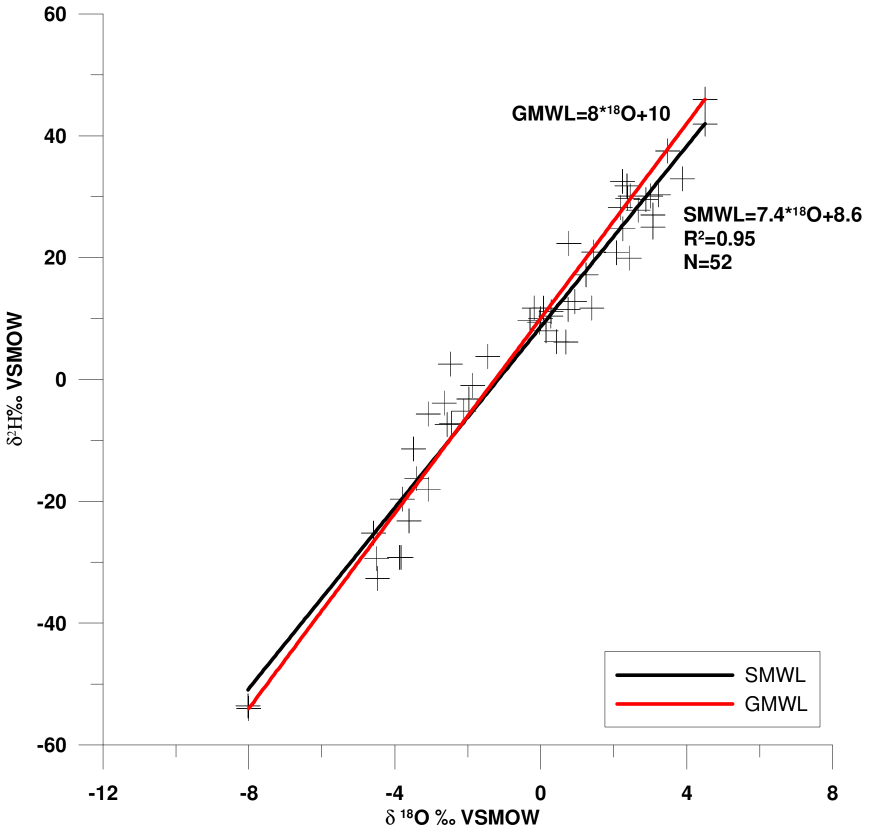

Figure 5.6.4: δ^{18}O vs. δD in rainwater samples collected from Sana'a basin

5.6.1.2 Parameters affecting the isotopes composition in Yemen's rainwater

The Yemen Highlands meteoric water line plots slightly below the global water line (i.e. lower *d*-excess). Such deviations result from differences in climatic factors, such as air temperature, secondary evaporation, seasonality of precipitation and moisture source (CLARK AND FRITZ, 1997), and occur in precipitation globally (SIMPKINS, 1995; ROZANSKI et. al, 1993; FRITZ et. al, 1987). The measured data shows that the stable isotope composition in rainwater falls in Yemen is primarily affected by the **altitude and temperature**. Thus, the rainwater samples collected from Yemen Highland (lower temperature) were more depleted in δ^{18}O and δD than values reported for the coastal stations (higher temperature) which were more enriched in heavy stable isotopes. The lowest δ^{18}O and δD values were found in samples collected from highland with -4.68 and from -32.70 and the highest values were found to be +6.13 and 36.66‰ in samples collected from western coastal plain, respectively.

Other parameters affect the isotopes compositions of Yemen rainwater are the air **humidity and rain amount**. Actually, the temperature, rain amount and the humidity are a function of the altitude. The increase in the altitude is associated with decrease in the temperature and increase in the rainfall amount, consequently a decrease in the humidity. Unfortunately, no rain amount and humidity data were available at the time of the storm event. The available data obtained from the nearest meteorological stations cannot be considered suitable for reliable interpretations because the small-scale variations of the amounts of precipitation and the data were not representative for the sampling stations. Figure 5.6.5 and 5.6.6 present the monthly mean climatic data which include the temperature, precipitation amount and humidity for the period from 1983 to 2002 measured in two representative stations in Yemen's highland and western coastal plain (Sana'a and Hodaidah). The data were used to discuss the effect of the rain amount and the air humidity on the isotopes compositions in Yemen's rainwater.

A reasonably strong correlation can be seen in figure 5.6.7 and 5.6.8 between mean $\delta^{18}O$ values calculated for the station WEC and mean monthly precipitation and humidity, respectively; however, there is scatter within the data. If the exact rain amount and humidity at the time of the storm event could be determined, the correlation might be stronger. Figures 5.6.7 and 5.6.8 show that the samples are more depleted in the heavy isotopes $\delta^{18}O$ and δD with the increase of the rain amount and humidity, whereas the samples become heavier with decrease of the rain amount and humidity as a result of evaporation leading to loss of the lighter isotopes as rain droplets fall through drier air. The humidity effects on the isotopic composition of Yemen rainwater can be confirmed comparing the d-excess values given in equation 5.6.1 and 5.6.2. Generally, the d-excess parameter increases with a deficit in the humidity (SHARP, 2007). The d-excess given in the equation 5.6.1, which is derived for Yemen's Highland (low humidity) is higher (8.2‰) than the value given for the coastal regions (7.1) which are characterized by higher humidity.

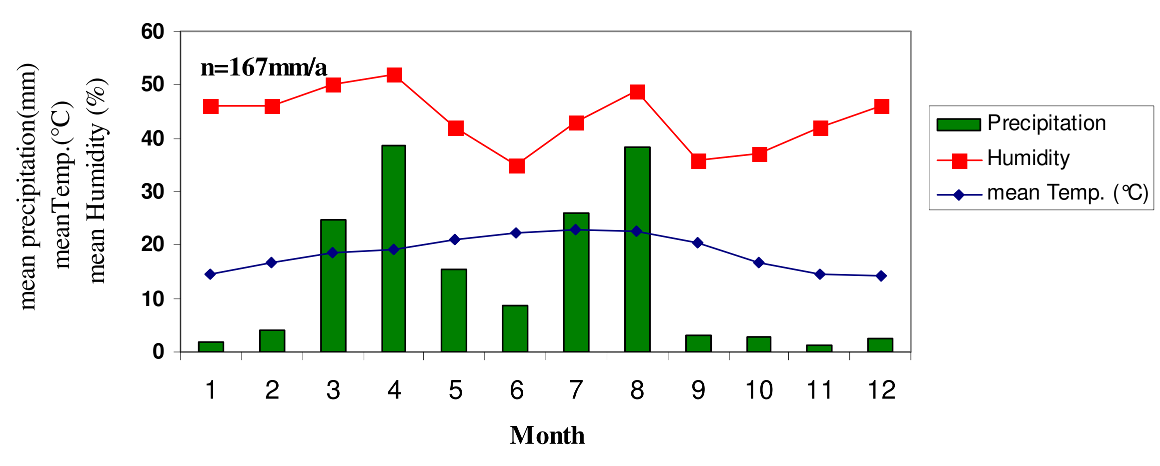

Figure 5.6.5: Mean monthly climatic data for the period 1984-2002 for Sana'a (AREA, 2005)

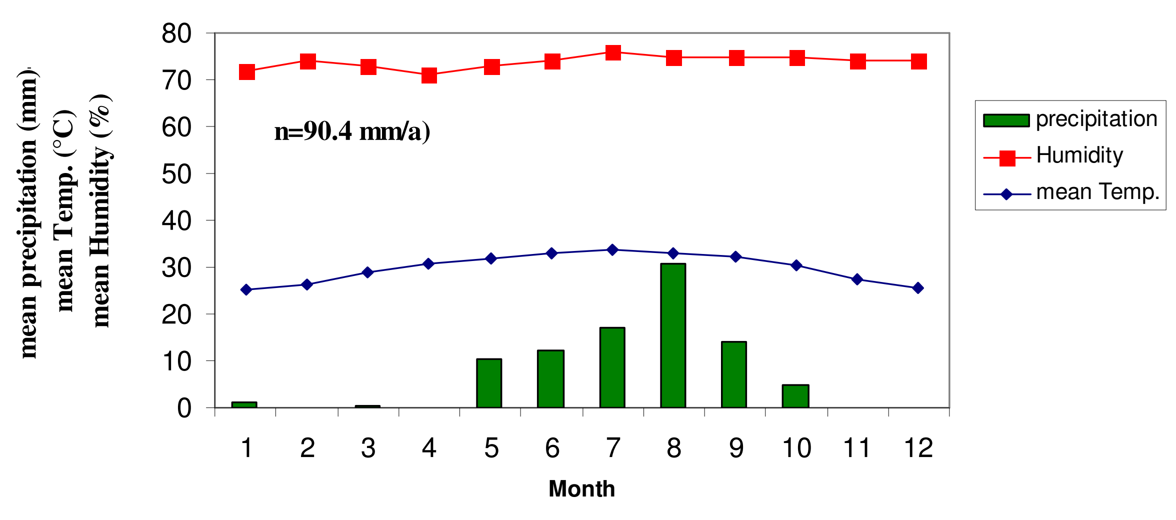

Figure 5.6.6: Mean monthly climatic data for the period 1984-2002 for Al-HODAIDAH (AREA, 2005)

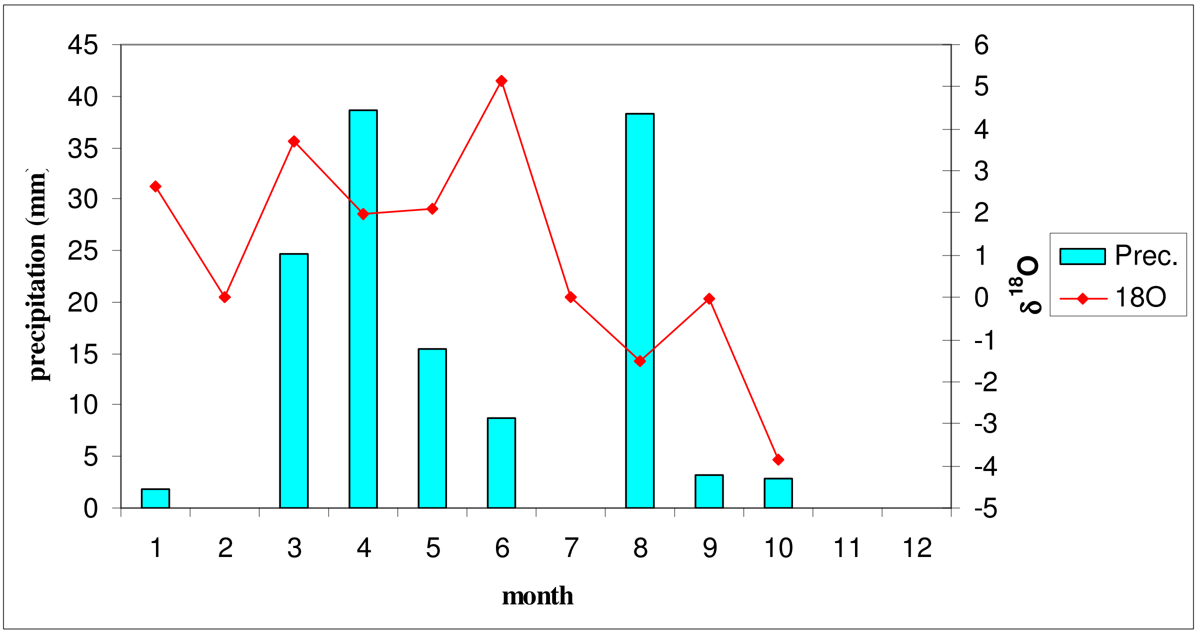

Figure 5.6.7: Mean monthly δ^{18}O (station: WEC) vs. mean monthly precipitation in Sana'a

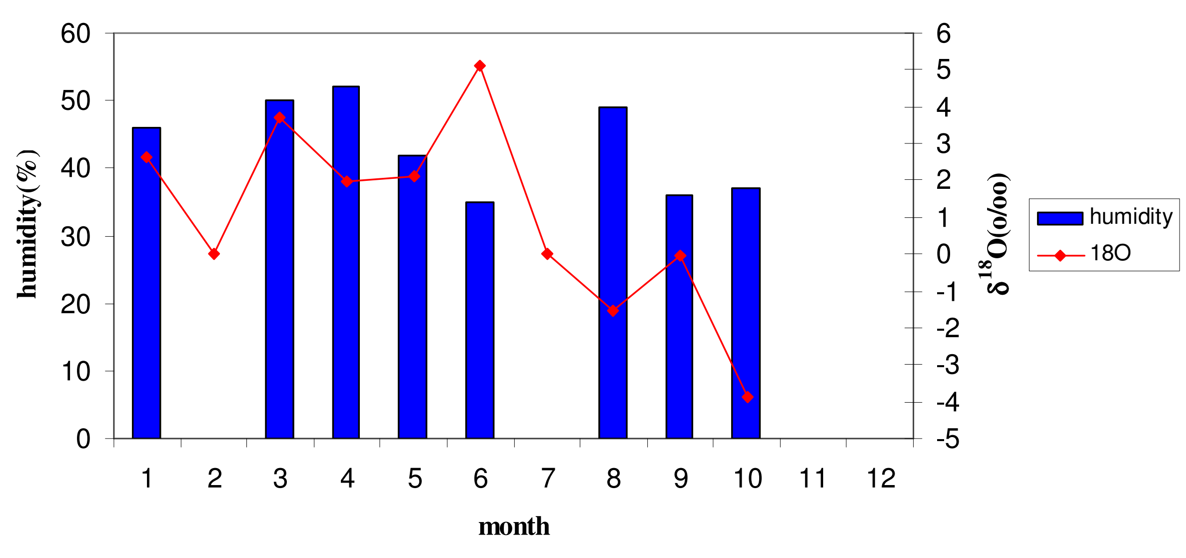

Figure 5.6.8: Mean monthly δ^{18}O (station: WEC) vs. mean monthly humidity in Sana'a

5.6.2 Stable isotopes composition of spring and groundwater in Sana'a basin

Stable isotopes oxygen-18 and deuterium compositions of water samples collected from 24 deep wells and 13 springs located in the Sana'a basin in October 2009 can provide useful information on the recharge sources of the groundwater. The data were used to determine the recharge origin and mixing process of the groundwater in the differences aquifer systems. The relation between δ^{18}O and δD for spring and groundwater samples in the study area is shown in figure 5.6.9. The analytical results of stable isotopic compositions together with those of the d-excess values are presented in tables 10 and 11 in the appendix. One sample collected from spring (SW-6) was excluded because the measured $\delta^{18}O$, δD and d-excess values were found to be outside the expected range. This spring was very dirty and the water is mixed with rain- and surface water from Wadis.

The number of samples collected in this study considered too small for reliable interpretations; therefore the isotope data were complemented by data from groundwater samples collected from deep and shallow wells and studied by A. SHAMSAN in 2005 and 2008 (Fig. 5.6.10). A comparison was made between the result obtained from the current study and analyses data for groundwater sample collected from the Sadah'h basin in October 2008. The data obtained from the Sada'h basin were plotted in figure 5.10.11.

The oxygen and hydrogen isotopic compositions of groundwater's samples collected from the deep wells range from -4.20 to – 1.25‰ and from -24.39 to -5.3‰ with an average of -2.61 and -12.49‰, respectively. The d-excess value ranges from +1.53 to +11.6‰ with an average of +12.30.

Samples collected from springs are divided into two groups according to their ^{18}O and D isotopes composition: one group plots along the GMWL and SMWL; the other group plots above the GMWL and LMWL. This is maybe because of re-evaporation of precipitation from local surface water in low-humidity regions, as in Sana'a region, creates vapour masses with isotopic contents that plot above the local meteoric water line (CLARK and FRITZ, 1997). Values for $\delta^{18}O$ and δD range from -3.05 to -0.45 ‰ and from -13.17 to -0.13‰ with an average to be -2.13 and -6.1‰, respectively. The d-excess was calculated to be +3.50 as minimum and +15.70 ‰ as maximum with an average of +10.96 ‰.

The difference between the isotopic values of water samples collected from wells and the samples collected from the springs could be due to: a) a temperature effect; the samples of springs are colder than the well samples due to the contact with the colder air temperature b) most of the springs are fed by several springs of higher recharge altitude compared with that of the groundwater c) pathways and residence time of spring water is shorter. The contribution of precipitation to groundwater recharge is strongly dependent upon the hydrogeological characteristics of the study area, including bedrock geology, soil cover, soil thickness, climate, and vegetation. This difference can be explained that the groundwater in the wells is mixed with other recharge source, e.g. the re-infiltration of irrigation water or sewage water to the wells.

Figures 5.6.9 and 5.6.10 show that the groundwater samples collected from volcanic and limestone aquifers plot below the SMWL and GMWL and exhibit the lowest d-excess values compared with the samples collected from sandstone and alluvium aquifer indicating relatively higher evaporation before recharge (groundwater in the volcanic and limestone aquifer origins from evaporated meteoric water). The values for $\delta^{18}O$ and δD range between -1.3 and -3.35‰ and -5.3 and -20.5‰ in the volcanic aquifer and -1.25 and -4.20‰ and -8.5‰ and -24.4 in the limestone aquifer, with a mean d-value of 4.9 and 1.5‰, respectively. In 2003 reported FORSTER from heavier $\delta^{18}O$ and δD values found in sub-basin 14 and 19 in the west and southeast of Sana'a City (volcanic aquifer) to be above 0.00‰ and greater than +5‰, respectively, which exhibit a marked tendency towards an evaporate effect (FOSTER, 2003) . In contrast, the samples collected from the sandstone and alluvium aquifer are more depleted in heavy stable isotope $\delta^{18}O$ and δD and show a mean d-excess values to be 11.6‰ in the samples of alluvium aquifer and 12.3‰ in sandstone aquifer. These values are near the d-excess of GWML (10‰) indicating that they are little affected by evaporation before recharge. These interpretations and results are confirmed by plotting the data obtained from studies carried out by SHAMSAN in 2005 and 2008 (Fig. 5.6.10). FOSTER (2003) reported from depletion in $\delta^{18}O$ in the alluvium aquifer with values to be -1.00 to -3.00‰. The $\delta^{18}O$ values measured in this study in the alluvium aquifer range between -1.67 and -3.47‰. The values given by FOSTER (2003) and SHAMSAN (2004 and 2008) show more or less similarity with the results of this study.

The stable isotope composition for a total of 12 groundwater samples collected from the Sada'h basin (about 242km north of Sana'a) in 2008 by the author were used in this study for comparison purpose. The Sada'ah and the Sana'a basin show a similarity in the geology and climatic conditions (temperature, rainfall amount). Geologically the groundwater aquifer in the Sada'ah basin comprises mainly of sandstone, limestone and alluvium quaternary deposits (DANIKH,VAN DER JUN, 1985). The samples are more depleted in the heavy isotopes ^{18}O and Deuterium and plot close to the GMWL and SMWL indicate to recharge from non-evaporated meteoric water (Fig. 5.6.10). The δ-values for ^{18}O and ^{2}H display a wide range and vary from –2.91 to 11.58‰ and from –5.03 to –33.38‰, respectively with d-excess values ranging from +6.86 to +12.28 ‰ with a mean of +9.53 ‰, which is slightly displaced toward the GMWL.

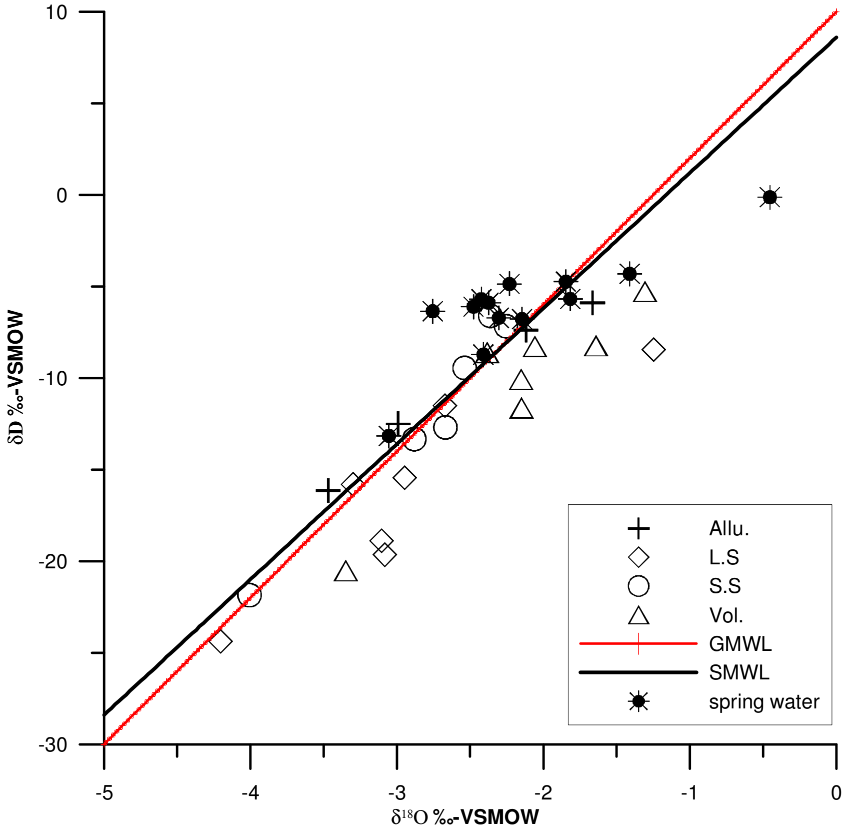

Figure 5.6.9: $\delta^{18}O$ vs. δD of the spring and groundwater - Sana'a basin

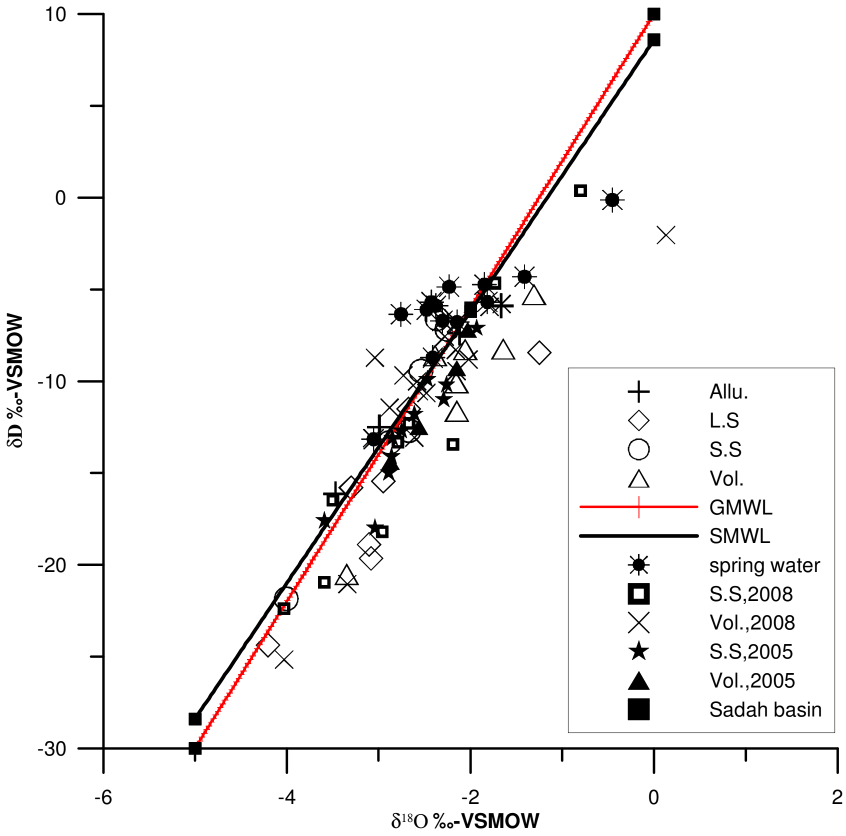

Figure 5.6.10: δ^{18}O versus δD data for Sana'a (samples 2005, 2008 and 2010) and Sada'h basin, 2008

5.6.3 Hydrochemical and stable isotopes data as indicator for recharge source in the Sana'a basin

The stable isotopes ^{18}O and Deuterium and hydrochemical results of this work provide some important insight into the dynamics of aquifer recharge. Generally, two major recharge sources were recognized; the **infiltration of sewage water**, particularly in the alluvium and sandstone aquifer below the urban area in the centre of Sana'a City and in the northern part of the basin, respectively; and the direct **infiltration of the precipitation** falls in the region. The recharge from the infiltration of the sewage water is associated with increase in the chloride and nitrate concentration, mainly in the alluvium and sandstone aquifer, and in some locations in the limestone aquifer in the northern part of the basin.

The recharge from direct infiltration of precipitation can divided into two groups; groundwater recharged from **evaporated meteoric origin**, particularly in the limestone and volcanic aquifer; and water was **little affected by evaporation** before recharge which was the case in the sandstone and alluvium aquifers.

The results show that the groundwater samples are more depleted in the heavy stable isotopes $\delta^{18}O$ and δD concentration than the rain falls in Sana'a region (Fig. 5.6.4 and 5.6.9). This is could be refers to groundwater recharge by precipitation occurs during a colder climate, higher humidity and greater intensity (>20 mm) and duration as the currently climate conditions, particularly in the northern part of the basin (mostly in the sandstone aquifer) where the samples are more depleted (Fig. 5.6.11). This assumption is supported by studies carried out by FOSTER (2003) and SHAMSAN (2004).

SHAMSAN (2004) dated the groundwater in the Tertiary volcanic and sandstone aquifers using ^{13}C, ^{14}C and ^{3}H. According to the measured ^{13}C and ^{14}C values, the groundwater in the both aquifer is estimate to be old water with an age reach 10.000 years, the values range between 6.04 and 10.53 PDB‰ and 22.8 and 75.1 PMC, respectively. The ^{3}H concentration in the groundwater was found to be very low (0.9 to 1.3 TU) indicating that there is no contemporary recharge reached the groundwater in both aquifer during the last 4 decades (SHAMSAN, 2004).

The results obtained from the study carried out by FOSTER (2003) indicate that there is no contemporary recharge having reached the sandstone aquifer and the groundwater in this aquifer considered being palaeo-groundwater (Fig.5.6.12). However, the ^{3}H concentration in the groundwater in alluvium aquifer show post-1965 tritium concentration indicating modern recharge in this aquifer (FOSTER, 2003) [2].

Lower EC (230-620 µS/cm) TDS (150-403 mg/l), Na/Ca ratios (tab. 5 in the appendix) and lower major ion concentrations of spring water in the mountainous area surrounding the Sana'a basin suggest that they have undergone shorter residence times, and that the area is a possible recharge source for the Sana'a basin (Fig.5.6.13).

The higher molar ratios of Na/Cl (Tab. 5 in the appendix) in the samples collected from limestone and volcanic aquifer suggest that the recharge source of the groundwater is different from that of the groundwater in the alluvium and sandstone aquifers and has undergone very strong water–rock interaction during the long residence time (Fig. 5.6.14).

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[2] Tritium (3H), with a half-life of 12.43, is used for dating young groundwater (less than 30 years old). It occurs with high concentration in the atmosphere due to the nuclear test during 1952-1963. The post-1960 groundwater shows tritium value greater than 50TU.

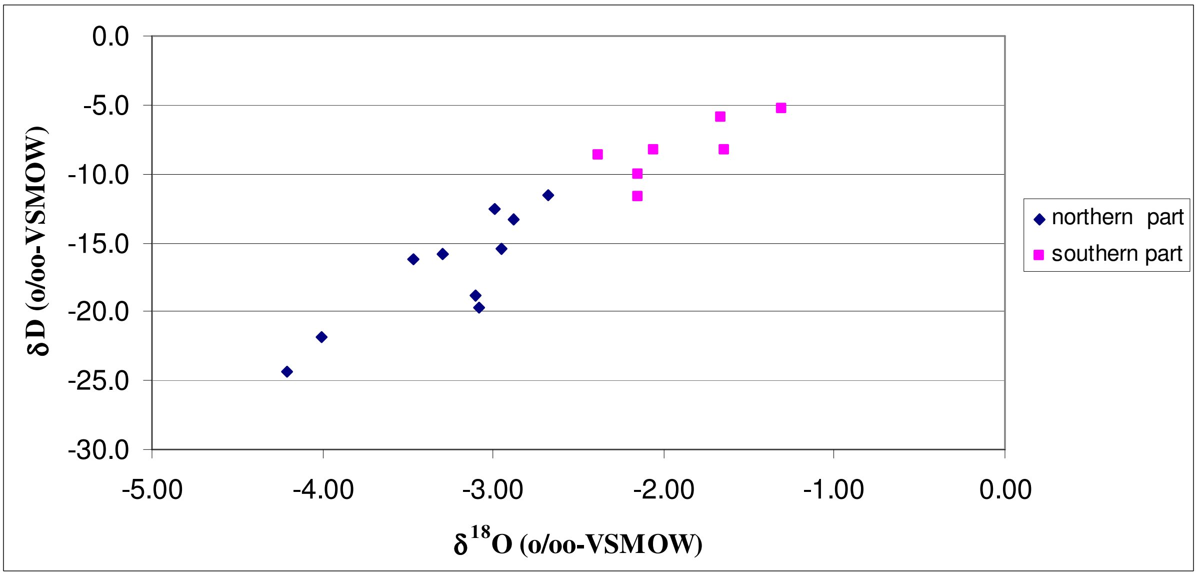

Figure 5.6.11: δ^{18}O versus δD in groundwater samples from northern and southern part of Sana'a basin

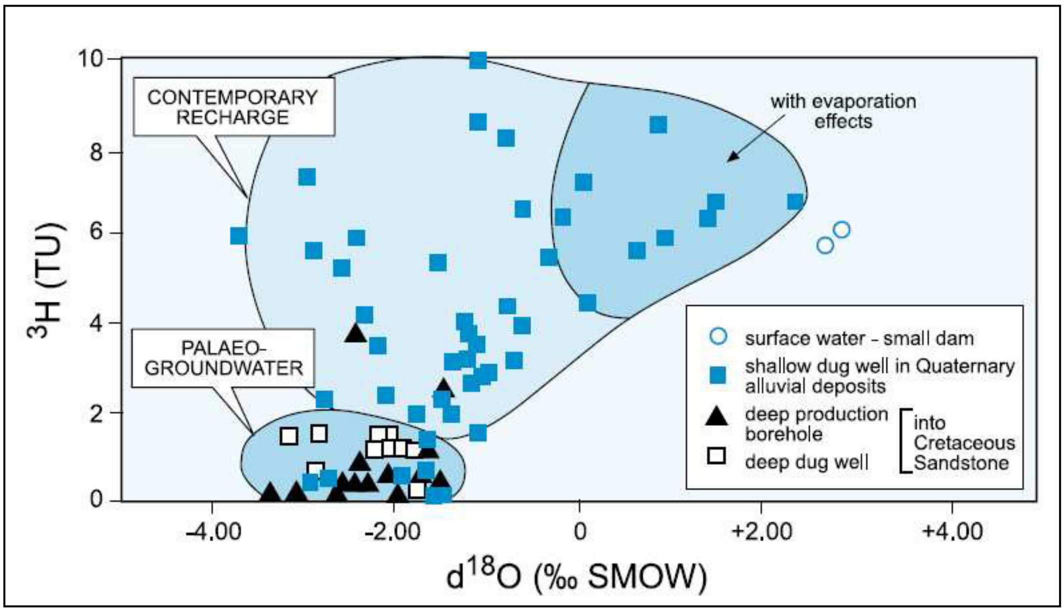

Figure 5.6.12: δ^{18}O versus ^{3}H in groundwater samples from Sana'a basin (from FOSTER, 2003)

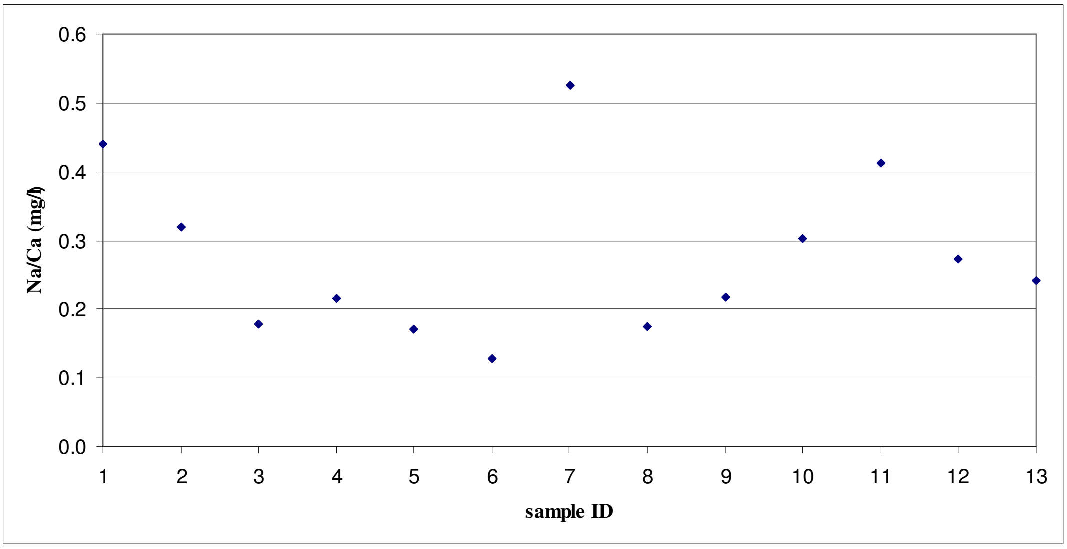

Figure 5.6.13: Na/Ca rations of spring water samples

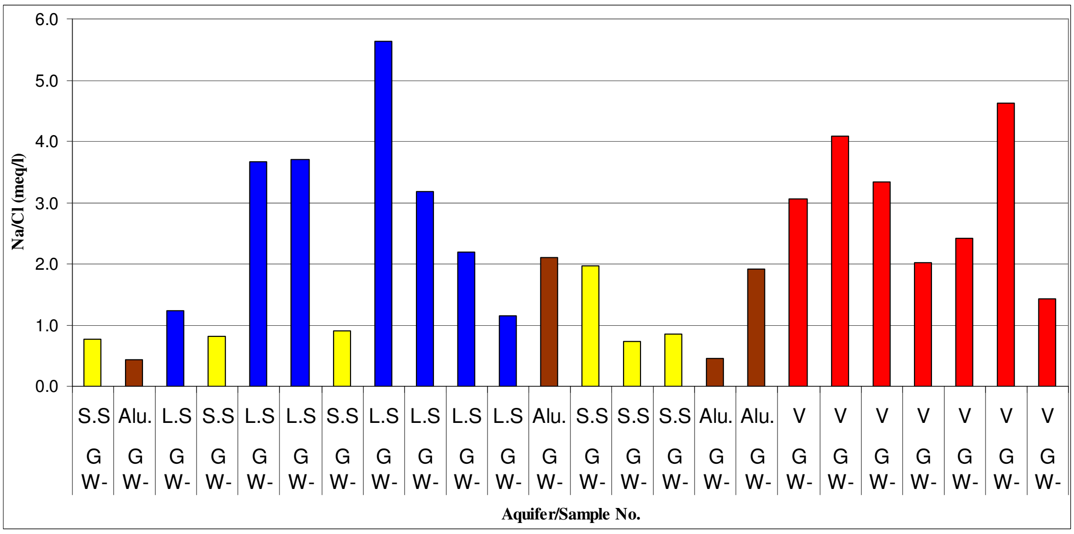

Figure 5.6.14: Na/Cl rations of the groundwater samples

6 Groundwater quality in Sana’a Basin and comparison with previous studies

Comparing the results of this study with data obtained from the SAWAS-project carried out in 1996, and data from studies carried out by SHAMSAN in 2005 and 2008 indicates a decline in groundwater quality in the Sana‘a basin. The comparison is discussed in the following section of this study.

Generally, this comparison is viable because of the reliability of the data sources, but the following points raised concerns:

1 - The sampling wells in the various studies are different

2 - The number of the total samples in the various studies is different

3 - In the current study, the different aquifer systems sampled and evaluated separately, but in previous studies, the alluvium and volcanic aquifer were considered as one system and the sandstone and limestone aquifer as one. Therefore, this system was implemented in the current study to get a better comparison.

6.1 Physicochemical data

The comparison of the physicochemical data of the presents study and the results of studies carried out in 1996 by SAWAS, and in 2005 and 2008 by A. SHAMSAN is tabulated in table 12 in the appendix and illustrated in figures 6.1 to 6.3. The maximum and minimum measured values of the physicochemical composition of the groundwater samples were used in this comparison. The alluvium and the volcanic aquifer are considered as one aquifer system and the sandstone and limestone as one system. It can be observed that the electrical conductivity of the ground water, the concentrations of sulphate and nitrate in the different aquifer systems increased, especially in the limestone and sandstone aquifers. The pH values increased only slightly. Chloride and nitrite concentrations were compared with the results of a study carried out by FOPPEN in 2002 in the alluvium aquifer. An increase in the concentrations of Cl and NO_3 was observed in this study (tab. 6.1).

6.1.1 Sandston and limestone aquifer

Figures 6.1 and 6.2 show that in the most recent analysis the maximum measured concentrations of cations and anions are increased in sandstone and limestone aquifer in the northern part of the basin. An increase in the measured EC and water temperature in 2010 was also recorded (Fig. 6.3) and is quite substantial. It could be due to the increase of groundwater abstraction in the last decades as a result of increasing settlement in this part of the basin. The increase in the concentrations of nitrates and chlorides in the groundwater in 2010 could be point to the infiltration of wastewater. The drainage water of the urban area (Sana’a City) is processed in this area.

The measured pH-values support the interpretation that the groundwater is contaminated by infiltration. Groundwater affected by wastewater has pH values of 0.5-1 units lower than groundwater not affected by wastewater indicating that acidification has taken place

(FOPPEN, 2002). Figure 6.3 and table 12 in the appendix show a slight decrease in pH-values in 2010 ranging between 0.1 and 0.7 units.

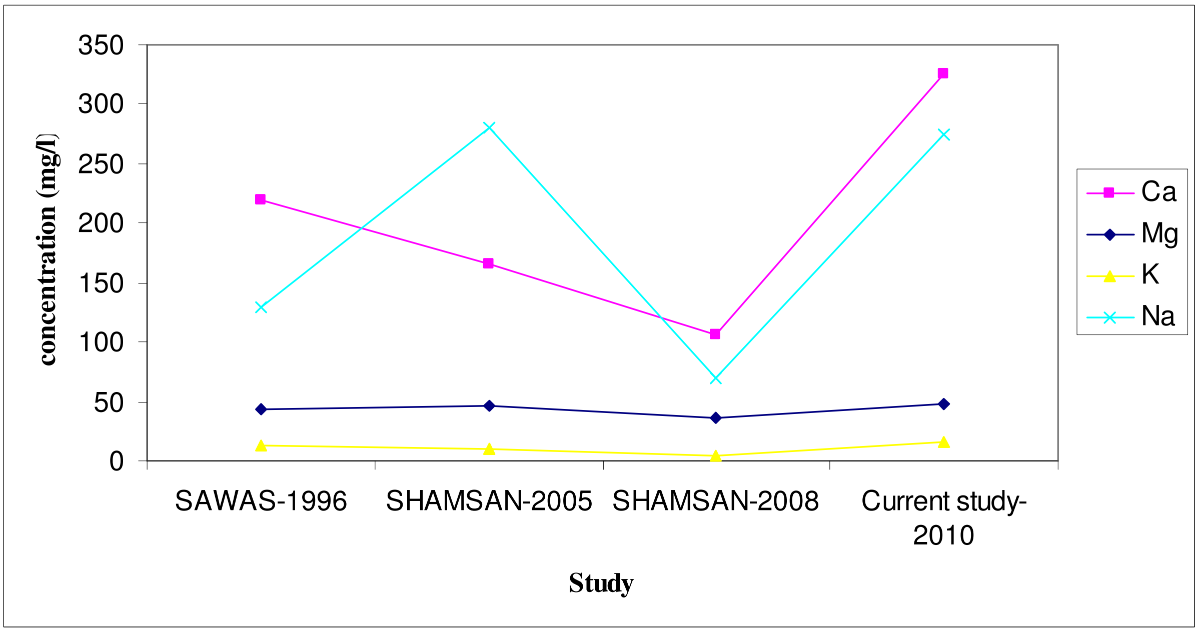

Figure 6.1: Maximum measured values of cations in the Sandstone and Limestone aquifer

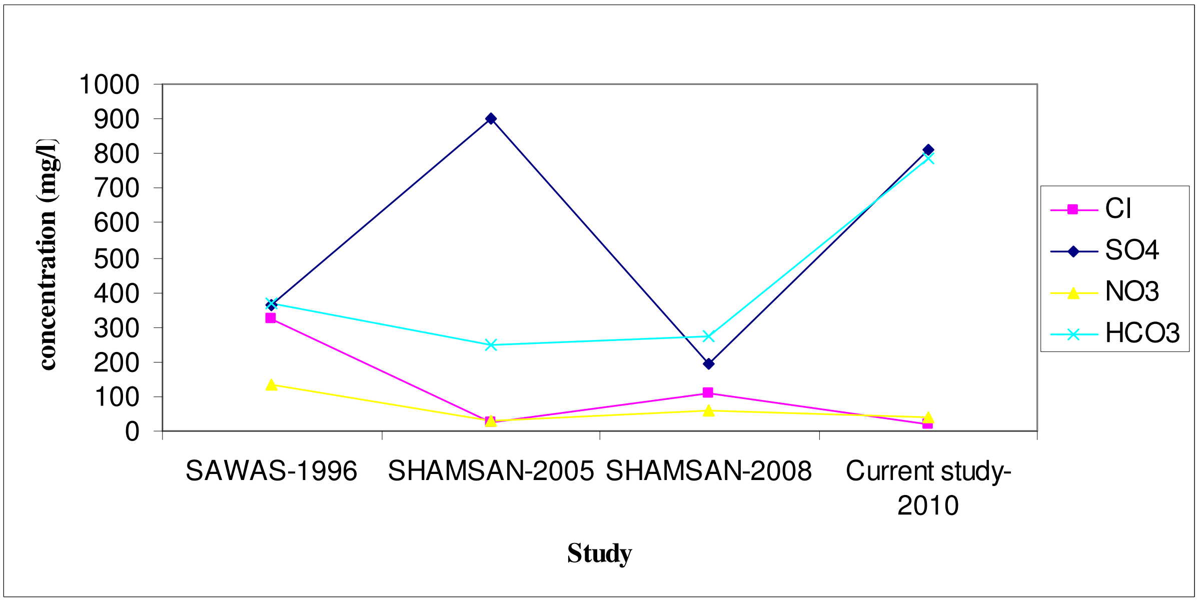

Figure 6.2: Maximum measured values of anions in the Sandstone and Limestone aquifer

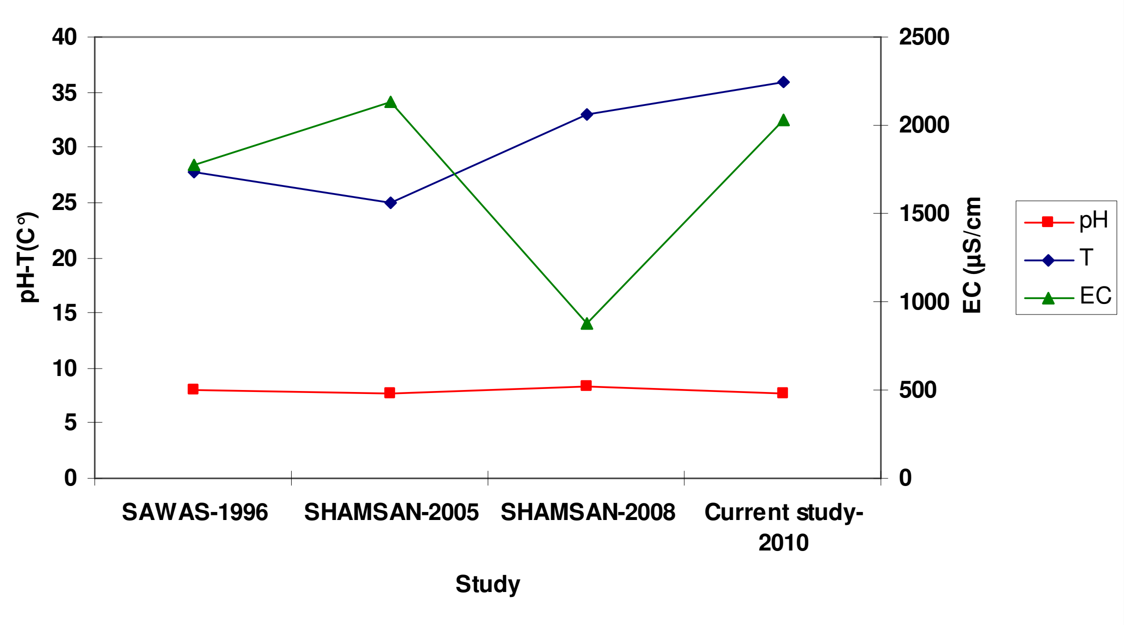

Figure 6.3: Maximum measured values of pH, T and EC in the Sandstone and Limestone aquifer

6.1.2 Alluvium and volcanic aquifer

In the volcanic and alluvium aquifers the highest concentration of all parameters were found in the data obtained by the study of SAWAS (1996) (Fig. 6.4 to 6.6). This is probably due to the higher number of total samples, on the other side; the most samples in the study of 1996 were taken from the wells located in the aquifers below the city of Sana'a (the urban area) where the groundwater is contaminated through the infiltration of sewage water via cesspits (in the old city) or from the sewage ponds northern Sana'a City (SAWAS, 1996). This fact was supported by a study carried out in 2002 by FOPPEN.

FOPPEN in 2002 reported a nitrate concentration in this aquifer below Sana'a City ranging from 1 to 3 mmol/l (106- 354.5 mg/l), chloride concentrations ranging from 3 to 10 mmol/l (35.5- 106 mg/l) and a dominate water type of $CaCl_2$ (FOPEN, 2002). Comparing the result of the current study with the study carried out by FOPPEN in 2002, it becomes clear that the nitrate concentration in the groundwater samples of this study is lower than in 2002 (tab. 6.1). This may be a sampling artifact, as different wells were sample in the two studies. The urban area below Sana'a city was sampled only four times in the current study (four wells located in the alluvium aquifer). As shown in the location map in figure 4.1, the sampled wells do not come from the most contaminated area in the north of Sana'a and the old city.

According to FOPPEN, the chloride concentration in the central and northern parts of Sana'a is equal to the chloride concentration in waste water and ranges from 223 to 558 mg/l (FOPPEN, 2002). This is believed to result from hundreds of years of human settlement and the associated production and infiltration of small amounts of wastewater. This hypothesis is supported by a study carried out by ITALCONSULT in 1973.

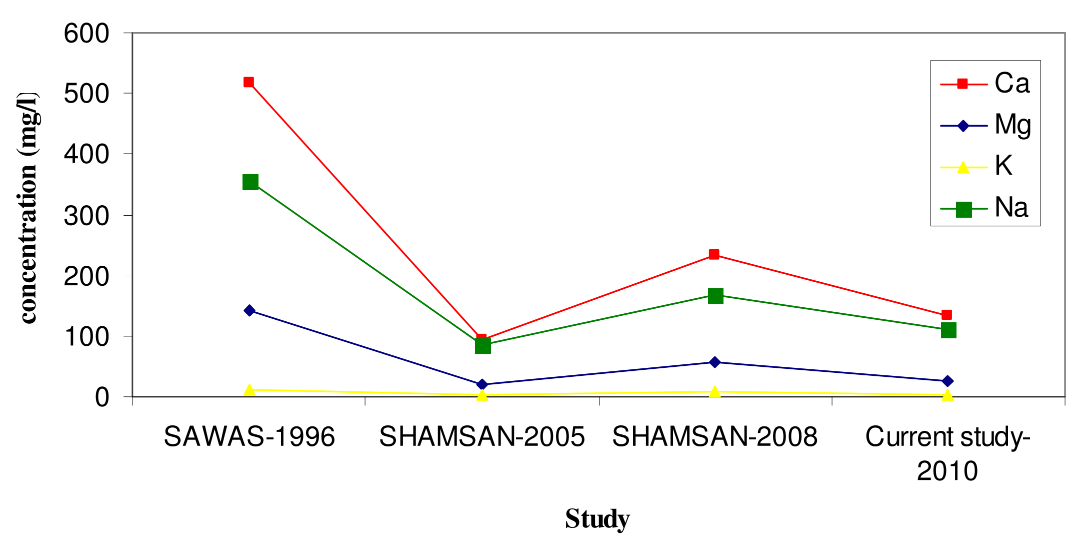

Figure 6.4: Maximum measured values of cations in the Alluvium and Volcanic aquifer

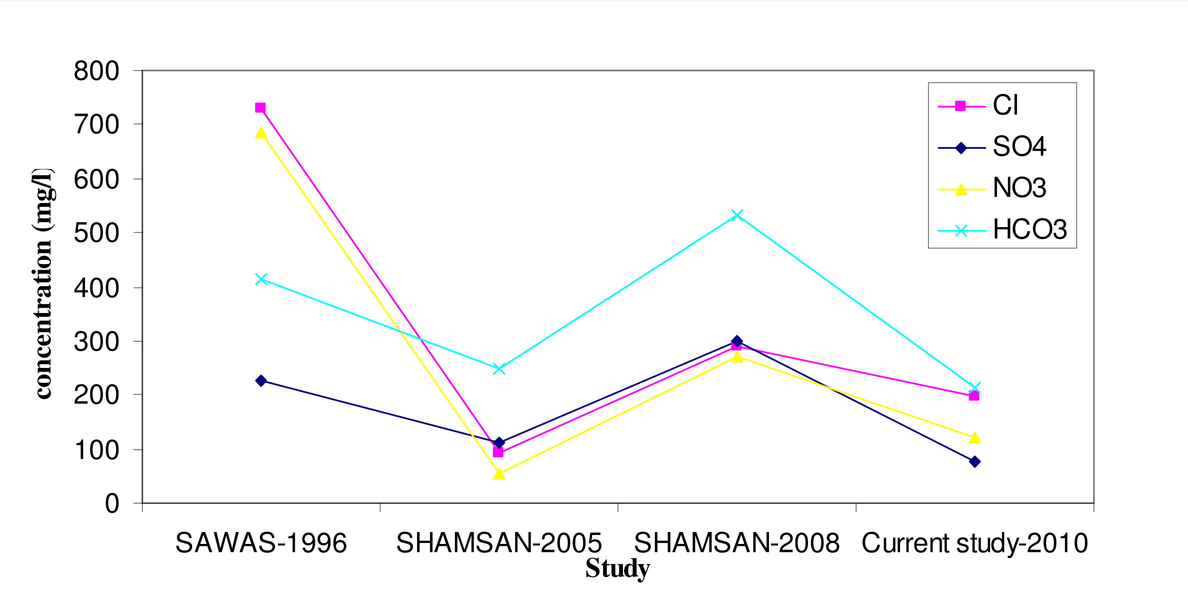

Figure 6.5: Maximum measured values of anions in the Alluvium and Volcanic aquifer

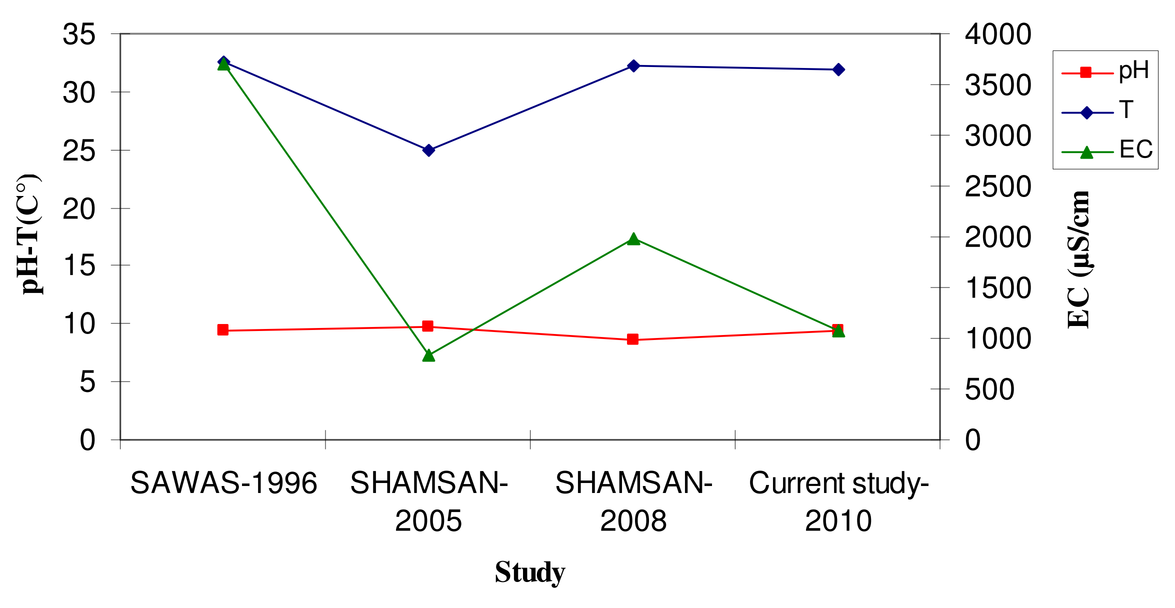

Figure 6.6: Maximum measured values of physicochemical parameters in Alluvium and Volcanic aquifer

Table 6.1: Maximum and minimum nitrite and chloride concentration measured in different studies

Parameters	**HAMDI, 2000**		**Foppen, 2002**		**current study, 2010**	
	Min	**Max**	**Min.**	**Max.**	**Min.**	**Max**
NO_3 (mg/L)	14	38	106	354.5	< 0.02	121
Cl (mg/L)	223	558	35.5	106	27	197

6.2 Stable isotopes composition of rainwater

There are no data existing for stable isotopes compositions in Yemen's rainwater; therefore rainfall isotopes data from Ethiopia as the nearest neighbouring country for Yemen were chosen for a regional comparison. The comparison carried out between the YHMWL and Addis Ababa meteoric water line derived from precipitation samples collected from GNIP stations in Addis Ababa. The city is located at an elevation of about 2400 m.a.s.l with a mean annual temperature of 17C° and an average rainfall of about 1200 mm/yr (KEBEDE, et. al, 2009).

The $\delta^{18}O$ and δD of rainfall at the IAEA station at Addis Ababa vary between -4‰ and 0‰, with the d-excess being in the range between 10 and 20‰. Spatial variation of the isotopic composition of Ethiopian rainfall is relatively small (KEBEDE ET AL., 2005; SCHOELL AND FABER, 1976). The weighted mean isotopic composition of non-evaporated rainfall at Addis Ababa is -2‰ for $\delta^{18}O$ and -1‰ for δD (KEBEDE ET AL., 2009). The local meteoric water line for Addis Ababa is defined by the equation (DEMLIE ET AL. 2008):

$$\boldsymbol{\delta 2H = 7.2*\delta 18O + 12‰} \qquad \text{(eq. 5.6.4)}$$

Comparing the YHMWL with the local meteoric water line for Addis Ababa, the slope of the YHMWL **(7.1)** is similar with the slope for the Addis Ababa meteoric water line **(7.2)**, but the d-excess **8.2‰** for YHMWL is different from that for Addis Ababa **12‰**; this may be a reflection of regional differences in the two study areas. The differences in δD and $\delta^{18}O$ values used to develop the lines result from differences in the altitude, amount of evaporation and precipitation that takes place in the two study areas. The city Addis Ababa is located at an elevation of about 2400 m.a.s.l with a mean annual temperature of 17C° and an average rainfall of about 1200 mm/yr (KEBEDE; ET. AL.2009). Other reason for the difference is probably that the LMWL for Addis Ababa was derived on the basis calculated of the ***weighted mean values*** which based on data about the rainfall amount. In this study the rainfall amount during the storm event is not considered for the construction of the LMWL.

The LMWL for Sana'a basin constructed in this study was compared with the line derived by SHAMSAN (2008) for the Sana'a basin and defined by the equation (SHAMSAN, 2008):

$$\boldsymbol{\delta^{2}H = 8*\delta^{18}O + 13‰} \qquad \text{(eq. 5.6.5)}$$

The slope of this line (8) is close to the slope derived in the current study (7.4), but the d-excess value 13‰ is higher than the value 8.6‰ recorded in this study. This is probably because of the following:

- In the study carried out by SHAMSAN in 2008 only rain events above 10mm was considered, but in this study the amount effect was not considered because of a lack of information on the amount of the rain.

- The line derived by SHAMSAN (2008) was based on the calculated ***weighted mean values.***
- The total rainwater samples collected in the both studies is different. The total samples number collected by SHAMSAN, 2008 is unknown

6.3 Comparison with WHO and NWRA standards

To ascertain the suitability of ground- and spring water of Sana'a basin for drinking as well as irrigation purpose, physicochemical parameters of the water samples taken from Sana'a basin are compared with the guideline recommended by WHO, 2004 and NWRA, 2000 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 either by NWRA or WHO, the concentration was compared with Europe Unions standards (EU-standard). The result of the comparison is presented in table 1 and 2 in the appendix.

Generally, it can be said that ground- and spring water in 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 the WHO-standard, but do not exceeded the standard values recommended by NWRA in 2000. Heavy metals Pb, Cu, Ni, Co, Cd are below the detection limit in all 24 groundwater samples. The heavy metals As, Mn, Al and Zn were found in low concentration in some of groundwater samples. The values exceeded neither the values recommended by WHO, 2004 nor by NWRA, 2000.

In contrast, Br concentrations in all of ground- and spring water samples exceeded the guidelines values recommended by EU.

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 (tab. 4 and 5 in the appendix).

A classification of water based on SAR was carried out to ascertain the suitability of water for irrigation purposes (see section 5.4.2). The calculated TDS and SAR indicate that the water of

Sana’a basin is suitable for irrigation purposes. The water was classified based on SAR as excellent.

Microbiological analyses were not conducted in this study. According to SAWAS (1996) the groundwater in the Quaternary alluvium, Tertiary volcanic and Cretaceous sandstone is microbiologically polluted. Different bacteria (e.g. coliform, faecal coliformm etc.) were found in analysed groundwater samples (SAWAS, 1996).

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).

As shown in figure 7.1, 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 (SAWAS, 1996 and Al-HAMDI, 2000).

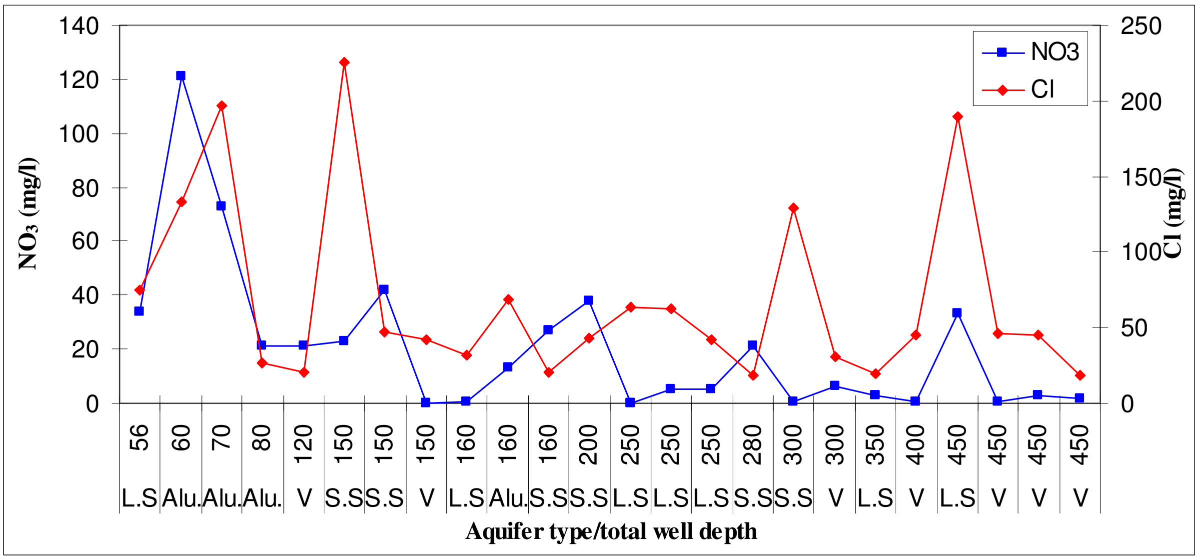

Figure 6.7: Nitrite and chloride concentration in the groundwater samples vs. total depth of the well

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Appendix

Table 1: Physicochemical characteristics of groundwater samples collected from Sana'a basin

Sample ID	Well description				Physico-chemical			Cations (mg/l)				Anions (mg/l)					TDS (mg/l)	Ion Error %
	Aquifer type	depth of well	depth to WT	Elevation (m)	pH	T (C°)	EC µs/cm	Mg	Na	K	Ca	CL	Br	NO3	SO4	HCO3		
GW-1	S.S	300	140	2233	7,0	26	790	20.3	64.5	4.9	82.6	129	0.4	0.5	125	214.2	513.5	4.91
GW-2 (dug)	Alu.	70	60	2244	8,0	23	1070	23.8	56.5	2.7	133	197	2	73	124	126	695.5	-0.63
GW-3	L.S	160	55.14	2181	7,5	27	1380	35.2	25.7	5.4	162	32	0.5	0.3	326	315	897	-1.25
GW-4	S.S	150	120	2093	7,1	28	1002	40.4	119	3.3	135	225	2.5	23	237	252	651.3	-0.79
GW-5	L.S	250	210	2009	6,3	36	1970	72	152	16.4	326	64	0.6	0.2	812	787.5	1280.5	-1.98
GW-6	L.S	250	220	2006	6,3	35	2030	74.5	149	15.5	321	62	0.8	5	780	781.2	1319.5	-1.55
GW-7	S.S	150	80	2130	5,6	32	680	23.9	27.6	5.1	85.2	47	0.7	42	98	258.3	442	-2.33
GW-8	L.S	56	39	2102	7,6	25	1300	26.5	274	3.6	44.6	75	1	34	330	378	845	1.05
GW-9	L.S	250	210	2130	7,0	32	1060	39.6	86.8	7.1	126	42	0.6	5	292	371.7	689	0.11
GW-10	L.S	350	342	2291	7,2	33	560	27.1	27.1	4.8	64	19	0.3	3	37	333.9	364	-0.39
GW-11	L.S	450	320	2152	7,2	28	1340	44	142	9.2	106	190	0.7	33	125	466.2	871	-1.31
GW-12	Alu.	160	32.92	2176	8,2	28	520	3.8	94	2.3	22	69	0.6	13	70	207.9	338	-5.84
GW-13	S.S	280	180	2546	7,6	27	350	8.6	23	3.7	41.3	18	0.3	21	17	195.3	227.5	-3.27
GW-14	S.S	200	170	2557	7,2	21	490	9.6	20.3	9.6	69.4	43	0.3	38	33	207.9	318.5	-2.40
GW-15	S.S	160	130	289	7,4	23	370	8.1	11.1	10.8	51	20	0.3	27	14	201.6	240.5	-3.67
GW-16 (dug)	Alu.	60	40	2264	8,1	24	980	24.6	38.8	2	125	133	1.2	121	52	214.2	637	-0.77
GW-17 (dug)	Alu.	80	60	2294	8,1	23	440	8.1	33.5	1.8	52.8	27	0.4	21	25	195.3	286	-0.11
GW-18	V	400	320	2338	9,4	31	400	0.2	89.4	1.1	2.9	45	0.6	0.8	46	151.1	260	-3.67
GW-19	V	150	120	2428	8,9	29	470	0.25	111.3	0.8	3.9	42	0.4	0	42	176.4	305.5	0.61
GW-20	V	450	255	2379	9,0	32	450	0.18	99.5	0.4	4.1	46	0.7	0.3	47	144.9	292.5	-0.58
GW-21	V	300	250	2384	7,7	27	450	7.9	40.6	1.4	52.5	31	0.5	6.5	76	157.5	292.5	-0.38
GW-22	V	450	250	2322	8,3	22	380	2.1	70.5	0.9	19.9	45	0.6	3	41	151.2	247	-2.25
GW-23	V	450	255	2558	8,2	26	280	1.8	54	1.1	13.5	18	0.3	1.5	18	182.7	182	-4.97
GW-24	V	120	84	2927	7,5	20	350	7.3	19.5	1.7	59.5	21	0.3	21	17	182.7	227.5	1.02
WHO-Standard					6.5-8.5		1500	150	200	200	200	250	0.01 (E)	50	250	240	1000	
NWRA-Standard *					6.5-9	25	2500	150	400	12	200	600	No GL.	50	400	500	1500	

Table 2: Physicochemical characteristics of spring water collected from Sana'a basin

Sample ID	Lithology	Location			Physico-chemical			Cations (mg/l)				Anions (mg/l)					TDS (mg/l)	Ion Error %
		N	E	Elevation (m.a.s.l)	EC µs/cm	pH	T (C°)	Mg	Na	K	Ca	CL	Br	NO3	SO4	HCO3		
SW-1	V	1689925	411332	2455	330	8.2	23	7.3	21.5	1	48.9	14	0.3	15	12	189	214.5	0.17
SW-2	L.S	1739706	444175	2103	550	7.2	21	18.2	24.8	2.8	77.5	27	0.4	11	44	359.1	357.5	0.09
SW-3	S.S	1710238	381567	2502	300	6	22	5	6.5	0.9	36.5	12	0.2	5	10	151.2	195	-4.31
SW-4	A contact with S.S	1710146	381505	2460	230	8.2	19	5.1	8.2	0.8	37.9	13	0.2	2	11	157.5	149.5	-5
SW-5	A contact with S.S	1711566	379465	2500	240	7.1	21	6.4	6.4	1.5	37.6	11	0.2	9	11	157.5	156	-4.44
SW-6	S.S	1710881	385063	2541	280	8.4	21	6.6	6.4	2.6	50.1	11	0.2	3	26	170.1	182	-4.58
SW-7	S.S	1715056	382618	2582	620	7.4	22	10.5	35.6	32.9	67.8	61	0.4	69	53	182.7	403	-2.14
SW-8	S.S	1717753	376514	2752	320	6.7	22	7.8	8.5	2.9	48.5	15	0.2	13	40	176.4	208	-1.10
SW-9	Vcontact with A	1714999	385890	2522	490	7.7	23	15	16.9	1	77.6	34	0.4	10	56	258.3	318.5	-5
SW-10	V	1713590	387923	2537	380	9.4	20	10.8	16.5	1	54.5	21	0.5	16	19	214.2	247	-2.65
SW-11	V	1701576	444017	2669	400	7.6	22	9.4	23.2	1.1	56.3	27	0.4	10	37	220.5	260	-2.26
SW-12	V	1691763	392027	2988	410	7.3	18	8.6	17.2	1.4	63.2	18	0.3	22	17	207.9	266.5	-3.48
SW-13	V	1691588	392109	3022	330	8.4	18	7.4	13.1	1	54.2	19	0.3	25	18	157.5	214.5	0.10
WHO - Standard					1500	6.5-8.5	-	150	200	200	200	250	0.01 (E)	50	250	240	1000	
NWRA-Standard					2500	6.5-9	25	150	400	12	200	600	No GL	50	400	500	1500	

- (E): EU-Standard
- The red marks means that the concentration exceeded the values recommended either by WHO or NWRA

Table 3: Heavy metals in groundwater samples collected from Sana'a basin (values in mg/l)

Sample ID	**Aquifer type**	**As**	**Pb**	**Cu**	**Ni**	**Co**	**Cd**	**Fe**	**Mn**	**Al**	**Zn**
GW-1	S.S	U	U	U	U	U	U	0.37	0.03	U	U
GW-2 (dug)	Alu.	U	U	U	U	U	U	0.09	U	0.06	0.03
GW-3	L.S	U	U	U	U	U	U	0.71	0.08	U	U
GW-4	S.S	U	U	U	U	U	U	0.84	U	U	U
GW-5	L.S	U	U	U	U	U	U	1	0.07	U	U
GW-6	L.S	U	U	U	U	U	U	0.3	U	U	0.2
GW-7	S.S	U	U	U	U	U	U	0.03	U	U	U
GW-8	L.S	U	U	U	U	U	U	0.19	U	U	U
GW-9	L.S	U	U	U	U	U	U	0.03	U	U	U
GW-10	L.S	U	U	U	U	U	U	0.04	U	U	U
GW-11	L.S	U	U	U	U	U	U	0.33	0.05	0.61	0.04
GW-12	Alu.	U	U	U	U	U	U	0.12	U	0.04	U
GW-13	S.S	U	U	U	U	U	U	0.05	U	U	0.04
GW-14	S.S	U	U	U	U	U	U	0.07	U	U	U
GW-15	S.S	U	U	U	U	U	U	U	U	U	U
GW-16 (dug)	Alu.	0.003	U	U	U	U	U	0.07	U	U	0.42
GW-17 (dug)	Alu.	U	U	U	U	U	U	U	U	U	U
GW-18	V	U	U	U	U	U	U	0.7	0.02	U	0.05
GW-19	V	0.003	U	U	U	U	U	0.24	U	0.08	U
GW-20	V	0.007	U	U	U	U	U	0.18	U	U	U
GW-21	V	U	U	U	U	U	U	0.07	U	U	U
GW-22	V	U	U	U	U	U	U	U	U	U	U
GW-23	V	U	U	U	U	U	U	0.05	U	U	0.23
GW-24	V	U	U	U	U	U	U	0.09	U	0.03	U
WHO-Standard		0.01	0.01	2.0	0.02	No GL	0.003	No GL	0.5	0.2	3.0
NWRA-standard*		0.01	0.05	1	0.02	No GL	0.005	1	0.2	0.3	15

- U: below the detected limit
- * The values given by NWRA refer to the maximal concentration which allowed in drink water
- The red marks means that the concentration exceeded the values recommended either by WHO or NWRA

Table 4: Calculated Ca^{+2} and Mg^{+2} hardness and SAR in the groundwater samples collected from Sana'a basin

Sample ID	**Aquifer type**	**SAR (meq/l)**	**Total hardness (mg/l)**	**Na/Ca (mg/l)**	**Na/Cl (meq/l)**	**SO4/Cl (meq/l)**	**MH(%)**
GW-1	S.S	1.17	289.73	0.8	0.8	3.4	19.7
GW-2	Alu.	0.84	430.08	0.4	0.4	5.8	15.2
GW-3	L.S	0.34	549.32	0.2	1.2	5.5	17.8
GW-4	S.S	1.63	503.14	0.9	0.8	6.1	23.0
GW-5	L.S	1.40	1110.20	0.5	3.7	4.6	18.1
GW-6	L.S	1.38	1107.95	0.5	3.7	4.4	18.8
GW-7	S.S	0.48	310.99	0.3	0.9	2.3	21.9
GW-8	L.S	5.68	220.15	6.1	5.6	1.2	37.3
GW-9	L.S	1.22	477.36	0.7	3.2	1.9	23.9
GW-10	L.S	0.51	271.11	0.4	2.2	0.4	29.7
GW-11	L.S	2.07	445.40	1.3	1.2	2.3	29.3
GW-12	Alu.	3.44	70.58	4.3	2.1	0.7	14.7
GW-13	S.S	0.60	138.51	0.6	2.0	0.2	17.2
GW-14	S.S	0.43	212.86	0.3	0.7	0.9	12.2
GW-15	S.S	0.27	160.71	0.2	0.9	0.3	13.7
GW-16	Alu.	0.59	413.36	0.3	0.4	2.4	16.4
GW-17	Alu.	0.80	165.21	0.6	1.9	0.3	13.3
GW-18	V	9.69	8.07	30.8	3.1	0.3	6.5
GW-19	V	10.44	10.78	28.5	4.1	0.2	6.0
GW-20	V	9.24	10.99	24.3	3.3	0.3	4.2
GW-21	V	0.98	163.64	0.8	2.0	0.8	13.1
GW-22	V	2.84	58.36	3.5	2.4	0.4	9.5
GW-23	V	2.59	41.13	4.0	4.6	0.1	11.8
GW-24	V	0.45	178.68	0.3	1.4	0.2	10.9
WHO-Standard			500				
NWRA-standard*			500				

Table 5: Calculated Ca^{+2} and Mg^{+2} hardness and SAR in the spring water samples collected from Sana’a basin

Sample ID	lithology	SAR (meq/l)	Total hardness (mg/l)	Na/Ca (mg/l)	Na/Cl (meq/l)	SO4/Cl (meq/l)	MH (%)
SW-1	V	0.54	152	0.4	2.4	0.1	13.0
SW-2	L.S	0.47	268	0.3	1.4	0.6	19.0
SW-3	S.S	0.19	112	0.2	0.8	0.2	12.0
SW-4	A contact with S.S	0.23	116	0.2	1.0	0.2	11.9
SW-5	A contact with S.S	0.18	120	0.2	0.9	0.3	14.5
SW-6	S.S	0.16	152	0.1	0.9	0.6	11.6
SW-7	S.S	0.75	213	0.5	0.9	1.2	13.4
SW-8	S.S	0.21	153	0.2	0.9	1.0	13.9
SW-9	Vcontact with A	0.33	256	0.2	0.8	1.5	16.2
SW-10	V	0.38	181	0.3	1.2	0.3	16.5
SW-11	V	0.53	179	0.4	1.3	0.6	14.3
SW-12	V	0.38	193	0.3	1.5	0.2	12.0
SW-13	V	0.31	166	0.2	1.1	0.4	12.0
WHO-Standard			500				
NWRA-standard*			500				

Table 6: Saturation indices (SI) of groundwater samples

Sample ID	Calcite	Dolomite	Anhydrite	Gypsum
GW-1	-0.35	-1.03	-1.74	-1.5
GW-2	-0.41	-1.29	-1.61	-1.4
GW-3	0.03	-0.33	-1.16	-0.9
GW-4	-0.15	-0.54	-1.38	-1.2
GW-5	0.57	0.77	-0.7	-0.5
GW-6	0.57	0.78	-0.72	-0.5
GW-7	-0.25	-0.8	-1.83	-1.6
GW-8	-0.48	-0.91	-1.7	-1.46
GW-9	-0.01	-0.25	-1.31	-1.07
GW-10	-0.23	-0.55	-2.3	-2.09
GW-11	0.03	-0.04	-1.7	-1.51
GW-12	-0.89	-2.36	-2.43	-2.2
GW-13	-0.60	-1.64	-2.8	-2.51
GW-14	-0.39	-1.38	-2.31	-2.07
GW-15	-0.50	-1.53	-2.8	-2.52
GW-16	-0.19	-0.81	-2	-1.8
GW-17	-0.52	-1.56	-2.51	-2.3
GW-18	-2.02	-	-3.57	-3.3
GW-19	-1.78	-	-3.45	-3.2
GW-20	-1.74	-	-3.23	-3.03
GW-21	-0.63	-1.82	-2.04	-1.8
GW-22	-1.05	-2.79	-2.67	-2.43
GW-23	-1.1	-3.04	-3.14	-2.9
GW24	-0.5	-1.61	-2.62	-2.3

Table 7: Saturation indices (SI) of spring water samples

Sample ID	Calcite	Dolomite	Anhydrite	Gypsum
SW-1	-0.55	-1.64	-2.83	-2.59
SW-2	-0.13	-0.6	-2.18	-1.94
SW-3	-0.74	-2.05	-2.98	-2.74
SW-4	-0.71	-2	-2.93	-2.7
SW-5	-0.72	-1.99	-2.94	-2.7
SW-6	-0.57	-1.78	-2.47	-2.23
SW-7	-0.48	-1.5	-2.15	-1.91
SW-8	-0.59	-1.73	-2.32	-2.08
SW-9	-0.26	-0.94	-2.05	-1.82
SW-10	-0.46	-1.36	-2.61	-2.37
SW-11	-0.44	-1.39	-2.32	-2.08
SW-12	-0.41	-1.42	-2.6	-2.36
SW-13	-0.58	-1.76	-2.616	-2.38

Table 8: Description of rainwater sampling-sites

Station name	Station ID	Total Samples	Location		
			East	North	Elevation (m)
Bajel	BJ	25	318747	1668053	224
Dhabra	DB	5	369962	1635634	1000
Mafhaq	MF	8	381781	1667838	1600
Al-Ameer	AM	5	360252	1662424	2200
Walan	WA	9	419363	1663585	2500
Sukhnah	SKH	9	331030	1635224	350
Amran	AMR	6	397100	1748600	2190
Taiz	TAIZ	10	393212	1500782	1311
Hajah	HJ	12	350401	1735363	1739
Rebat	RB	42	345162	1623751	598
Dhamar	DH	10	434345	1608670	2360
Hasabah(Sana'a basin)	HS	19	415794	1702878	2246
WEC (Sana'a basin)	WEC	42	412044	1699288	2285
Sayoon	SY	3	900000	1750000	700
Hodaidah	HOD	12	279506	1636321	14
Bani Al-ameri	RI	34	363120	1615328	2016
Dares (Sana'a basin)	DAR	4	415289	1702498	2245
Total	17	255			

Table 9: Isotopic composition in Yemen's rainwater

sampleID	Date	Temperatur	δ^{18}O (o/oo)	1 s	δD(o/oo)	1 s	d- excess	Elevation (m)
AM-01/08	02.05.2008	25	0.65	0.02	14.3	0.4	9.1	2200
AM-02/08	08.05.2008	24	-0.17	0.06	2.4	0.3	3.8	2200
AM-03/08	30.05.2008	24	2.44	0.03	17.2	0.2	-2.3	2200
AM-04/08	03.06.2008	18	-2.63	0.04	-18.9	0.2	2.2	2200
AM-05/08	24.10.2008	20	-1.53	0.03	-0.8	0.5	11.5	2200
AMR-1	5.5.2008	19	1.69	0.01	23.6	0.3	10.1	2190
AMR-2	5.9.2008	20	2.75	0.03	18.9	0.4	-3.1	2190
AMR-3	5.10.2008	19	-3.9	0.02	-18.1	0.2	13.1	2190
AMR-4	5.15.2008	18	0.64	0.03	12.1	0.4	6.9	2190
AMR-5	5.29.2008	18	-3.92	0.04	-16.9	0.2	14.5	2190
AMR-6	5.30.2008	19	-4.45	0.02	-27.6	0.2	8	2190
BJ-01/09	12.05.2009	27	3.93	0.01	25.8	0.2	-5.6	224
BJ-02/09	18.05.2009	31	0.90	0.02	7.0	0.4	-0.2	224
BJ-03/09	19.05.2009	30	1.58	0.02	11.6	0.4	-1.1	224
BJ-04/09	30.06.2009	24	2.26	0.00	19.3	0.3	1.2	224
BJ-05/09	10.08.2009	28	0.57	0.03	13.0	0.3	8.4	224
BJ-06/09	17.08.2009	25	0.82	0.02	9.5	0.3	2.9	224
BJ-07/09	25.08.2009	27	-4.03	0.02	-16.3	0.1	16.0	224
BJ-08/09	30.08.2009	29	0.45	0.01	19.2	0.5	15.5	224
BJ-09/09	03.09.2009	30	0.68	0.01	11.8	0.3	6.3	224
BJ-1/08	6.8.2008	31	2.13	0.02	5.3	0.2	-11.7	224
BJ-10/09	07.09.2009	29	2.83	0.01	20.3	0.4	-2.3	224
BJ-2/08	6.28.2008	32	2.06	0.02	16.7	0.2	0.2	224
BJ-3/08	7.8.2008	31	2.23	0.03	19.6	0.3	1.7	224
BJ-4/08	8.17.2008	34	1.18	0.02	15.4	0.2	5.9	224
BJ-5/08	9.2.2008	32	-0.94	0.07	-0.5	0.2	7	224
BJ-6/08	9.16.2008	30	2.9	0.03	22.5	0.2	-0.8	224
BJ-7/08	10.31.2008	28	-2.64	0.02	-3.5	0.3	17.6	224
BJ-1/010	06.08.010	25	0.58	0.04	18.2	0.3	13.6	224
BJ-1/010	06.08.010	25	0.55	0.03	17.7	0.4	13.4	224

BJ-2/010	15.08.010	28	0.60	0.03	2.5	0.2	-2.2	224
BJ-2/010	15.08.010	28	0.59	0.05	2.2	0.3	-2.4	224
BJ-3/010	26.08.010	29	-1.89	0.04	-1.9	0.3	13.2	224
BJ-3/010	26.08.010	29	-1.86	0.02	-2.5	0.3	12.4	224
BJ-4/010	28.08.010	27	-0.03	0.06	9.4	0.2	9.6	224
BJ-4/010	28.08.010	27	-0.03	0.06	8.3	0.3	8.6	224
DAR-1	5.30.2008	19	-4.47	0.02	-32.7	0.4	0	2245
DAR-2	7.25.2008	17	-1.87	0.01	-1	0.2	14	2245
DAR1-010	06.05.010	15.5	2.07	0.01	20.8	0.6	4.3	2245
DAR2-010	11.07.010	14.5	-8.03	0.04	-53.6	0.3	10.7	2245
DB-1	01.05.2008	25	-3.11	0.02	-15.5	0.4	9.4	1000
DB-2	03.05.2008	22	-1.61	0.04	-0.9	0.2	11.9	1000
DB-3	19.05.2008	25	-0.6	0.03	4.8	0.3	9.7	1000
DB-4	06.08.2008	25	-1.16	0.01	1.8	0.4	11.1	1000
DB-5	20.08.2008	25	-0.37	0.05	8.4	0.4	11.3	1000
DH-1	10.04.2008	26	0.14	0.02	14.2	0.4	13.1	2360
DH-2	15.04.2008	25	3.19	0.03	29.7	0.2	4.2	2360
DH-3	30.05.2008	26	0.72	0.05	-7.8	0.2	-13.6	2360
DH-4	01.06.2008	25	-1.66	0.03	-1.1	0.2	12.2	2360
DH-5	02.06.2008	27	-2.56	0.02	-8.9	0.2	11.6	2360
Dh1-010	13.02.010	22	-1.62	0.06	10.0	0.3	23.0	2360
Dh2-010	14.04.010	14	-0.09	0.04	-4.0	0.3	-3.3	2360
Dh3-010	04.08.010	17	1.19	0.04	17.1	0.4	7.6	2360
Dh6-08	28.08.2008	19	-1.04	0.08	0.7	0.2	9.0	2360
Dh7-08	06.11.2008	17	7.10	0.03	33.3	0.4	-23.5	2360
HJ-1	5.8.2008	23.5	0.8	0.03	14.8	0.4	8.4	1739
HJ-1.2	6.20.2008	24	0.56	0.03	16	0.3	11.6	1739
HJ-2	5.18.2008	23.6	2.09	0.04	23.7	0.3	7	1739
HJ-2.2	7.6.2008	23	1.91	0.03	14.1	0.2	-1.2	1739
HJ-3	5.30.2008	23.8	-0.12	0.03	0.8	0.4	1.7	1739
HJ-3.2	7.8.2008	23.5	4.78	0.01	27.7	0.4	-10.5	1739
HJ-4	5.31.2008	23.5	-2.67	0.04	-9.3	0.2	12.1	1739
HJ-4.2	7.9.2008	23	-0.62	0.03	4.6	0.3	9.6	1739
HJ-5.2	7.11.2008	23.7	0.5	0.03	9	0.3	5	1739

HJ-6.2	7.12.2008	20	-1.34	0.03	3.1	0.3	13.8	1739
HJ-7.2	7.23.2008	23	2.51	0.02	8	0.2	-12.1	1739
HJ-8.2	7.30.2008	23.5	-0.31	0.03	-0.6	0.3	1.8	1739
HOD-01/09	29.03.2009	27	-0.48	0.01	10.7	0.3	14.6	14
HOD-02/09	22.08.2008	32	6.13	0.01	36.7	0.4	-12.4	14
HOD-03/09	25.08.2009	28	-2.50	0.02	-6.5	0.5	13.5	14
HOD-04/09	08.09.2009	35	1.99	0.03	17.6	0.4	1.7	14
HOD-1/08	5.29.2008	27	2.68	0.03	9.7	0.3	-11.8	14
HOD-2/08	5.31.2008	29	0.38	0.04	6.5	0.4	3.5	14
HOD-3/08	10.30.2008	26	-1.9	0.02	2.6	0.4	17.9	14
HOD-4/08	11.1.2008	27	-1.61	0.03	5.4	0.5	18.2	14
HOD-5/08	11.1.2008	28	-2.17	0.02	0.5	0.3	17.9	14
HOD1-010	09.07.2010	32	2.67	0.08	18.5	0.4	-2.8	14
HOD2-010	25.08.010	32	-2.58	0.04	-8.6	0.1	12.0	14
HOD3-010	26.08.010	31	0.51	0.05	10.1	0.4	6.0	14
HS-1/08	5.5.2008	17	4.5	0.02	41.9	0.2	5.8	2246
HS-2/08	5.9.2008	20	3.07	0.02	27	0.2	2.4	2246
HS-3/08	5.30.2008	19	-3.83	0.04	-29.2	0.3	1.5	2246
HS-4/08	5.31.2008	20	-4.5	0.02	-29.4	0.3	6.6	2246
HS-01/09	24.08.2009	22	-4.58	0.03	-25.2	0.6	11.4	2246
HS-2/09	13.02.2010	19	-2.48	0.03	2.5	0.4	22.4	2246
HS-3/09	06.03.2010	20	-3.09	0.03	-5.7	0.2	19.1	2246
HS-4/09	31.03.2010	20	0.77	0.02	22.3	0.4	16.2	2246
HS-10/010	12.05.010	16	3.48	0.03	37.5	0.3	9.7	2246
HS-11/010	07.08.010	19	-3.09	0.03	-18.0	0.3	6.7	2246
HS-12/010	09.08.010	18	-3.61	0.01	-23.2	0.3	5.7	2246
HS-13/010	10.08.010	17	-1.97	0.03	-3.2	0.3	12.6	2246
HS-14/010	02.09.010	26	-0.29	0.04	9.7	0.3	12.0	2246
HS-4/010	14.04.010	19	-3.40	0.06	-16.3	0.4	10.9	2246
HS-5/010	19.04.010	14	3.07	0.01	25.0	0.2	0.4	2246
HS-6/010	24.04.010	18	3.23	0.02	30.3	0.4	4.4	2246
HS-7/010	28.04.010	15	0.14	0.04	8.0	0.4	6.8	2246
HS-8/010	06.05.010	16	1.45	0.05	20.9	0.3	9.3	2246
HS-9/010	09.05.010	19	3.02	0.01	30.1	0.4	5.9	2246

JB-1	5.9.2008	20	-0.57	0.02	3.8	0.3	8.3	2422
MF-1	5.6.2008	23	-0.17	0.03	10.3	0.2	11.7	1600
MF-2	5.9.2008	22	0.17	0.01	10.5	0.4	9.2	1600
MF-3	6.1.2008	24	-1.08	0.02	1.6	0.3	10.2	1600
MF-4	6.2.2008	21	-0.96	0.02	1.4	0.3	9.1	1600
MF-5	6.3.2008	22	-0.93	0.04	2.6	0.3	10	1600
MF-6	7.12.2008	22	-5.62	0.03	-38.8	0.5	6.2	1600
MF-7	7.30.2008	21	-4.76	0.03	-31.8	0.1	6.3	1600
MF-8	10.24.2008	21	-3.51	0.01	-13.3	0.4	14.8	1600
RB 01/09	20.04.2009	27	-0.27	0.02	6.0	0.4	8.1	598
RB 02/09	10.05.2009	30	1.55	0.07	19.0	0.4	6.6	598
RB 03/09	11.05.2009	28	0.44	0.04	13.4	0.5	9.9	598
RB 04/09	29.06.2009	29	0.31	0.01	10.9	0.3	8.4	598
RB 05/09	02.07.2009	29	0.65	0.04	10.9	0.3	5.8	598
RB 06/09	08.07.2009	28	4.14	0.02	25.4	0.4	-7.7	598
RB 07/09	10.07.2009	29	-0.74	0.03	-1.7	0.5	4.2	598
RB 08/09	12.07.2009	30	3.55	0.02	24.4	0.3	-3.9	598
RB 09/09	16.07.2009	29	0.20	0.07	3.8	0.2	2.2	598
RB 10/09	22.07.2009	29	-0.53	0.04	8.1	0.5	12.3	598
RB 11/09	25.07.2009	28	-0.28	0.05	-3.2	0.2	-0.9	598
RB 12/09	10.08.2009	29	-0.39	0.03	7.5	0.3	10.6	598
RB 13/09	30.08.2009	28	-1.95	0.03	1.2	0.4	16.8	598
RB-14-09	28.09.2009	30	0.73	0.06	12.3	0.3	6.5	598
RB-15-09	07.10.010	29	1.81	0.02	22.1	0.1	7.6	598
RB-16-09	18.10.2009	28	2.77	0.03	21.9	0.4	-0.3	598
RB-1/08	5.7.2008	27	2.54	0.02	22.4	0.4	2.1	598
RB-2/08	5.9.2008	25	-0.17	0.02	7.2	0.3	8.6	598
RB-3/08	5.29.2008	24	-0.14	0.04	8	0.3	9.1	598
RB-4/08	9.18.2008	29	1.57	0.03	19.7	0.3	7.1	598
RB-5/08	10.23.2008	28	-1.51	0.03	5.3	0.3	17.4	598
RB-6/08	10.28.2008	27	-1.79	0.02	1.2	0.1	15.5	598
RB-7/08	11.3.2008	25	-0.77	0.01	7.1	0.4	13.3	598
RB-01-010	06.03.010	25	-1.32	0.05	-1.0	0.4	9.5	598
RB-10/010	10.06.010	30	0.07	0.06	5.0	0.5	4.5	598

RB-10/010	10.06.010	30	0.08	0.02	4.7	0.4	4.1	598
RB-2/010	02.04.010	28	2.57	0.04	23.1	0.3	2.5	598
RB-2/010	02.04.010	28	2.61	0.02	22.9	0.3	2.0	598
RB-3/010	14.04.010	29	-0.61	0.05	-5.9	0.3	-1.0	598
RB-3/010	14.04.010	29	-0.63	0.04	-5.8	0.3	-0.7	598
RB-4/010	19.04.010	28	-0.08	0.06	3.8	0.2	4.4	598
RB-4/010	19.04.010	28	0.00	0.03	2.8	0.2	2.8	598
RB-5/010	27.04.010	29	2.10	0.05	22.7	0.3	5.9	598
RB-5/010	27.04.010	29	2.12	0.07	22.6	0.3	5.7	598
RB-6/010	03.05.010	30	1.41	0.07	16.8	0.3	5.5	598
RB-6/010	03.05.010	30	1.41	0.05	16.1	0.2	4.9	598
RB-7/010	05.05.010	27	-0.12	0.05	6.8	0.5	7.8	598
RB-7/010	05.05.010	27	-0.10	0.05	6.5	0.2	7.3	598
RB-8/010	11.05.010	31	-0.46	0.03	-2.1	0.3	1.6	598
RB-8/010	11.05.010	31	-0.43	0.02	-2.5	0.2	1.0	598
RB-9/010	23.05.010	30	-0.52	0.02	7.4	0.5	11.5	598
RB-9/010	23.05.010	30	-0.53	0.04	6.5	0.2	10.8	598
RI-01/09	08.05.2009	25	-0.77	0.02	7.4	0.4	13.6	2016
Ri-01/09*	08.05.2009	25	-0.71	0.01	6.3	0.5	12.0	2016
RI-02/09	12.05.2009	23	-1.24	0.02	7.1	0.3	17.1	2016
RI-03/09	13.05.2009	22	0.78	0.02	13.5	0.3	7.2	2016
RI-04/09	17.05.2009	22	-2.15	0.02	-2.8	0.6	14.4	2016
RI-05/09	18.05.2009	21	-4.39	0.02	-21.5	0.4	13.6	2016
RI-06/09	02.06.2009	23	-1.72	0.02	-5.7	0.2	8.0	2016
RI-07/09	03.06.2009	21	0.13	0.03	9.7	0.4	8.7	2016
RI-08/09	18.06.2009	22	-4.68	0.02	-24.2	0.4	13.3	2016
RI-09/09	29.06.2009	22	1.10	0.01	14.1	0.2	5.4	2016
RI-1	03.06.2008	22	-2.28	0.03	-17.9	0.2	0.3	2016
RI-10/09	30.06.2009	21	0.06	0.03	12.2	0.2	11.6	2016
RI-2	05.06.2008	20	-2.27	0.03	-18.6	0.2	-0.4	2016
RI-3	24.07.2008	22	-0.04	0.03	-0.7	0.3	-0.4	2016
RI-4	30.07.2008	21	-1.93	0.03	1.7	0.2	17.1	2016
RI-5	03.08.2008	22	-3.52	0.02	-15.5	0.2	12.7	2016
RI-6	18.08.2008	20	-4.12	0.02	-21.3	0.4	11.7	2016

Ri-11/09	27.04.010	24	0.10	0.03	14.8	0.2	14.0	2016
Ri-12/09	04.05.010	24	2.57	0.02	31.5	0.4	11.0	2016
Ri-13/09	05.05.010	24	1.80	0.02	13.4	0.2	-1.0	2016
Ri-1/010	01.04.010	24	-0.59	0.01	8.6	0.4	13.3	2016
Ri-2/010	02.04.010	23	-2.26	0.02	-5.8	0.3	12.3	2016
Ri-3/010	04.04.010	23	-3.89	0.02	-15.8	0.3	15.3	2016
Ri-4/010	10.04.010	23	-3.18	0.04	-15.1	0.3	10.3	2016
Ri-5/010	14.04.010	25	-4.36	0.01	-24.8	0.1	10.1	2016
Ri-6/010	20.04.010	23	-0.11	0.03	8.4	0.2	9.4	2016
Ri-7/010	23.04.010	25	-0.58	0.02	6.6	0.3	11.3	2016
Ri-8/010	24.04.010	23	-3.95	0.01	-15.3	0.3	16.3	2016
Ri-9/010	25.04.010	25	1.22	0.02	21.2	0.4	11.4	2016
Ri-10/010	26.04.010	25	0.27	0.02	18.0	0.4	15.8	2016
Ri-11/010	27.04.010	24	0.51	0.02	16.8	0.5	12.7	2016
Ri-12/010	04.05.010	24	-1.22	0.05	5.4	0.2	15.1	2016
Ri-13/010	05.05.010	24	-0.41	0.03	10.3	0.4	13.6	2016
SKH-1	16.05.2008	31	1.78	0.02	15.9	0.2	1.7	350
SKH-2	20.05.2008	34	0.99	0.02	14.5	0.2	6.5	350
SKH-3	30.05.2008	29	0.5	0.03	5.9	0.3	1.9	350
SKH-4	13.06.2008	31	0.17	0.02	5	0.2	3.7	350
SKH-5	27.06.2008	33	2.62	0.01	16.6	0.4	-4.4	350
SKH-6	11.07.2008	33	1.35	0.02	13.3	0.5	2.5	350
SKH-7	26.07.2008	31	-0.06	0.02	9.5	0.4	10	350
SKH-8	10.08.2008	30	2.27	0.02	19.2	0.3	1.1	350
SKH-9	17.08.2008	35	-0.19	0.03	3.9	0.5	5.4	350
SY-1	05.08.2008	28	3.52	0.04	4.6	0.6	-23.6	700
SY-2	28.10.2008	25	3.48	0.02	5.4	0.2	-22.5	700
SY-3	04.11.2008	23	3.56	0.01	5.2	0.2	-23.2	700
TAIZ-03/08	24.08.2008	23	-0.47	0.02	2.8	0.3	6.6	1311
TAIZ-04/08	26.08.2008	19	3.41	0.04	24.7	0.4	-2.6	1311
TAIZ-05/08	27.08.2008	21	2.18	0.04	18.6	0.4	1.2	1311
TAIZ-06/08	28.08.2008	20	-0.83	0.04	-6.4	0.4	0.2	1311
TAIZ-07/08	02.09.2008	20	1.05	0.04	13.2	0.2	4.8	1311
TAIZ-08/08	04.09.2008	20	1.12	0.03	16.1	0.3	7.1	1311

TAIZ-09/08	16.09.2008	18	2.02	0.06	23.8	0.2	7.7	1311
TAIZ-1/08	16.08.2008	24	-0.05	0.03	6.8	0.2	7.1	1311
TAIZ-10/08	23.09.2008	17	5.41	0.03	39.0	0.5	-4.3	1311
TAIZ-2/08	18.08.2008	25	3.82	0.03	21.4	0.2	-9.1	1311
TDA-1/08	31.05.2008	35	0.13	0.02	6	0.3	4.9	14
WA-1	03.05.2008	17	-1.53	0.04				2500
WA-1	09.05.2008	19	-1.46	0.02	2.5	0.4	14.1	2500
WA-2	01.06.2008	18	-1.61	0.02	5.3	0.2	18.2	2500
WA-3	25.07.2008	20	-1.63	0.02	-7.1	0.2	6	2500
WA-3*	02.08.2008	23	-1.61	0.02	-7.2	0.5	5.7	2500
WA-4	12.08.2008	20	0.56	0.01	16.2	0.3	11.7	2500
WA-5	21.08.2008	18	2.32	0.03	30.6	0.5	12.1	2500
WA-6	03.05.2008	18	-0.71	0.01	5.6	0.3	11.2	2500
WA-7	09.05.2008	19	-1.22	0.04	7.1	0.4	16.9	2500
WEC-1	08.05.2008	17	1.4	0.01	11.7	0.4	0.5	2285
WEC-2	30.05.2008	20	-2.11	0.03	-5.2	0.5	11.7	2285
WEC-3	04.06.2008	19	5.13	0.03	26.3	0.4	-14.8	2285
WEC-4	31.10.2008	17	-3.87	0.03	-29.2	0.2	1.8	2285
WEC-5	24.01.2010	23	2.38	0.02	29.7	0.5	10.6	2285
WEC-6	25.01.2010	23	2.88	0.04	29.5	0.4	6.5	2285
WEC-7	05.03.2010	19	0.43	0.07	6.2	0.5	2.8	2285
WEC-8	06.03.2010	20	-3.49	0.07	-11.4	0.4	16.5	2285
WEC-9	07.03.2010	20	4.96	0.04	25.8	0.3	-13.8	2285
WEC-10	28.03.2010	19	7.55	0.03	52.0	0.5	-8.4	2285
WEC-11	29.03.2010	21	6.00	0.03	52.0	0.4	4.0	2285
WEC-12	29.03.2010	22	9.57	0.02	59.0	0.5	-17.6	2285
WEC-13	29.03.2010	22	2.67	0.04	27.8	0.3	6.4	2285
WEC-14	30.03.2010	22	4.96	0.03	46.6	0.4	6.9	2285
WEC-15	31.03.2010	19	2.24	0.03	32.5	0.2	14.6	2285
WEC-16	31.03.2010	19	2.19	0.06	28.2	0.2	10.6	2285
WEC-17	01.04.2010	20	6.50	0.03	38.2	0.4	-13.8	2285
WEC-18	13.04.2010	28	10.54	0.02	64.1	0.3	-20.2	2285
WEC-19	14.04.2010	21	-2.44	0.05	-7.2	0.2	12.4	2285
WEC-20	14.04.2010	23	0.69	0.03	6.1	0.4	0.6	2285

WEC-21	17.04.2010	21	-2.64	0.06	-3.9	0.2	17.2	2285
WEC-22	18.04.2010	24	-1.46	0.03	3.8	0.3	15.4	2285
WEC-23	18.04.2010	21	-2.56	0.02	-7.4	0.2	13.0	2285
WEC-24	19.04.2010	20	0.93	0.02	12.8	0.4	5.4	2285
WEC-25	19.04.2010	30	6.30	0.04	32.3	0.4	-18.1	2285
WEC-26	20.04.2010	27	5.37	0.04	27.8	0.5	-15.1	2285
WEC-27	21.04.2010	20	5.80	0.03	41.9	0.5	-4.5	2285
WEC-28	22.04.2010	20	3.88	0.01	32.9	0.2	1.8	2285
WEC-29	23.04.2010	20	0.08	0.04	11.7	0.4	11.1	2285
WEC-30	27.04.2010	20	6.85	0.05	50.8	0.3	-3.9	2285
WEC-31	28.04.2010	20	-0.18	0.03	11.7	0.3	13.1	2285
WEC-32	28.04.2010	20	0.28	0.05	10.4	0.1	8.1	2285
WEC-33	29.04.2010	23	0.29	0.03	11.1	0.4	8.7	2285
WEC-34	03.05.2010	23	1.24	0.03	17.2	0.2	7.3	2285
WEC-35	05.05.2010	20	2.43	0.05	19.9	0.2	0.4	2285
WEC-36	07.05.2010	20	2.25	0.06	24.7	0.4	6.7	2285
WEC-37	11.05.2010	20	2.36	0.04	31.8	0.4	12.9	2285
WEC-38	12.05.2010	19	6.86	0.07	49.3	0.5	-5.5	2285
WEC-39	13.05.2010	19	2.45	0.05	30.1	0.2	10.4	2285
WEC-40	12.08.2010	18	0.75	0.03	11.5	0.3	5.5	2285
WEC-41	23.08.2010	19	-3.80	0.06	-19.7	0.3	10.7	2285
WEC-42	02.09.2010	18	-0.03	0.03	9.4	0.4	9.6	2285
Max.		**35**	**10.54**	**0.08**	**64.12**	**0.60**	**22.97**	**2500**
Min.		**14**	**-8.03**	**0.00**	**-53.57**	**0.10**	**-23.60**	**14**
Average		**24**	**0.32**	**0.03**	**8.61**	**0.32**	**5.95**	**1464**

Table 10: Isotopic composition of groundwater samples from Sana'a basin

Sample	Aquifer	δ^{18}O (o/oo) vs. SMOW	1 σ	δD (o/oo) vs. SMOW	1 σ	d excess
GW-1	S.S	-2.88	0.01	-13.3	0.5	9.7
GW-2	Alu.	-3.47	0.02	-16.1	0.4	11.6
GW-3	L.S	-3.30	0.03	-15.8	0.5	10.6
GW-4	S.S	-4.01	0.04	-21.9	0.5	10.2
GW-5	L.S	-3.08	0.05	-19.7	0.6	5.0
GW-6	L.S	-3.11	0.05	-18.9	0.5	6.0
GW-7	S.S	-2.54	0.03	-9.5	0.3	10.9
GW-8	L.S	-2.67	0.04	-11.5	0.3	9.9
GW-9	L.S	-2.95	0.03	-15.5	0.4	8.1
GW-10	L.S	-4.20	0.02	-24.4	0.4	9.3
GW-11	L.S	-1.25	0.04	-8.5	0.3	1.5
GW-12	Alu.	-2.99	0.02	-12.5	0.4	11.4
GW-13	S.S	-2.67	0.04	-12.7	0.3	8.7
GW-14	S.S	-2.36	0.04	-6.6	0.4	12.3
GW-15	S.S	-2.26	0.03	-7.2	0.4	10.9
GW-16	Alu.	-2.12	0.02	-7.4	0.4	9.6
GW-17	Alu.	-1.67	0.03	-5.9	0.5	7.4
GW-18	V	-2.15	0.02	-11.6	0.3	5.6
GW-19	V	-3.35	0.03	-20.5	0.7	6.3
GW-20	V	-1.64	0.04	-8.2	0.5	4.9
GW-21	V	-1.31	0.03	-5.3	0.3	5.2
GW-22	V	-2.15	0.03	-10.1	0.5	7.1
GW-23	V	-2.06	0.06	-8.3	0.4	8.2
GW-24	V	-2.39	0.02	-8.6	0.4	10.5

Table 11: Isotopic composition of spring water samples from Sana'a basin

Sample	$\delta^{18}O$ (o/oo) vs. SMOW	1 σ	δD (o/oo) vs. SMOW	1 σ	d excess
SW-1	-1.82	0.01	-5.7	0.2	8.9
SW-2	-2.15	0.02	-6.8	0.3	10.4
SW-3	-2.42	0.01	-5.7	0.3	13.7
SW-4	-2.23	0.02	-4.9	0.4	13.0
SW-5	-2.48	0.01	-6.1	0.4	13.7
SW-6*	-0.45	0.02	-0.1	0.3	3.5
SW-7	-2.37	0.05	-5.9	0.2	13.1
SW-8	-2.76	0.03	-6.4	0.4	15.7
SW-9	-1.85	0.02	-4.7	0.5	10.0
SW-10	-1.41	0.01	-4.3	0.3	7.0
SW-11	-3.05	0.03	-13.2	0.1	11.3
SW-12	-2.41	0.03	-8.7	0.7	10.6
SW-13	-2.30	0.02	-6.7	0.2	11.7

*This sample was not considered by the interpretation of the data

Table 12: Comparison the physicochemical data

parameter	**SAWAS, 1996**				**SHAMSAN, 05**				**SHAMSAN, 08**				**Current study, 2010**			
	All. And Vol.		**Ss. and Ls.**		**All. And Vol.**		**Ss. and Ls.**		**All. and Vol.**		**Ss. and Ls.**		**All. and Vol.**		**Ss. and Ls.**	
	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.	Min.	Max.
EC (µS/cm)	300	3702	432	1771	399	829	439	2130	438	1987	451	875	280	1070	350	2030
pH	6.6	9.33	7	8	7.1	9.8	7	7.9	6.4	8.6	6.4	8.3	7.5	9.4	5.6	7.6
T (C°)	17	32.5	20	27.8	15	25	16	25	14.2	33.2	14.8	32.9	20	32	21	36
Ca (mg/l)	2.4	518	22.2	220	3.2	93	40	165	26	234	31	106	2.9	133	41.3	326
Mg(mg/l)	0.05	141	0.82	44	5.8	19	9.4	46	10	56	10	37	0.18	24.6	8.1	74.5
K (mg/l)	0.2	12.5	2.1	12.4	0.5	2.9	2	9.5	1.02	9.72	1.42	3.98	0.4	2.7	3.3	16.4
Na (mg/l)	14	356	27.2	129	35	84	41	280	8	169	8	69	19.5	111.3	11.1	274
Cl (mg/l)	7	730	17.9	323	25	93	24	78	13	290	13	107	18	197	18	225
SO$_4$ (mg/l)	3.1	225	9.77	364	36	110	35	900	15	300	12	196	17	76	14	812
NO$_3$ (mg/l)	0.3	686	2.4	134	3	53	1.3	28	6.6	270	6.6	59.4	<0.02	121	0.2	42
HCO3 (mg/l)	44	415	70.8	366	151	248	205	363	117	532	124	273	126	214.2	195.3	787.5