

Session 5

Groundwater quality monitoring and data reporting

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Guidelines for Monitoring Strategies in Transboundary Aquifers: Goals, Methods and Tools.
The Case of the DRIN project (ALB-MTN)

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2. Monitoring quality requirements
3. Gathering quality field data
4. Data treatment and plotting
5. Data interpretation
6. Real case: The case of the Skadar/Shkoder Buna/Bojana transboundary aquifer



Hora	Descens	Cabal	T	Cond	pH	Eh	O2	NO3	NO2	NH4
0:00	4,38									
0:04	4,36			31	6,45	71	6,45	145	6,380	
0:08	4,34			32	6,45	71	6,45	150	6,384	
0:12	4,32			33	6,45	71	6,45	155	6,388	
0:16	4,30			34	6,45	71	6,45	160	6,392	
0:20	4,28			35	6,45	71	6,45	165	6,396	
0:24	4,26			36	6,45	71	6,45	170	6,400	
0:28	4,24			37	6,45	71	6,45	175	6,404	
0:32	4,22			38	6,45	71	6,45	180	6,408	
0:36	4,20			39	6,45	71	6,45	185	6,412	
0:40	4,18			40	6,45	71	6,45	190	6,416	
0:44	4,16			41	6,45	71	6,45	195	6,420	
0:48	4,14			42	6,45	71	6,45	200	6,424	
0:52	4,12			43	6,45	71	6,45	205	6,428	
0:56	4,10			44	6,45	71	6,45	210	6,432	
1:00	4,08			45	6,45	71	6,45	215	6,436	
1:04	4,06			46	6,45	71	6,45	220	6,440	
1:08	4,04			47	6,45	71	6,45	225	6,444	
1:12	4,02			48	6,45	71	6,45	230	6,448	
1:16	4,00			49	6,45	71	6,45	235	6,452	
1:20	3,98			50	6,45	71	6,45	240	6,456	

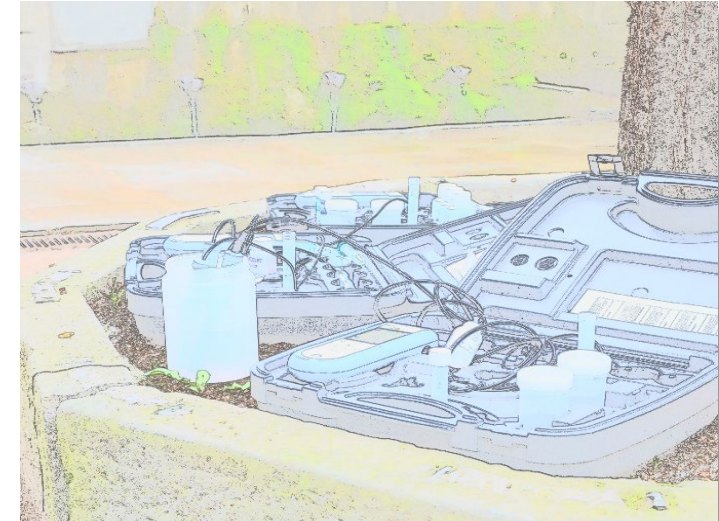
Photos: J. M.-P

1. Justification

Gathering data must be based on common and well-established methods.

They should consider,

- a) Fulfilling the **legal requirements**,
- b) Meeting high **field-work** and **analytical** standards,
- c) Adequate **data treatment & plotting**,
- d) Interpreting** results according to the problem need, which may require some geochemical modelling.



Photos: J M-P

2. Monitoring quality requirements

For surveillance monitoring:

- a) The **core suite** will comprise DO, pH, EC, nitrate, ammonium, temperature, a suite of major and trace ions plus, where appropriate, selected indicators. Include redox potential (Eh) as well,
- b) Parameters indicative of the **risks to** and **impacts on** groundwater from identified pressures,
- c) It is not necessary to monitor each of the **priority substances** including in the WFD and subsequent legislation.

2. Monitoring quality requirements

For operational monitoring:

- a) In addition to the core parameters, **selective parameters** will need to be monitored at specific locations, where groundwater bodies can be "at risk".
- b) Groundwater **threshold** values must be taken as references for quality status.
- c) Parameter selection will be made on a **case-by-case basis**, and be influenced by other information including existing water quality data and local knowledge.
- d) The chemical monitoring suites must be **reviewed on a regular basis** to ensure that they provide representative information.

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3. Gathering quality field data

Why hydrochemistry?

- a) Water is not just H₂O; it has ***solutes*** in it.
- b) Solutes inform about ***geochemical processes***, bringing up some knowledge about the hydrogeological system.
- c) Some solutes may be ***harmful*** for human uses, even for the whole environment in a broader sense.
- d) It is an indicator of environmental health and determines which ***actions*** must be conducted to preserve water resources quality.
- e) ... and it is fun!!!



Photos: J M-P

3. Gathering quality field data

What data are we looking for?

Table 10.2 Common Inorganic Solutes in Water

Cations	Anions	Other
Major Constituents		
Calcium (Ca^{2+})	Bicarbonate (HCO_3^-)	Dissolved CO_2 (H_2CO_3^*)
Magnesium (Mg^{2+})	Chloride (Cl^-)	Silica ($\text{SiO}_2(\text{aq})$)
Sodium (Na^+)	Sulfate (SO_4^{2-})	
Potassium (K^+)		
Minor Constituents		
Iron ($\text{Fe}^{2+}, \text{Fe}^{3+}$)	Carbonate (CO_3^{2-})	Boron (B)
Strontium (Sr^{2+})	Fluoride (F^-)	
	Nitrate (NO_3^-)	

Plus, metals or trace elements, organic products (natural and man-made) and isotopes.

Fiits, 2013.



Photos: J M-P

3. Gathering quality field data

Field sample collection: how?

- Collecting samples is an easy, ... but **tricky** task!
- Empty the borehole **volume** three times at least, and wait for constant EC and T.
- Select the right type of **bottle** (material, color, sterilized, acid rinse, ...), the necessary water volume, if additives are needed, ... Avoid air-bubble! Filter the sample! Store it cold!
- Check **procedures** at “Standard Methods”,
- Ask the lab, ask **colleagues**, ...
- So, ... take a **large car** (or van) to the field!!!



Photos: J M-P

3. Gathering quality field data

Field sample collection: how?



Photos: J M-P

4. Data treatment and plotting

Solutes in groundwater mainly depend on the following *processes*:

- a) Water-rock interaction: mineral equilibria
- b) Ion exchange / sorption
- c) Mixing between different sources
- d) Seawater intrusion
- e) Groundwater pollution: non-natural introduced chemicals

For most of these processes, we assume that the governing reactions are in *equilibrium*; that means, the ratio between products (solutes) and reactants (minerals) depend on the equilibrium constant.

4. Data treatment and plotting

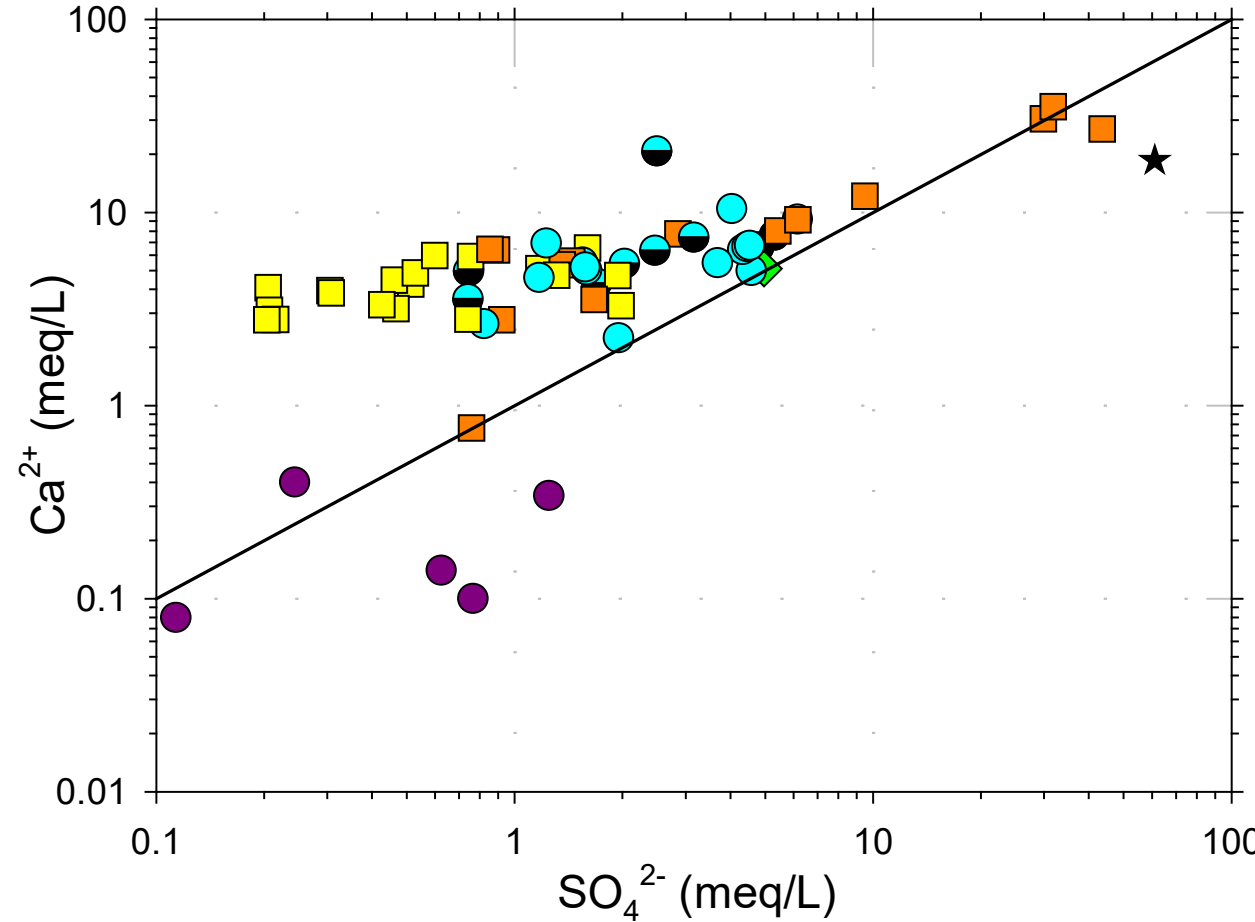


Table 10.7 Reactions and Solubility Products for Common Minerals at 25°C and Atmospheric Pressure

Mineral	Reaction	Log(K_{SO})	
Salts:			
Halite	$\text{NaCl} \rightleftharpoons \text{Na}^+ + \text{Cl}^-$	1.54	(1)
Sylvite	$\text{KCl} \rightleftharpoons \text{K}^+ + \text{Cl}^-$	0.98	(1)
Fluorite	$\text{CaF}_2 \rightleftharpoons \text{Ca}^{2+} + 2 \text{F}^-$	-10.6	(2)
Sulfates:			
Gypsum	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O}$	-4.58	(2)
Anhydrite	$\text{CaSO}_4 \rightleftharpoons \text{Ca}^{2+} + \text{SO}_4^{2-}$	-4.36	(2)
Barite	$\text{BaSO}_4 \rightleftharpoons \text{Ba}^{2+} + \text{SO}_4^{2-}$	-9.97	(2)
Carbonates:			
Calcite	$\text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$	-8.48	(2)
Aragonite	$\text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-}$	-8.34	(2)
Dolomite	$\text{CaMg}(\text{CO}_3)_2 \rightleftharpoons \text{Ca}^{2+} + \text{Mg}^{2+} + 2\text{CO}_3^{2-}$	-17.1	(2)
Siderite	$\text{FeCO}_3 \rightleftharpoons \text{Fe}^{2+} + \text{CO}_3^{2-}$	-10.9	(2)

Fiits, 2013.

4. Data treatment and plotting

Electroneutrality principle (meq/L):

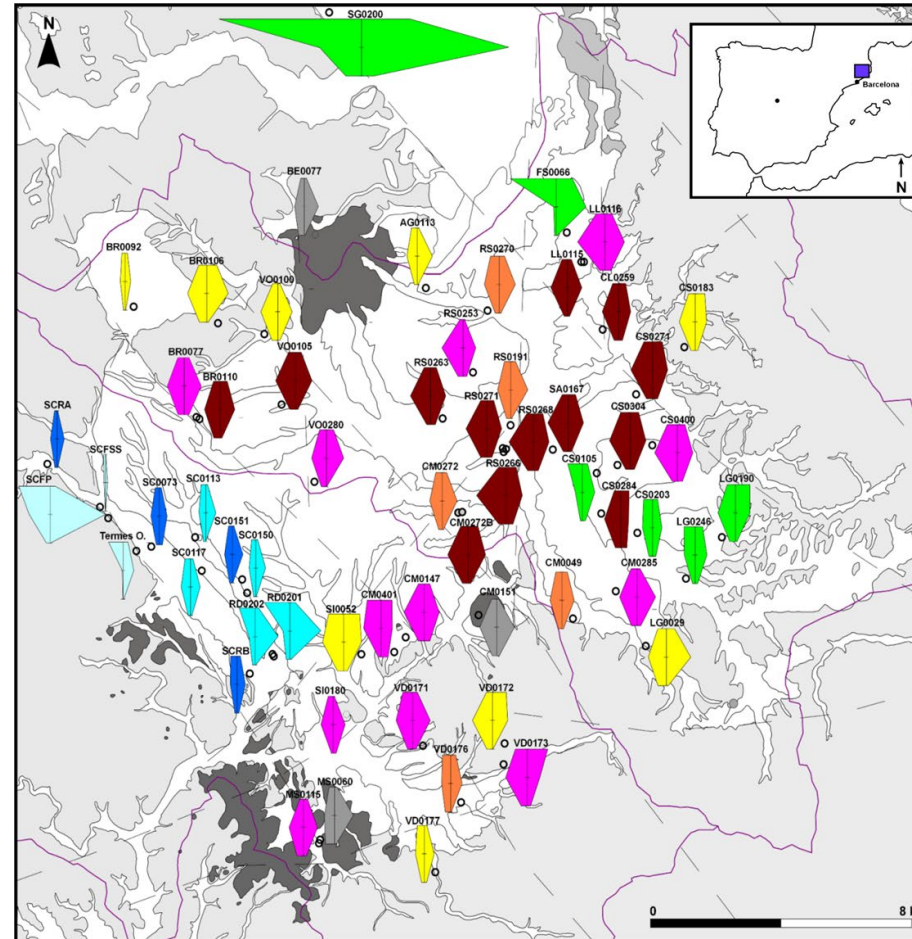
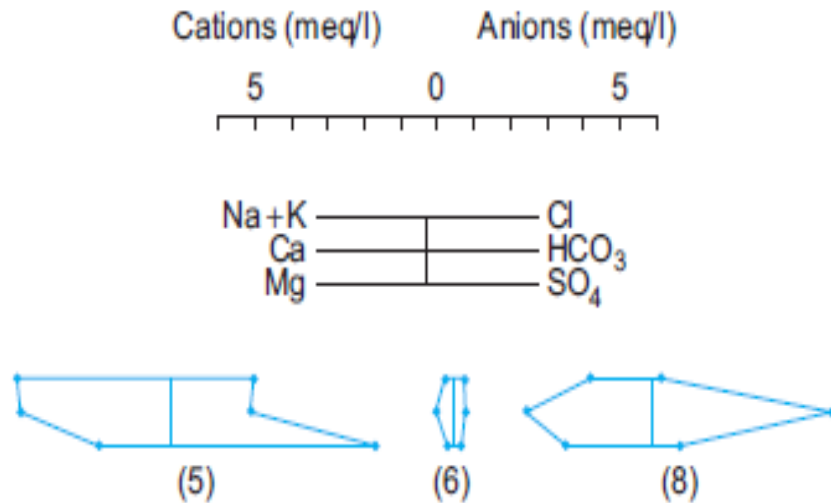
$$\sum \text{anions} = \sum \text{cations}$$

$$\text{Error (\%)} = 100 \frac{\sum \text{cations} - \sum \text{anions}}{\sum \text{cations} + \sum \text{anions}}$$

Σ Anions (meq/L)	Accepted error
0 – 3.0	± 0.2 meq/L
3.0 – 10.0	$\pm 2\%$
10.0 - 800	$\pm 2-5\%$

4. Data treatment and plotting

Stiff diagram; units: meq/L



Stiff Diagrams
May 2006

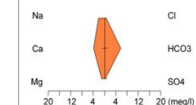
Legend

- Paleozoic Materials
- Paleogen materials
- Neogen+Quaternary volcanic materials
- Neogen+Quaternary sedimentari materials
- Main Faults
- Basin limit
- Sample point

Sampling

- Regional fault or granit (F > 2 mg/l)
- Granit or granit and Neogene
- Sedimentary Neogene with low nitrate
- Sedimentary Neogene with high nitrate
- Surface wells
- Volcanic or with volcanic materials
- Surface waters and wells Sta. Coloma
- Deep wells Sta. Coloma
- Springs Sta. Coloma

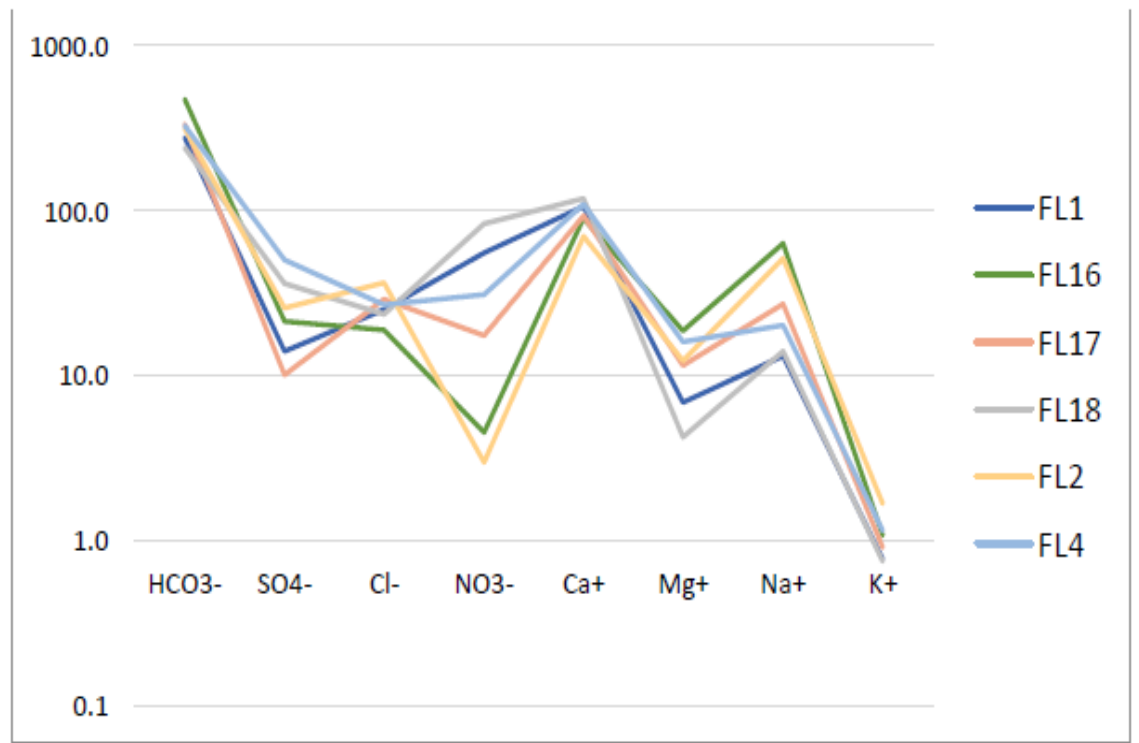
Stiff diagrams



Menció A, 2010, *PhD Diss.* UdG

4. Data treatment and plotting

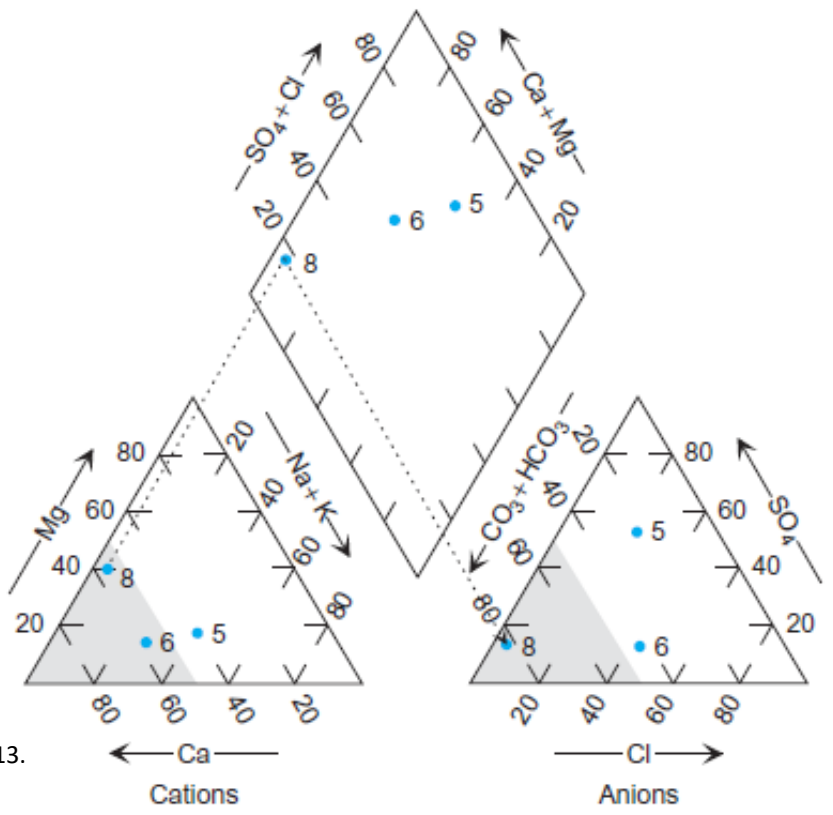
Schoeller-Berkaloff plot; units: meq/L



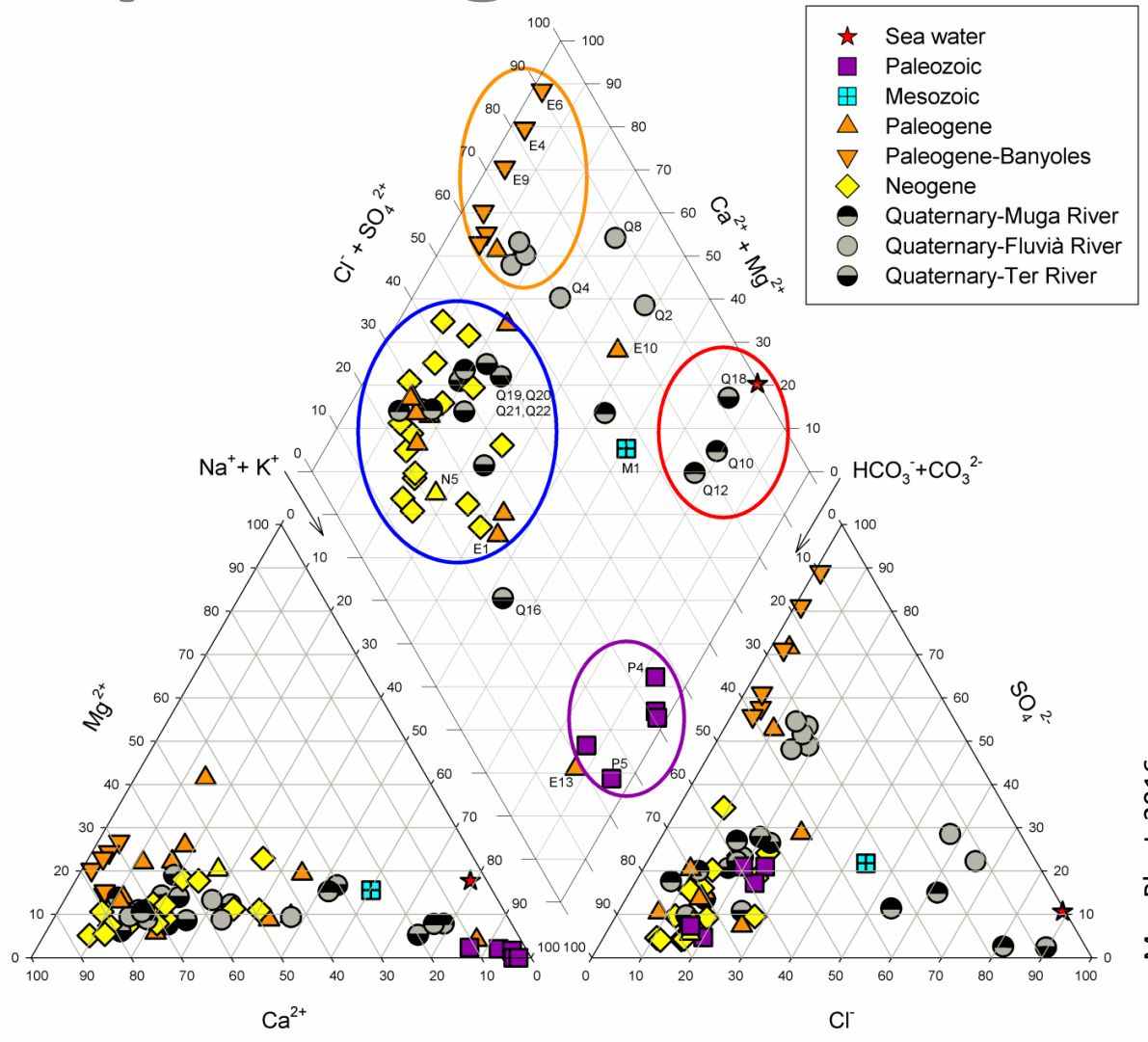
Vílchez Peña, A, 2020, MSc Thesis. UdG

4. Data treatment and plotting

Piper-Hill plots; units: meq/L



Fiits, 2013.



Mas-Pla, J, 2016

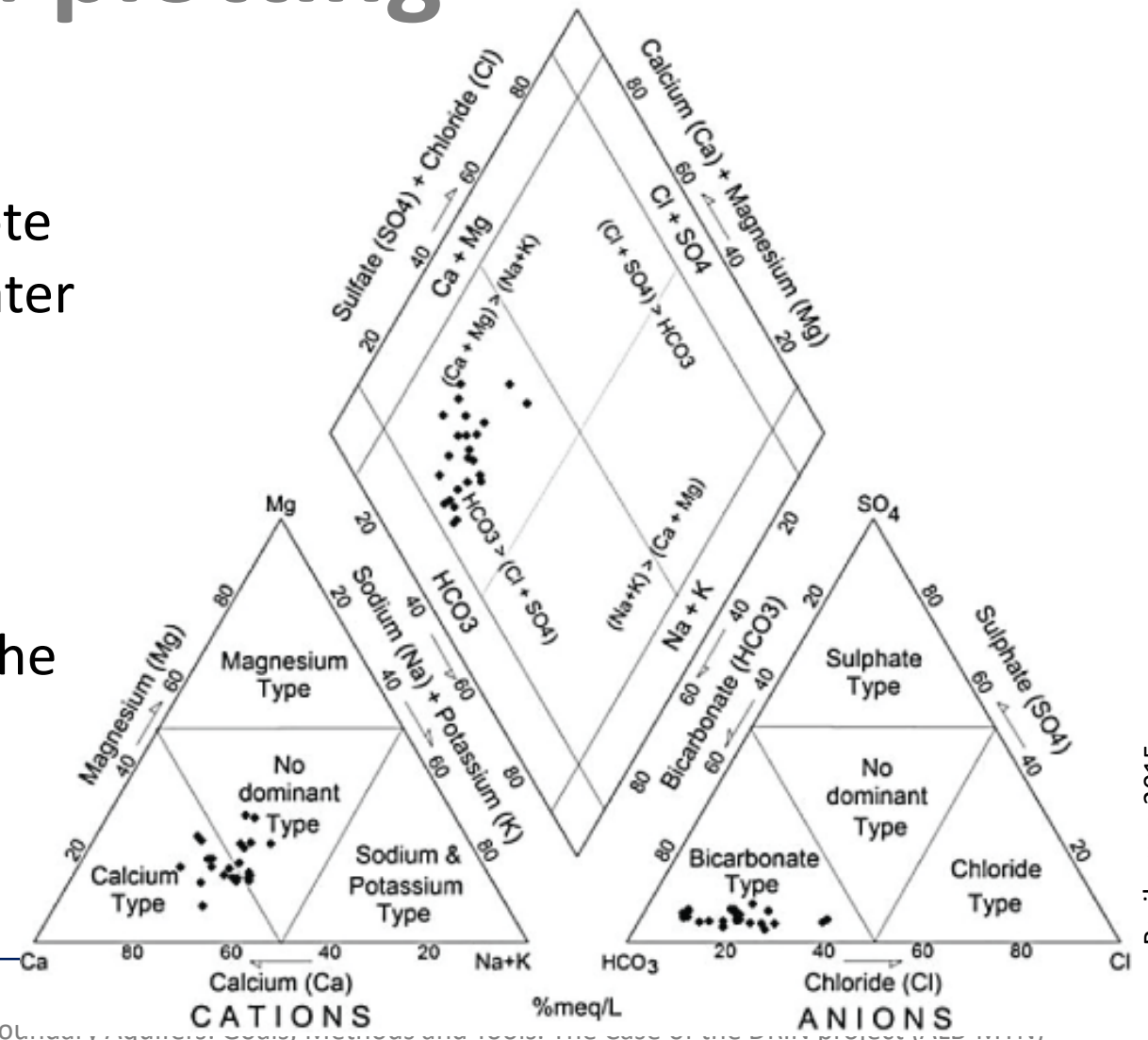
4. Data treatment and plotting

Piper-Hill plots; Hydrochemical facies

Hydrochemical facies is a term used to denote the diagnostic chemical aspect of ground-water solutions occurring in hydrologic systems.

The facies reflects **the response of chemical processes operating within the lithological framework**, and also the pattern of flow of the water.

(Back W, 1966, USGS Professional Paper 498-A)



Ravikumar, 2015

4. Data treatment and plotting

Piper-Hill “diamond” plot → Hydrochemical facies

Facies:

A - Sulfate-calcium*

B - Chloride-sodium**

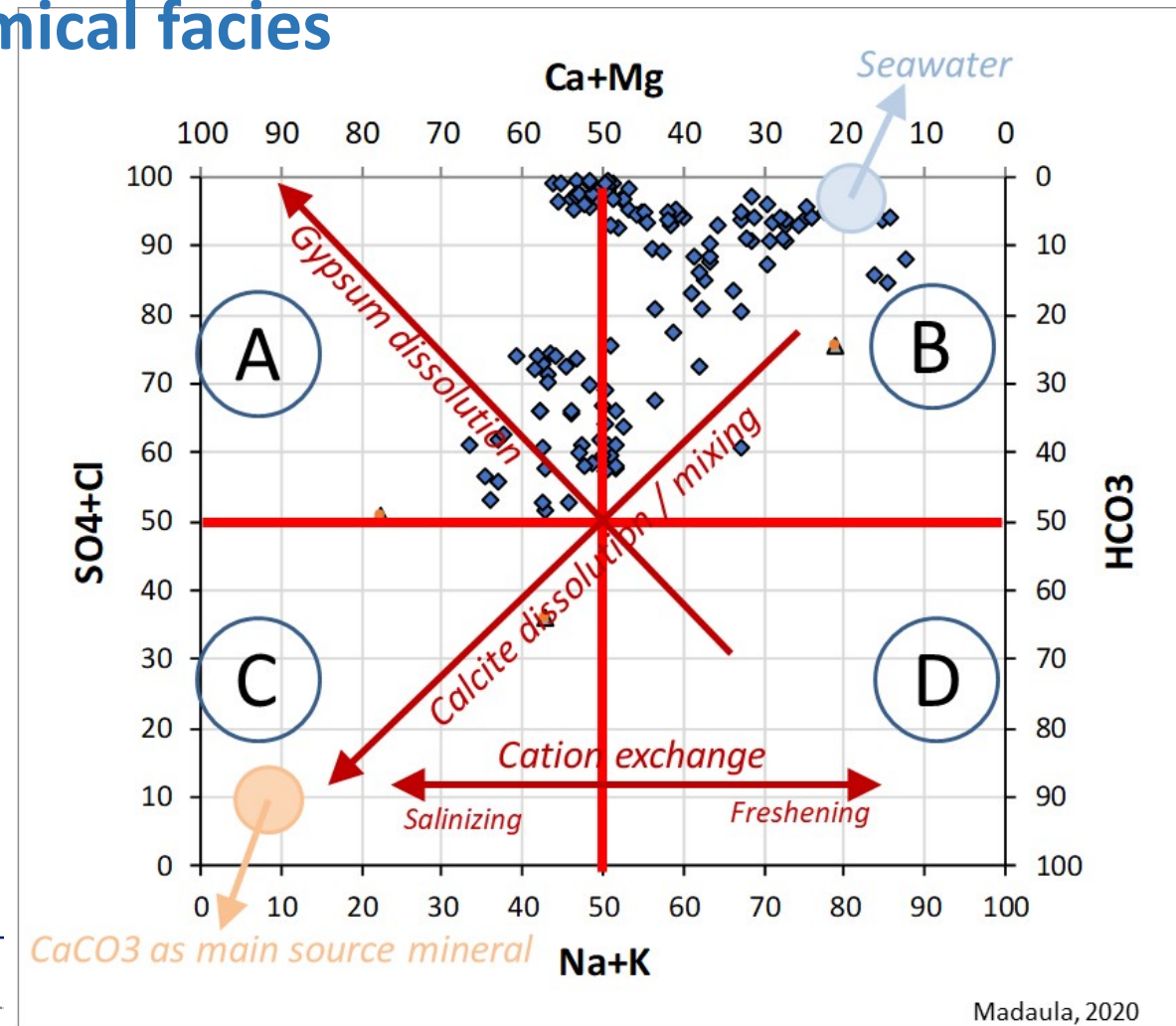
C - Bicarbonate-calcium

D - Bicarbonate sodium***

*.- Mg & K are always low

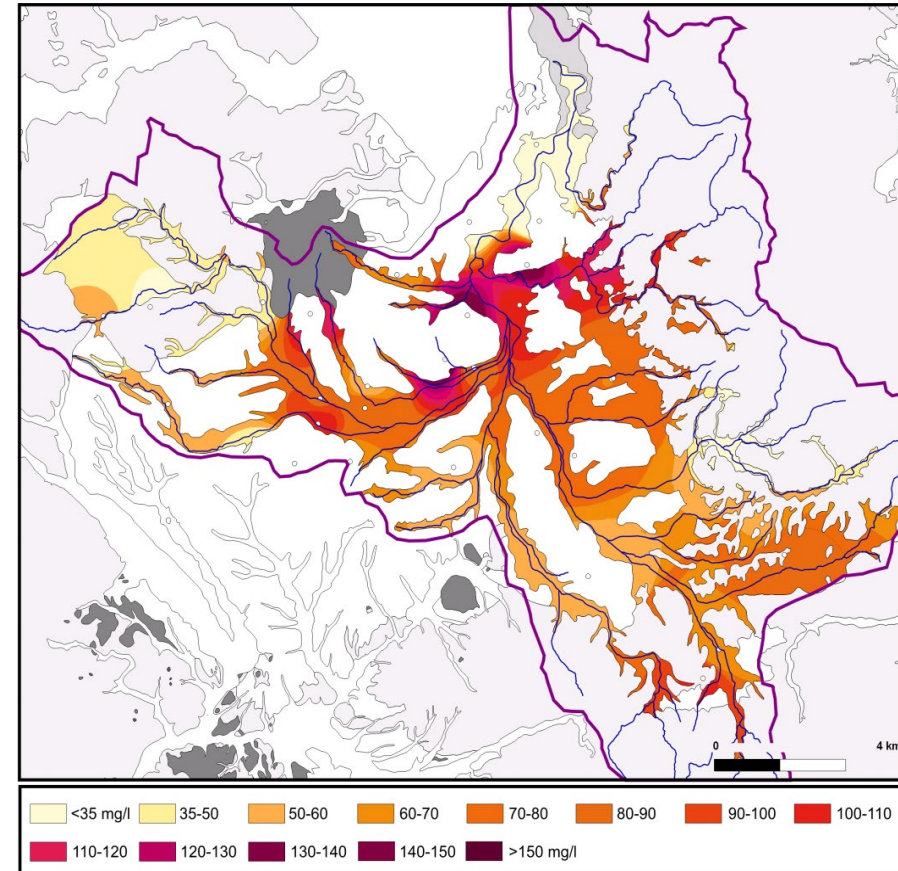
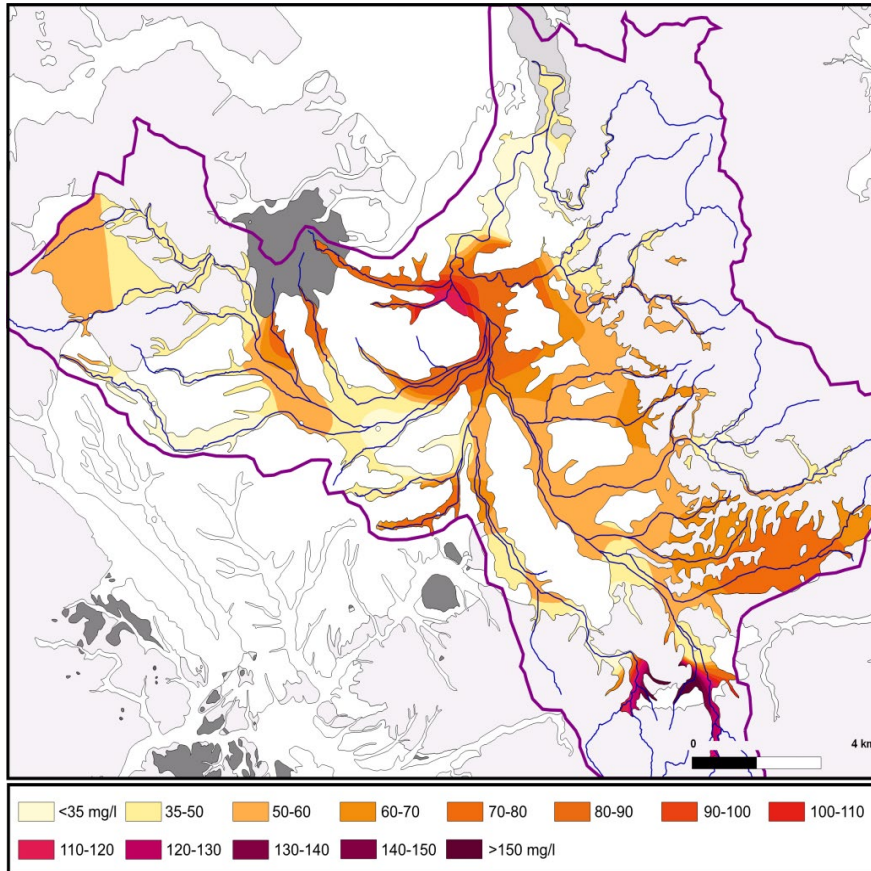
**.- SO_4 - Na is rare,

***.- HCO_3 - Na is common in igneous aquifers, usually with high pH values.



4. Data treatment and plotting

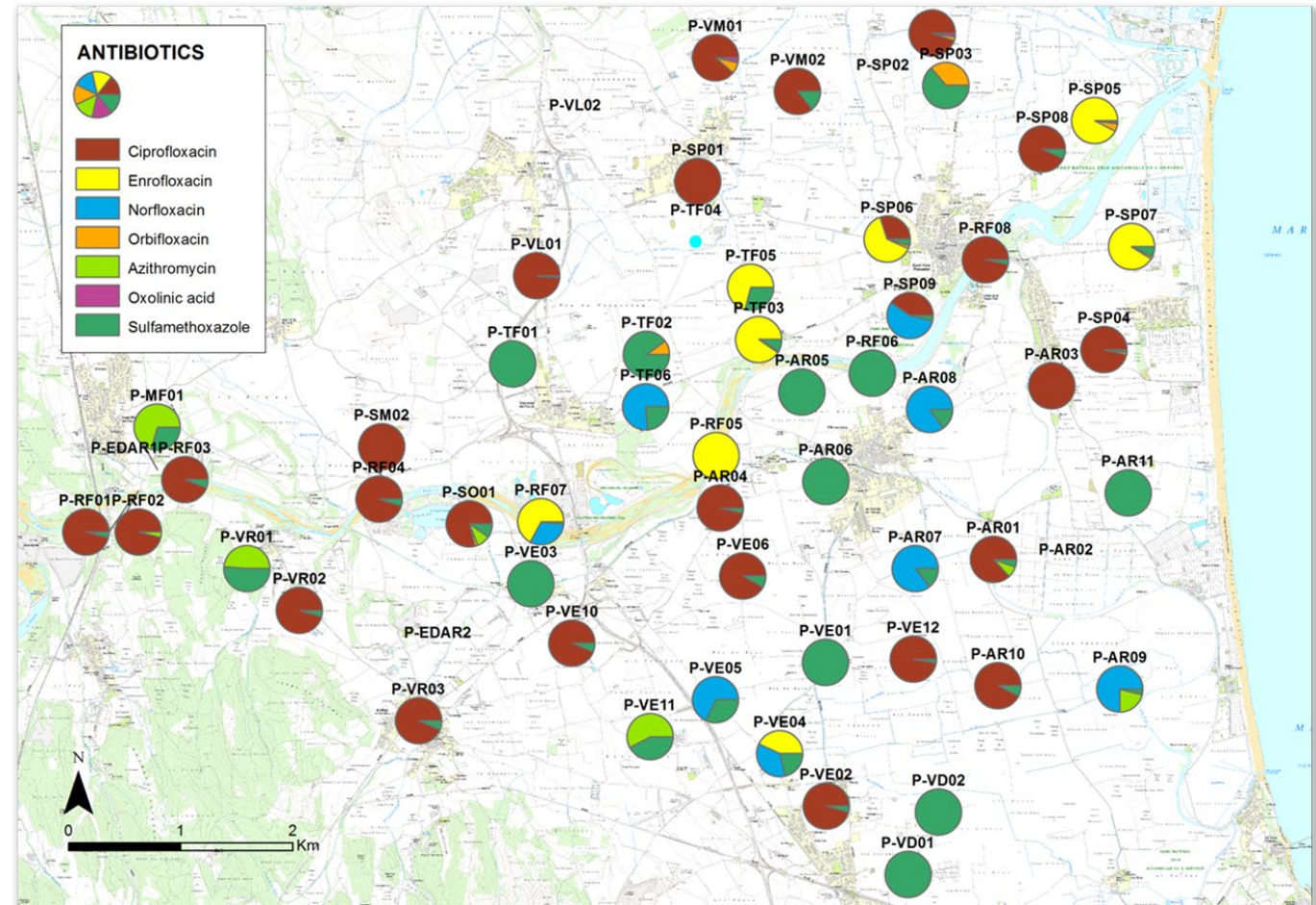
Plotting interpolated data



Menció A, 2010, PhD Diss. UdG

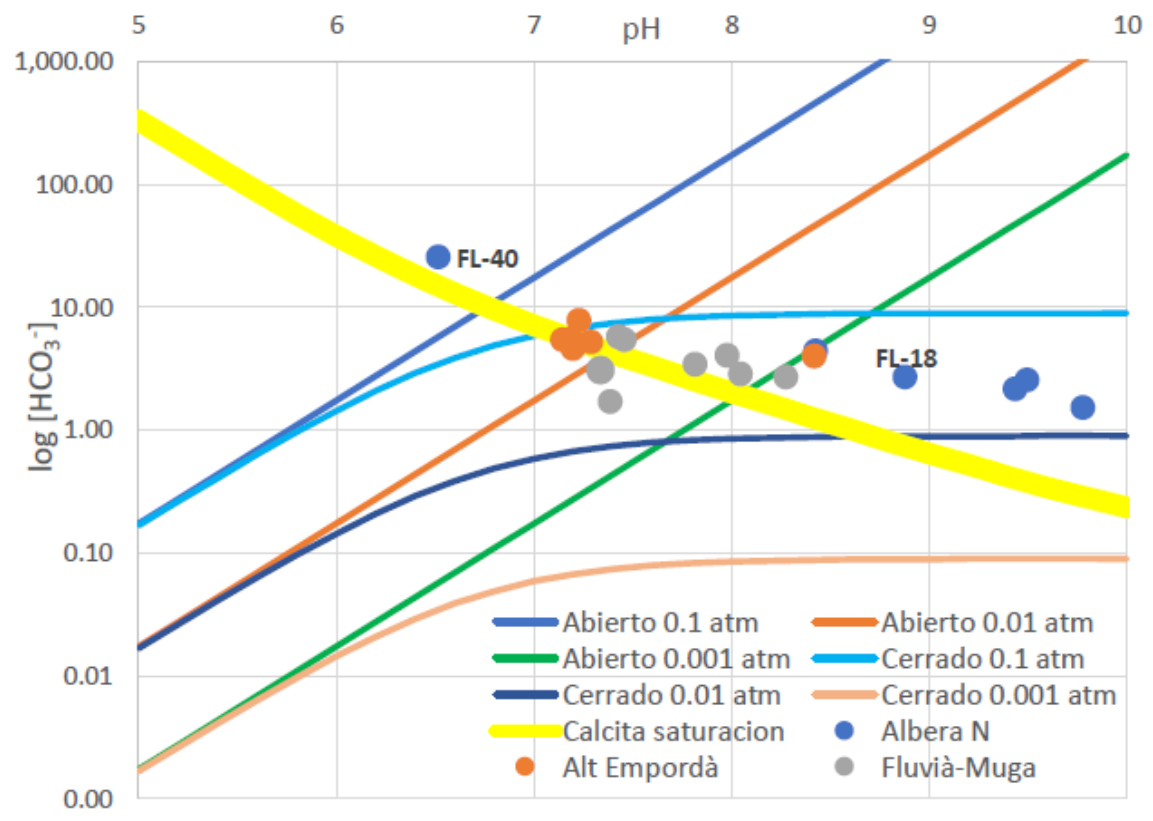
4. Data treatment and plotting

Plotting interpolated data



5. Data interpretation

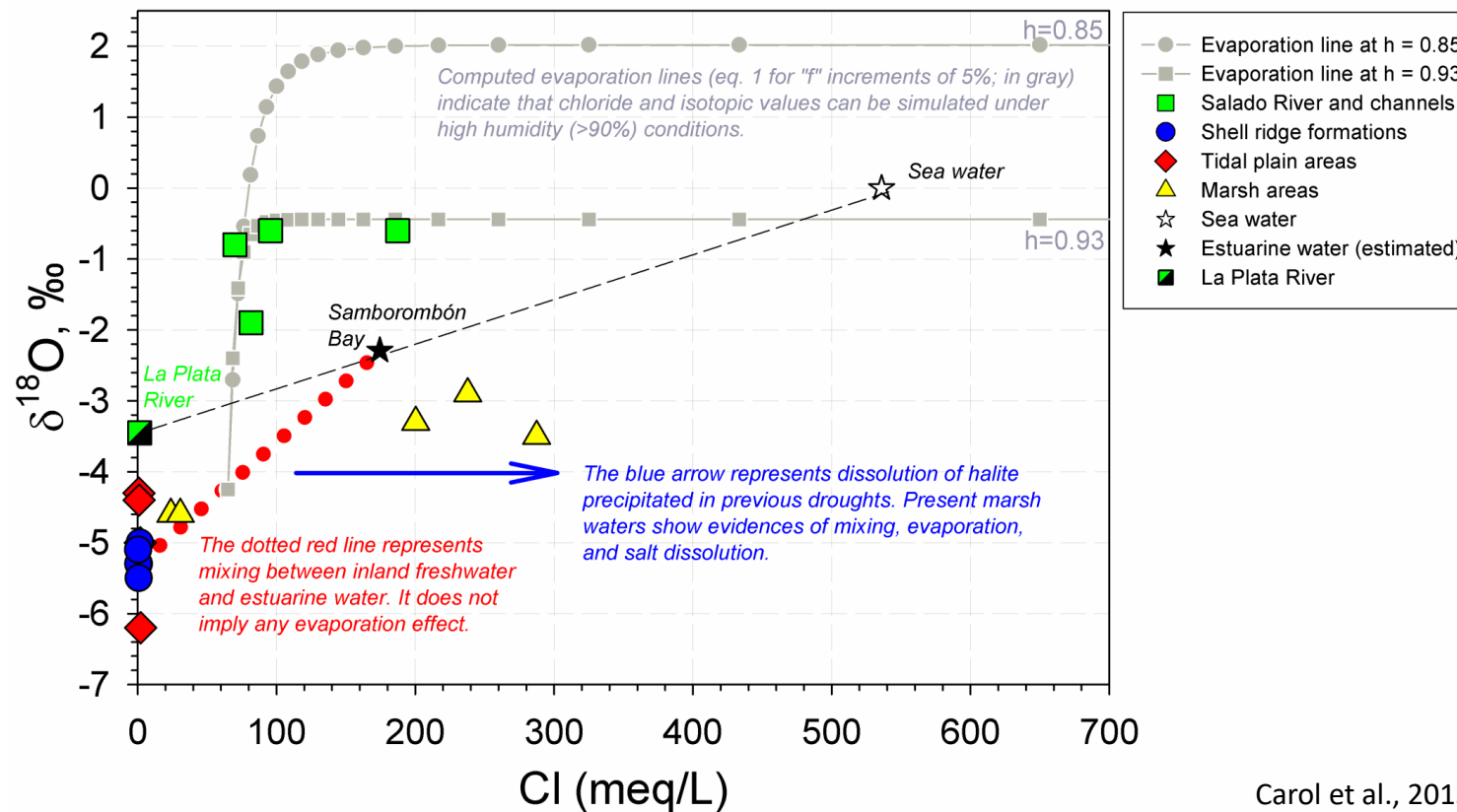
Interpreting hydrochemical plots



Vílchez Peña, A, 2020, *MSc Thesis*. UdG

5. Data interpretation

Interpreting hydrochemical plots

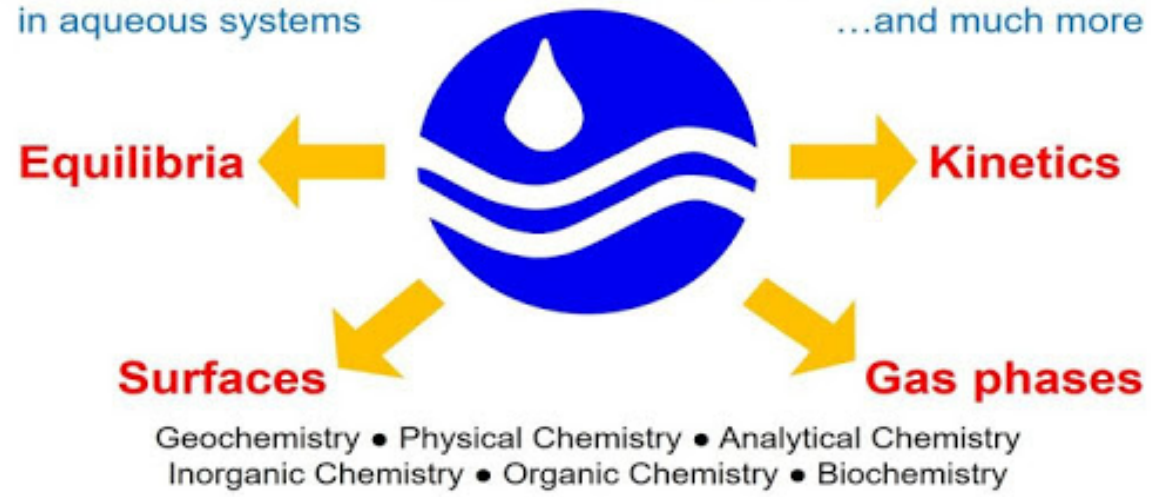


Carol et al., 2013. *Applied Geochemistry*, 34: 152-163

5. Data interpretation

Geochemical modelling

PHREEQC = pH-Redox-Equilibrium Calculations
in aqueous systems ...and much more



PHREEQC Interactive - [Phrq1 VilaJuiga PMP]

File Edit View Options Window Help

Initial conditions Forward and inverse modeling

Output files

- Phrq1 VilaJuiga PMP
 - Reading data base.
 - Reading input data for simulation 1.
 - Reading input data for simulation 2.

Initial solution 1. CAN-2

-----Solution composition-----

Elements	Molality	Moles
Alkalinity	2.131e-03	2.131e-03
Ca	4.992e-05	4.992e-05
Cl	7.054e-04	7.054e-04
K	2.558e-05	2.558e-05
Na	3.785e-03	3.785e-03
S(6)	3.749e-04	3.749e-04
Si	4.495e-04	4.495e-04

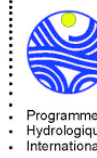
-----Description of solution-----

pH = 9.440
pe = 4.000
Specific Conductance (µS/cm, 13°C) = 293
Density (g/cm³) = 0.99956
Volume (L) = 1.00074
Activity of water = 1.000
Ionic strength (mol/kgw) = 4.322e-03
Mass of water (kg) = 1.000e+00
Total carbon (mol/kg) = 1.816e-03
Total CO2 (mol/kg) = 1.816e-03
Temperature (°C) = 13.40
Electrical balance (eq) = 3.246e-04
Percent error, 100*(Cat-|An|)/(Cat+|An|) = 4.37
Iterations = 5
Total H = 1.110158e+02
Total O = 5.551497e+01

Input Output Database Error

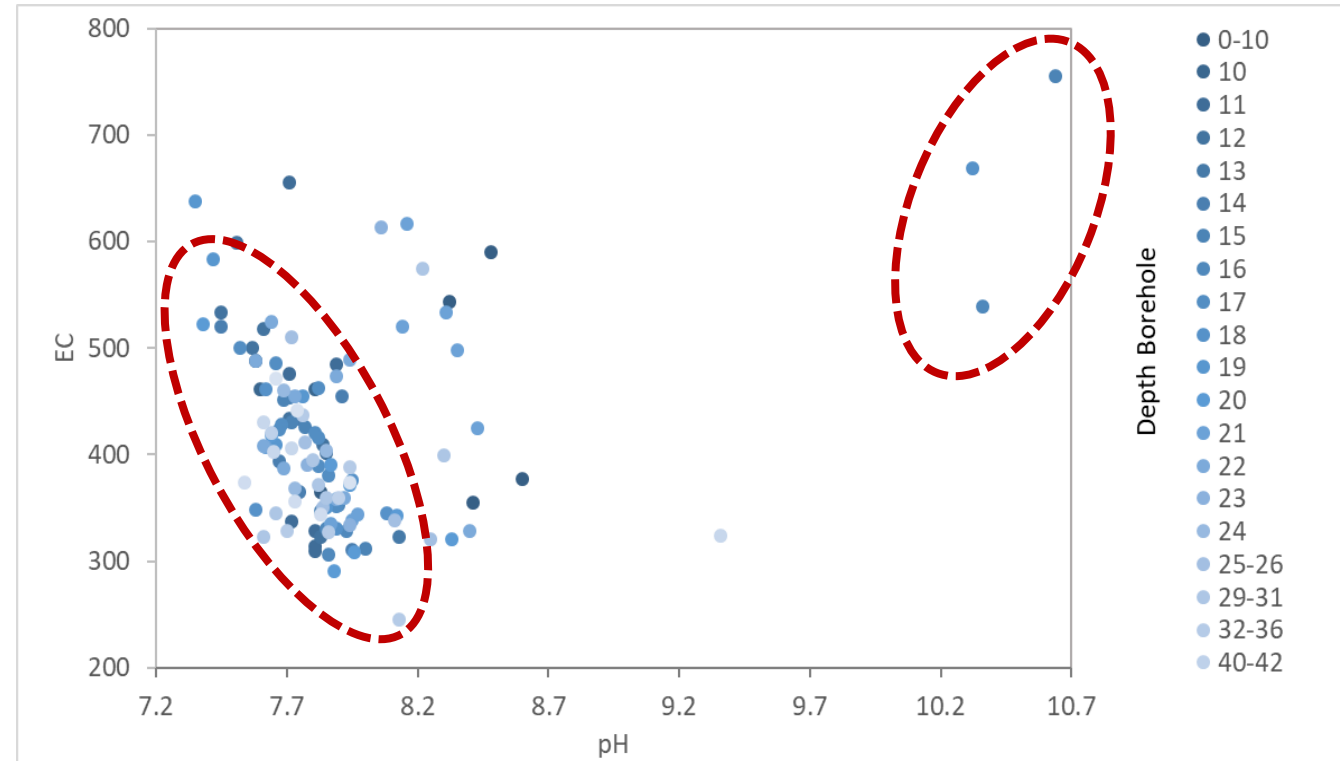
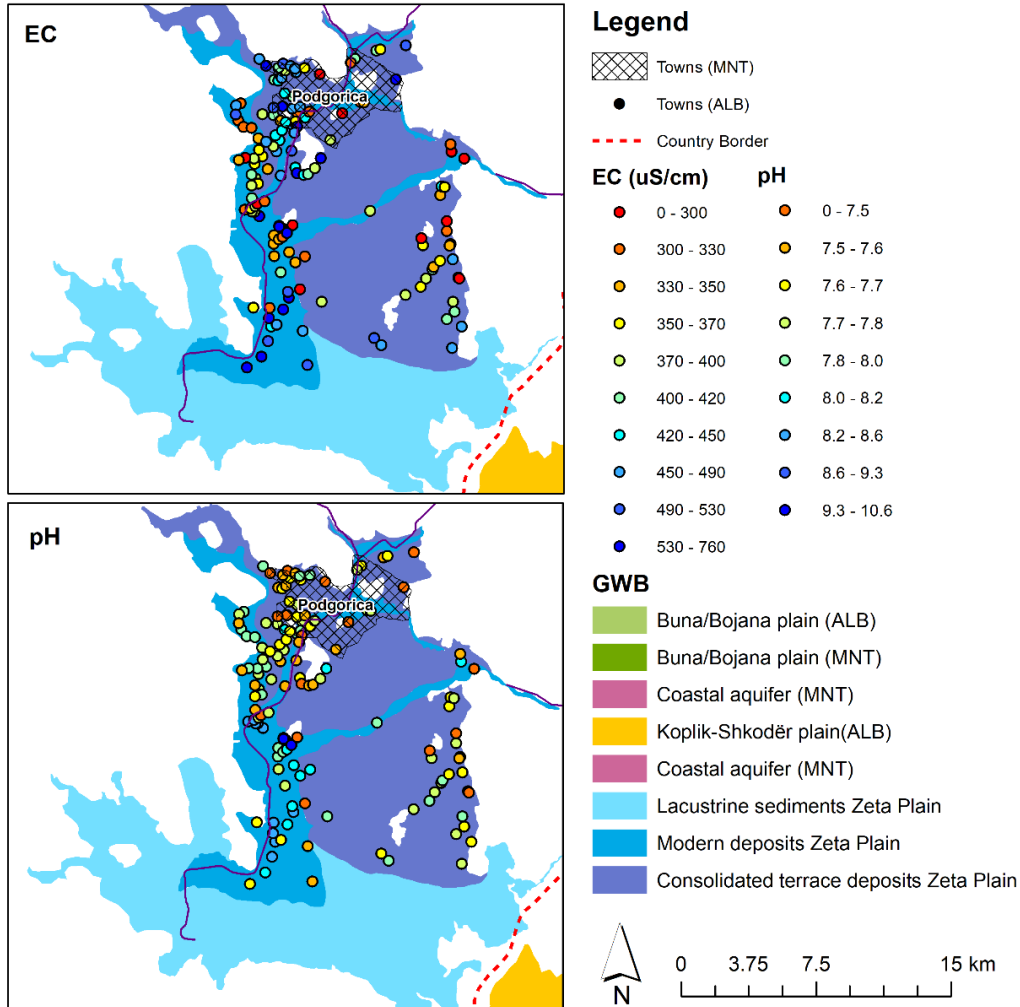
Ready NUM

6. Real case



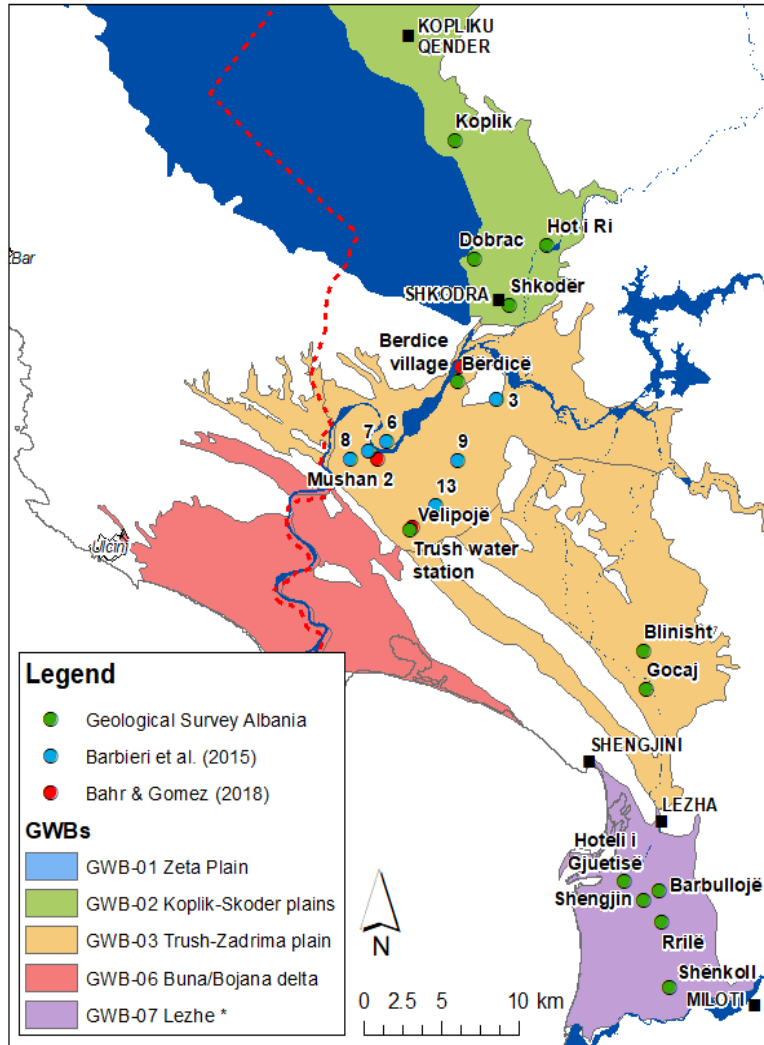
The case of the Skadar/Shkoder - Buna/Bojana transboundary aquifer

Surveillance monitoring

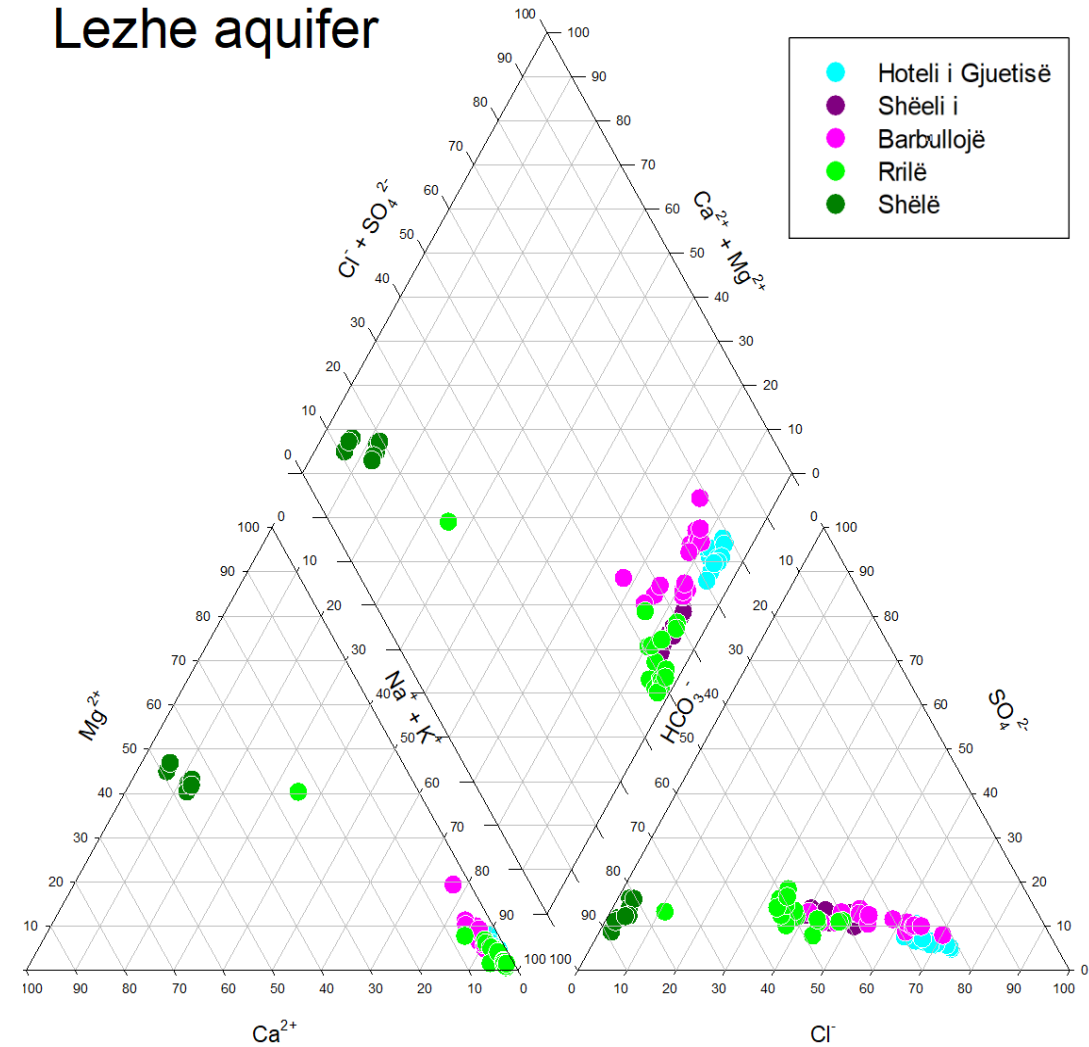


Del Val L, Mas-Pla J 2019. Drin Project. UNESCO Data from Montenegro Officials

Surveillance monitoring



Lezhe aquifer



Further reading



- EU-WFD Guidelines Document 26 on “Risk assessment and the use of Conceptual models for Groundwater”.
- Enemark, T., Peeters, L.J.M., Mallants, D., Batelaan, O., Hydrogeological conceptual model building and testing: A review, Journal of Hydrology (2018), doi: <https://doi.org/10.1016/j.jhydrol.2018.12.007>

Thank you!



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