

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

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1. Lab results

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.

I use the Excel file Atom_Mol_Weights.xlsx to get the molar weights of each ion, and directly converse the units by the following equations.

$$\text{mmol/l} = \frac{\text{mg/l}}{\text{mw}}$$

, where mw is the molecular weight (g/mol).

$$\text{meq/l} = \frac{\text{mg/l}}{\text{mw}} * ch$$

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

Table 1.1 the conversation results for the major ions

Number	Name	Na ⁺			K ⁺			Ca ²⁺		
		mg/l	mmol/l	meq/l	mg/l	mmol/l	meq/l	mg/l	mmol/l	meq/l
58	Matola river	2077.0	90.3	90.3	38.8	1.0	1.0	843.0	21.0	42.1
60	Lake	32.3	1.4	1.4	3.4	0.1	0.1	12.2	0.3	0.6
66	Incomati effluent	38.9	1.7	1.7	3.4	0.1	0.1	14.5	0.4	0.7
67	Matola wetland	1861.0	80.9	80.9	27.9	0.7	0.7	587.0	14.6	29.3
70	65-Incomati	87.9	3.8	3.8	5.9	0.1	0.1	28.7	0.7	1.4
10	16	112.3	4.9	4.9	5.5	0.1	0.1	25.6	0.6	1.3
12	23	102.1	4.4	4.4	9.8	0.3	0.3	43.4	1.1	2.2
26	PZ21 F	61.5	2.7	2.7	4.8	0.1	0.1	12.6	0.3	0.6
28	PZ19 F	25.7	1.1	1.1	3.4	0.1	0.1	4.3	0.1	0.2
30	PZ20 F	4.8	0.2	0.2	0.7	0.0	0.0	2.4	0.1	0.1
45	PZ02 F	260.0	11.3	11.3	25.6	0.7	0.7	106.7	2.7	5.3

47	PZ18 F	65.7	2.9	2.9	11.0	0.3	0.3	43.3	1.1	2.2
61	Poço tio Mulungu	104.9	4.6	4.6	10.9	0.3	0.3	55.8	1.4	2.8
14	PZ14 C	1064.0	46.3	46.3	17.8	0.5	0.5	271.0	6.8	13.5
23	PZ17 C	278.6	12.1	12.1	12.2	0.3	0.3	135.0	3.4	6.7
27	PZ21 C	6.8	0.3	0.3	2.8	0.1	0.1	7.9	0.2	0.4
29	PZ19 C	18.2	0.8	0.8	3.9	0.1	0.1	4.1	0.1	0.2
31	PZ20 C	24.2	1.1	1.1	2.9	0.1	0.1	5.6	0.1	0.3
46	PZ02 C	144.1	6.3	6.3	14.7	0.4	0.4	55.3	1.4	2.8
48	PZ18 C	136.6	5.9	5.9	15.7	0.4	0.4	53.1	1.3	2.6
68	PZ13 C	286.0	12.4	12.4	13.0	0.3	0.3	234.0	5.8	11.7

Number	Name	Mg ²⁺			Cl ⁻			HCO ₃ ⁻		
		mg/l	mmol/l	meq/l	mg/l	mmol/l	meq/l	mg/l	mmol/l	meq/l
58	Matola river	768.0	31.6	63.2	6573.1	185.4	185.4	427.1	7.0	7.0
60	Lake	6.0	0.2	0.5	15.8	0.4	0.4	106.1	1.7	1.7
66	Incomati effluent	7.1	0.3	0.6	87.3	2.5	2.5	59.8	1.0	1.0
67	Matola wetland	571.0	23.5	47.0	5406.8	152.5	152.5	386.7	6.3	6.3
70	65- Incomati	22.3	0.9	1.8	137.5	3.9	3.9	96.7	1.6	1.6
10	16	11.5	0.5	0.9	96.4	2.7	2.7	253.6	4.2	4.2
12	23	8.0	0.3	0.7	102.5	2.9	2.9	244.8	4.0	4.0
26	PZ21 F	3.9	0.2	0.3	56.3	1.6	1.6	134.2	2.2	2.2
28	PZ19 F	3.1	0.1	0.3	49.4	1.4	1.4	18.3	0.3	0.3
30	PZ20 F	0.5	0.0	0.0	10.9	0.3	0.3	2.4	0.0	0.0
45	PZ02 F	57.0	2.3	4.7	732.5	20.7	20.7	195.2	3.2	3.2
47	PZ18 F	17.6	0.7	1.4	68.4	1.9	1.9	212.3	3.5	3.5
61	Poço tio Mulungu	16.2	0.7	1.3	113.4	3.2	3.2	140.3	2.3	2.3
14	PZ14 C	366.0	15.1	30.1	2094.5	59.1	59.1	414.8	6.8	6.8
23	PZ17 C	70.3	2.9	5.8	770.9	21.7	21.7	207.4	3.4	3.4
27	PZ21 C	2.0	0.1	0.2	11.6	0.3	0.3	45.1	0.7	0.7
29	PZ19 C	2.4	0.1	0.2	38.0	1.1	1.1	12.2	0.2	0.2
31	PZ20 C	2.8	0.1	0.2	32.5	0.9	0.9	64.7	1.1	1.1
46	PZ02 C	22.2	0.9	1.8	260.5	7.3	7.3	190.3	3.1	3.1
48	PZ18 C	28.9	1.2	2.4	156.4	4.4	4.4	287.9	4.7	4.7
68	PZ13 C	116.0	4.8	9.5	946.6	26.7	26.7	237.9	3.9	3.9

Number	Name	SO ₄ ²⁻			NO ₃ ⁻			Total Fe		
		mg/l	mmol/l	meq/l	mg/l	mmol/l	meq/l	mg/l	mmol/l	meq/l
58	Matola river	1436.8	15.0	29.9	0.0	0.0	0.0	0.0	0.0	0.0
60	Lake	2.8	0.0	0.1	0.0	0.0	0.0	0.6	0.0	0.0

66	Incomati effluent	61.7	0.6	1.3	0.6	0.0	0.0	0.1	0.0	0.0
67	Matola wetland	854.5	8.9	17.8	0.0	0.0	0.0	0.1	0.0	0.0
70	65-Incomati	86.6	0.9	1.8	0.0	0.0	0.0	0.3	0.0	0.0
10	16	17.7	0.2	0.4	0.3	0.0	0.0	0.0	0.0	0.0
12	23	29.6	0.3	0.6	0.0	0.0	0.0	0.0	0.0	0.0
26	PZ21 F	3.1	0.0	0.1	0.4	0.0	0.0	0.8	0.0	0.0
28	PZ19 F	4.2	0.0	0.1	3.4	0.1	0.1	0.1	0.0	0.0
30	PZ20 F	3.9	0.0	0.1	0.0	0.0	0.0	0.1	0.0	0.0
45	PZ02 F	50.0	0.5	1.0	0.0	0.0	0.0	0.0	0.0	0.0
47	PZ18 F	44.7	0.5	0.9	2.8	0.0	0.0	0.0	0.0	0.0
61	Poço tio Mulungu	120.9	1.3	2.5	19.5	0.3	0.3	0.0	0.0	0.0
14	PZ14 C	242.3	2.5	5.0	24.9	0.4	0.4	0.0	0.0	0.0
23	PZ17 C	141.1	1.5	2.9	0.0	0.0	0.0	0.0	0.0	0.0
27	PZ21 C	0.1	0.0	0.0	0.0	0.0	0.0	3.0	0.1	0.1
29	PZ19 C	5.0	0.1	0.1	0.5	0.0	0.0	0.0	0.0	0.0
31	PZ20 C	0.3	0.0	0.0	0.1	0.0	0.0	1.3	0.0	0.1
46	PZ02 C	9.3	0.1	0.2	0.0	0.0	0.0	0.0	0.0	0.0
48	PZ18 C	77.3	0.8	1.6	2.4	0.0	0.0	0.0	0.0	0.0
68	PZ13 C	46.9	0.5	1.0	0.0	0.0	0.0	0.4	0.0	0.0

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?

The reason for this phenomenon is that the concentration of bicarbonate is relatively low, and bicarbonate is not stable. Under acidic conditions, bicarbonate is natural to react with hydrogen ions to form unstable carbonic acid, which then volatiles as carbon dioxide. In the alkaline environment, the bicarbonate is easy to react with hydroxide ions to form carbonate. Thus, bicarbonate is easier to miss than other ions, which are more conservative.

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

The assumption which I make is that the sum of all positive and negative charges in water is zero, which means the electrical balance is in an equilibrium state.

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

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.

To examine the accuracy of the analysis, one can calculate the electrical balance (E.B.):

$$E.B. (\%) = \frac{\sum cations + \sum anions}{\sum cations - \sum anions} * 100$$

Table 1.2 electric balance for each sample

Number	Name	E.B. (%)	Number	Name	E.B. (%)
58	Matola river	-6.2	47	PZ18 F	2.8
60	Lake	8.0	61	Poço tio Mulungu	3.8
66	Incomati effluent	-20.7	14	PZ14 C	11.7
67	Matola wetland	-5.6	23	PZ17 C	-5.9
70	65-Incomati	0.0	27	PZ21 C	2.9
10	16.0	0.0	29	PZ19 C	-3.5
12	23.0	0.0	31	PZ20 C	-7.6
26	PZ21 F	-0.2	46	PZ02 C	2.6
28	PZ19 F	-4.6	48	PZ18 C	2.7
30	PZ20 F	-4.1	68	PZ13 C	3.9
45	PZ02 F	-6.3			

The absolute E.B. values up to 2% are inevitable in the laboratory, and the absolute values up to 5% are generally accepted. Thus, the values, which are marked by red in the above table, over 5% are necessary to review the analysis. On the contrary, the E.B. values of 10, 12, and 70 are very adjacent to zero, which means a perfect performance of electric balance for these samples.

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

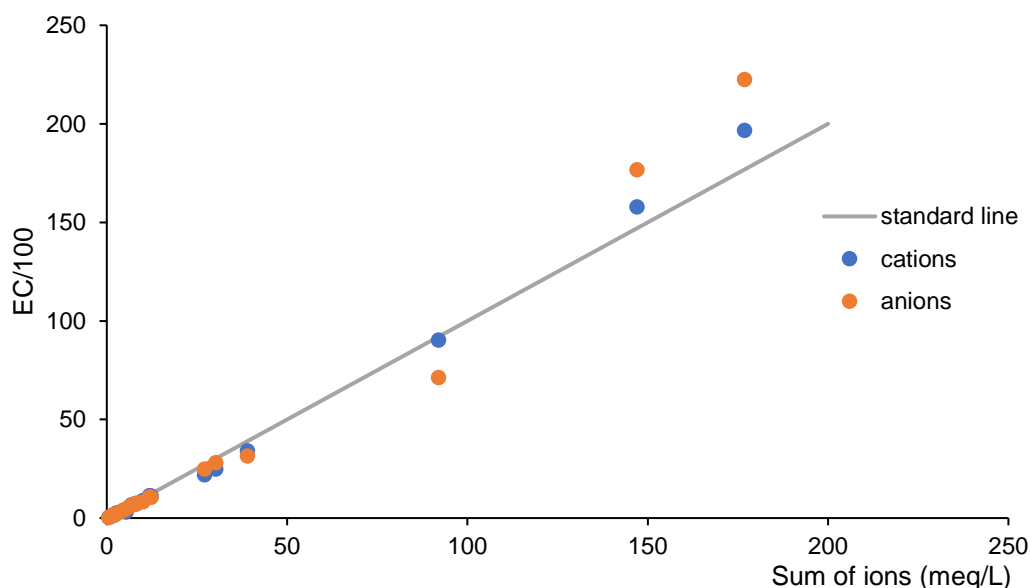


Figure 1.1 Correlation between the sum of cations and anions and EC/100 values

Based on the thumb rule in freshwater (up to EC of 2000 us/cm), the absolute value of the sum of cations or anions is equal to EC/100. In figure 1.1, the spots of cations and anions are near to the standard line, which reflects the thumb rule. And this thumb rule is limited by the value of EC. We can see that from the figure 1.1 difference between ions and the standard line is very high when the value of EC/100 is much higher than 20. So, we can get the conclusion that the thumb rule is fit for freshwater, which EC value is not over 2000 us/cm.

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.

Table 1.3 electric balance in the four samples with the largest error

Number	Name	$\sum cations$	$\sum anions$	E.B.%	EC/100
60.00	Lake	2.63	2.24	7.96	2.70
66.00	Incomati effluent	3.11	4.74	-20.74	5.37
14.00	PZ14 C	90.38	71.41	11.72	92.00
31.00	PZ20 C	1.70	1.98	-7.57	2.00

Sample 60: Anions are too low. Chloride and sulfate are recommended to repeat.

Sample 66: Cations are too low. Sodium is recommended to repeat.

Sample 14: Anions are too low. Chloride and sulfate are recommended to repeat.

Sample 31: Cations are too low. Calcium and magnesium are recommended to repeat.

g) Calculate the contribution of the anions HCO_3^- 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.

Table 1.4 contribution of HCO_3^- and Cl^- to the EC (in %)

Number	Name	Cl^- (%)	HCO_3^- (%)	Domination ions
58	Matola river	104.9	4.0	Cl
60	Lake	16.5	64.4	HCO_3
66	Incomati effluent	45.9	18.2	Cl
67	Matola wetland	103.7	4.3	Cl
70	65-Incomati	48.0	19.6	Cl
10	16	35.3	53.9	MIX
12	23	35.1	48.7	MIX
26	PZ21 F	35.9	49.8	MIX
28	PZ19 F	63.3	13.6	Cl
30	PZ20 F	57.1	7.4	Cl
45	PZ02 F	76.2	11.8	Cl
47	PZ18 F	28.4	51.2	MIX
61	Poço tio Mulungu	31.8	22.9	MIX
14	PZ14 C	64.2	7.4	Cl
23	PZ17 C	72.0	11.3	Cl
27	PZ21 C	27.6	62.5	HCO_3
29	PZ19 C	65.9	12.3	Cl
31	PZ20 C	45.8	53.0	MIX
46	PZ02 C	59.7	25.4	Cl
48	PZ18 C	37.3	39.9	MIX
68	PZ13 C	68.5	10.0	Cl

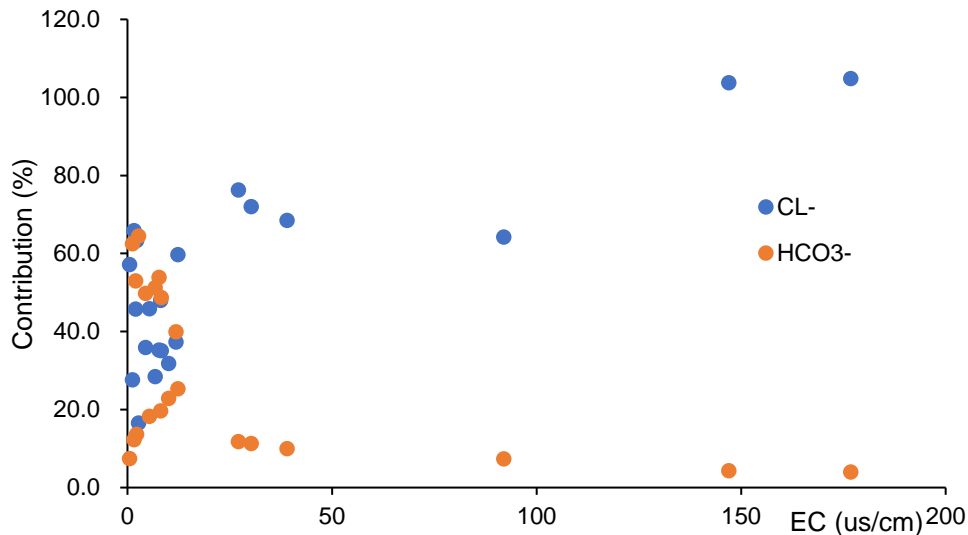


Figure 1.2 the contribution of Cl^- and HCO_3^- versus the electric conductivity

The electrical conductivity is the indicator of salinity. From the table and figure above, we can get the contribution of Cl^- and HCO_3^- in salinity. When the EC value is high, the fraction of Cl^- is much higher than HCO_3^- , which means the chloride is the major anions in the water sample. And the origin of chloride in the salty water is maybe from the seawater intrusion. And in some freshwater samples like 60 and 27, the bicarbonate occupies the major position. The origin of the bicarbonate is maybe calcite solution. Besides these two major situations, there is also a mixing state with similar values of chloride and bicarbonate.

2. Visualization of results on water quality and water type

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).

As can be seen from the figure, the concentration of each ion in each sample has the same trend, that is, the concentration of sodium ion, calcium ion, chloride ion sulfate ion on the high side and the concentration of iron ion, manganese ion and nitrate ion on the low side. Compared with the standard value provided by WHO, the water quality of most samples was better than the standard value except for a few samples whose ion concentration exceeded the standard.

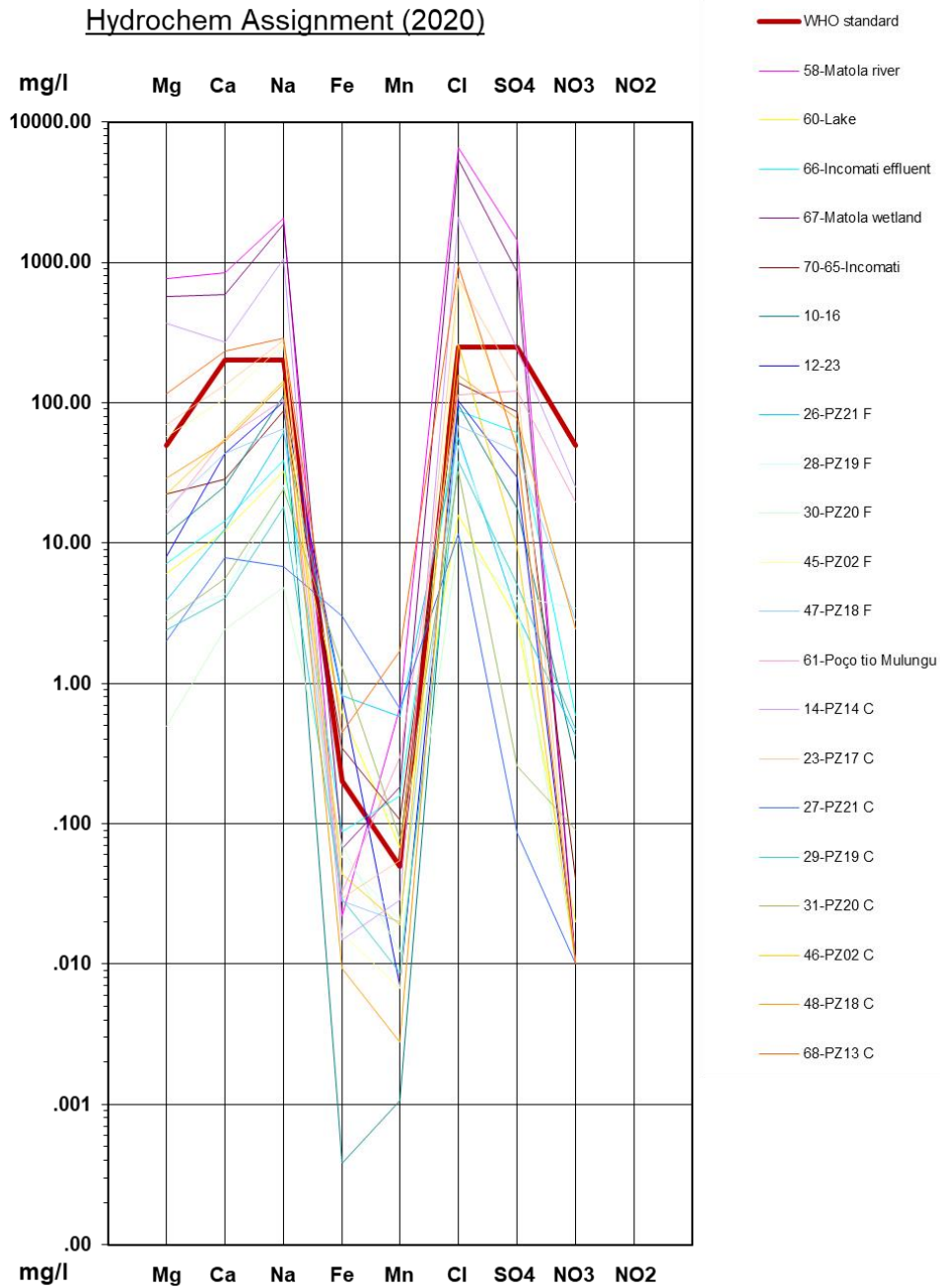


Figure 2.1 the Schoeller diagram for all samples

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?

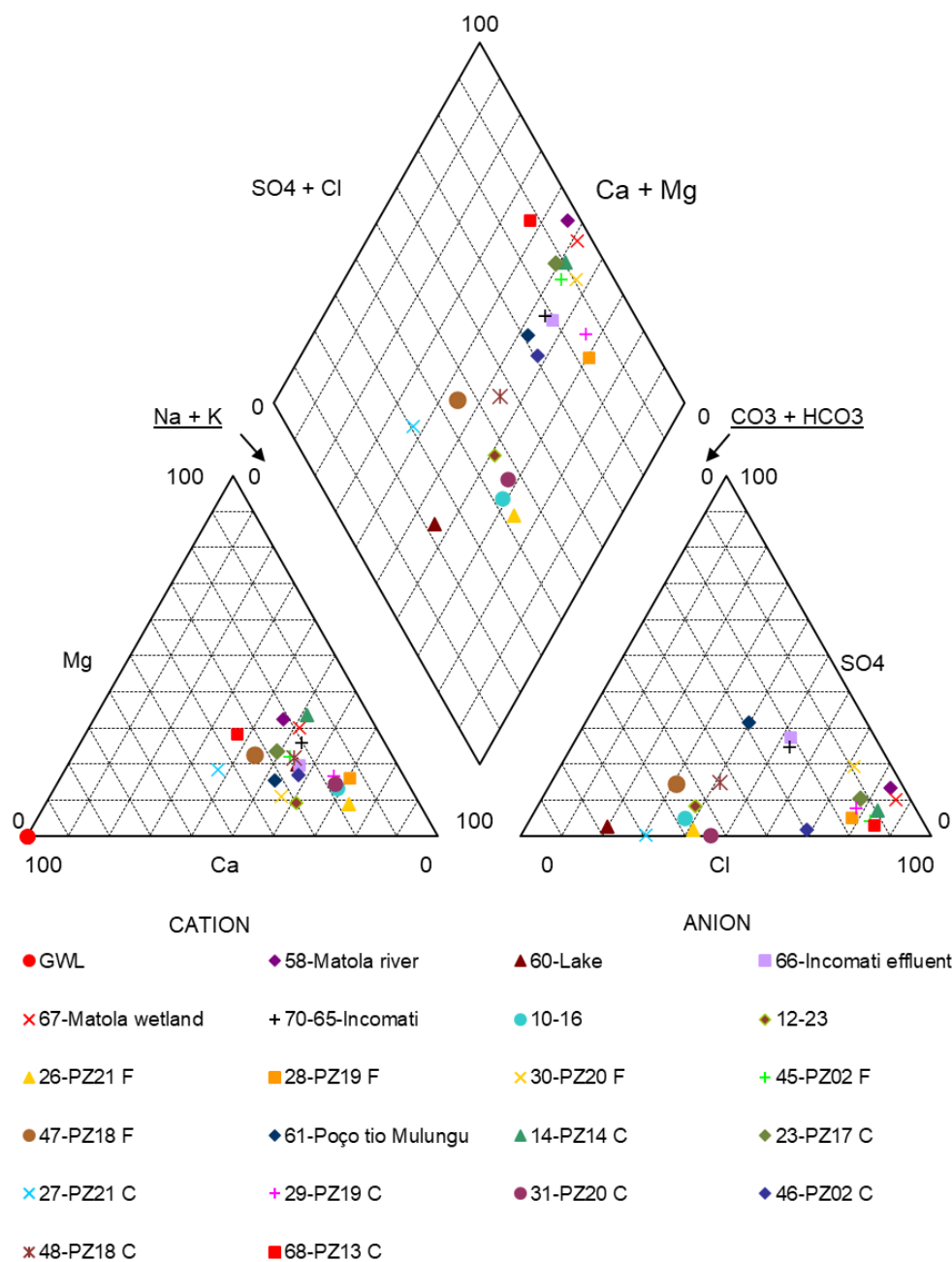


Figure 2.2 the Piper diagram for all samples

Table 2.1 Dominant cations and anions of all samples

Number	Name	Dominant cation	Dominant anion
58	Matola river	Na + K	Cl ⁻ + SO ₄ ²⁻
60	Lake	Na + K	HCO ₃
66	Incomati effluent	Na + K	Cl ⁻ + SO ₄ ²⁻
67	Matola wetland	Na + K	Cl ⁻ + SO ₄ ²⁻
70	65-Incomati	Na + K	Cl ⁻ + SO ₄ ²⁻

10	16	Na + K	HCO ₃
12	23	Na + K	HCO ₃
26	PZ21 F	Na + K	HCO ₃
28	PZ19 F	Na + K	Cl ⁻ + SO ₄ ²⁻
30	PZ20 F	Na + K	Cl ⁻ + SO ₄ ²⁻
45	PZ02 F	Na + K	Cl ⁻ + SO ₄ ²⁻
47	PZ18 F	Ca + Mg	HCO ₃
61	Poço tio Mulungu	Na + K	Cl ⁻ + SO ₄ ²⁻
14	PZ14 C	Na + K	Cl ⁻ + SO ₄ ²⁻
23	PZ17 C	Na + K	Cl ⁻ + SO ₄ ²⁻
27	PZ21 C	Ca + Mg	HCO ₃
29	PZ19 C	Na + K	Cl ⁻ + SO ₄ ²⁻
31	PZ20 C	Na + K	HCO ₃
46	PZ02 C	Na + K	Cl ⁻ + SO ₄ ²⁻
48	PZ18 C	Na + K	Cl ⁻ + SO ₄ ²⁻
68	PZ13 C	Ca + Mg	Cl ⁻ + SO ₄ ²⁻

Actually not. Only the lake sample with No. 60 is away from the groundwater samples. The other surface samples are near the plots of groundwater samples. It means that there is much interaction between surface water and groundwater in this study area except the lake.

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.

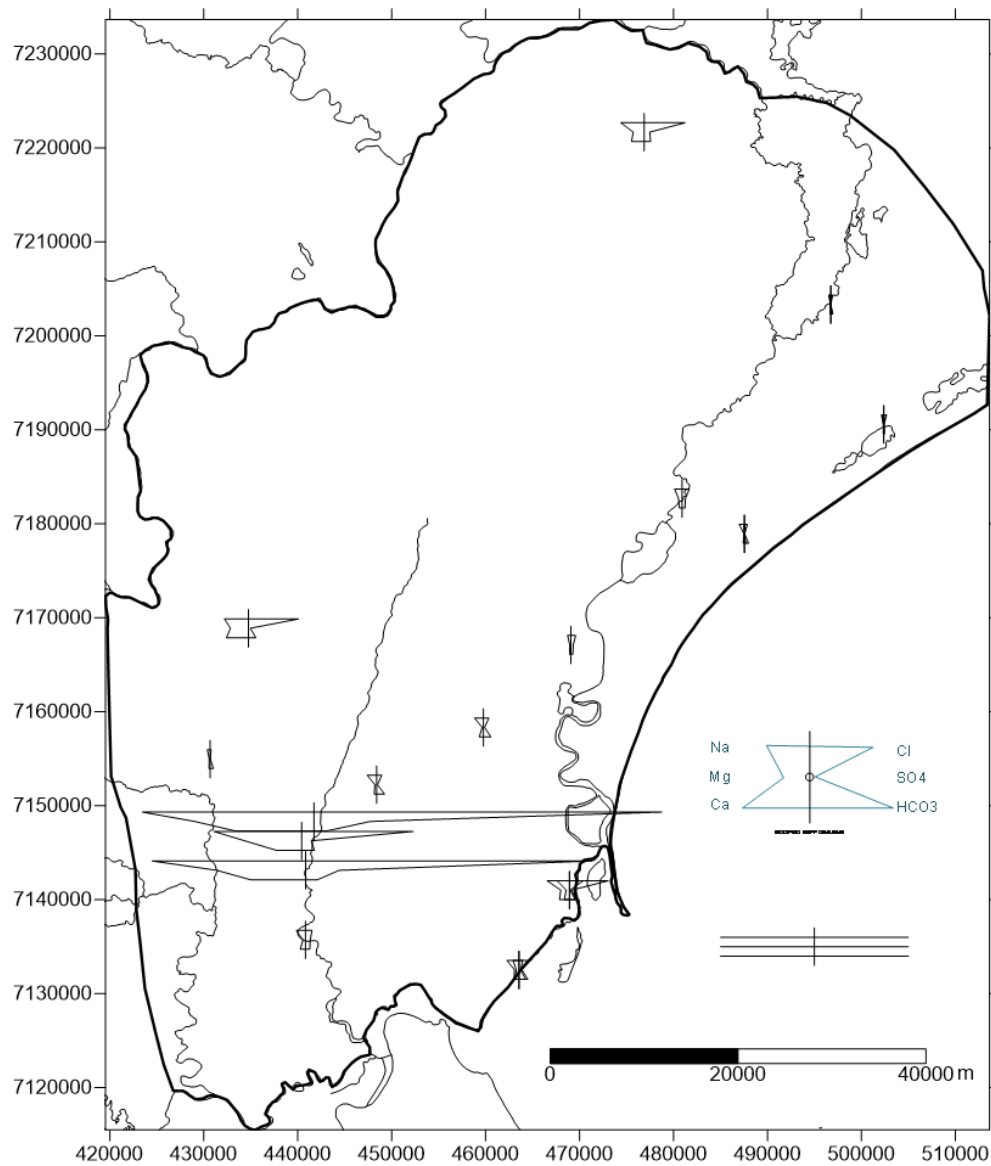


Figure 2.2 the Stiff diagrams plotted on a map.

Table 2.2 the brackish samples

Number	Name	Type	UTM E (m)	UTM N (m)	Elevation (m)	distance from coast	Hydraulic head
58	Matola river	SW	441729.0	7148326.4	30	30	20
67	Matola wetland	SW	440835.6	7143123.4	11	25	20
45	PZ02 F	SGW	468933.5	7141017.0	9	1	7.82
61	Poço tio Mulungu	SGW	440822.2	7135726.6	8	10	10
14	PZ14 C	DGW	440417.0	7146262.4	37	30	17.08
23	PZ17 C	DGW	476875.0	7221686.6	22	45	16.44
46	PZ02 C	DGW	468933.5	7141017.0	9	1	7.82
48	PZ18 C	DGW	463548.6	7132522.1	10	0.1	7.68
68	PZ13 C	DGW	434755.7	7168883.2	106	45	85.43

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.

For samples 45, 46, and 48, the dominant component of each sample is sodium chloride, and their sampling spots are along the coast. Thus for these three samples, the origin of the brackish water has a high possibility of seawater intrusion.

For samples 14, 58, and 67, the sampling spots are near the Matelo River and far away from the coast. So, the probability of recent seawater intrusion is low. And another climate condition in this river area is high evapotranspiration. Thus, my hypothesis for the origin of brackish water in this discharge area is that groundwater dissolves some rocks like halite with the groundwater flow from the recharge area to the discharge area. And for sample 61, it is a downstream area of samples 14, 58, and 67, and its concentration of salinity is not very high. Thus my hypothesis is the origin of sample 61 is from upstream water.

As for the samples 23 and 68, they are far away from the coastline, which is higher than 40 kilometers. The probability of recent seawater intrusion is really low. It is impossible. The dominant ion in sample 23 is sodium and chloride. Thus the saltwater can be found in the site of sample 23. And the dominant cation of 68 is calcium. Thus the origin of brackish water for sample 68 is the calcite or other rocks dissolution.

3. Calculation of recharge and rainfall contribution to groundwater

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

There are two assumptions we make to consider these samples to have Cl⁻ concentrations of average rainwater. The first one is that the origin of recharge water in these three places is only precipitation, no including other sources. The second one is that Cl⁻ is considered conservative, which means its concentration is not altered by other hydrochemical processes.

b) Calculate the recharge (as % of rainfall) for all groundwater samples with an EC below or equal to 1000 μ S/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.

Table 3.1 the recharge (as % of rainfall) for all groundwater samples

Number	Name	Cl (mmol/l)	Recharge (% of rainfall)
10	16	2.72	11.28
12	23	2.89	10.61

26	PZ21 F	1.59	19.32
28	PZ19 F	1.39	22.03
30	PZ20 F	0.31	100.00
47	PZ18 F	1.93	15.91
61	Poço tio Mulungu	3.20	9.59
27	PZ21 C	0.33	93.94
29	PZ19 C	1.07	28.65
31	PZ20 C	0.92	33.51
		Mean	34.48
		Median	20.67
		Maximum	100.00
		Minimum	9.59

The mathematical analysis is in the table above. The mean value is 34.48, and the median value is 20.67. The maximum is sample 10, which is seen as the rainwater.

It is not realistic. The sample 30 is not the real precipitation water, so the error exists. The suggestions are sampling the rainfall directly and using the measurement values of rainfall water instead of the value from the surface or groundwater. The accuracy will be improved by this suggestion way.

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.

Table 3.2 the contribution of groundwater from rainwater and other sources

Num.	Name	Concentration factor	Rainwater (%)				Other sources (%)			
			Na ⁺	Ca ²⁺	Cl ⁻	HCO ₃ ⁻	Na ⁺	Ca ²⁺	Cl ⁻	HCO ₃ ⁻
30	PZ20 F	1.00	0.21	0.06	0.31	0.04	0.00	0.00	0.00	0.00
10	16	8.86	1.86	0.54	2.72	0.35	3.02	0.10	0.00	3.80
12	23	9.42	1.98	0.57	2.89	0.38	2.46	0.51	0.00	3.64
26	PZ21 F	5.18	1.09	0.31	1.59	0.21	1.59	0.00	0.00	1.99
28	PZ19 F	4.54	0.95	0.28	1.39	0.18	0.16	-0.17	0.00	0.12
47	PZ18 F	6.29	1.32	0.38	1.93	0.25	1.54	0.70	0.00	3.23
61	Poço tio Mulungu	10.43	2.19	0.63	3.20	0.42	2.37	0.76	0.00	1.88
27	PZ21 C	1.06	0.22	0.06	0.33	0.04	0.07	0.13	0.00	0.70
29	PZ19 C	3.49	0.73	0.21	1.07	0.14	0.06	-0.11	0.00	0.06
31	PZ20 C	2.98	0.63	0.18	0.92	0.12	0.43	-0.04	0.00	0.94

All the chloride is from the rainwater, which is the assumption taken in this part. Only little bicarbonate is from rainwater, and its origin is the dissolution of calcite. For the cation sodium and calcium, the source is both rainwater and other

sources. The other source is the dissolution of calcite and silicate.

4. Mineral weathering and surface water-groundwater interactions

a) Calculate the SI for calcite and the partial CO₂ 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, Ca²⁺ and HCO₃⁻ concentrations and the Ca²⁺/HCO₃⁻ ratio.

Table 3.2 the contribution of groundwater from rainwater and other sources

Number	pH	Ca ²⁺ mmol/L	HCO ₃ ⁻ mmol/L	Ca/HCO ₃ %	CO ₂ (g)	Calcite SI[-]
10	8.0	0.64	4.16	15.37	-2.62	0.39
12	7.9	1.08	4.01	26.99	-2.48	0.45
14	7.4	6.79	6.83	99.47	-1.93	0.65
23	7.6	3.37	3.40	99.10	-2.31	0.41
26	7.0	0.31	2.20	14.29	-1.91	-1.12
27	5.8	0.20	0.74	26.70	-1.17	-2.94
28	6.4	0.11	0.30	35.77	-2.09	-3.08
29	6.0	0.10	0.20	50.54	-1.91	-3.62
30	4.8	0.06	0.04	151.62	-1.21	-5.59
31	6.2	0.14	1.06	13.26	-1.38	-2.60
45	8.2	2.67	3.20	83.22	-2.97	0.91
46	8.2	1.38	3.12	44.24	-2.90	0.67
47	7.6	1.08	3.48	31.05	-2.27	0.12
48	8.0	1.33	4.72	28.08	-2.59	0.70
58	7.4	21.29	7.09	300.52	-1.91	0.87
60	7.4	0.30	1.74	17.50	-2.38	-0.77
61	6.3	1.39	2.30	60.55	-1.18	-1.33
66	6.8	0.36	0.98	36.93	-2.05	-1.69
67	7.3	14.79	6.40	231.08	-1.87	0.69
68	7.0	5.85	3.91	149.75	-1.65	0.01
70	6.9	0.72	1.59	45.17	-1.88	-1.19

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.

The lower values are obtained.

We use the activity coefficient equal to one by ignoring activities and aqueous complexes, while in the real world, the activity coefficient is lower than one, so the manual calculation gets the lower values.

c) Plot the Ca²⁺ vs. HCO₃⁻ concentrations and Na⁺ vs. HCO₃⁻ 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.

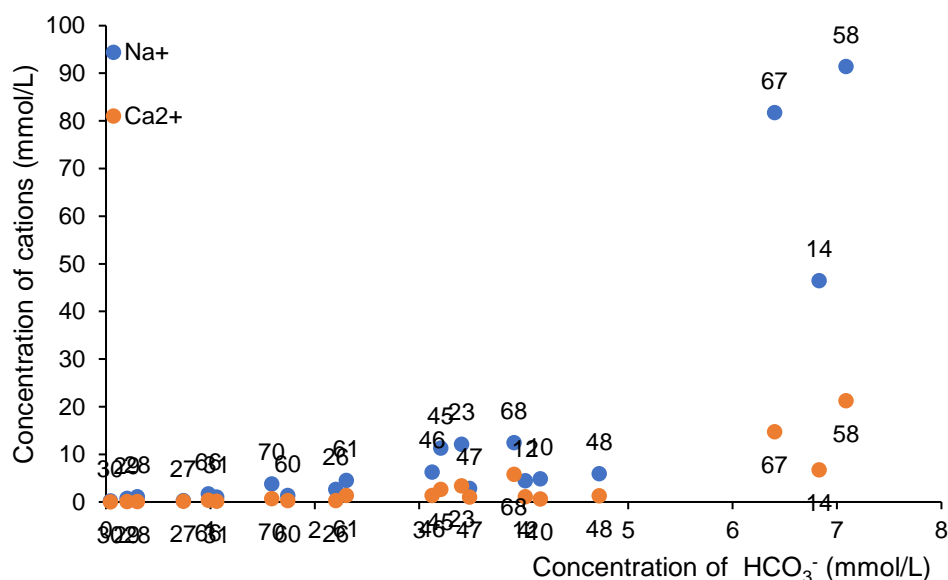


Figure 4.1 the Ca^{2+} and Na^{+} vs. HCO_3^{-} concentrations

We can classify the process by the calcium and sodium concentration and the relationship with the concentration of bicarbonate. Calcite dissolution occurred in the sample 14, 58 and 67, which has a high concentration of sodium, calcium, and bicarbonate. Silicate weathering occurred in samples 10, 12, 23, 45, 46, 47, 48, and 68, which has a relatively high concentration of sodium, calcium, and bicarbonate. The process of silicate weathering needs more time than the process of calcite dissolution. This leads to the concentration of sodium, calcium, and bicarbonate in the sampling of silicate weathering is less than the sampling of calcite dissolution. And the other samples left are no (or very little) interaction with minerals.

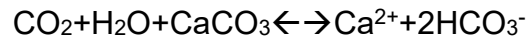
d) Based on the table and graph try to explain which surface water samples show the clearest interaction with groundwater (you can also look at other ions such as Cl^{-}). Also mention which assumptions you are making in your hypothesis.

Samples 58 and 67 show the clearest interaction with groundwater.

The assumption I make is that the origin of sodium, calcium, and bicarbonate is only from the silicate weathering and calcite dissolution instead of other sources from the surface water. And another reason is from the topography. Sample 58 and 67 is at the riverside and wetland, which is low elevation. This area is likely to be the discharge area, which has great interaction between surface water and groundwater.

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.

It is an open system. In this system, carbon dioxide directly contacts with water bodies containing calcite, rather than joining the water to form carbonic acid and react with calcite. The reaction equation is as follows.



5. Nitrate and sulphate reduction

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

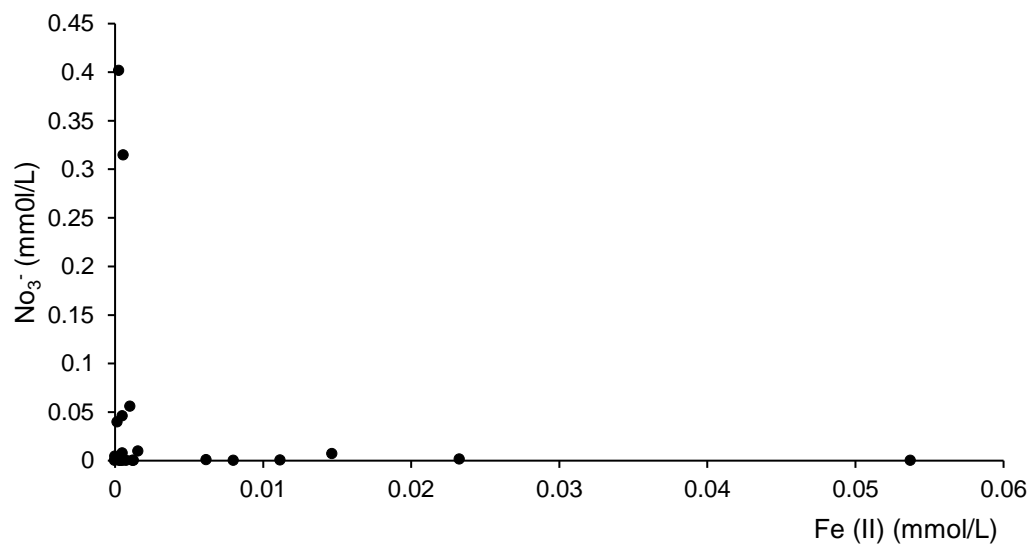


Figure 5.1 the Fe (II) vs. NO_3^- concentrations

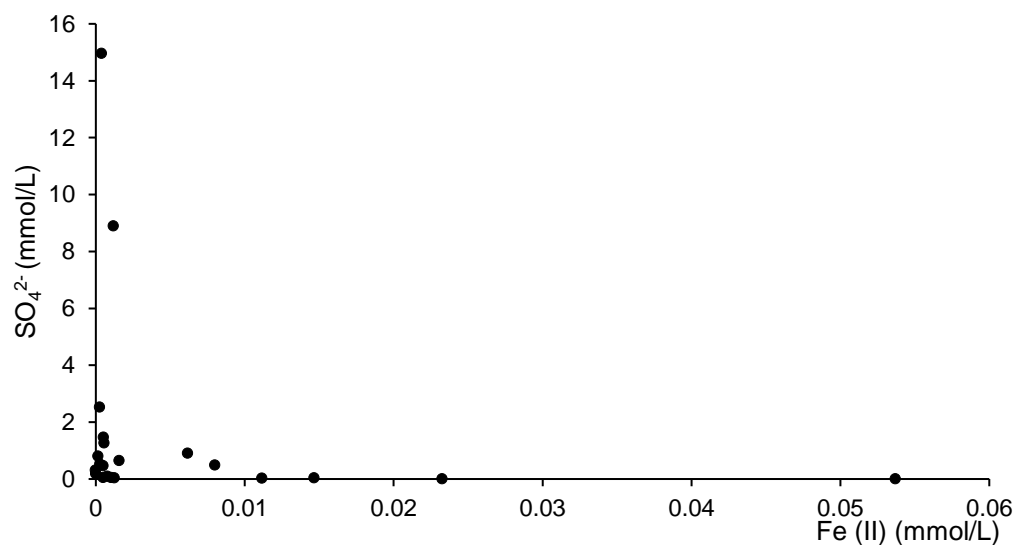


Figure 5.2 the Fe (II) vs. SO_4^{2-} concentrations

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.

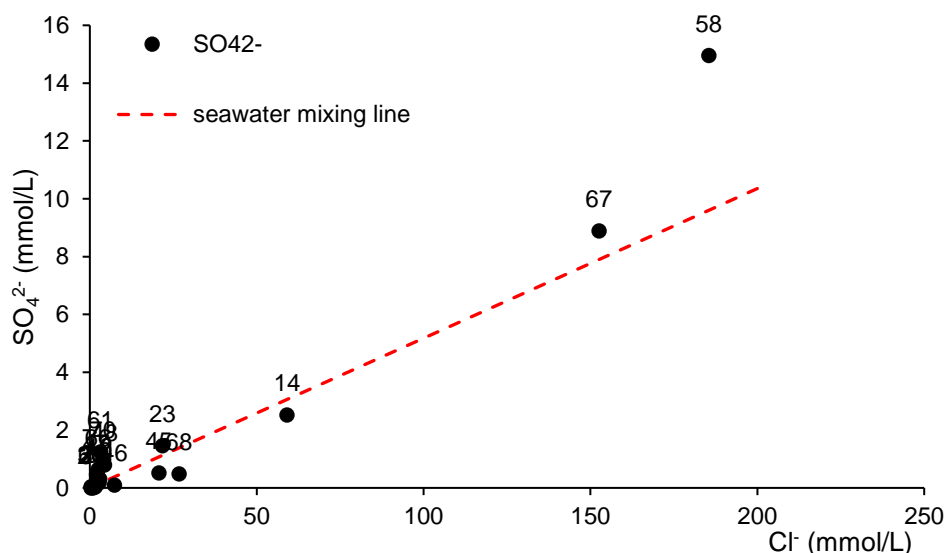


Figure 5.3 the SO_4^{2-} vs. Cl^- concentrations and seawater mixing line

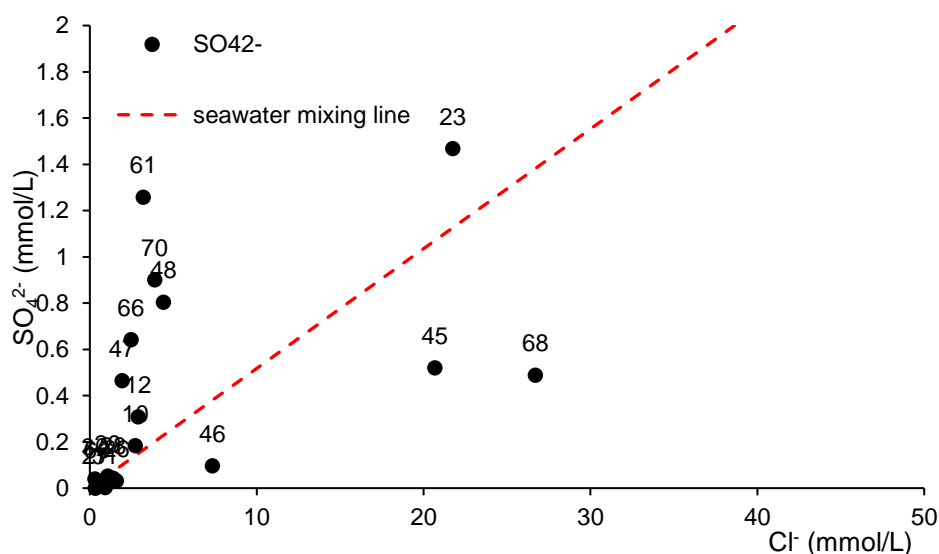


Figure 5.4 the SO_4^{2-} vs. Cl^- concentrations in the lower range of chloride

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?

The more reduced state: samples 27, 31, 26, and 60. Because they are with more Fe^{2+} .

The more oxidized state: samples 14, 61, 58, and 67. Because they are with more SO_4^{2-} and NO_3^- .

For the samples 27 and 31, they are deep groundwater, so they are lack oxygen and oxidizing agent after a long time to react. For sample 60, it is a recharge area and less interaction with the groundwater. The origin of sample 60 is precipitation, which is long exposure to air. So it keeps the more reduced state.

6. Mixing with saltwater/seawater and cation exchange

a) For these samples calculate the fraction of seawater (use sample 10 located nearby as natural groundwater), and the ratios of Na^+/Cl^- and $\text{Ca}^{2+}/\text{HCO}_3^-$

Table 6.1 the fraction of seawater and ratios of Na^+/Cl^- and $\text{Ca}^{2+}/\text{HCO}_3^-$

Number	Fraction (%)	Na^+/Cl^- (%)	$\text{Ca}^{2+}/\text{HCO}_3^-$ (%)
58	32.4	48.7	300.5
67	26.6	53.1	231.1
45	3.2	54.7	83.2
14	10.0	78.3	99.5
23	3.4	55.7	99.1
68	4.3	46.6	149.8

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.

Table 6.2 the concentrations of major ions from conservative mixing

Number	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
45	20.2	1.0	4.1	1.1
14	52.9	1.6	4.0	3.1
23	21.1	1.0	4.1	1.2
68	25.3	1.1	4.1	1.4

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

Table 6.3 the differences between the “conservative” and observed concentrations for the major four ions

Number	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
45	-8.9	1.7	-0.9	-0.6
14	-6.6	5.1	2.8	-0.6

23	-9.0	2.4	-0.7	0.3
68	-12.9	4.8	-0.2	-0.9

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

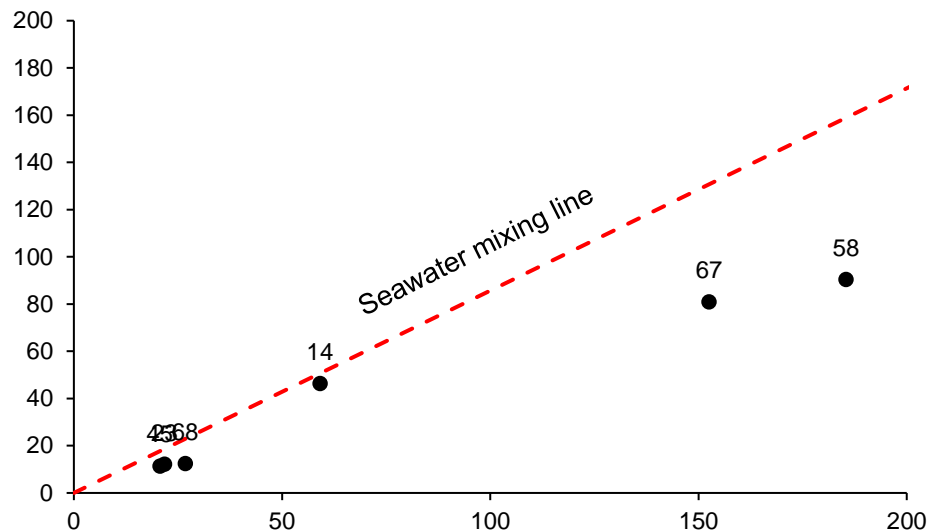


Figure 6.1 the Na^+ vs. Cl^- concentrations

e) Plot the Na^+/Cl^- and $\text{Ca}^{2+}/\text{HCO}_3^-$ ratios vs. Cl^- concentrations.

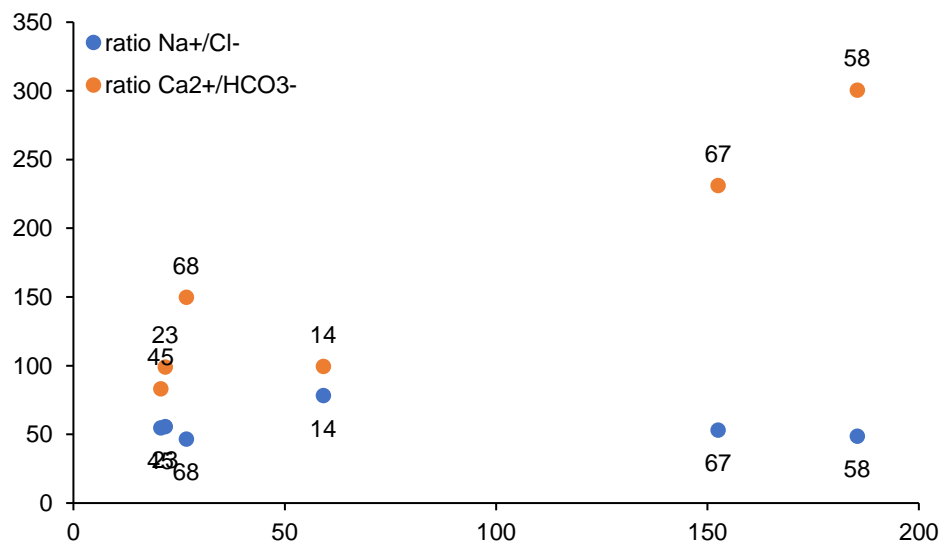


Figure 6.2 the Na^+/Cl^- and $\text{Ca}^{2+}/\text{HCO}_3^-$ ratios vs. Cl^- concentrations

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

From table 6.3, we can get the difference of Na^+ between the actual situation and the ideal situation is negative, while the difference of Ca^{2+} is positive. From figure 6.1, we can see that with the actual concentration of Cl^-

increasing the concentration of Na is much less than the ideal seawater mixing line. It means some of Na⁺ from the seawater intrusion disappear. Figure 6.2 also can give the same information as the other two figures. The reason for this phenomenon is the cation exchange, and the reaction equation is as follows.

