HYDROCHEMISTRY

Abstract

Explaining saline and freshwater occurrence in the Great Maputo Area of Southern Mozambique

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Assignment Hydrochemistry – Explaining saline and freshwater occurrence in the Great Maputo Area of Southern Mozambique

A paper was recently published by Nogueira et al. (2019) on the hydrochemistry of the Great Maputo aquifer and interacting surface waters (river, wetland) in Southern Mozambique, in the scope of MSc thesis research conducted at IHE. The location of the study area is shown in Figure 1, which also includes a cross-section. More details on the research work can be found in the referred paper.

In this assignment, we will work with a subset of 21 groundwater and surface water samples collected from the area, and we will study the data from the various perspectives dealt with in the classroom. The data can be found in the file Assignment_Hydrochem_2020.xlsx, which can be downloaded from eCampus. Also available on eCampus are the published paper, a few shp files of the area, the software PHREEQC for Windows (for hydrochemical modelling) and EASY_QUIM (for unit calculations and drawing of several diagrams), and the Excel file Atom_Mol_Weights.xlsx, with atomic/molecular weights and seawater ratios.
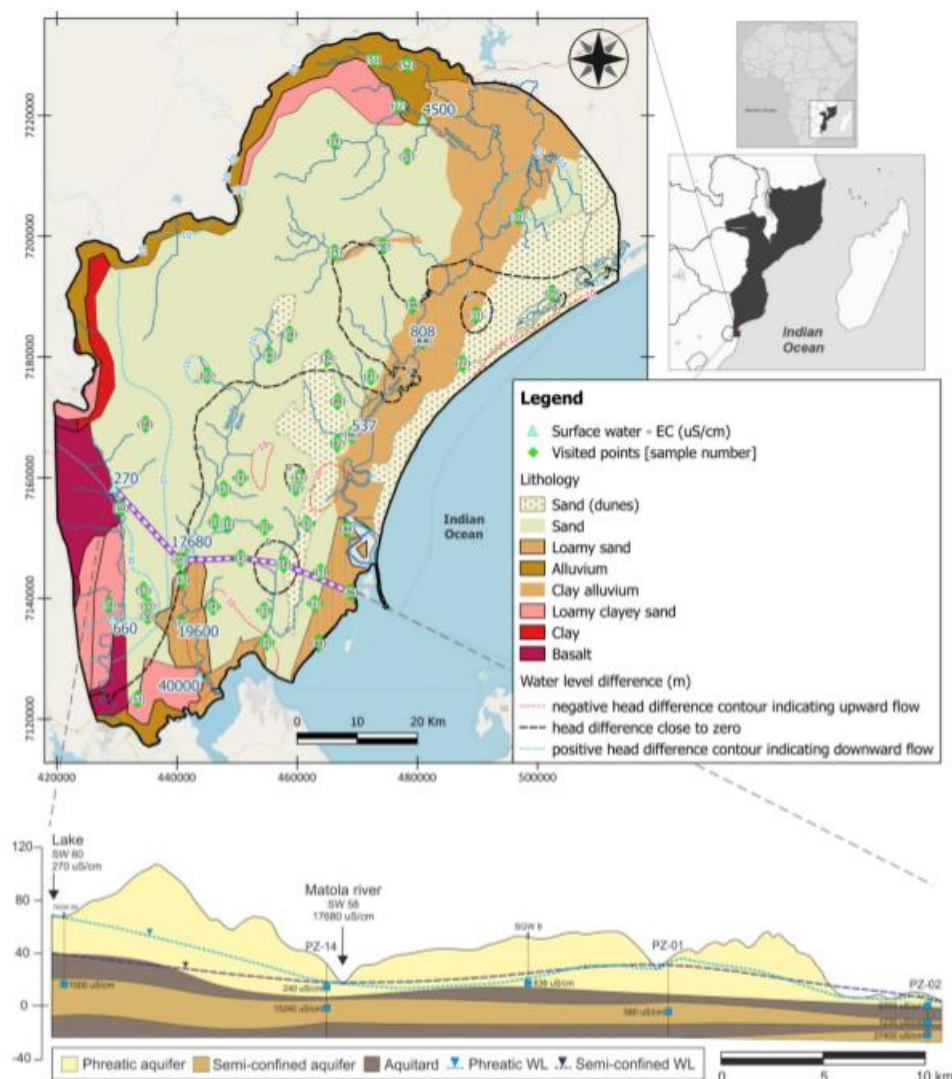

Fig. 1. Location and geological context of the study area, in map (top) and cross-section (bottom). Also shown are sampling points for a campaign held in May 2017, as well as surface water EC values and calculated groundwater head differences between the phreatic and semi-confined aquifers. Source: Nogueira et al. (2019)

1. Lab results

Before we can do a hydrochemical study, we need to check the completeness and correctness of the results and transform the units to mmol/l, since all chemical reactions represent molar transfers. We can then also transform to meq/l and can check the quality of the analysis by calculating the electrical balance (E.B.), as well as drawing a number of graphs.

 a) Transform the units to mmol/l and meq/l. You can use the Excel file Atom_Mol_Weights.xlsx, or the software EASY_QUIM, or PHREEQC for Windows. Indicate the software you used and provide the results for the major ions in a table.

Answer:

The units are transformed to mmol/l by the equation, given as

$$mmol/l = \frac{mg/l}{\textbf{mw}} \tag{1.1}$$

, where **mw** is the atomic or molecular weight (g/mol) obtained by the Excel file Atom_ Mol_Weights.xlsx.

The software EASY_QUIM transforms the units to meq/l with the equation as

$$meq/l = \frac{mg/l}{\textbf{mw}} \times \textbf{ch} \tag{1.2}$$

, where **ch** is charge of the ion. The results for the major ions show in table 1.1

Table 1.1 The major ions with the units of mmol/l and meq/l

Number	Name	Na$^+$	K$^+$	Ca^{2+}	Mg^{2+}	Cl$^-$	HCO$_3^-$	SO$_4^{2-}$	NO$_3^-$
						mmol/l			
58	Matola river	90.34	0.99	21.03	31.60	185.40	7.00	14.96	0.0002
60	Lake	1.40	0.09	0.30	0.25	0.45	1.74	0.03	0.0003
66	Incomati effluent	1.69	0.09	0.36	0.29	2.46	0.98	0.64	0.0095
67	Matola wetland	80.95	0.71	14.65	23.49	152.51	6.34	8.90	0.0002
70	65-Incomati	3.82	0.15	0.72	0.92	3.88	**1.6**	0.90	0.0006
10	16	4.88	0.14	0.64	0.47	2.72	**4.2**	0.18	0.0045
12	23	4.44	0.25	1.08	0.33	2.89	**4.0**	0.31	0.0002
26	PZ21 F	2.68	0.12	0.31	0.16	1.59	2.20	0.03	0.0069
28	PZ19 F	1.12	0.09	0.11	0.13	1.39	0.30	0.04	0.0556
30	PZ20 F	0.21	0.02	0.06	0.02	0.31	0.04	0.04	0.0002
45	PZ02 F	11.31	0.65	2.66	2.34	20.66	3.20	0.52	0.0002
47	PZ18 F	2.86	0.28	1.08	0.72	1.93	3.48	0.46	0.0458
61	Poço tio Mulungu	4.56	0.28	1.39	0.67	3.20	2.30	1.26	0.3145
14	PZ14 C	46.28	0.46	6.76	15.06	59.08	6.80	2.52	0.4016
23	PZ17 C	12.12	0.31	3.37	2.89	21.75	3.40	1.47	0.0002
27	PZ21 C	0.29	0.07	0.20	0.08	0.33	0.74	0.00	0.0002
29	PZ19 C	0.79	0.10	0.10	0.10	1.07	0.20	0.05	0.0075
31	PZ20 C	1.05	0.07	0.14	0.11	0.92	1.06	0.00	0.0015
46	PZ02 C	6.27	0.38	1.38	0.91	7.35	3.12	0.10	0.0002
48	PZ18 C	5.94	0.40	1.32	1.19	4.41	4.72	0.80	0.0394
68	PZ13 C	12.44	0.33	5.84	4.77	26.70	3.90	0.49	0.0002
						meq/l			
58	Matola river	90.30	0.99	42.15	63.47	-185.2	-7.0	-29.9	-0.0002
60	Lake	1.40	0.09	0.61	0.50	-0.4	-1.7	-0.1	-0.0003
66	Incomati effluent	1.69	0.09	0.73	0.59	-2.5	-1.0	-1.3	-0.0095
67	Matola wetland	80.91	0.71	29.35	47.19	-152.3	-6.3	-17.8	-0.0002
70	65-Incomati	3.82	0.15	1.44	1.84	-3.9	**-1.6**	-1.8	-0.0006
10	16	4.88	0.14	1.28	0.95	-2.7	**-4.2**	-0.4	-0.0045
12	23	4.44	0.25	2.17	0.66	-2.9	**-4.0**	-0.6	-0.0002
26	PZ21 F	2.67	0.12	0.63	0.32	-1.6	-2.2	-0.1	-0.0069
28	PZ19 F	1.12	0.09	0.22	0.25	-1.4	-0.3	-0.1	-0.0556
30	PZ20 F	0.21	0.02	0.12	0.04	-0.3	0.0	-0.1	-0.0002
45	PZ02 F	11.30	0.65	5.34	4.71	-20.6	-3.2	-1.0	-0.0002
47	PZ18 F	2.86	0.28	2.17	1.45	-1.9	-3.5	-0.9	-0.0458
61	Poço tio Mulungu	4.56	0.28	2.79	1.34	-3.2	-2.3	-2.5	-0.3145
14	PZ14 C	46.26	0.46	13.55	30.25	-59.0	-6.8	-5.0	-0.4016
23	PZ17 C	12.11	0.31	6.75	5.81	-21.7	-3.4	-2.9	-0.0002
27	PZ21 C	0.29	0.07	0.40	0.16	-0.3	-0.7	0.0	-0.0002
29	PZ19 C	0.79	0.10	0.20	0.20	-1.1	-0.2	-0.1	-0.0075
31	PZ20 C	1.05	0.07	0.28	0.23	-0.9	-1.1	0.0	-0.0015
46	PZ02 C	6.27	0.38	2.77	1.83	-7.3	-3.1	-0.2	-0.0002
48	PZ18 C	5.94	0.40	2.66	2.39	-4.4	-4.7	-1.6	-0.0394
68	PZ13 C	12.43	0.33	11.70	9.59	-26.7	-3.9	-1.0	-0.0002

b) A few samples have missing values for bicarbonate. What could be the reason that this has occurred for this anion, and not for the other major cations and anions?

Answer:

The reason for missing values for bicarbonate could be that the calcite had precipitated in the bottle without acid, thus decreasing HCO_3^- concentration, or the experimental operation error is that the anions were analyzed in the acidified sample bottle, which leads to release carbon dioxide to the atmosphere. However, the cations and anions were analyzed in different containers and the cations were analyzed in the acidified sample bottles. Therefore, Ca^{2+} concentration can be detected. Compared with the bicarbonate, the other anions relatively chemical stability, and their concentrations were not altered when determining the fraction of anions in solution.

c) Estimate the missing bicarbonate concentrations through the electrical balance. What assumption are you making? Include the results in the table of question a).

Answer:

The assumption is that the Cl^-, HCO_3^-, SO_4^{2-}, and NO_3^- ions are the dominant anions in the samples, while the other anions are negligible, and the Na^+, K^+, Ca^{2+}, and Mg^{2+} ions are the dominant cations in the sample, which means the other cations are insignificant. According to the electrical balance, the sum of cations and anions in meq/L = 0, given as

$$\sum cations + \sum anions = 0$$

. The results show in table 1 with bold red words.

d) Calculate the E.B. for each sample (indicate the software in which you calculated it). Provide the results in a table or add them to the table of question a). Briefly comment on the results.

Answer：

Table 1.2 Electric balance for each sample

Number	Name	E.B.	Number	Name	E.B.
58	Matola river	-6.01%	47	PZ18 F	2.86%
60	Lake	7.34%	61	Poço tio Mulungu	3.71%
66	Incomati effluent	-21.00%	14	PZ14 C	11.91%
67	Matola wetland	-5.46%	23	PZ17 C	-5.80%
70	65-Incomati	0.00%	27	PZ21 C	-7.14%
10	16	0.00%	29	PZ19 C	-3.51%
12	23	0.00%	31	PZ20 C	-9.50%
26	PZ21 F	-1.45%	46	PZ02 C	2.69%
28	PZ19 F	-4.63%	48	PZ18 C	2.74%
30	PZ20 F	-4.59%	68	PZ13 C	3.83%
45	PZ02 F	-6.13%			

The results of the electrical balance are obtained by equation (1.3) with the sum of cations and anions. In the laboratory, the absolute E.B. values up to 2% are inevitable and the values up to 5% are generally accepted. Thus, the values of electrical balance in samples 66, 14 and 31 with 21%, 11.91% and 9.5% respectively, have larger errors, which are necessary to review the analysis. On the contrary, the samples collected at the location of number 26, 47, 46 and 48 have proper calculations, which account for 1.45%, 2.86%, 2.69% and 2.74% respectively. Meanwhile, samples 12, 70, and 10 are calculated the bicarbonate concentration by the electrical balance, which means the E.B. values are zero.

e) Compare the sum of anions and cations (in meq/l) to EC/100, by plotting on one graph: sum of anions vs EC/100 and sum of cations vs. EC/100. What do you conclude?
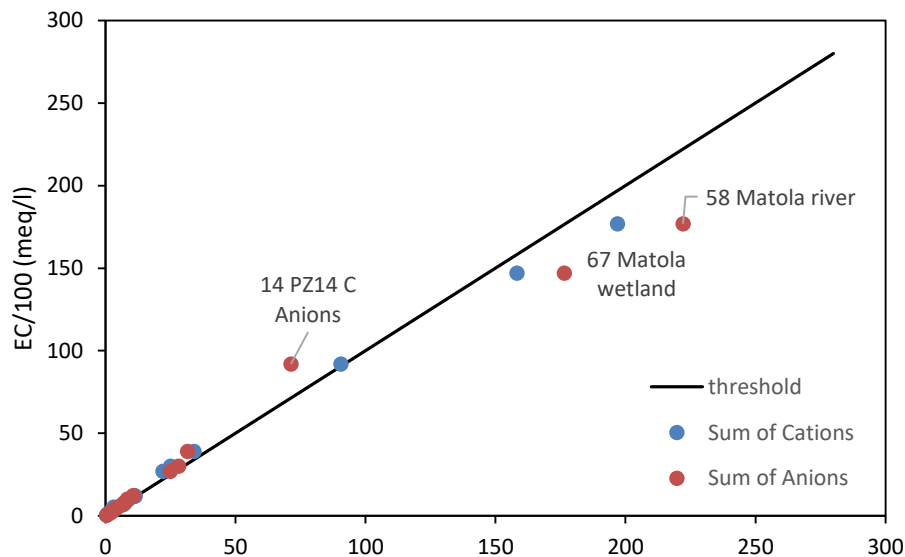
Answer：

FIGURE 1.1 Correlation between the EC/100 values and the sum of Cations and Anions

Figure 1.1 presents that most of the sum values approximately reach the EC/100 values. However, the Cations and EC/100 match, while the anions are low in sample 14(PZ14C), which the anions may be missing from the calculation of other ions (e.g., fluoride). Meanwhile, the EC/100 values of sample 58(Matola river) and 67(Matola wetland) are much lower than the anions, which might be caused by inevitable laboratory errors. Because the samples have a high concentration of sodium ions and chloride ions, the EC values more than 1500 μs/cm and the samples are the brackish water, and researchers need to dilute the samples for measuring results. Therefore, the dilute process leads to laboratory errors.

f) For the four samples with the largest error in question d), indicate whether you think measured cation or anion concentrations are too high or too low and for which ions you recommend to repeat the analysis in the laboratory.

Answer:

TABLE 1.3 Four samples with the largest error and EC/100 values

Number	Name	$\sum$ Cations	$\sum$ Anions	E.B.	EC/100
60	Lake	2.60	2.24	7.34%	2.7
66	Incomati effluent	3.09	4.73	-21.00%	5.37
14	PZ14 C	90.51	71.25	11.91%	92
31	PZ20 C	1.64	1.98	-9.50%	2

The four samples with the largest error show in table 1.3, and the cations and anions should be the EC/100 values. Thus the sum values of cations in samples 66(Incomati effluent) and 31 (PZ20C) are too low, which I recommend repeating the analysis for sodium according to table 1.1. On the other hand, the samples 14 and 60 have the lower anions and the sulfates need to reanalyze. Because the Calcium Sulfate and Magnesium Sulfate do not ionize well.

g) Calculate the contribution of the anions HCO₃⁻ and Cl⁻ to the EC (in %) for all samples. Provide the results in a table, and plot them in a graph vs. EC. Briefly comment on the results, in terms of where and why you think each of the two ions dominates.

Answer:

TABLE 1.4 Contribution of the anions HCO_3^- and Cl^- to the EC (in %)

| Number	Name	Cl^- meq/l	HCO_3^- meq/l	EC (uS/cm)	Cl^- %	HCO_3^- %
58	Matola river	185.16	7	17680	104.73%	3.96%
60	Lake	0.45	1.74	270	16.67%	64.44%
66	Incomati effluent	2.46	0.98	537	45.81%	18.25%
67	Matola wetland	152.3	6.34	14700	103.61%	4.31%
70	65-Incomati	3.87	1.6	808	47.90%	19.45%
10	16	2.72	4.2	771	35.28%	54.00%
12	23	2.89	4.0	824	35.07%	48.79%
26	PZ21 F	1.59	2.2	442	35.97%	49.77%
28	PZ19 F	1.39	0.3	220	63.18%	13.64%
30	PZ20 F	0.31	0.04	53.7	57.73%	7.45%
45	PZ02 F	20.63	3.2	2710	76.13%	11.81%
47	PZ18 F	1.93	3.48	679	28.42%	51.25%
61	Poço tio Mulungu	3.19	2.3	1005	31.74%	22.89%
14	PZ14 C	59	6.8	9200	64.13%	7.39%
23	PZ17 C	21.72	3.4	3020	71.92%	11.26%
27	PZ21 C	0.33	0.74	118.3	27.90%	62.55%
29	PZ19 C	1.07	0.2	162.5	65.85%	12.31%
31	PZ20 C	0.91	1.06	200	45.50%	53.00%
46	PZ02 C	7.34	3.12	1230	59.67%	25.37%
48	PZ18 C	4.41	4.72	1182	37.31%	39.93%
68	PZ13 C	26.66	3.9	3900	68.36%	10.00%
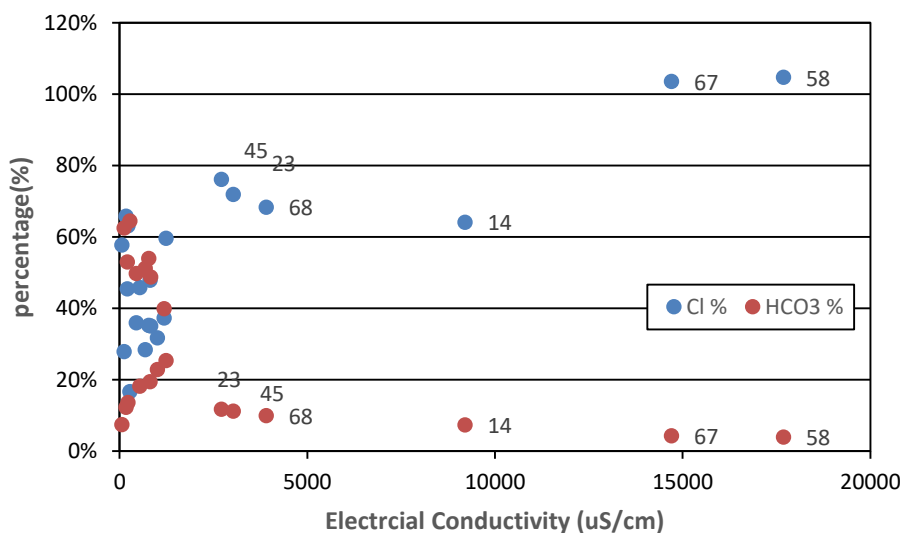
FIGURE 1.2 Percentage of the anions HCO_3^- and Cl^- versus Electrical Conductivity

The electrical conductivity is the indicator of salinity and the EC values more than 1000 μS/cm means the water has more salinity than freshwater, called brackish water. The chloride ions dominate the

brackish water because salinity is the saltiness or dissolved sodium chloride content of a body of water. Thus the samples in which EC values more than 1000 µS/cm are dominated by the chloride ions, especially in the samples 58(Matola river) and 67(Matola wetland) where have high salinity and high Cl- concentration.

The samples 60,10,47,27, and 31, have high concentrations of bicarbonate ion with low EC values. Because different rock types influence the chemical water components. For example, the water may transmit in limestones, which calcite may dissolution in the water. Thus the dominant anions in those sample are bicarbonate.

2. Visualisation of results on water quality and water type

We can now make a number of graphs to help us interpret the data with respect to water quality standards and occurrence of (natural) contamination, and also with respect to water types and a first indication of their meaning. Figure 2 presents the piezometric map of the phreatic aquifer.
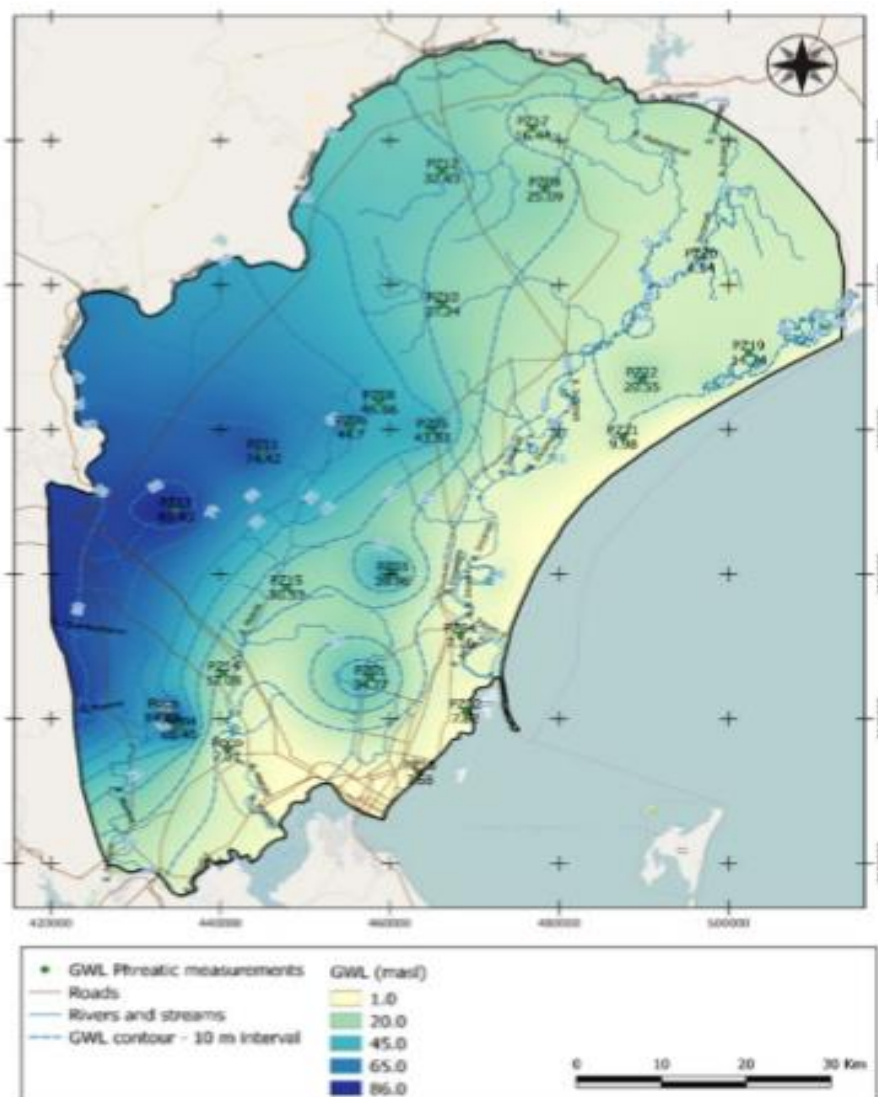

Fig. 2. Groundwater level contour map of the phreatic aquifer; source: Nogueira (2017)

a) Present the Schoeller diagram for all samples and briefly comment on the graph. The drinking water recommended values from the WHO are included (only the value for nitrate is an actual health-related guideline).
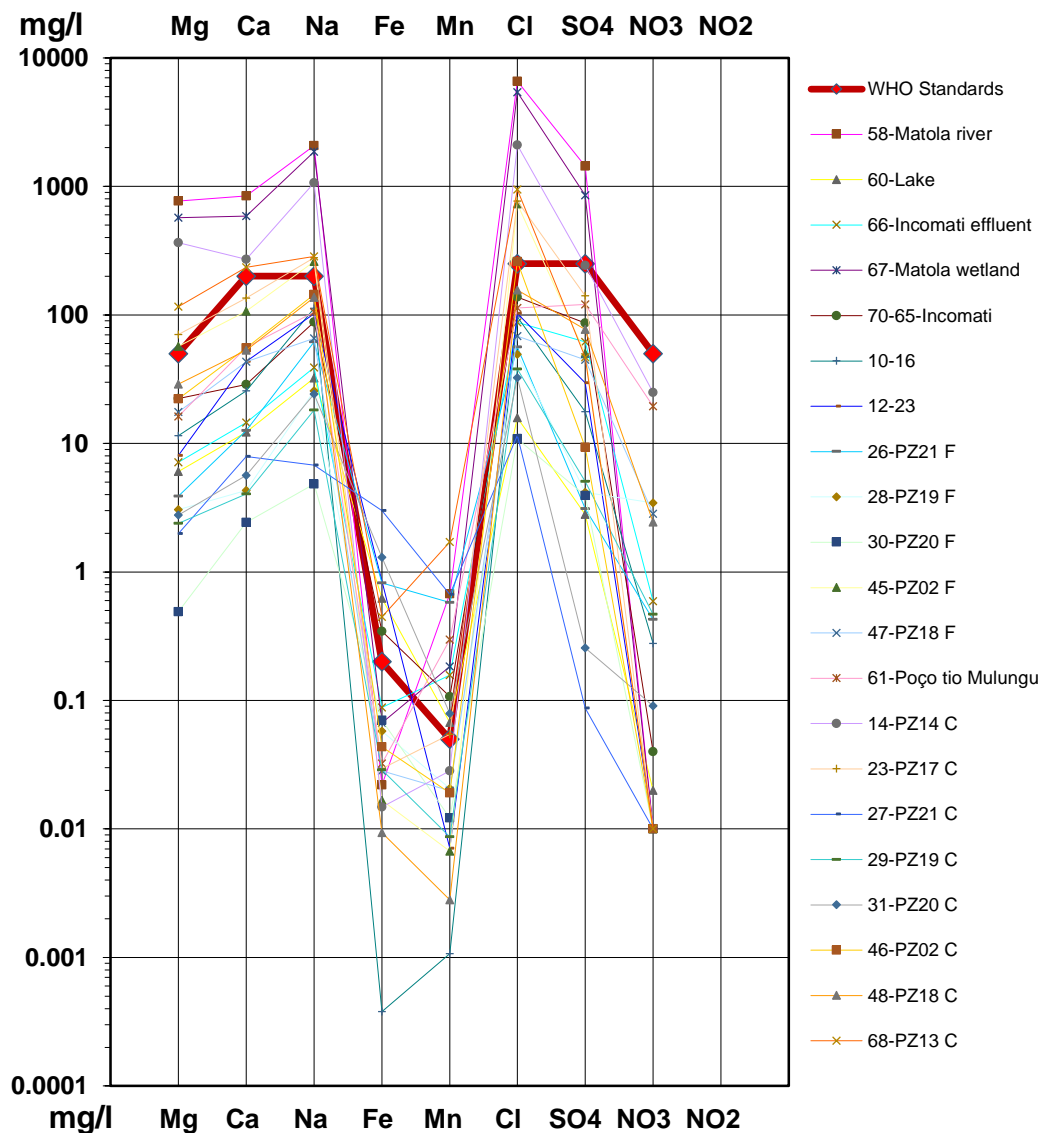

FIGURE 2.1 Schoeller diagram for all samples

Figure 1.2 presents that the concentrations of the ions for the most samples are smaller than the recommended values from WHO. However, samples 58, 67 and 14 have high levels of the hardness, sodium, chloride and sulfate ions compared with WHO standards. Although, the WHO does not suggest that the thresholds of health concern found in drinking-water about those ions.

To protected for bottle-fed infant and other parts of the population, the guideline value for nitrate set as 50mg/l, as nitrate ion, based on an absence of health effects(methemoglobinemia and thyroid effects) in epidemiological studies(WHO,2017). Fortunately, the concentrations of nitrate ion for all samples are smaller than the threshold, as shown in fig.2.1.

b) Present the Piper diagram for all samples and indicate the dominant water types (i.e. dominant cation and anion in the samples). Do the surface water samples plot away from the groundwater samples on the graph? What can this indicate?
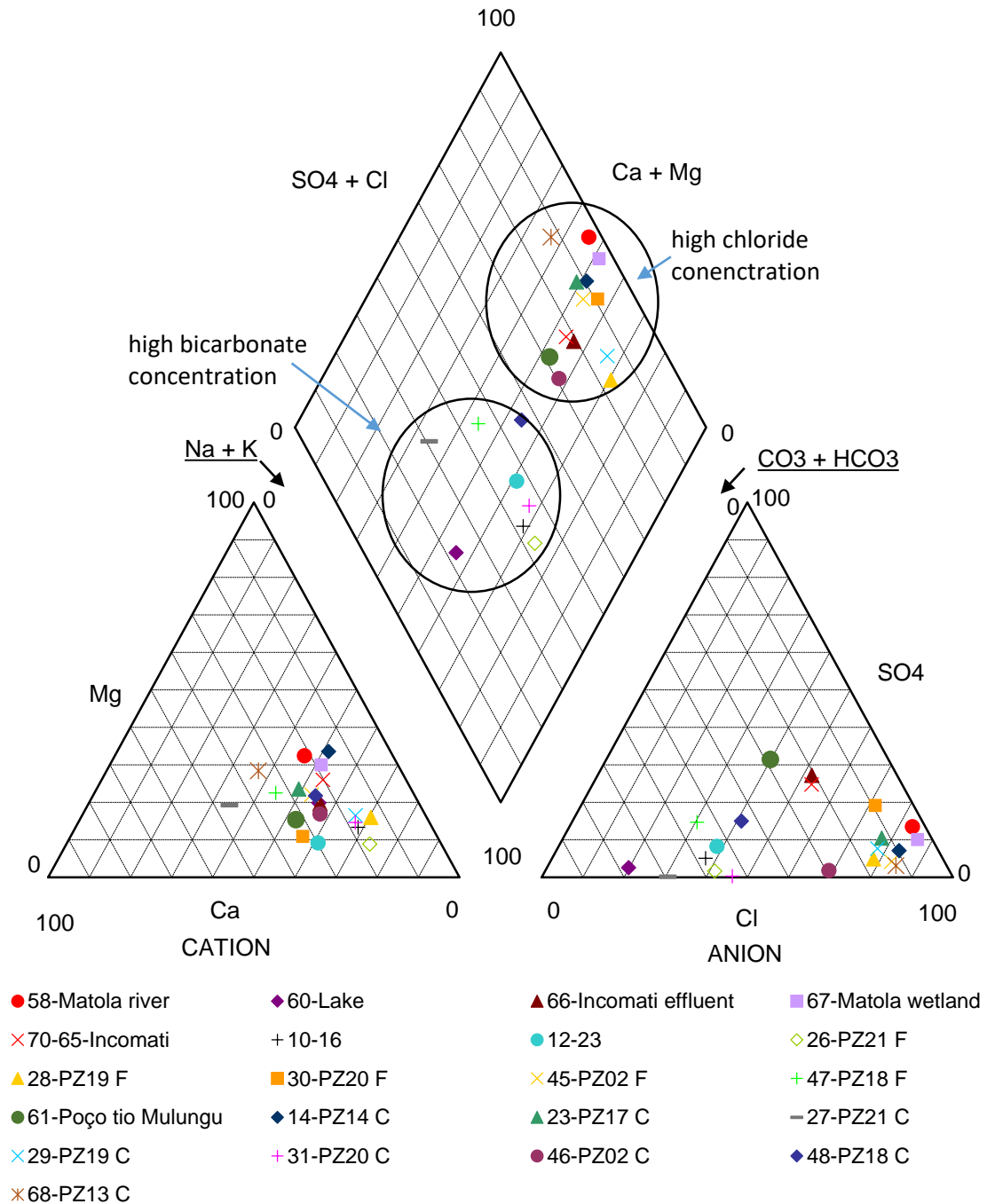

FIGURE 2.2 Piper diagram of all samples

Table 2.1 Dominant cations and anions of all samples

Number	Name	Type	Dominant cation	Dominant cation
58	Matola river	SW	Na	Cl
60	Lake	SW	Na	HCO₃
66	Incomati effluent	SW	Na	Cl
67	Matola wetland	SW	Na	Cl
70	65-Incomati	SW	Na	Cl
10	16	SGW	Na	HCO₃
12	23	SGW	Na	HCO₃
26	PZ21 F	SGW	Na	HCO₃
28	PZ19 F	SGW	Na	Cl
30	PZ20 F	SGW	Na	Cl
45	PZ02 F	SGW	Na	Cl
47	PZ18 F	SGW	Ca + Mg	HCO₃
61	Poço tio Mulungu	SGW	Na	Cl
14	PZ14 C	DGW	Na	Cl
23	PZ17 C	DGW	Na	Cl
27	PZ21 C	DGW	Ca	HCO₃
29	PZ19 C	DGW	Na	Cl
31	PZ20 C	DGW	Na	HCO₃
46	PZ02 C	DGW	Na	Cl
48	PZ18 C	DGW	Na	Cl
68	PZ13 C	DGW	Ca + Mg	Cl

Table 2.1 indicates that the dominant cations are sodium ion and potassium ion in most of the samples, which more than 50%, except the samples 27(PZ21 C) and 68(PZ13 C). Sample 27 dominate by calcium ion, and Calcium ion and Magnesium ion dominate the solutions 68 and 47. The bicarbonate ion dominates the anions of the samples 60, 27, 26, 12, 31, 47 and 10. And the dominant anion of other samples is chloride ion.

Yes, the surfer water sample 60, collected in a lake, plots away from the groundwater samples, which means the lake is a low correlation with the groundwater and the groundwater does not discharge to the lake or recharge from the lake. Because the chemical components of the drainage to the lake are the same as the original resources lead to the chemical components of lake and groundwater similar. By contrast, other surface water samples plot near the groundwater samples. It represents that the surface exchanges water with the groundwater.

c) Present the Stiff diagrams plotted on a map (you can do this by exporting from EASYQUIM in bna format and importing into Surfer; use a maximum of one or two scales, and indicate this in the legend). For the brackish samples (EC>1000 uS/cm) indicate in a table the elevation, approximate distance from coast and origin (surface water or shallow/deep groundwater). Also check the hydraulic heads of the phreatic aquifer shown on the map of Fig. 2.
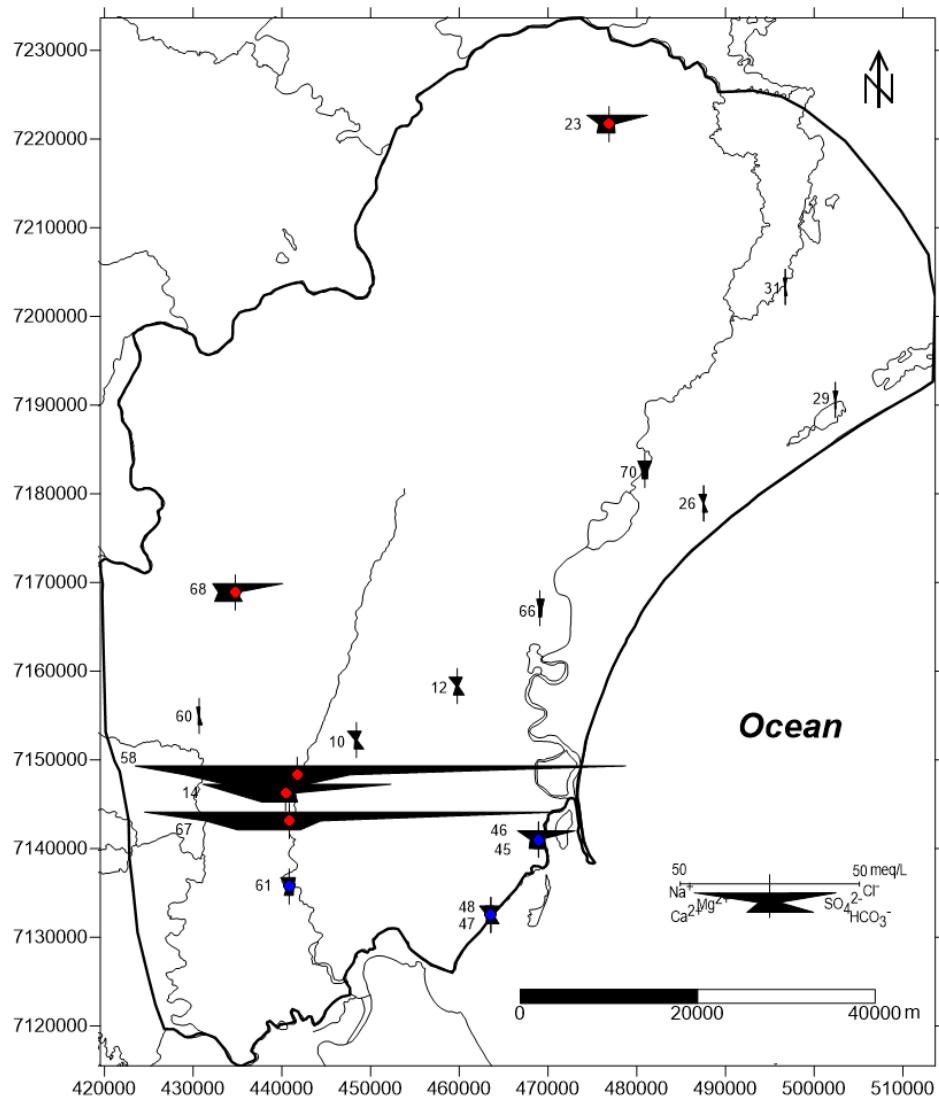
Answer:

FIGURE 2.3 Stiff diagram for all samples

Table 2.2 Elevations and distances for the brackish samples (EC>1000 uS/cm)

Number	Name	Type	UTM E (m)	UTM N (m)	Elevation (m)	EC (uS/cm)	Distance(km)
58	Matola river	SW	441729.0	7148326.4	30	17680.0	28
67	Matola wetland	SW	440835.6	7143123.4	11	14700.0	25
45	PZ02 F	SGW	468933.5	7141017.0	9	2710.0	0.72
61	Poço tio Mulungu	SGW	440822.2	7135726.6	8	1005.0	11
14	PZ14 C	DGW	440417.0	7146262.4	37	9200.0	27
23	PZ17 C	DGW	476875.0	7221686.6	22	3020.0	44
46	PZ02 C	DGW	468933.5	7141017.0	9	1230.0	0.72
48	PZ18 C	DGW	463548.6	7132522.1	10	1182.0	0.01
68	PZ13 C	DGW	434755.7	7168883.2	106	3900.0	43

d) Provide possible hypothesis for the origin of the brackish water with the information you gathered until now. In particular elaborate on the probability of recent seawater intrusion for each brackish sample.

Answer:

Samples 46, 48 and 45 obtain along the coast in the deeper aquifer and shallow aquifer with low elevation and the dominant ion in the samples is sodium chloride. The freshwater have high possibility intruded by the seawater.

The electrical conductivity values are more than 9000 uS/cm in sample 58, 67, and 14, which measure in shallow aquifer and surface. Meanwhile, the mean potential evapotranspiration is much high in this area, between 1000 and 1500 mm/year (Nogueira, G., et al, 2019). The hypothesis is that the brackish water in the river is discharged from the groundwater, which dissolves the evaporites such as halite. Meanwhile the distances from those samples to the coast are more than 20 kilometers, and the low probability of seawater intrusion occurred.

The EC values of sample 61 in the shallow aquifer with 1005 uS/cm is not very high and the sodium chloride is the dominant ion in the water, which present connate saltwater or trapped seawater with low hydraulic head. The seawater intrusion may happened because of low distance and dominant ion in the sample.

The sites obtained sample 68 and 23 which are far away from the ocean with more than 40 kilometers, are impossible intruded by seawater. The sample 68 collect in the deeper aquifer with EC value of 3900 uS/cm, influenced by calcite dissolution due to the calcium ion dominating the solution. And the presence of connate saltwater in the site obtained sample 23 because of the dominant ion in the sample which is sodium chloride.

3. Calculation of recharge and rainfall contribution to groundwater

Samples 27, 30 (groundwater) and 60 (lake water) have very low Cl^- concentrations that can be considered equal to that of average rainwater (including dry and wet deposition).

a) What assumptions are we making when considering these samples to have Cl- concentrations of average rainwater?

Answer:

The rainwater is the only source to recharge the chloride ion to those water, including groundwater and lake water.

Based on this assumption, and a number of other simplifications (see lecture notes) we can calculate the recharge of the aquifer using the Cl^- mass balance. We can only do this where groundwater has not been affected by any other sources of Cl^-. In this case we use an EC threshold of 1000 µS/cm to represent pristine groundwater not affected by other sources. We will use sample 30 as our "rainwater".

b) Calculate the recharge (as % of rainfall) for all groundwater samples with an EC below or equal to 1000 µS/cm (include sample 61). Briefly comment on the obtained values (in terms of average, median, maximum, minimum). Can they indeed be considered realistic, despite the simplifications? Provide one suggestion on how to further evaluate this.

Answer:

The percentage of recharge from rainfall to groundwater can calculate with an equation, given as

$$R = \frac{m_{cl^-,rainwater}}{m_{cl^-,groundwater}} \times 100\%$$

, where m_{cl^-} is the molarity or weight of rainwater and groundwater. The results are shown in Table 3.1.

Table 3.1 Recharge (as % of rainfall) for all groundwater samples with an EC below or equal to 1000 µS/cm (include sample 61)

Number	Type	Cl⁻	EC	Recharge
		mmol	(uS/cm)	(% of rainfall)
30	Rainwater	0.31	53.7	
60	SW	0.45	270.0	68.83%
66	SW	2.46	537.0	12.45%
70	SW	3.88	808.0	7.91%
10	SGW	2.72	771.0	11.28%
12	SGW	2.89	824.0	10.61%
26	SGW	1.59	442.0	19.32%
28	SGW	1.39	220.0	22.03%
47	SGW	1.93	679.0	15.91%
61	SGW	3.20	1005.0	9.59%
27	DGW	0.33	118.3	93.94%
29	DGW	1.07	162.5	28.65%
31	DGW	0.92	200.0	33.51%
Average	27.84%		Median	17.61%
Maximum	93.94%		Minimum	7.91%

The table presents that the average value of the recharge (as % of rainfall) is 27.84%. And the recharge with 17.61% is the median value obtained by the average of recharges in sample 26 and 47. The maximum values are from the low Cl⁻ concentrations of sample 27, which account for 93.94%. The recharge located in sample 70 to the groundwater is the minimum percentage of rainfall with 7.91%.

The samples could not be considered realistic, despite the simplification. The values indicate the hydrochemistry process occurring in rainwater percolating through the soil and unsaturated zones and in groundwater. However, the recharge in sample 27, which collect in deep layer aquifer with 93.94% is not realistic, even more than the percentage in the shallow aquifer, because of evaporation. The evaporation must consume the infiltration, and it is impossible to percolate so high a fraction of rainfall.

The Cl⁻ concentration has changed with increasing soil depth, influenced by many rainfalls due to different resident times. The suggestion is that according to the depth of groundwater samples, estimating the resident time and selecting the precipitation is to calculate the recharge.

c) For the groundwater samples of question 3b) calculate the contribution of rainwater to Na+, Ca2+, Cl- and HCO3- as well as the fraction not derived from rainwater. Provide the results in a table and provide a brief interpretation of the results.

Answer:

Number	Type	concentration factor	Rainwater (mmol/L)				Other sources (mmol/L)			
			Ca^{2+}	Na^+	Cl^-	HCO_3^-	Ca^{2+}	Na^+	Cl^-	HCO_3^-
60	SW	1.5	0.3	0.1	0.45	0.1	1.1	0.2	0	1.7
66	SW	8.0	1.7	0.5	2.46	0.3	0.0	-0.1	0	0.7
70	SW	12.6	2.7	0.8	3.88	0.5	1.2	-0.1	0	1.1
10	SGW	8.9	1.9	0.5	2.72	0.4	3.0	0.1	0	3.8
12	SGW	9.4	2.0	0.6	2.89	0.4	2.5	0.5	0	3.6
26	SGW	5.2	1.1	0.3	1.59	0.2	1.6	0.0	0	2.0
28	SGW	4.5	1.0	0.3	1.39	0.2	0.2	-0.2	0	0.1
47	SGW	6.3	1.3	0.4	1.93	0.3	1.5	0.7	0	3.2
61	SGW	10.4	2.2	0.6	3.20	0.4	2.4	0.8	0	1.9
27	DGW	1.1	0.2	0.1	0.33	0.0	0.1	0.1	0	0.7
29	DGW	3.5	0.7	0.2	1.07	0.1	0.1	-0.1	0	0.1
31	DGW	3.0	0.6	0.2	0.92	0.1	0.4	0.0	0	0.9

Table 3.2 indicates the results of the contribution of rainwater to four ions and the fraction from other sources.

The low HCO_3^- concentration from the rainwater cannot contribute significantly to the groundwater. Instead, their sources in groundwater might be the calcite or magnesium carbonate dissolution from limestones and dolomites, especially in the shallow aquifer with high HCO_3^- concentration

On the other hand, the Na^+ concentration from other sources in samples 66, 70, 28 and 29 is negative. That might be an effect of industrial Cl^- productions. In such cases, Na^+ is preferred as a conservative ion. However, samples 12, 47 and 67 on Na^+ concentration from the other source are high, which might be influenced by silicate weathering.

Meanwhile, the rainwater and other sources of both influences on the Ca^{2+} concentration are high. The calcite aquifer in shallow might be dissolute the calcite into the water and impacts the results.

4. Mineral weathering and surface water-groundwater interactions

Let us now look at the possible existence of carbonate mineral dissolution and/or silicate mineral weathering. We do this by calculating the saturation index (SI) for calcite (as calcite dissolution is an equilibrium driven process) and the partial CO_2 pressure for each sample, and by plotting Ca^{2+} and Na+ concentrations versus HCO_3^- concentrations in scatter plots. It is not easy to distinguish between carbonate dissolution and silicate weathering when the dominating silicate mineral is anorthite (Ca-silicate). However often albite (Na-silicate) can be an abundant silicate mineral or composite minerals occur with both Na and Ca (defining the "plagioclase series"). This will largely reflect itself in the Ca^{2+}/HCO_3^- ratio. Moreover, silicate weathering is a much slower process than calcite dissolution.

a) Calculate the SI for calcite and the partial CO_2 pressure for all samples in PHREEQC, by using the file ex_Spreadsheet_v2.phrq (follow the steps indicated in the file). Present the values in a table together with pH, Ca^{2+} and HCO_3^- concentrations and the Ca^{2+}/HCO^{3-} ratio.

Table 4.1 Results calculated in PHREEQC

Number	pH	Ca^{2+}	HCO_3-	Ca^{2+}/HCO^{3-}	Calcite	$PCO_2(g)$

		Concentration (mmol/L)		ratio(%)	SI [-]	log
58	7.35	21.29	7.09	300%	0.87	-1.91
60	7.44	0.30	1.74	18%	-0.77	-2.38
66	6.82	0.36	0.98	37%	-1.69	-2.05
67	7.30	14.79	6.40	231%	0.69	-1.87
70	6.85	0.72	1.60	45%	-1.19	-1.87
10	8.02	0.64	4.20	15%	0.39	-2.62
12	7.87	1.08	4.00	27%	0.44	-2.49
26	7.04	0.31	2.20	14%	-1.12	-1.91
28	6.37	0.11	0.30	36%	-3.08	-2.09
30	4.78	0.06	0.04	152%	-5.60	-1.22
45	8.20	2.67	3.20	83%	0.91	-2.97
47	7.60	1.08	3.48	31%	0.12	-2.27
61	6.30	1.39	2.30	61%	-1.33	-1.18
14	7.43	6.79	6.83	99%	0.65	-1.93
23	7.58	3.37	3.40	99%	0.41	-2.31
27	5.84	0.20	0.74	27%	-2.94	-1.17
29	6.02	0.10	0.20	51%	-3.61	-1.91
31	6.20	0.14	1.06	13%	-2.60	-1.38
46	8.15	1.38	3.12	44%	0.67	-2.90
48	8.03	1.33	4.72	28%	0.70	-2.59
68	6.95	5.85	3.91	150%	0.01	-1.65

b) If you would manually calculate the saturation index for each sample, based on the concentrations measured in the lab and ignoring activities and aqueous complexes, would you expect to find lower or higher values? Please explain in one sentence.

Answers:

The lower values are obtained.

The reason for getting the lower values is that the activity coefficient (γ) equal to one and ion concentrations calculated manually are smaller due to ignoring activities and aqueous complexes, but the coefficient generally smaller than one, which represents the complex and activity correction as the fraction of each ion concentration.

c) Plot the Ca^{2+} vs. HCO_3^- concentrations and Na^+ vs. HCO_3^- concentrations on the same graph; add the sample labels. Based on this graph and the values in the table (question a) try to indicate and briefly explain in which samples most likely: i) calcite dissolution occurred; ii) silicate weathering occurred or iii) no (or very little) interaction with minerals took place.
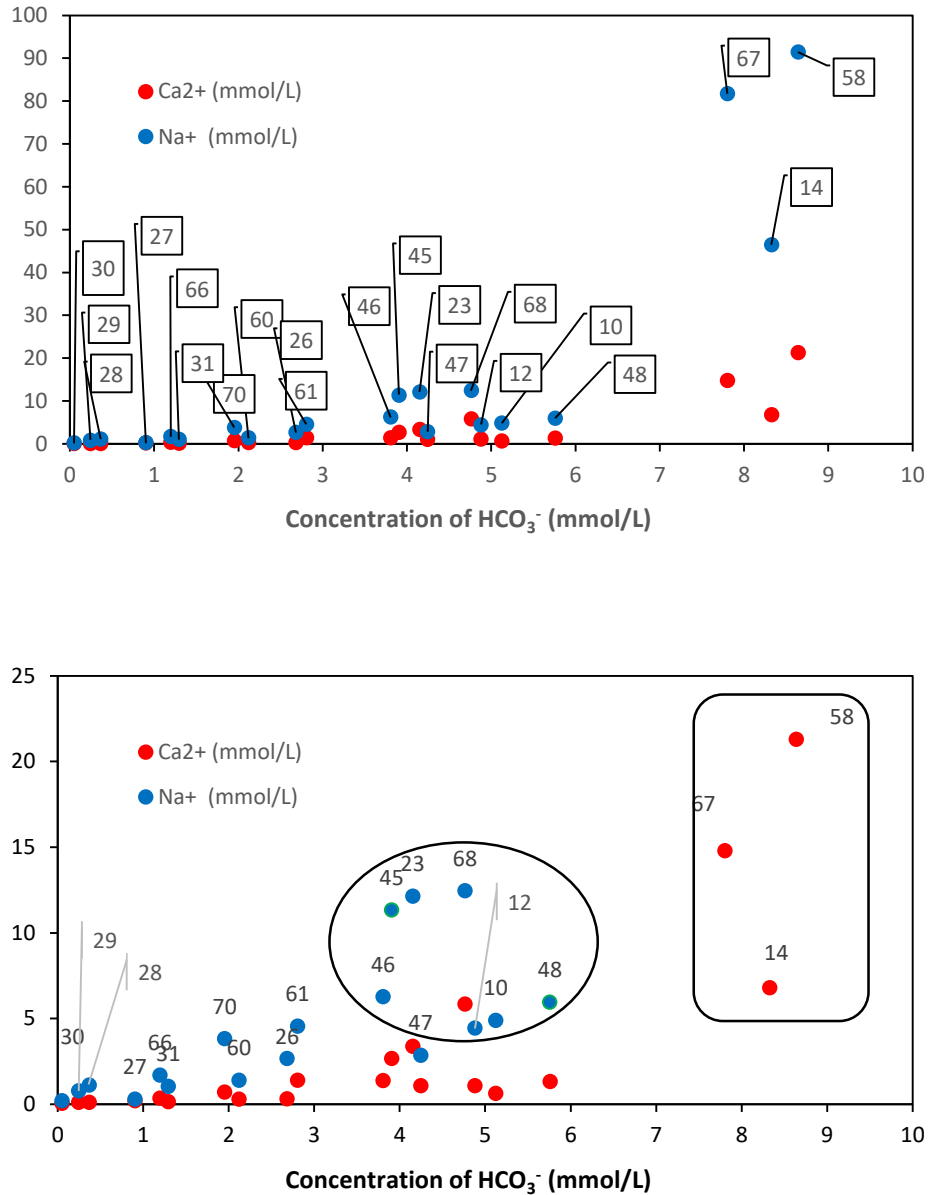
Answer:

FIGURE 4.1 Ca²⁺ vs. HCO₃⁻ concentrations and Na⁺ vs. HCO₃⁻ concentrations

The top diagram of fig. 4.1 reduces the maximum y-axis value to 25, given as the bottom diagram, to analyze the relatively low concentration of sodium and calcium ions. The analyzed results are shown in the table, as follow:

i) calcite dissolution occurred			Reason
58	Matola river	SW	the samples indicated in fig. 4.1 with a black rectangle, obtained in deep aquifer or shallow aquifer, have the relatively high concentrations of calcium and bicarbonate ions, compared with other samples, and the solution is supersaturated with SI more than 0.2 and the high Na concentration may remain due to strapped seawater
14	PZ14 C	DGW	
67	Matola wetland	SW	
68	PZ13 C	DGW	the partial carbon dioxide of sample 68 relatively high increasing the reaction of calcite dissolution with a high concentration of calcium

ii) silicate weathering occurred			Reason
45	PZ02 F	SGW	
46	PZ02 C	DGW	
48	PZ18 C	DGW	The weathering from the albite produce the sodium ion as
47	PZ18 F	SGW	well as bicarbonate in the silicates rocks, and the Na+
23	PZ17 C	DGW	concentrations are relatively high in samples, indicated with
68	PZ13 C	DGW	a black circle in fig 4.1, while the levels of bicarbonate are
12	23	SGW	not very low.
10	16	SGW	

iii) no (or very little) interaction with minerals took place.			Reason
60	Lake	SW	
66	Incomati effluent	SW	
26	PZ21 F	SGW	
28	PZ19 F	SGW	the concentrations of all ions are low, including
30	PZ20 F	SGW	bicarbonate, which is smaller than 3 mmol/L
27	PZ21 C	DGW	
29	PZ19 C	DGW	
31	PZ20 C	DGW	

d) Based on the table and graph try to explain which surface water samples show the clearest interaction with groundwater (you can also look at other ions such as Cl-). Also mention which assumptions you are making in your hypothesis.

Answer:

The surface water samples 66 show the clearest interaction with groundwater.

The only source of the surface water is from precipitation, and the water transmits through the aquifer without any dissolution.

e) Describe the processes that occur when calcite-saturated groundwater comes in contact with the atmosphere, for instance when groundwater discharges into a river or wetland.

Answer:

When groundwater discharges into a river, the groundwater becomes free surface water with reducing the dissolution of CO_2 concentration in the water, because the carbon dioxide content in the atmosphere is lower than that in the soil. According to the solubility product (K) of the reaction between calcite and carbon dioxide, given as

$$K = \frac{[Ca^{2+}][HCO_3^-]}{P_{CO_2}} = 10^{-6.0}$$

, degassing of CO_2 leads to the precipitation of calcite when the groundwater is calcite-saturated.

5. Nitrate and sulphate reduction

To detect possible signs of reduction processes happening we can look at the "disappearance" of these oxidants (electron acceptors) and possible "appearance" of reductants (electron donors).

a) Plot Fe(II) vs. NO_3^- concentrations and vs. SO_4^{2-} concentrations; add the labels to the graph.
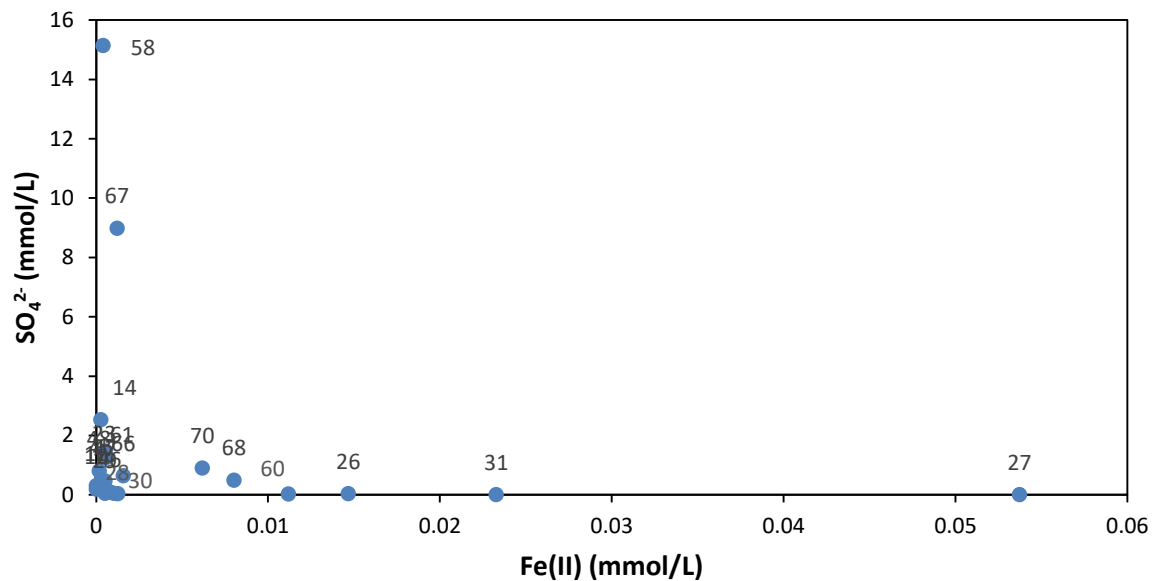

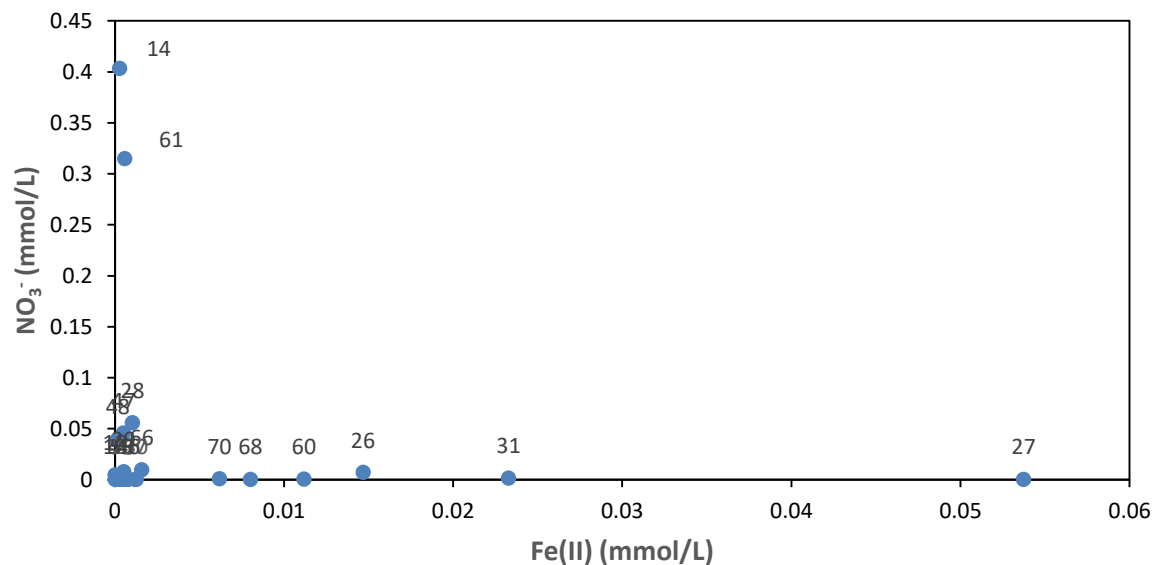FIGURE 5.1 Fe(II) vs. SO_4^{2-} concentrations

FIGURE 5.2 Fe(II) vs. NO_3^- concentrations

b) Plot SO_4^{2-} vs. Cl^- concentrations and add the seawater mixing line (and the sample labels). Include one plot of the lower range of concentrations (i.e. "zoom in") to see how the samples plot around the seawater mixing line.
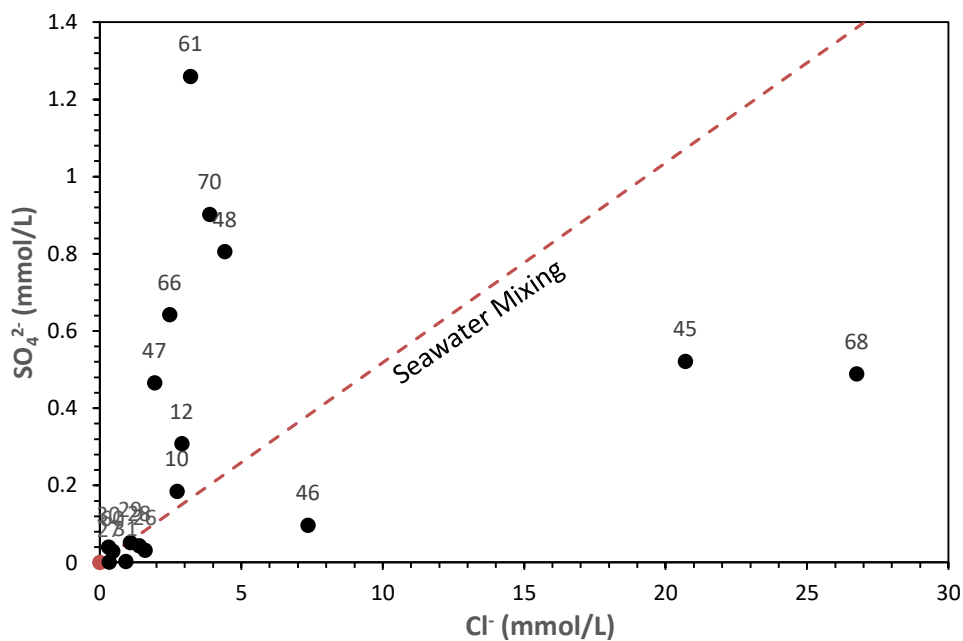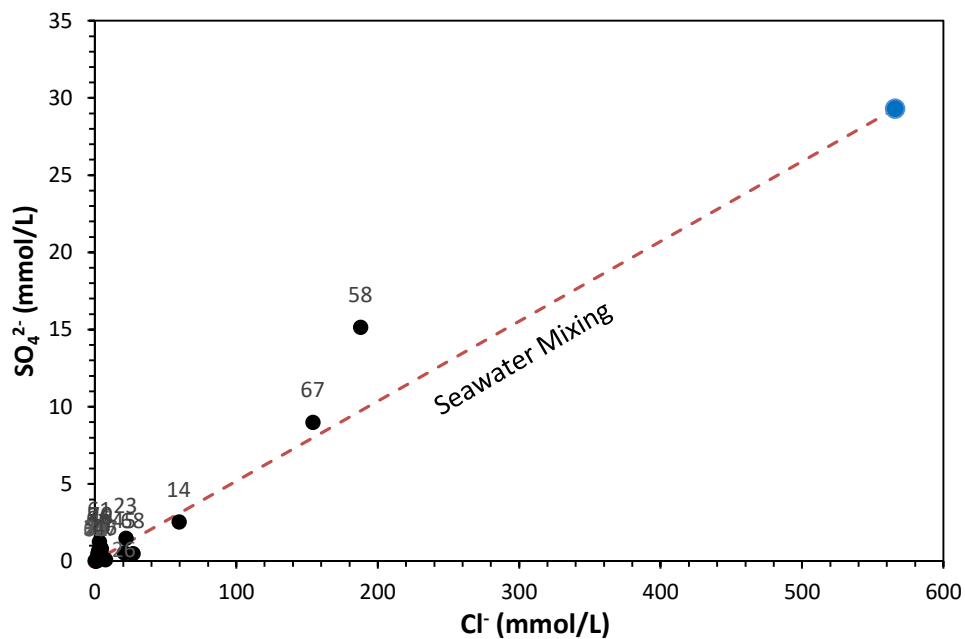
FIGURE 5.3 SO_4^{2-} vs. Cl^- concentrations with seawater mixing line

c) Based on the two plots above, which samples seem to be in a more reduced state, and which show evidence of a more oxidized state? What could be the explanation of the more reduced state of the samples you found?

Answer:

Atoms tend to take on low valences, while water is in a reduced state. Thus the higher concentration of ferrous iron, water is in a more reduced state. Sample 70, 68, 60, 26, 31 and 27 seem to be in a more reduced state as shown in fig.5.1 and 5.2. However, figure 5.3 presents the sample 70 and 68 plot far away from the seawater mixing line, which means that the intrusion of seawater or

freshening of saltwater might have occurred in those areas and influence in sulphate concentration. Thus the points of sample 70 and 68 are outliers. Reversely, with increasing the concentration of sulfate and nitrate, the water is in a more oxidized state such as sample 61, 14, 58 and 67.

The more reduced state of Sample 60, collected in the lake with relatively high elevation, maybe due to the eutrophication of surface water impacted by fertilizer leakage and the increased biomass of phytoplankton consume the more dissolved oxygen in the lake leads to the more reduced state of water. Similarly, the sample 26 collected in the shallow groundwater locates near the city, called Manhica. Therefore, the water has a high possibility to be polluted by wastewater discharged from the city with a high concentration of organic matter such as sugars and it may result in that the water is in the more reduced state. Meanwhile, the reason which results in Sample 31 and 27 in the more reduced states might be a reduction reaction with a high concentration of organic matter in the deep aquifer.

6. Mixing with saltwater/seawater and cation exchange

Let us now look at the possible occurrence of mixing with seawater and possibly related cation exchange. For this, we use the six samples with the highest EC.

a) For these samples calculate the fraction of seawater (use sample 10 located nearby as natural groundwater), and the ratios of Na^+/Cl^- and Ca^{2+}/HCO_3^-

Answer:

Fraction of seawater in a sample based on the concentration (m) of the conservative Cl^- ion, is calculated as

$$f_{sea} = \frac{m_{Cl^-,sample} - m_{Cl^-,freshwater}}{m_{Cl^-,sea} - m_{Cl^-,freshwater}}$$

, where the Cl^- concentration of the sea is 566 mmol/L and the Cl^- concentration of the freshwater using sample 10 is 4.2 mmol/L. The results are shown in Table 6.1.

Table 6.1 Fraction of seawater and the ratios of Na^+/Cl^- and Ca^{2+}/HCO_3^-

Number	Fraction(f_{sea})	Na^+/Cl^-	Ca^{2+}/HCO_3^-
58	32%	49%	301%
67	27%	53%	231%
14	10%	78%	99%
68	4%	47%	150%
23	3%	56%	99%
45	3%	55%	83%

b) Calculate the concentrations of Na^+, Ca^{2+}, HCO_3^- and SO_4^{2-} if they were to come only from conservative mixing of natural groundwater and seawater.

Answer:

The expected concentration of ion *i* in conservative mixing of freshwater and seawater (no hydrochemical reactions), given as

$$m_{i,mix} = f_{sea} \times m_{i,sea} + (1 - f_{sea}) \times m_{i,freshwater}$$

, as show the results in Table 6.2.

Table 6.2 Conservative concentrations of Na^+, Ca^{2+}, HCO_3^- and SO_4^{2-}

Number(mmol/L)	Na^+,	Ca^{2+}	HCO_3^-	SO_4^{2-}
58	160.6	3.9	3.6	9.6
67	132.6	3.3	3.7	7.9
14	52.9	1.6	4.0	3.1
68	25.3	1.1	4.1	1.4
23	21.1	1.0	4.1	1.2
45	20.2	1.0	4.1	1.1

c) Calculate the differences between the "conservative" and observed concentrations for these four ions for the six samples.

Table 6.2 Differences between the "conservative" and observed concentrations for these four ions

Number(mmol/L)	Na^+,	Ca^{2+}	HCO_3^-	SO_4^{2-}
58	-70.3	17.1	3.4	5.3
67	-51.6	11.3	2.6	1.0
14	-6.6	5.1	2.8	-0.6
68	-12.9	4.8	-0.2	-0.9
23	-9.0	2.4	-0.7	0.3
45	-8.9	1.7	-0.9	-0.6

d) Plot the Na⁺ vs. Cl⁻ concentrations on a graph and include the seawater mixing line.
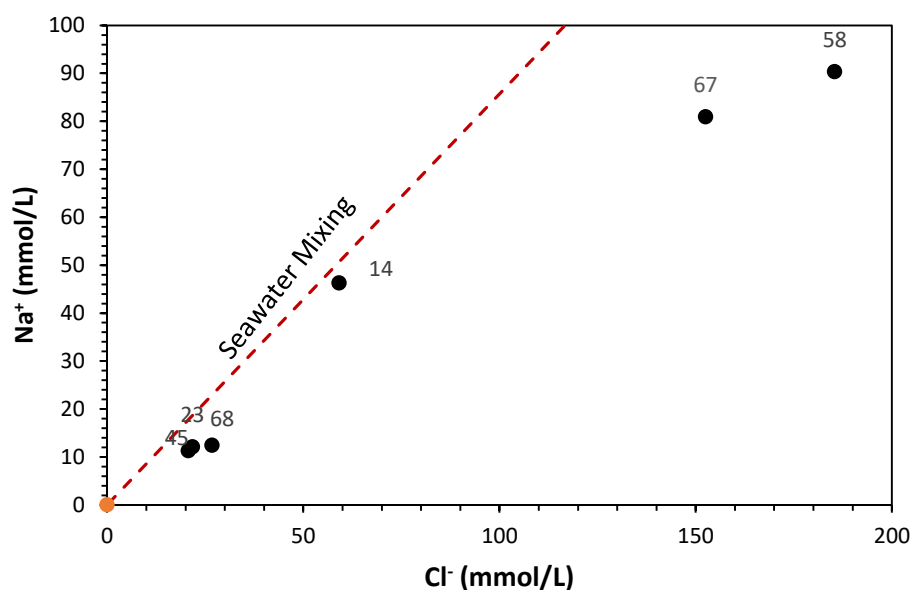

FIGURE 6.1 Na⁺ vs. Cl⁻ concentrations with the seawater mixing line.

e) Plot the Na⁺/Cl⁻ and Ca²⁺/HCO₃⁻ ratios vs. Cl⁻ concentrations.

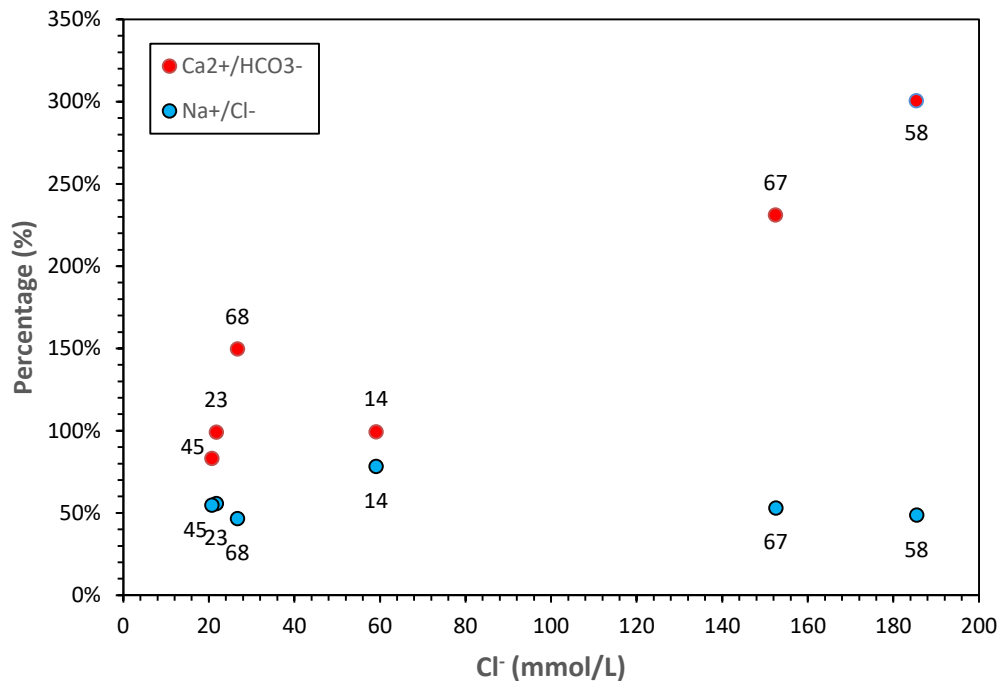FIGURE 6.2 Na⁺/Cl⁻ and Ca²⁺/HCO₃⁻ ratios vs. Cl⁻ concentrations

f) Briefly interpret the results of questions 6c, 6d and 6e. Write down the reactions you think are occurring.

Answer:

The results of questions 6c, 6d represent that the relatively high sodium concentrations disappear after mixing seawater and the ratios of Na⁺/Cl⁻ plot far away from the seawater mixing line and lower than that line in sample 58 and 67. Meanwhile, the rates of Ca²⁺/HCO₃⁻ are much higher than those of Na⁺/Cl⁻ with high Cl⁻ concentration, as shown in fig 6.2 with 301% and 231% in sample 58 and 67 respectively. To sum up, that phenomenon might be caused by cation exchange complex due to seawater intrusion, given as

$$2Na^+ + Ca\text{-}X_2 \rightarrow 2Na\text{-}X + Ca^{2+}$$
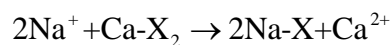
, where X = aquifer cation exchange complex.

Reference

Nogueira, G., Stigter, T. Y., Zhou, Y., Mussa, F., & Juizo, D. (2019). Understanding groundwater salinization mechanisms to secure freshwater resources in the water-scarce city of Maputo, Mozambique. *Science of The Total Environment*, *661*, 723-736.

World Health Organization. (2017). Guidelines for drinking-water quality: first addendum to the fourth edition.**3**