

# 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.

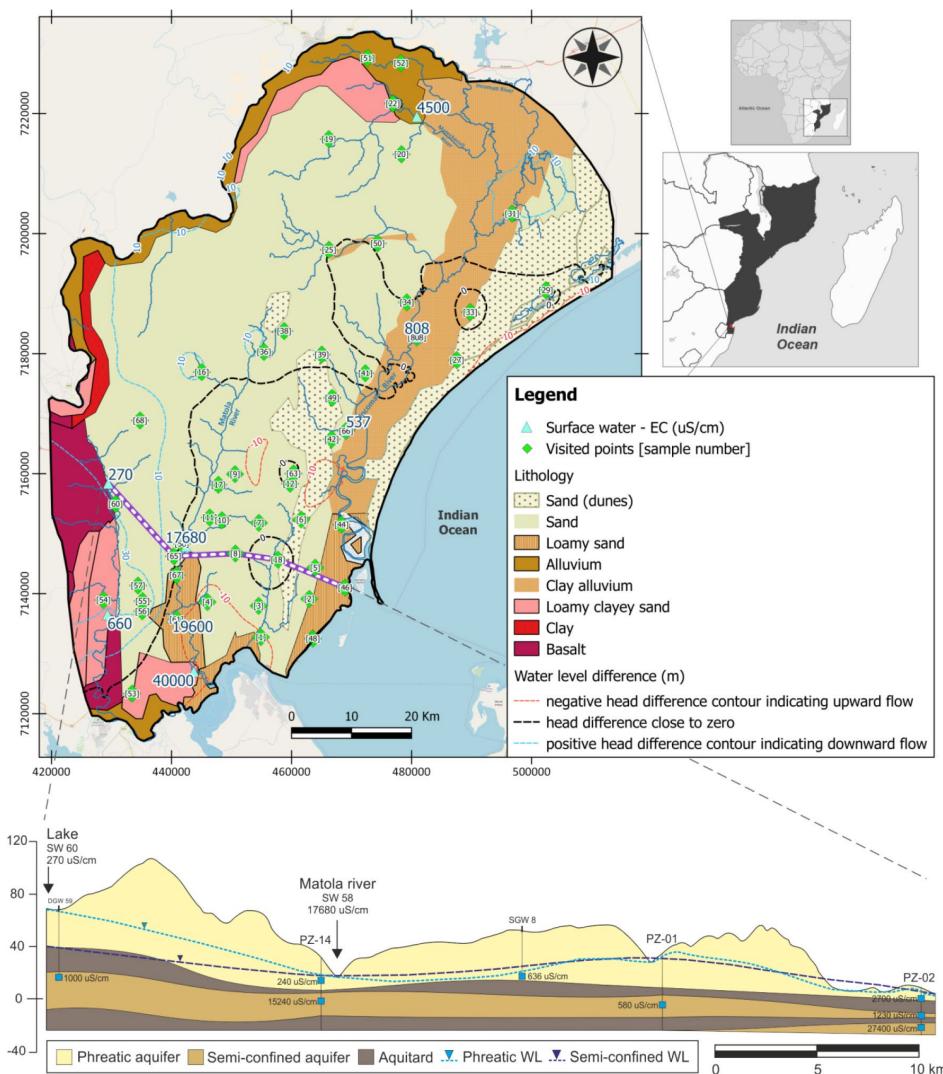


Fig. 1. Location and geological context of the study area, in map (top) and cross-section (bottom). Also shown are sampling points for a campaign held in May 2017, as well as surface water EC values and calculated groundwater head differences between the phreatic and semi-confined aquifers. Source: Nogueira 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.
- 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?
- c) Estimate the missing bicarbonate concentrations through the electrical balance. What assumption are you making? Include the results in the table of question a).
- 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.
- 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?
- 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.
- g) Calculate the contribution of the anions  $\text{HCO}_3^-$  and  $\text{Cl}^-$  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.

## 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.

- 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).
- 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?

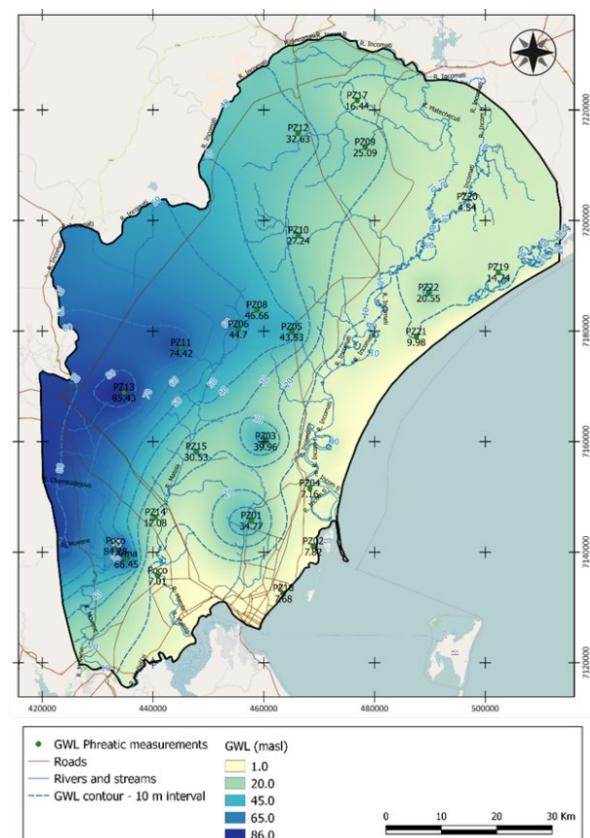


Fig. 2. Groundwater level contour map of the phreatic aquifer; source: Nogueira (2017)

- 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 ( $\text{EC} > 1000 \mu\text{S}/\text{cm}$ ) 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.
- d) Provide possible hypotheses 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.

### 3. Calculation of recharge and rainfall contribution to groundwater

Samples 27, 30 (groundwater) and 60 (lake water) have very low  $\text{Cl}^-$  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  $\text{Cl}^-$  concentrations of average rainwater?

Based on this assumption, and a number of other simplifications (see lecture notes) we can calculate the recharge of the aquifer using the  $\text{Cl}^-$  mass balance. We can only do this where groundwater has not been affected by any other sources of  $\text{Cl}^-$ . In this case we use an EC threshold of  $1000 \mu\text{S}/\text{cm}$  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  $1000 \mu\text{S}/\text{cm}$  (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.
- c) For the groundwater samples of question 3b) calculate the contribution of rainwater to  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$  and  $\text{HCO}_3^-$  as well as the fraction not derived from rainwater. Provide the results in a table and provide a brief interpretation of 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  $\text{CO}_2$  pressure for each sample, and by plotting  $\text{Ca}^{2+}$  and  $\text{Na}^+$  concentrations versus  $\text{HCO}_3^-$  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  $\text{Ca}^{2+}/\text{HCO}_3^-$  ratio. Moreover, silicate weathering is a much slower process than calcite dissolution.

- a) Calculate the SI for calcite and the partial  $\text{CO}_2$  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,  $\text{Ca}^{2+}$  and  $\text{HCO}_3^-$  concentrations and the  $\text{Ca}^{2+}/\text{HCO}_3^-$  ratio.
- 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.

- c) Plot the  $\text{Ca}^{2+}$  vs.  $\text{HCO}_3^-$  concentrations and  $\text{Na}^+$  vs.  $\text{HCO}_3^-$  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.
- 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  $\text{Cl}^-$ ). Also mention which assumptions you are making in your hypothesis.
- 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.

## 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  $\text{Fe(II)}$  vs.  $\text{NO}_3^-$  concentrations and vs.  $\text{SO}_4^{2-}$  concentrations; add the labels to the graph.
- b) Plot  $\text{SO}_4^{2-}$  vs.  $\text{Cl}^-$  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.
- 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?

## 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 highest EC.

- a) For these samples calculate the fraction of seawater (use sample 10 located nearby as natural groundwater), and the ratios of  $\text{Na}^+/\text{Cl}^-$  and  $\text{Ca}^{2+}/\text{HCO}_3^-$ .
- b) Calculate the concentrations of  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$  and  $\text{SO}_4^{2-}$  if they were to come only from conservative mixing of natural groundwater and seawater.
- c) Calculate the differences between the “conservative” and observed concentrations for these four ions for the six samples.
- d) Plot the  $\text{Na}^+$  vs.  $\text{Cl}^-$  concentrations on a graph and include the seawater mixing line.
- e) Plot the  $\text{Na}^+/\text{Cl}^-$  and  $\text{Ca}^{2+}/\text{HCO}_3^-$  ratios vs.  $\text{Cl}^-$  concentrations.
- f) Briefly interpret the results of questions 6c, 6d and 6e. Write down the reactions you think are occurring.

## References

- Nogueira G., 2017. Tracing the hydrochemical water types and salinization mechanisms in the Great Maputo area as a function of groundwater recharge, hydrogeological properties and human activities. MSc thesis, UNESCO-IHE, Delft, the Netherlands, 120 pp.
- 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