

Coupling geochemical and isotopic tracers ($\delta^{18}\text{O}$; $\delta^2\text{H}$; $^{87}\text{Sr}/^{86}\text{Sr}$) to quantify groundwater mixing in carbonate environments

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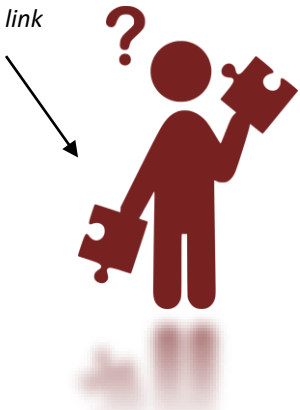


Session HS8.2.4

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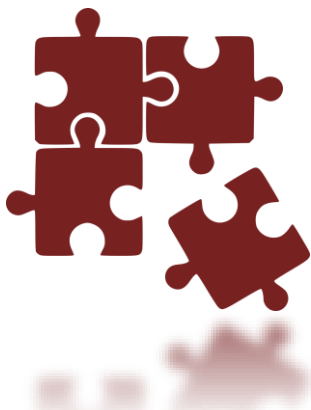
Main issues and objective



Context and methodologies



Qualification of groundwater



Model and quantification of mixing process

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 Pictures

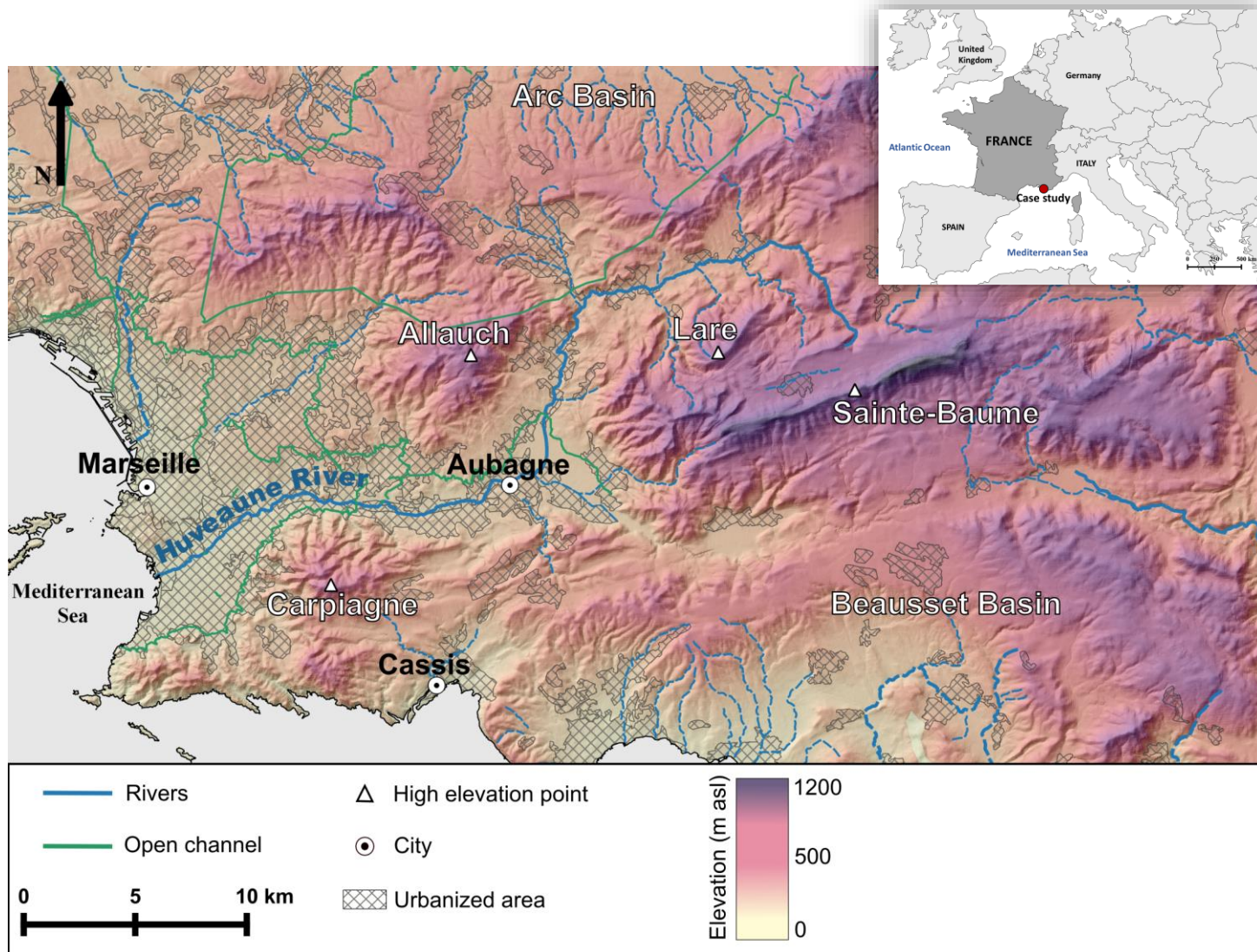
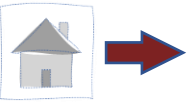
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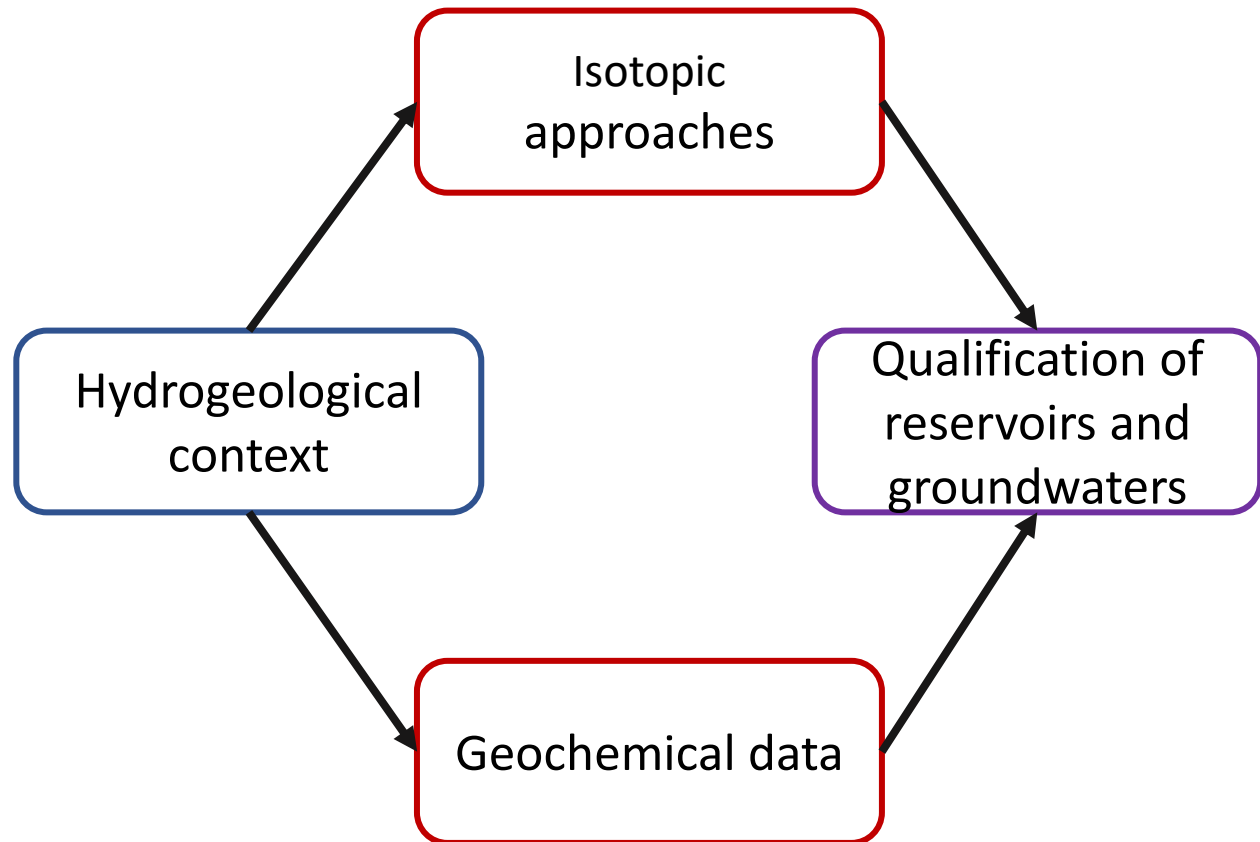
Main issues



- High density populated area with historically water supply from the Marseille canal
- Local and massive carbonate aquifers on the Sainte Baume mountains, classified as strategic water resource (SDAGE 2016-2021)

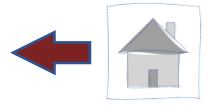
What does the coupling of geochemical and isotopic approaches bring to the understanding of the hydrogeological functioning of a complex hydrosystem (origin of water, existence of a mixture between aquifer, water-rock interaction?)

Objective



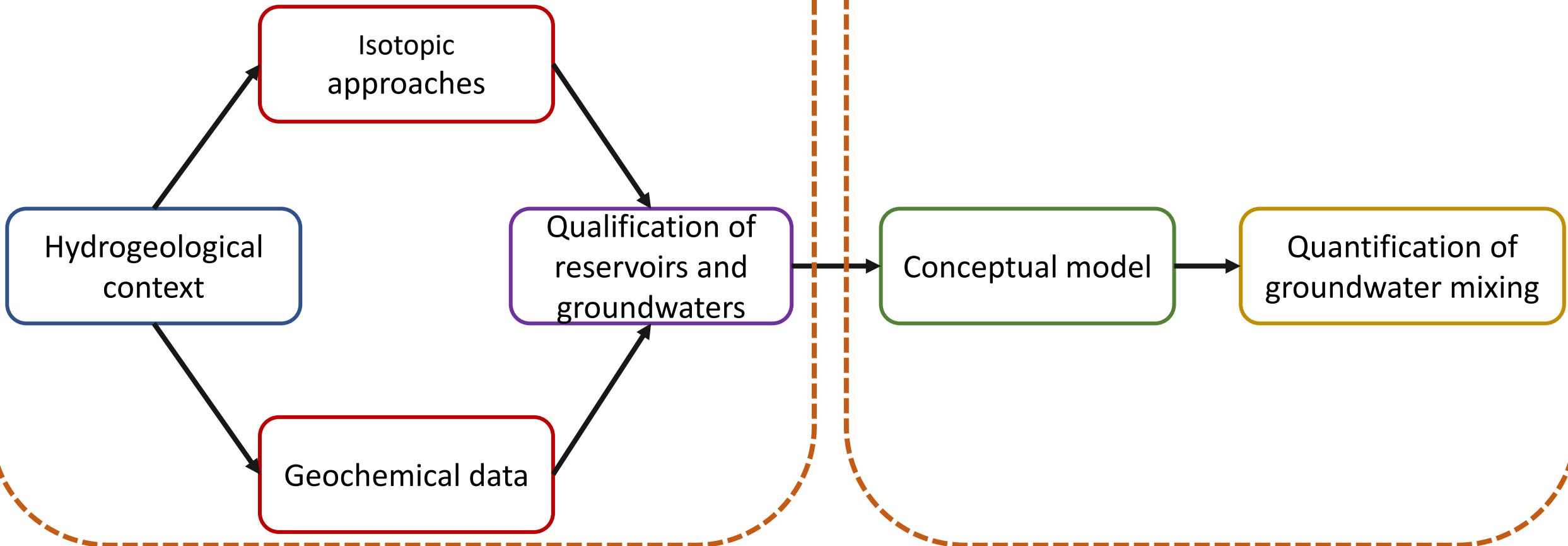
Qualification of groundwater mixing based on hydrogeochemical approaches

Objective

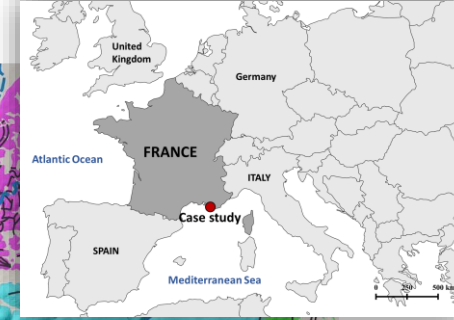
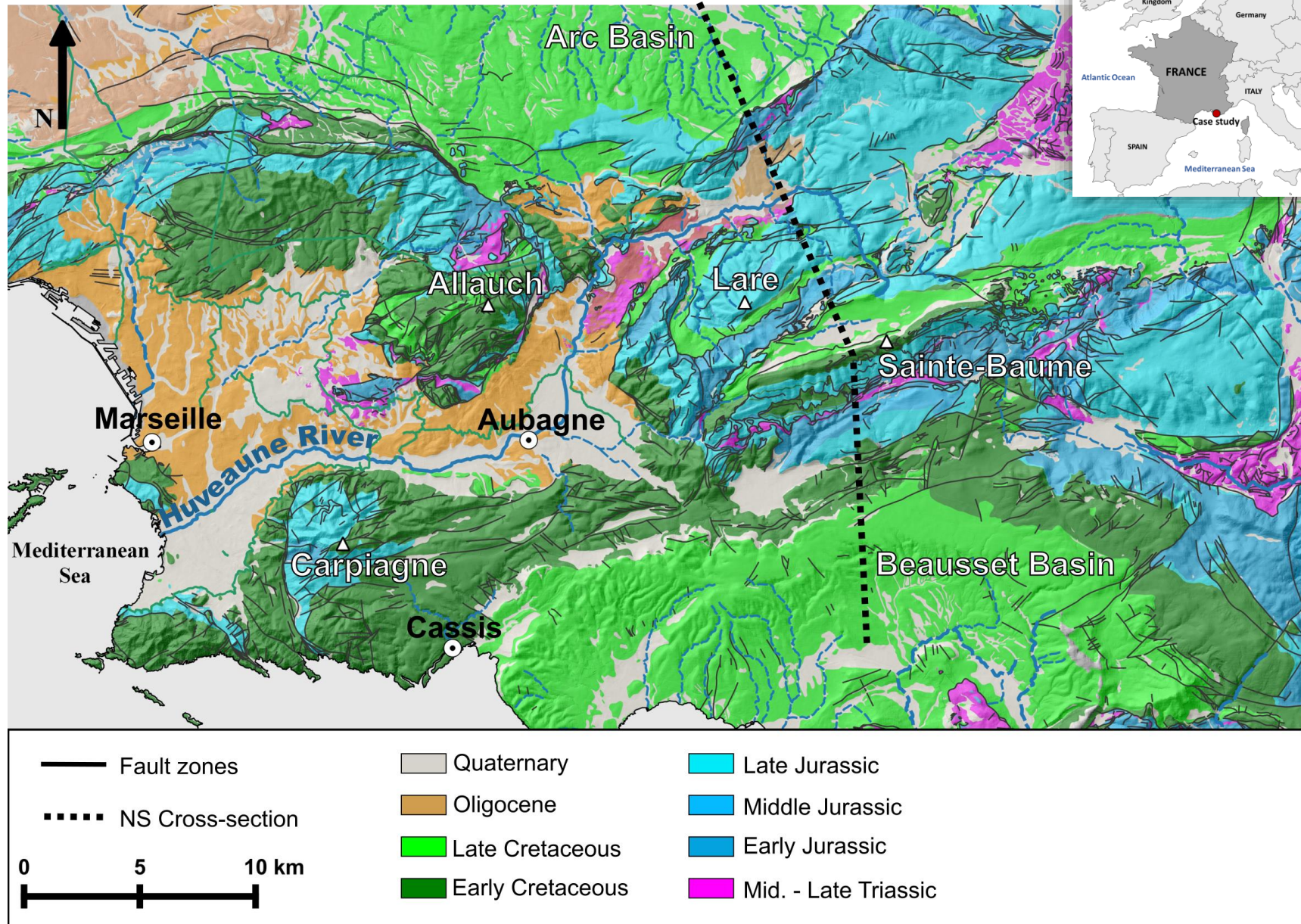
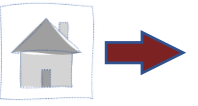


Qualification of groundwater mixing based on hydrogeochemical approaches

Quantification of groundwater mixing from conceptual model

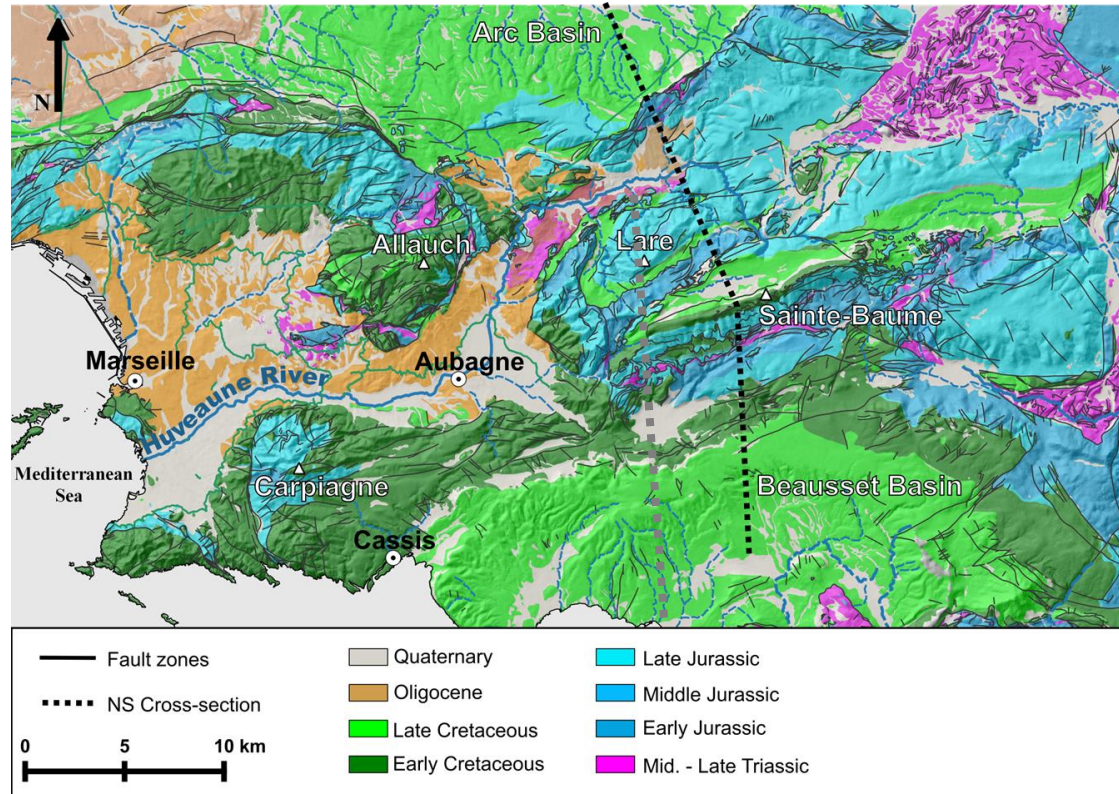
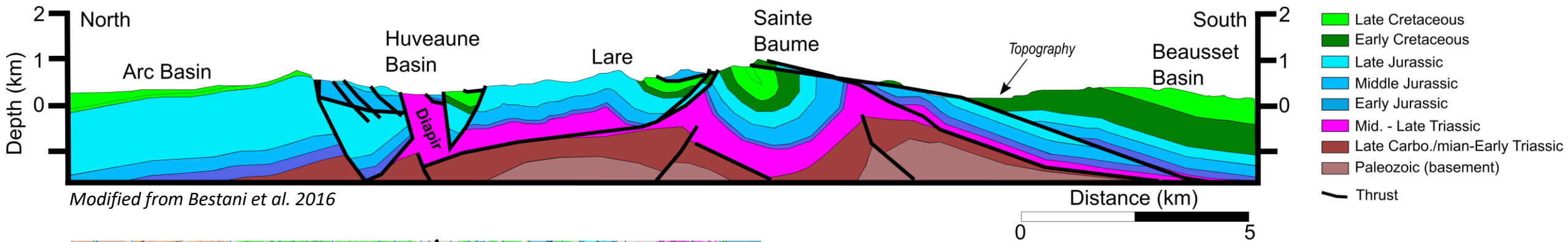


Geological context



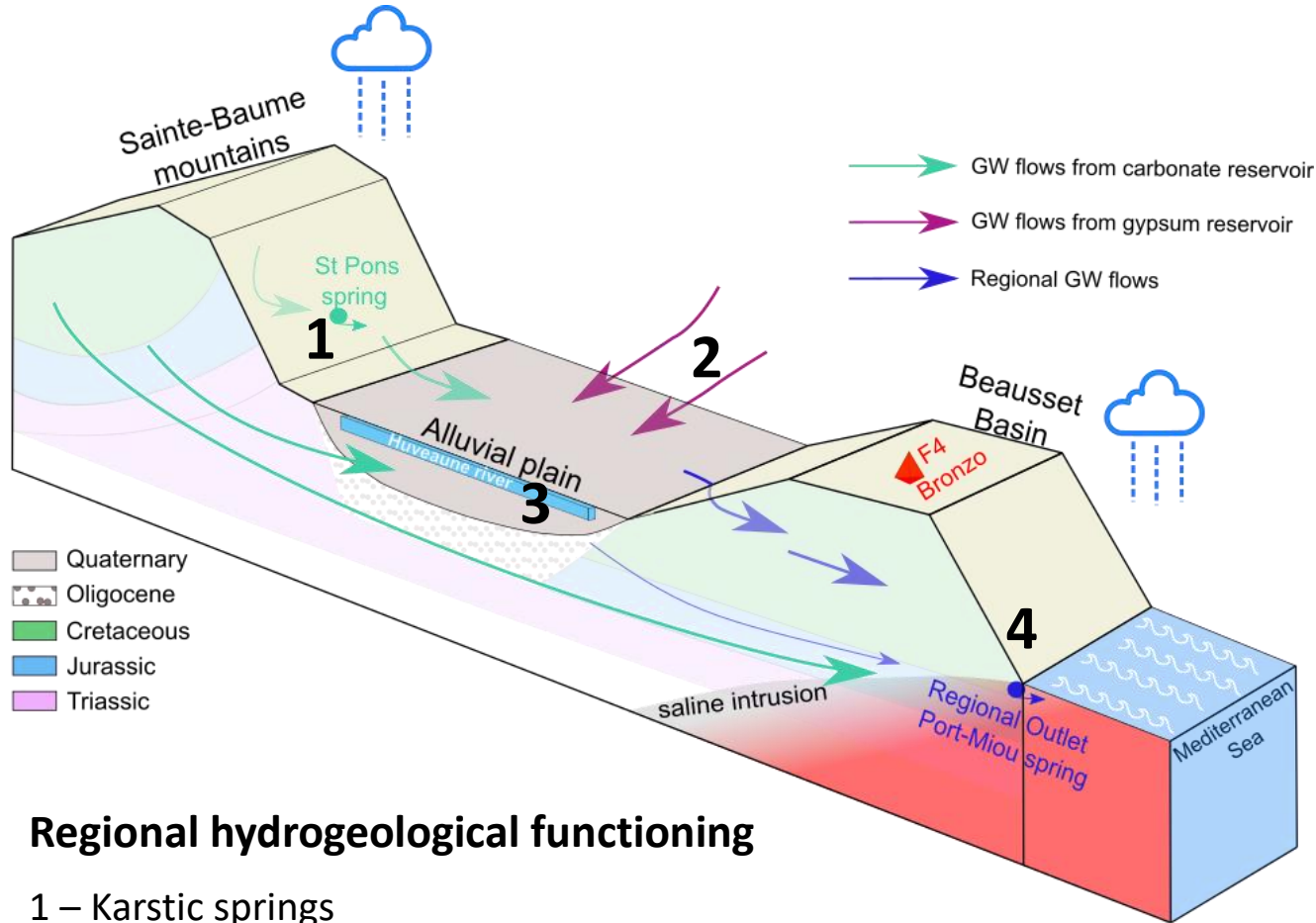
- Complex geodynamic context with sedimentary deposits mainly marked by Durancian compression (Late Cretaceous), Pyrenean compression (Early Cretaceous to Eocene) and Oligocene extension
- Alluvial plain with detrital deposits from Trias to Cretaceous

Geological context



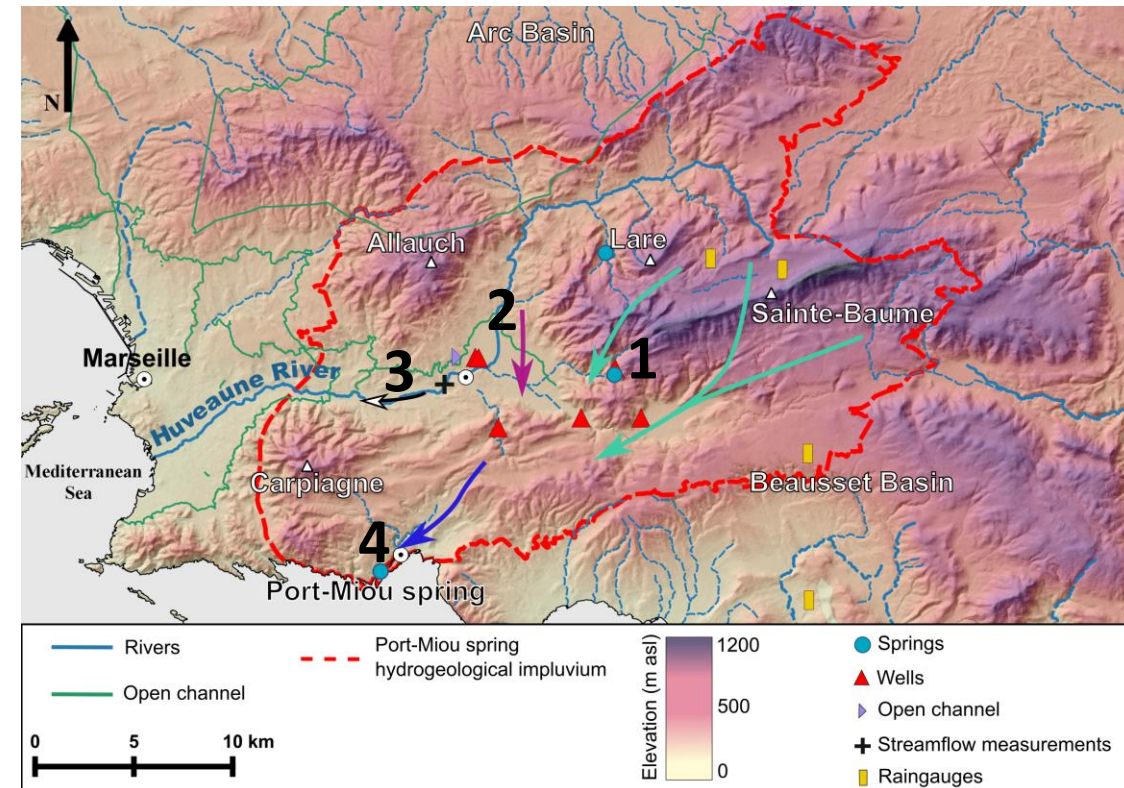
- North-South structural cross-section marked on the geological map (dotted line)
- Complex geological structure with synclinal and anticlinal forms
- Thrust of Beausset Basin on the Sainte Baume mountains (Pyrenean compression)
- Huveaune Basin and diapir induce from Oligocene extension

Hydrogeological context

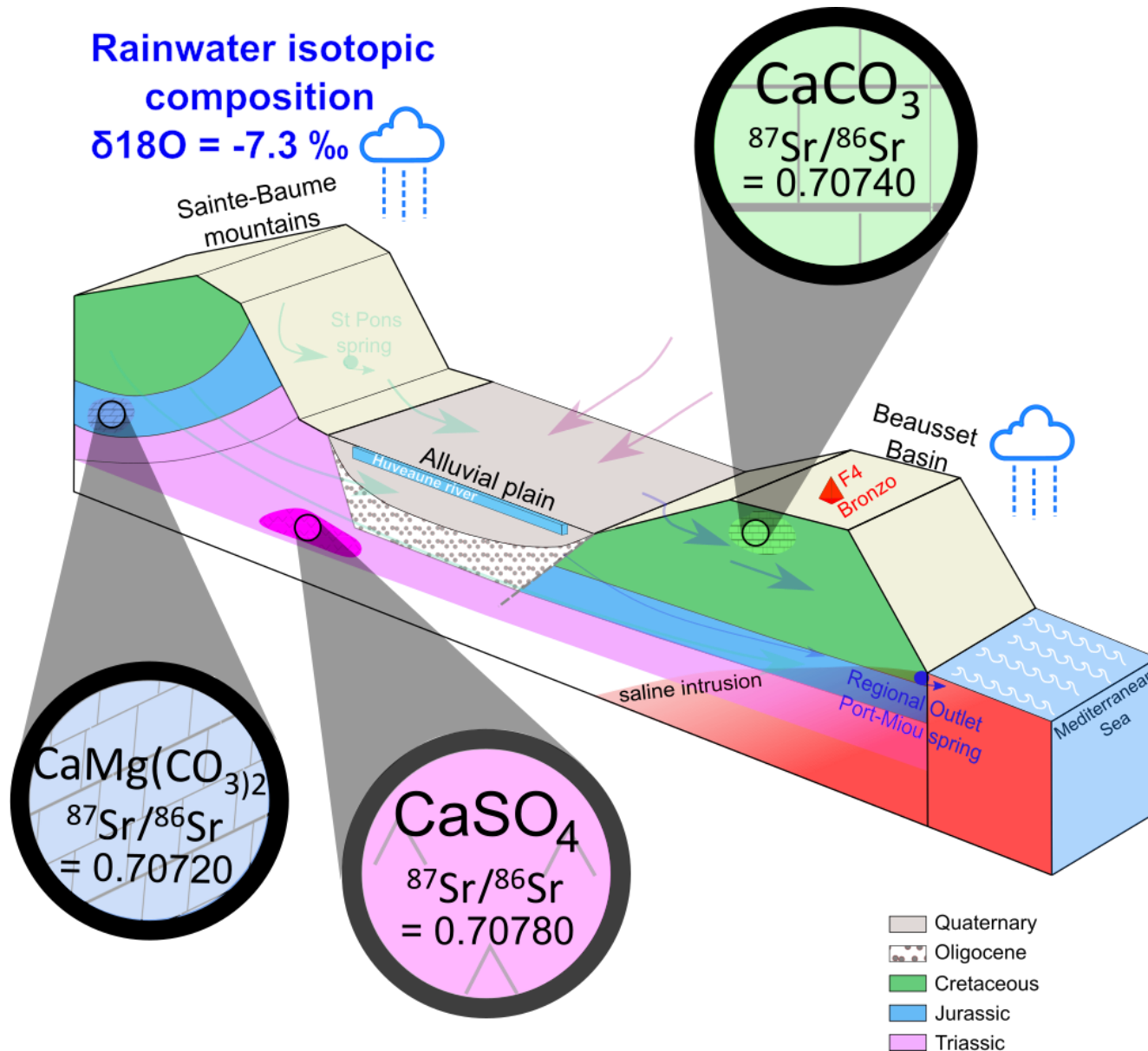


Regional hydrogeological functioning

- 1 – Karstic springs
- 2 – Alluvial plain
- 3 – Huveaune river – $1\text{ m}^3/\text{s}$
- 4 – Regional outlet Port-Miou spring – 3 to $8\text{ m}^3/\text{s}$

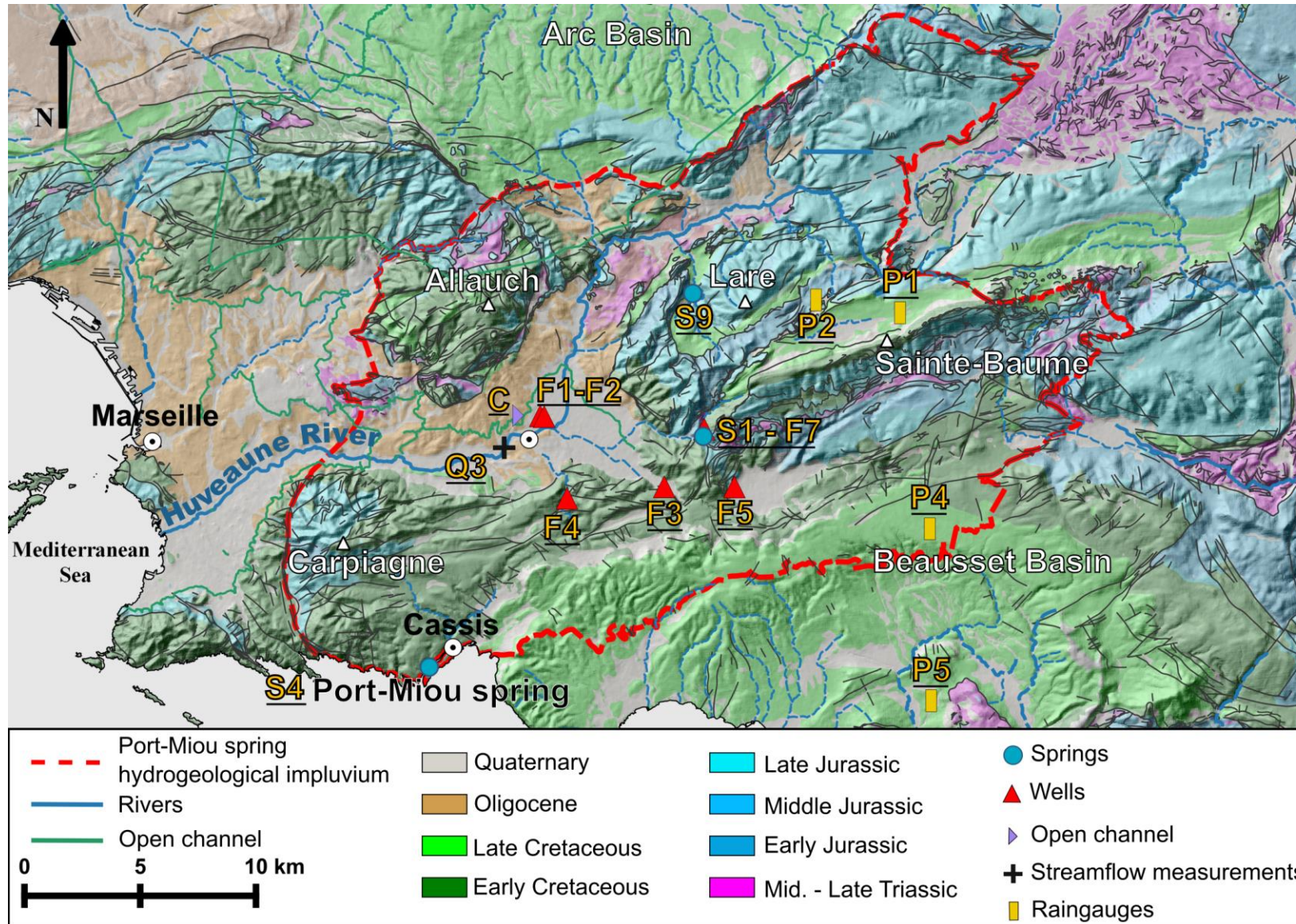
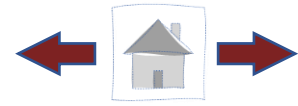


Methodologic approaches



- Major ions as tracer of **water-rocks interactions** (Ca^{2+} , Mg^{2+} , Sr^{2+} , SO_4^{2-} , NO_3^- , Na^+ , Cl^-)
- Strontium isotope ($^{87}\text{Sr}/^{86}\text{Sr}$) as tracer of **water-rocks interactions**, depending on the age of the deposits
- Water stable isotope ($\delta^{18}\text{O}/\delta^2\text{H}$) as tracer of the **area of the recharge**

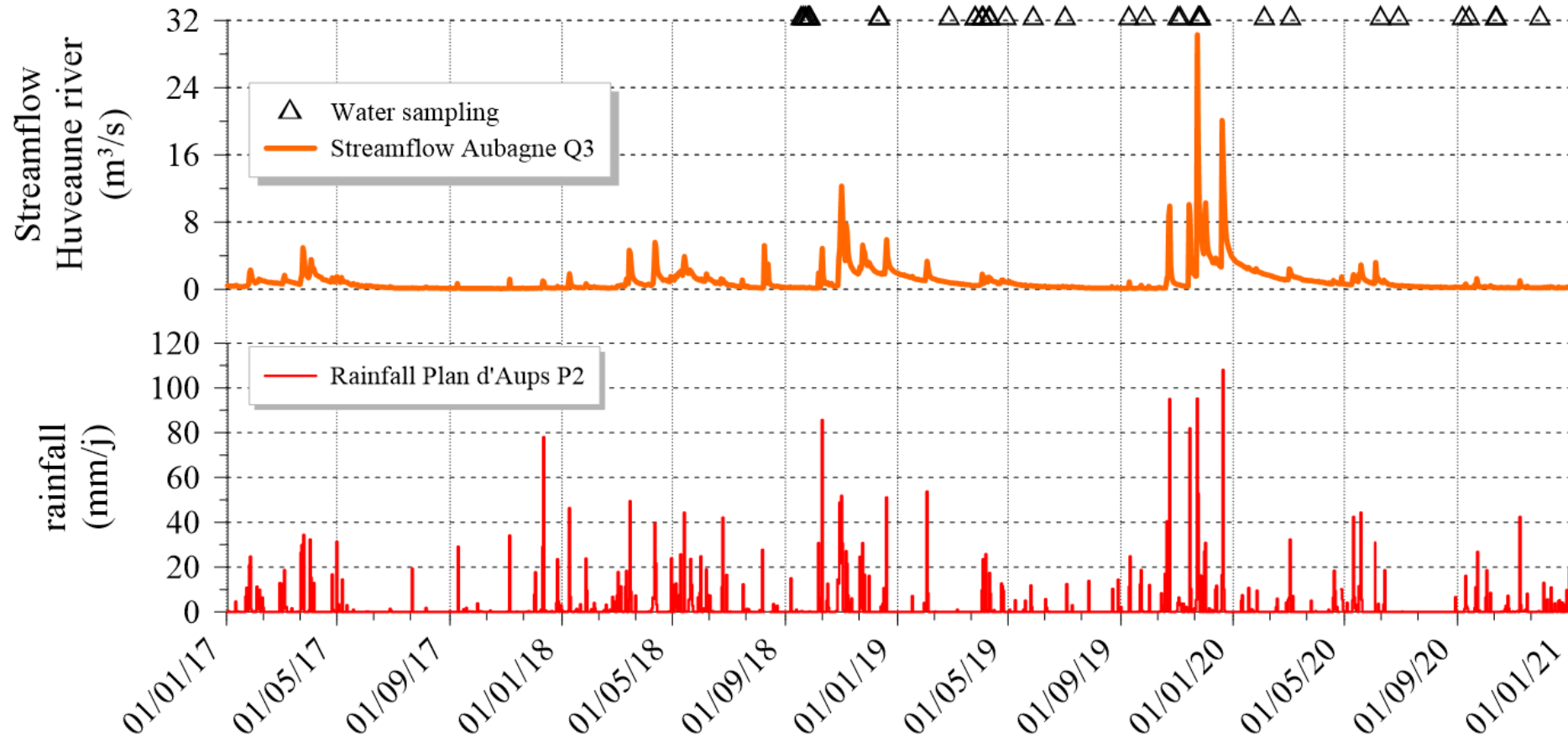
Observation network



Spatial repartition of the observation network representative of various geological and hydrological context

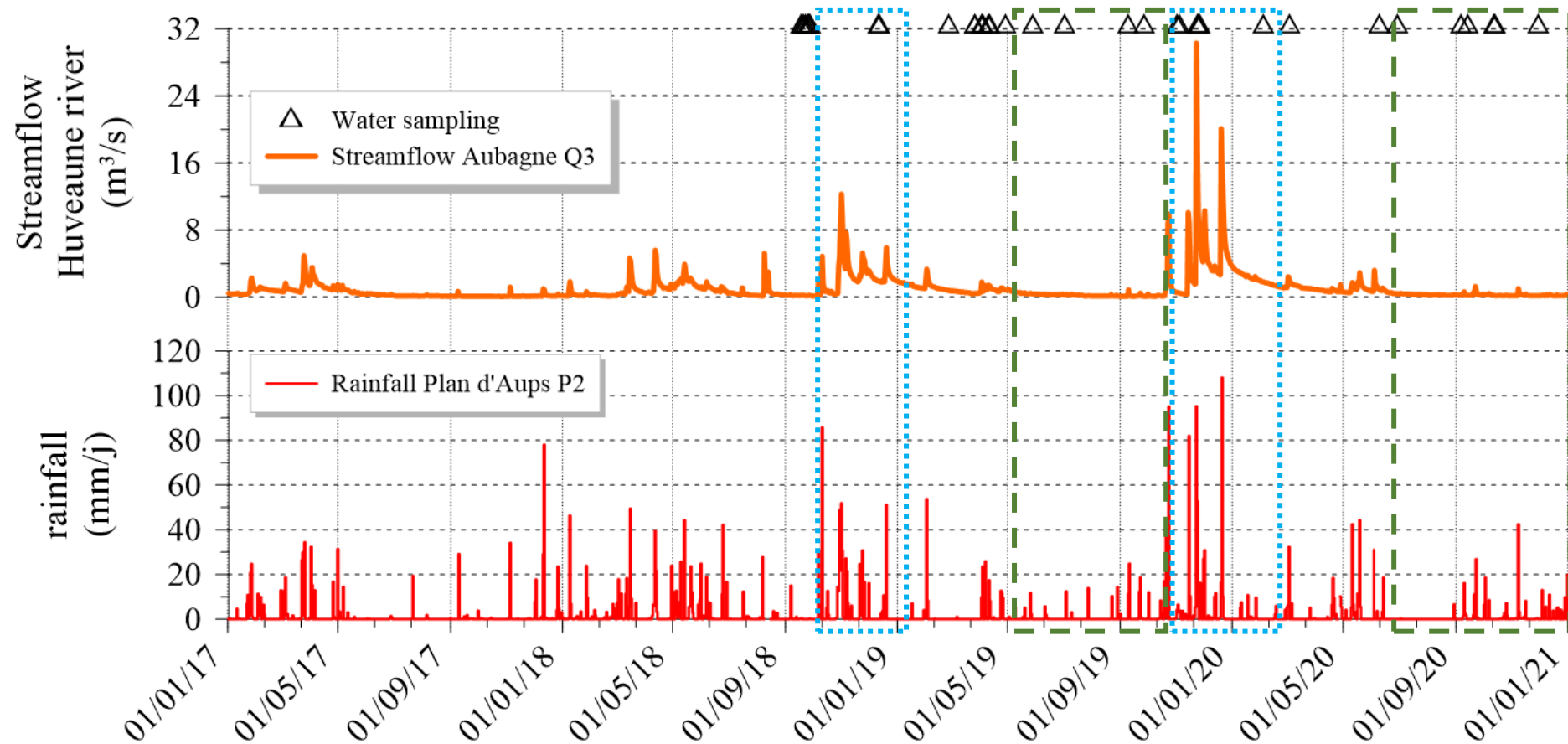
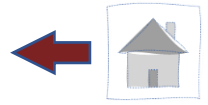
- Rainfall (P) and streamflow measurements (Q)
- Irrigation water from Marseille open channel (C)
- Boreholes (F) and karstic springs (S) to measure physico-chemical parameters and collect water for major ions and isotopic analysis in contrasted geological context
- Port-Miou spring (S4) – regional groundwater outlet

Hydrological context



- Streamflow measurements on three stations on the Huveaune River (*the most downstream showed here*)
- Rainfall measurements on four raingauge representative of different elevation and distance to the sea (*highest elevation showed here*)

Hydrological context

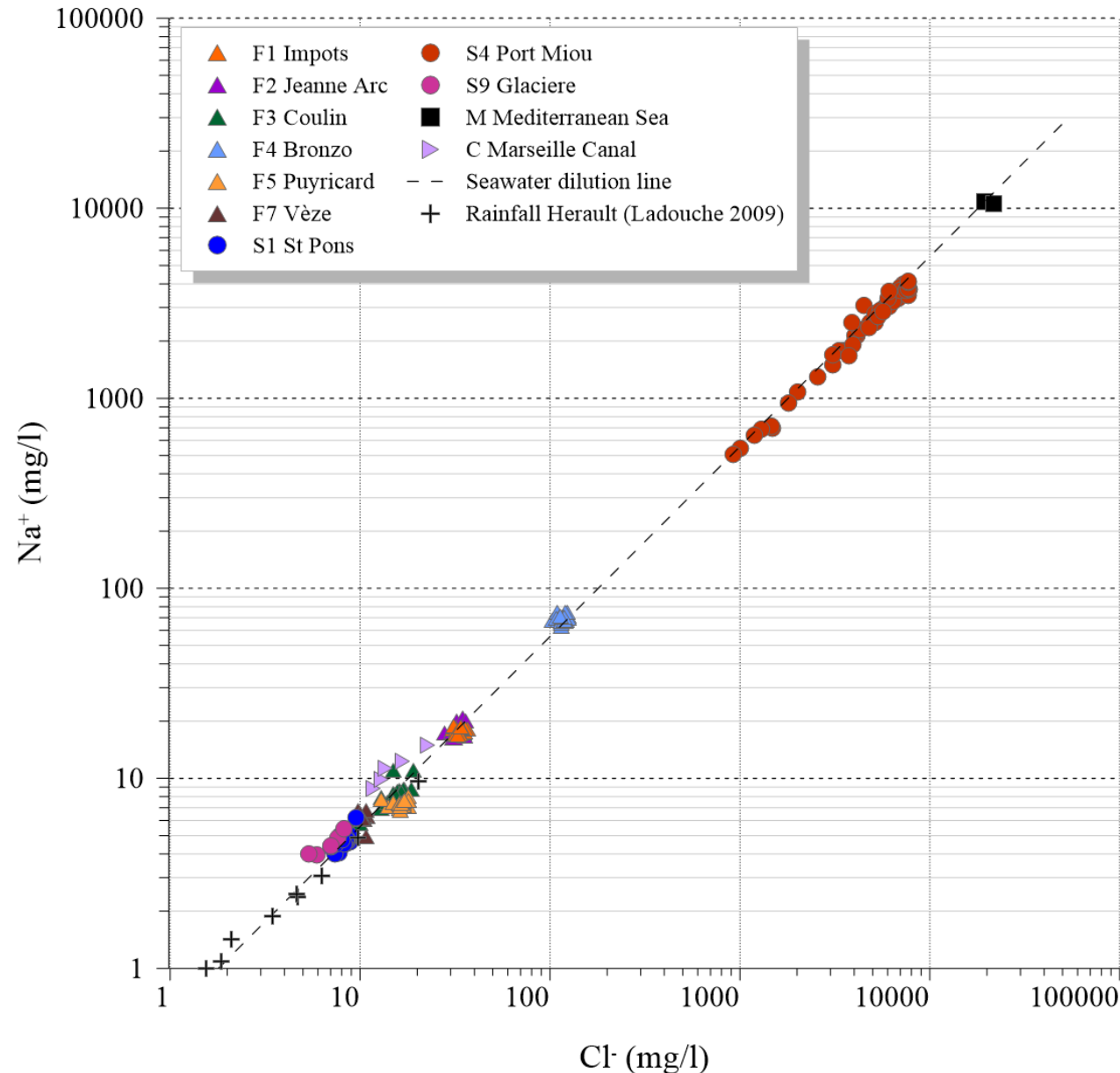
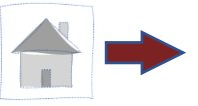


 High water period

 Low water period

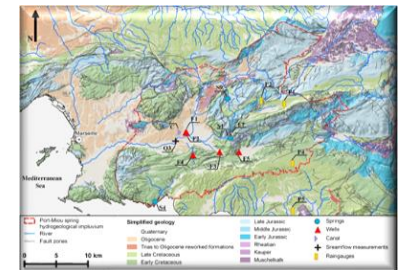
- Mensual water sampling representative of contrasted hydrological conditions

Na-Cl correlation for regional water

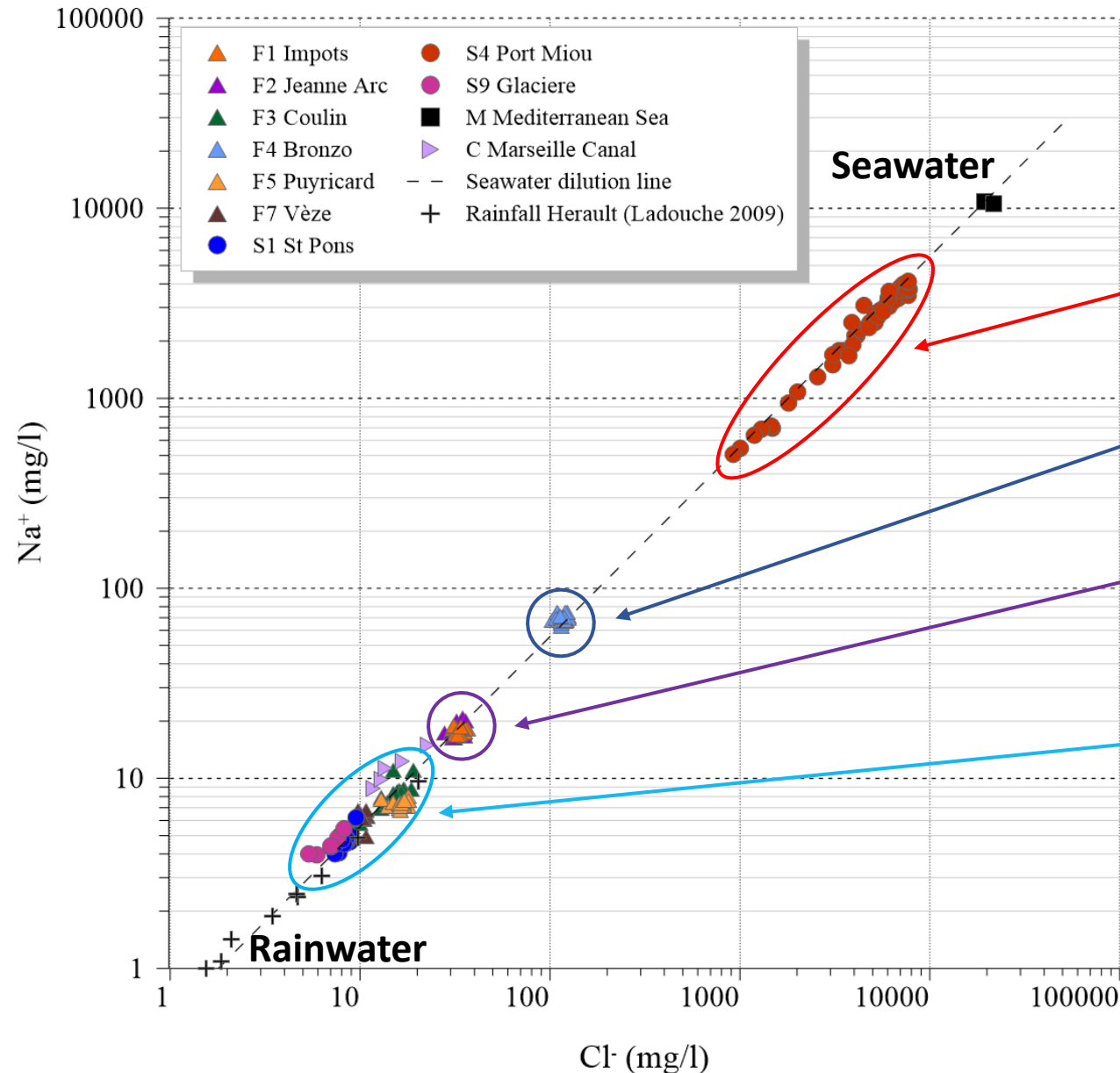


- **Binary diagram associated with seawater (SW) mixing line to identify gain or loss in major ions**
- [Cl⁻] range from 5 to more than 20,000 mg/l
- [Na⁺] range from 5 to 10,000 mg/l
- Good correlation for each water samples between sodium and chloride ions and the seawater mixing line
- ➔ show the influence of marine water source for the chemical composition of GW

Click to context



Identification of GW groups



- Identification of 4 groups of GW based on these diagrams – Na vs Cl

Brackish water from Port-Miou Springs (regional GW outlet)

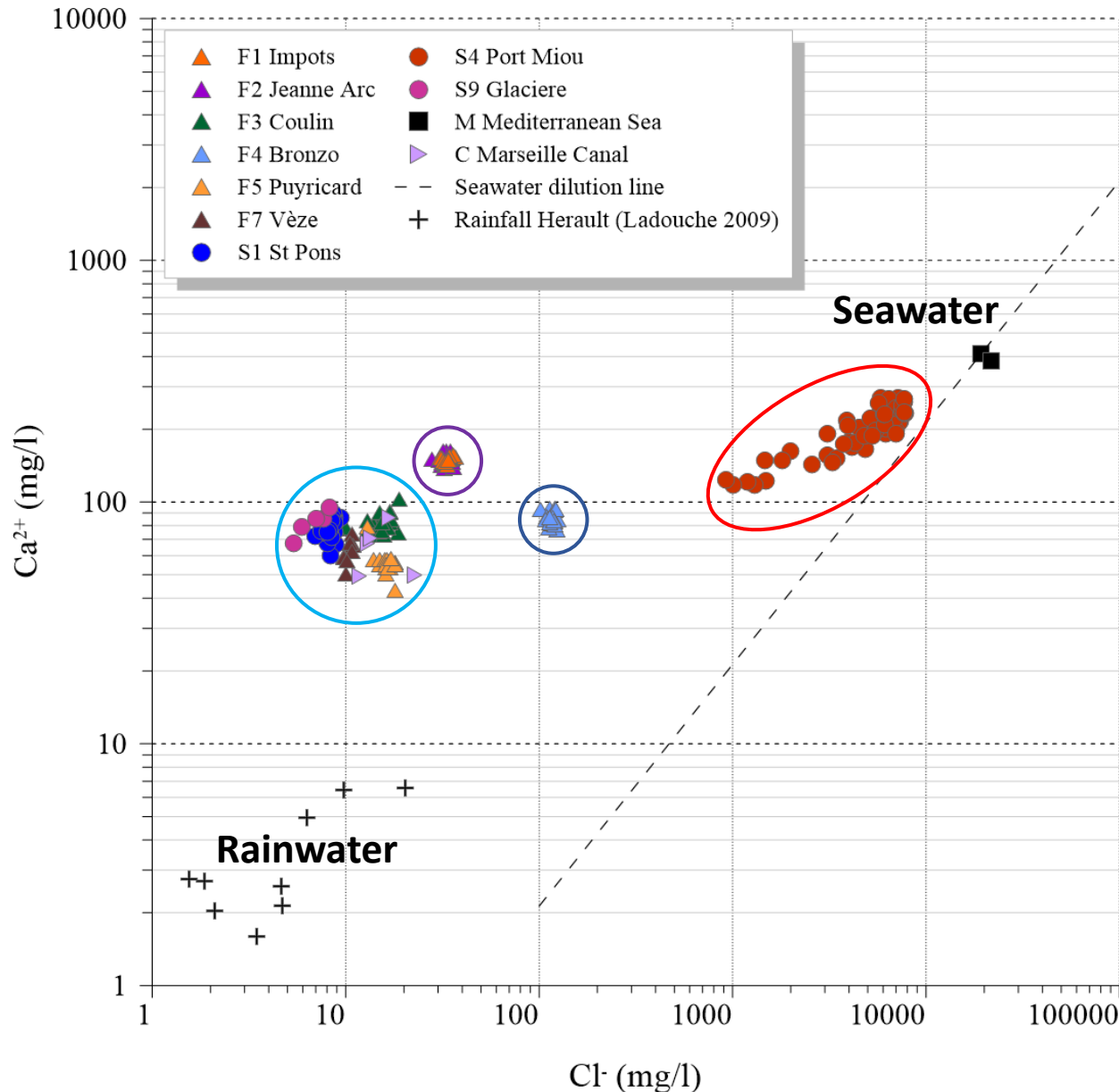
F4 Bronzo – influence of NaCl on GW Saline intrusion ?

Boreholes in alluvial plain

Karstic springs and boreholes positioned in carbonate reservoir

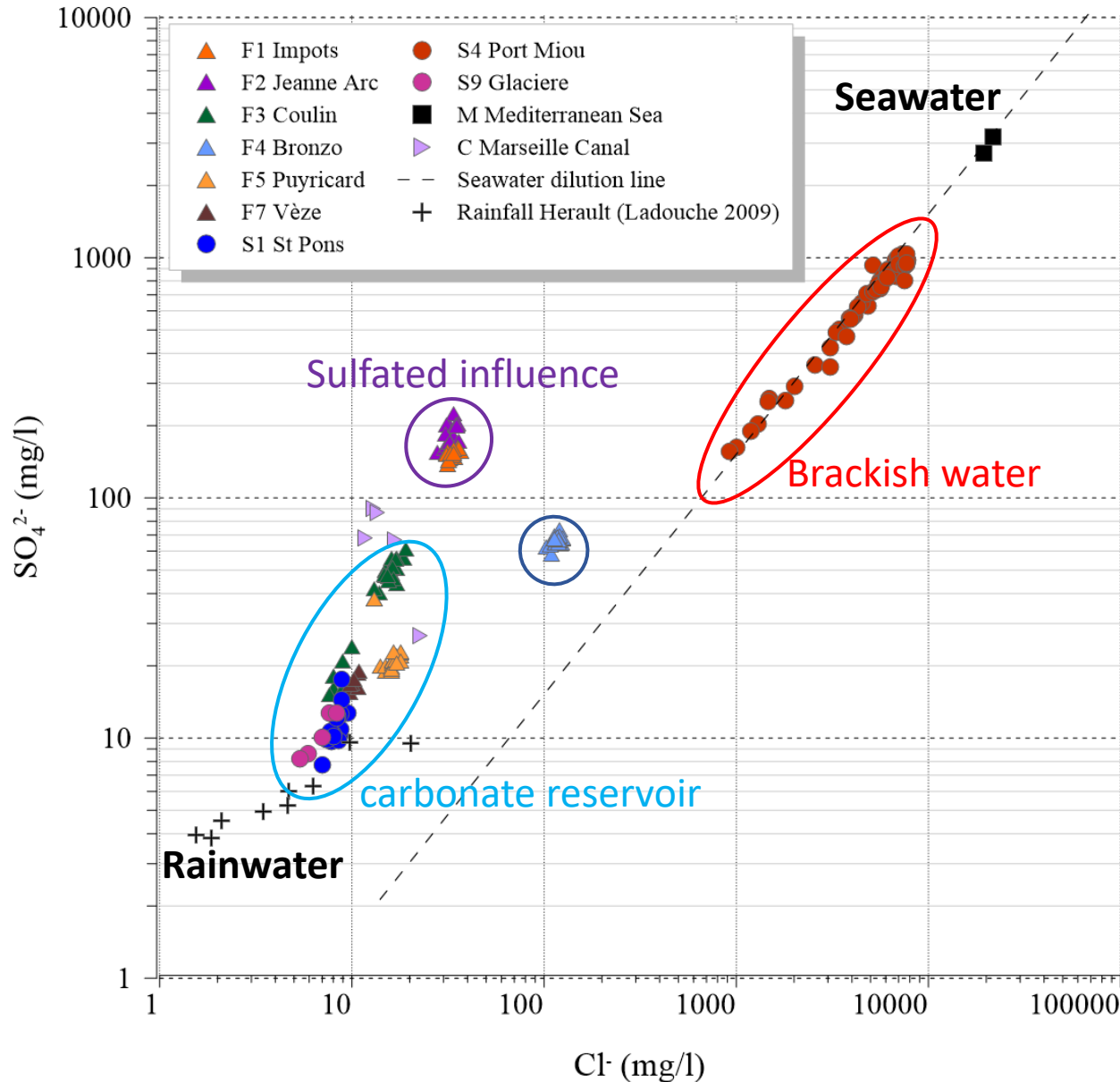
Water from irrigation open channel comes from Durance River with Alpine origin ("Marseille canal")

Enrichment in calcium



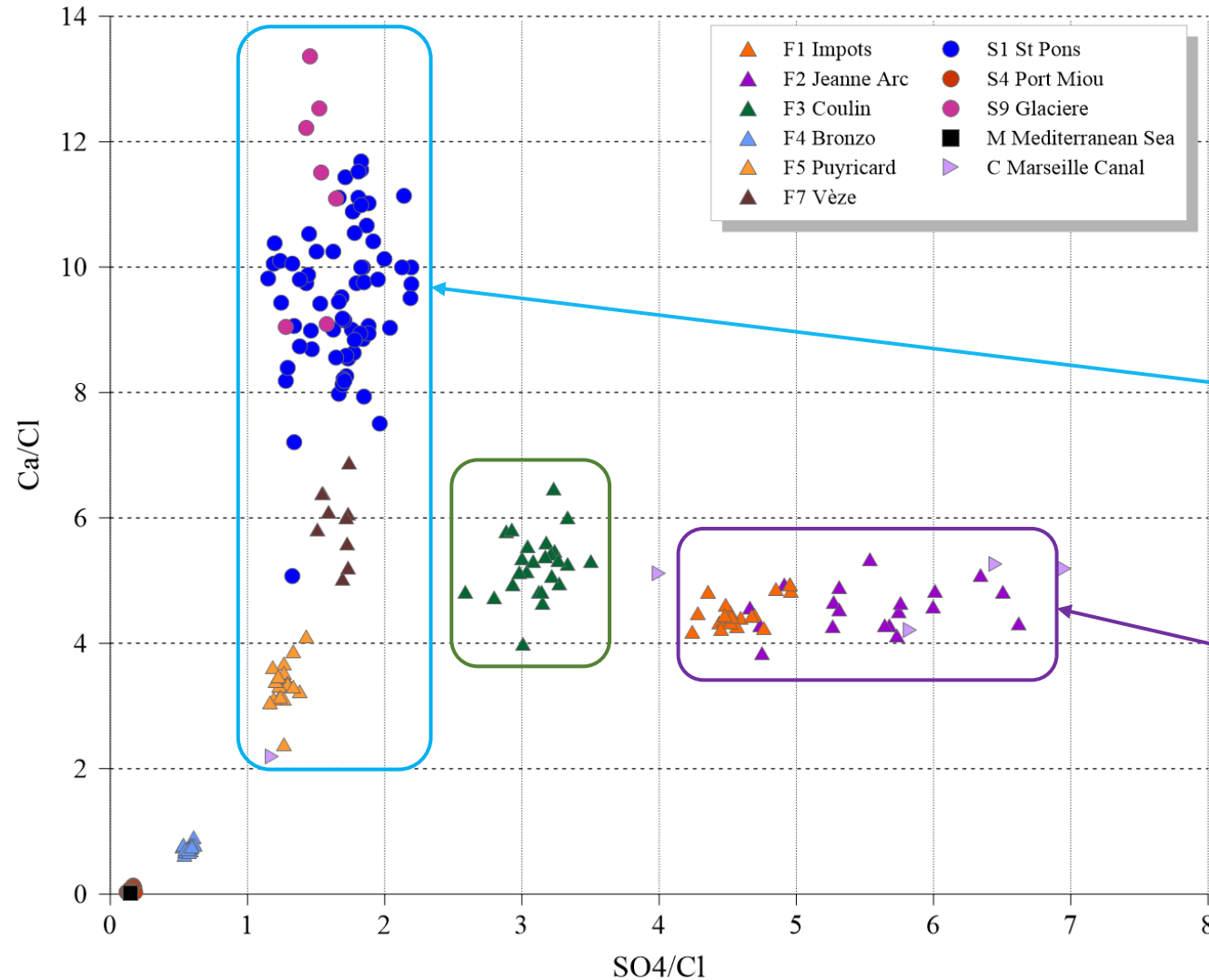
- Identification of 4 groups of GW based on these diagrams – Ca vs Cl
 - Enrichment in calcium for all GW
 - Distribution similar for magnesium and strontium (*not showed here*)
- ➔ Major ions to distinguish water-rocks interactions
- Distinction between karstic springs or boreholes and alluvial plain from calcium concentration
 - Ca/Cl binary diagram suggests mixing between GW and SW for F4 Bronzo

Enrichment in sulfate



- **Sulfate ion to identify influence from gypsum reservoir**
- High enrichment on GW sampled on the alluvial plain (F1, F2)
➔ Hydrogeological relationship between the alluvial plain and the Triassic gypsum found upstream
- High dispersion of chemical composition of karstic springs and carbonate boreholes

Mixing process based on major ions



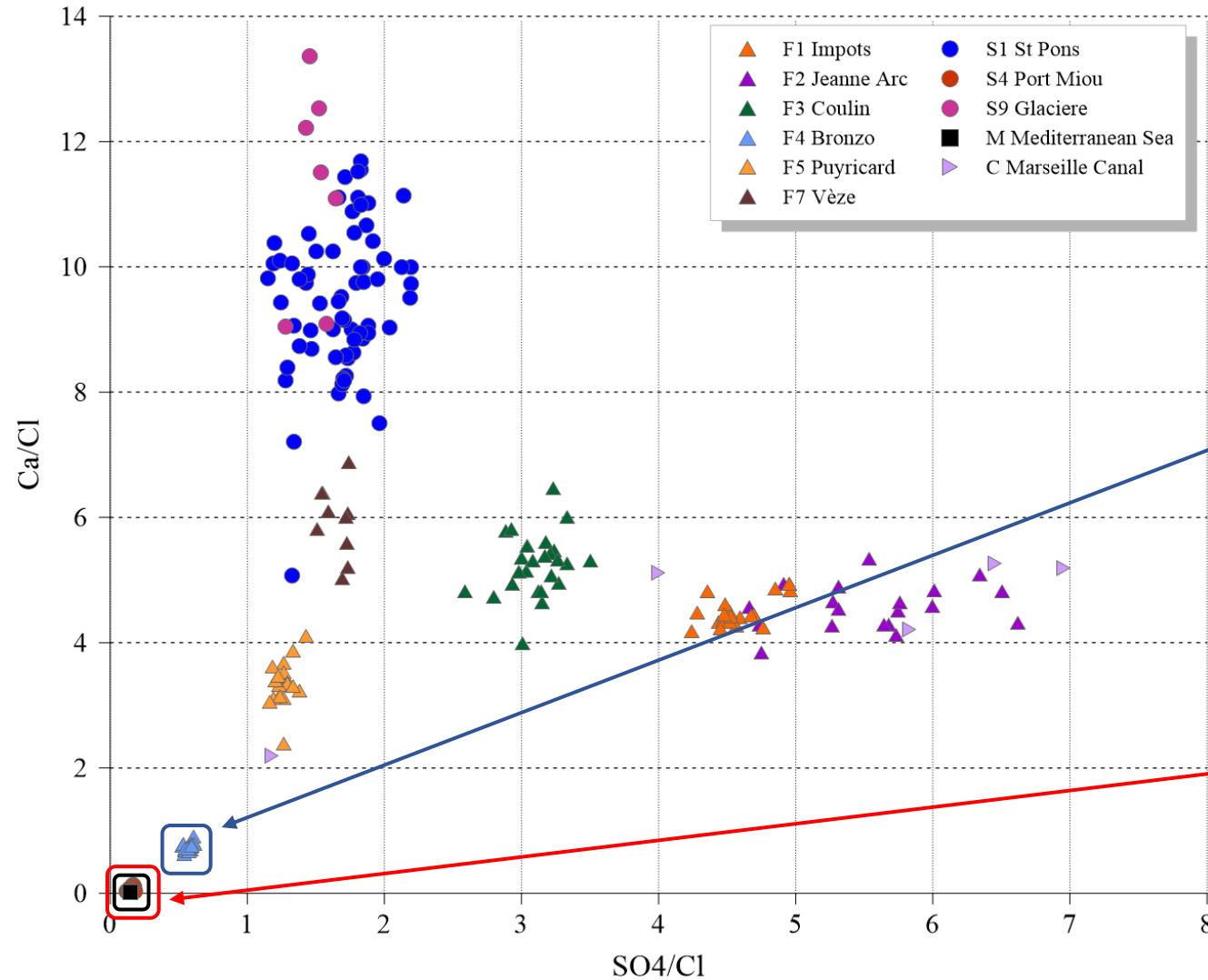
- **Molar ratio to identify mixing waters from distinct geological reservoirs and to discriminate chemical composition of sampling sites**
- The previous groups appears clearly with more dispersion for each sites

→ High dispersion of calcium for the karstic and carbonate samples associated with varying recharge from calcitic to dolomitic reservoir

→ High dispersion of sulfate on the alluvial plain from gypsum reservoir

One exception with F3 Coulin which appears as a mixing of carbonate and sulfated GW

Mixing process based on major ions



- **Qualitative information on the hydrogeological functioning**

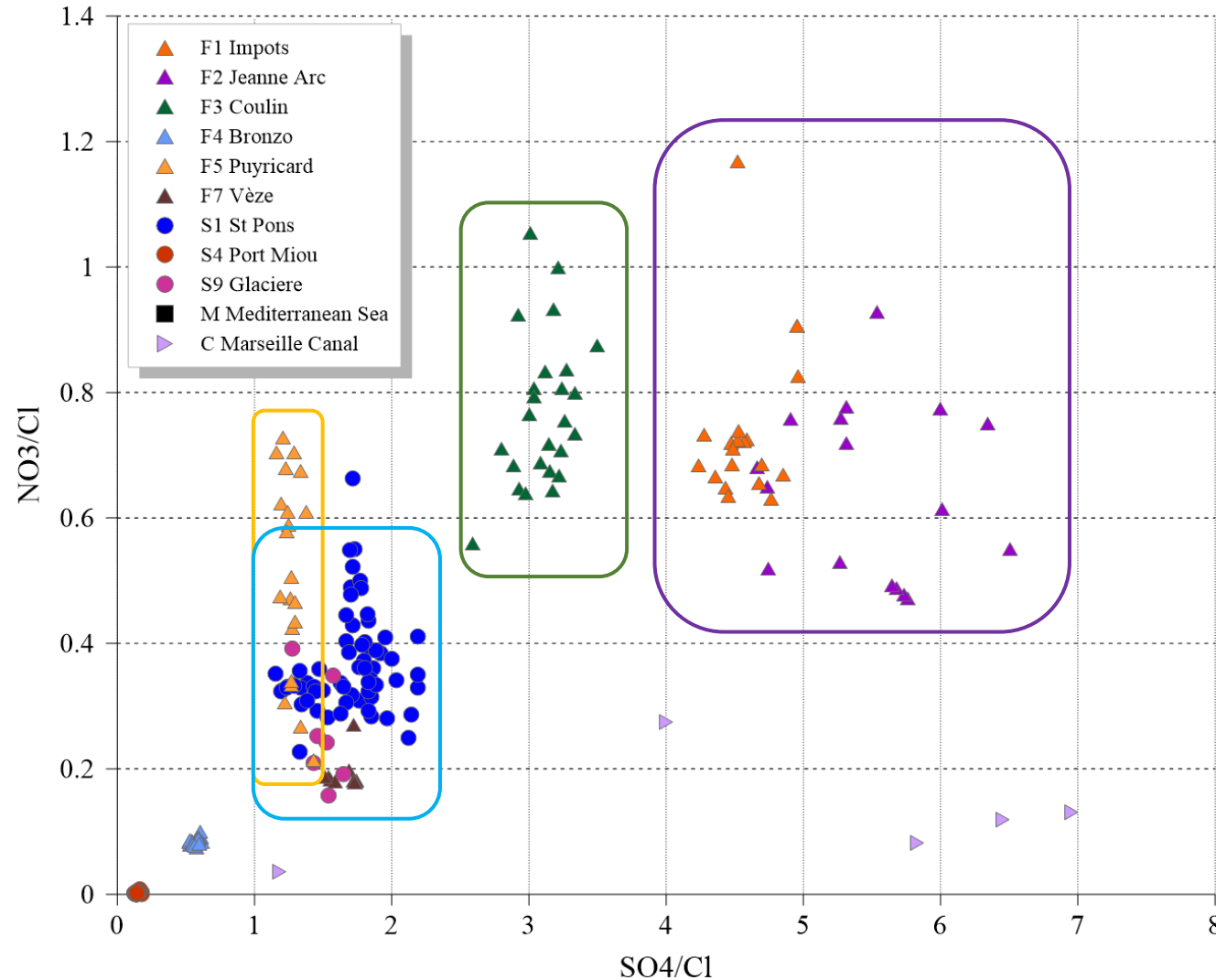
- No variation of Ca/Cl vs SO₄/Cl for F4 Bronzo

 → Indicated a large reservoir capable of buffering the chemical composition of GW

- S4 Port-Miou and seawater

  → Chemical composition of S4 is correlated to the chemical composition of seawater

Anthropogenic influence on GW



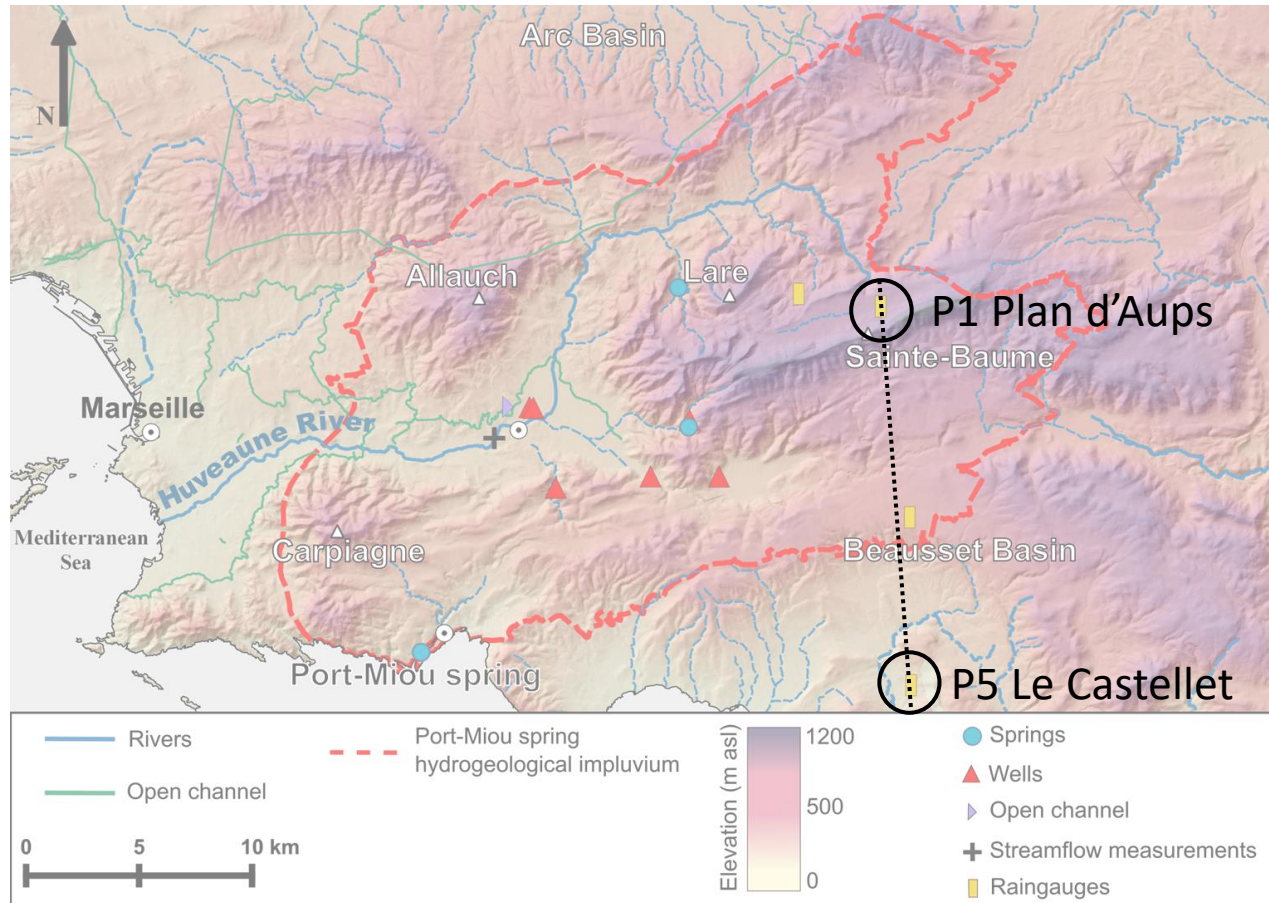
- Nitrate to indicate anthropogenic influence through agricultural practices

 F5 Puyricard and F3 Coulin → high variation of NO_3/Cl that indicate varying inputs of nitrates during time

 S1, S9 and F7 → few influence from NO_3 or SO_4 indicate no mixing from reservoir marked by these ions

 F1 and F2 → high variation of NO_3/Cl and SO_4/Cl that indicate mixing between sulfated reservoir and anthropogenic influence
Potential influence of water from irrigation canal

Rainwater stable isotopic composition



- **Qualification of rainwater isotopic composition ($\delta^{18}\text{O}/\delta^2\text{H}$) in two contrasted sampling sites**

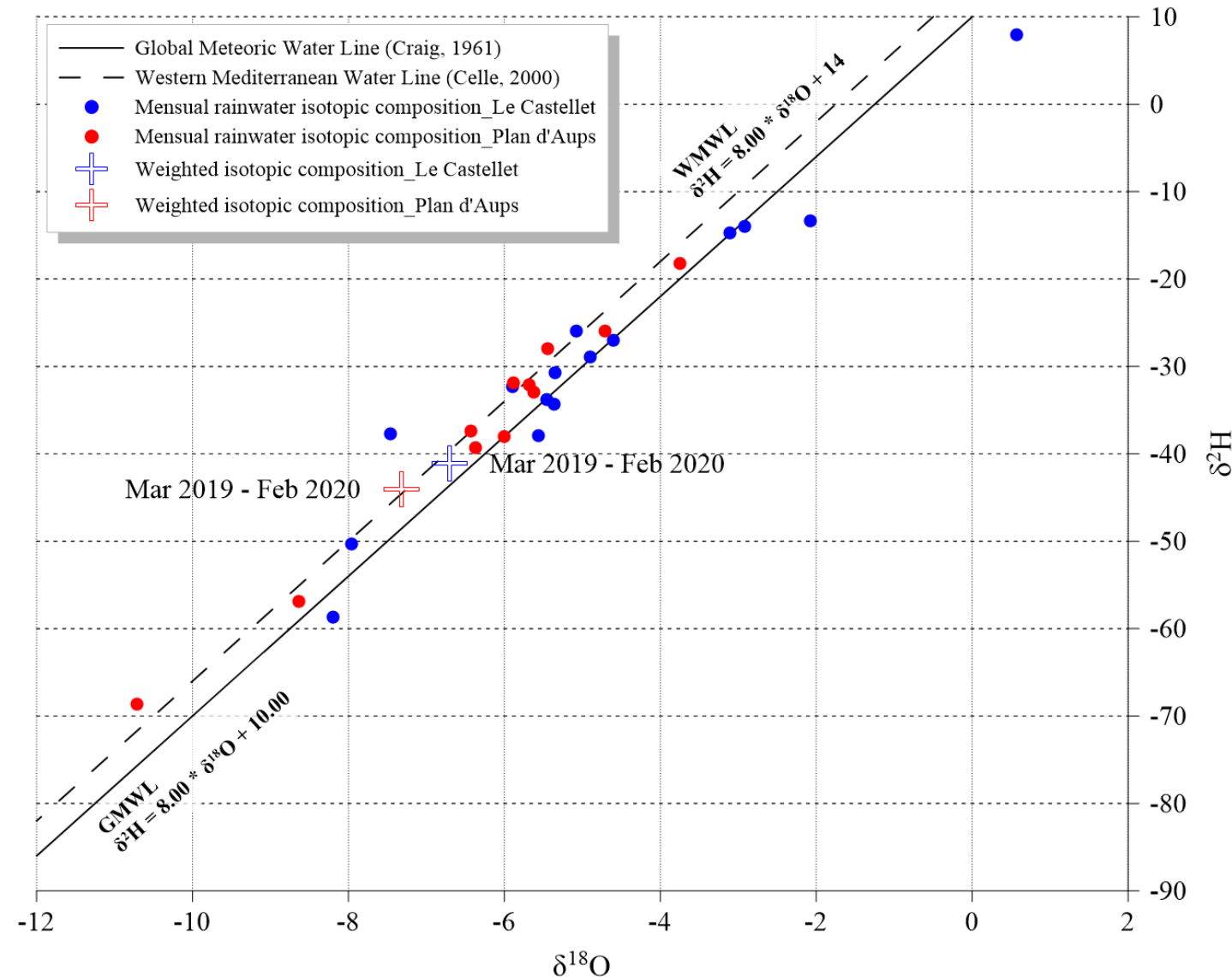
- Plan d'Aups
 - 682 m asl
 - North of Sainte Baume range (1200 m asl)
 - About 20 km from the sea
- Le Castellet
 - 103 m asl
 - About 8 km from the sea



..... North-South altimetric profile

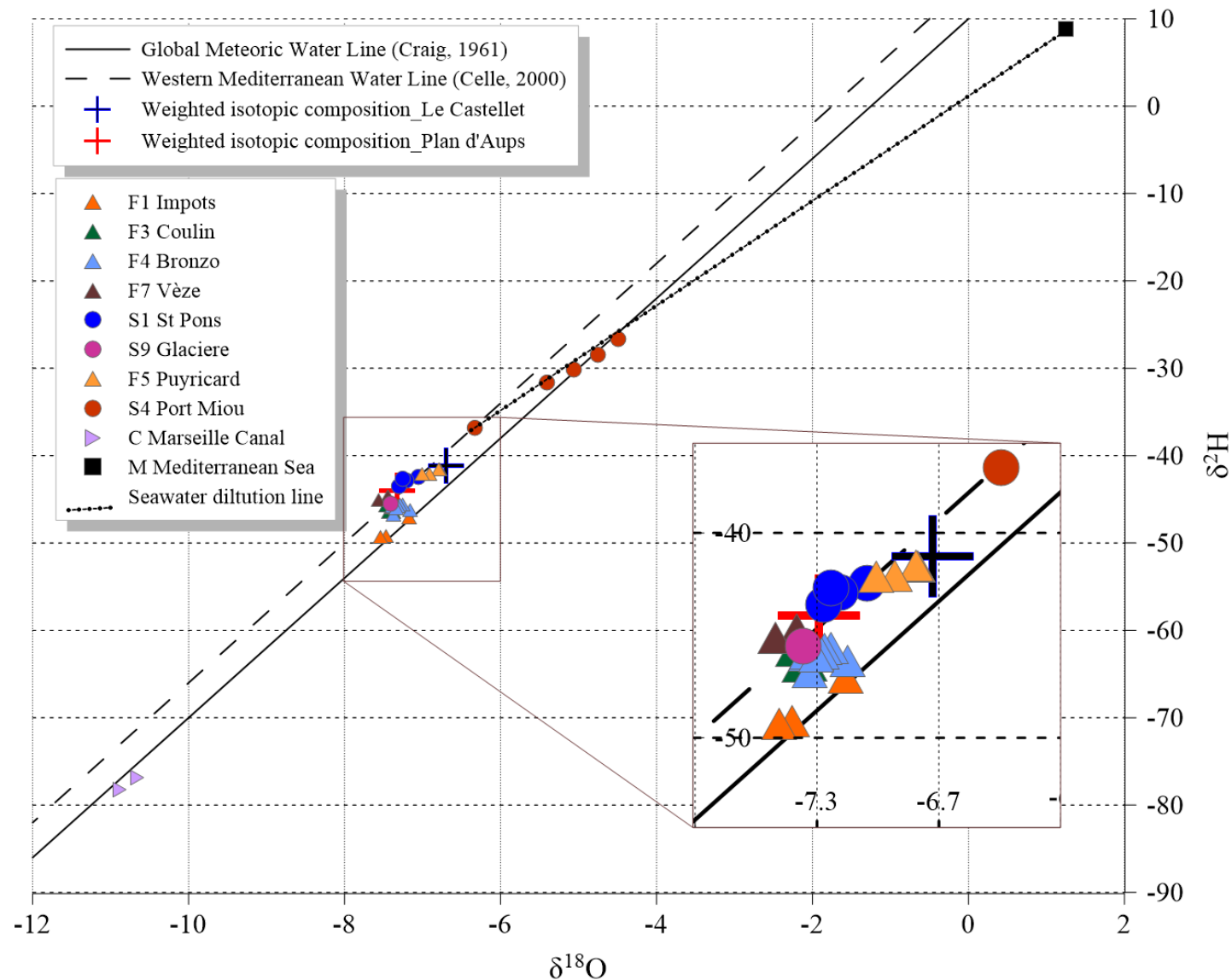


Rainwater weighed isotopic composition



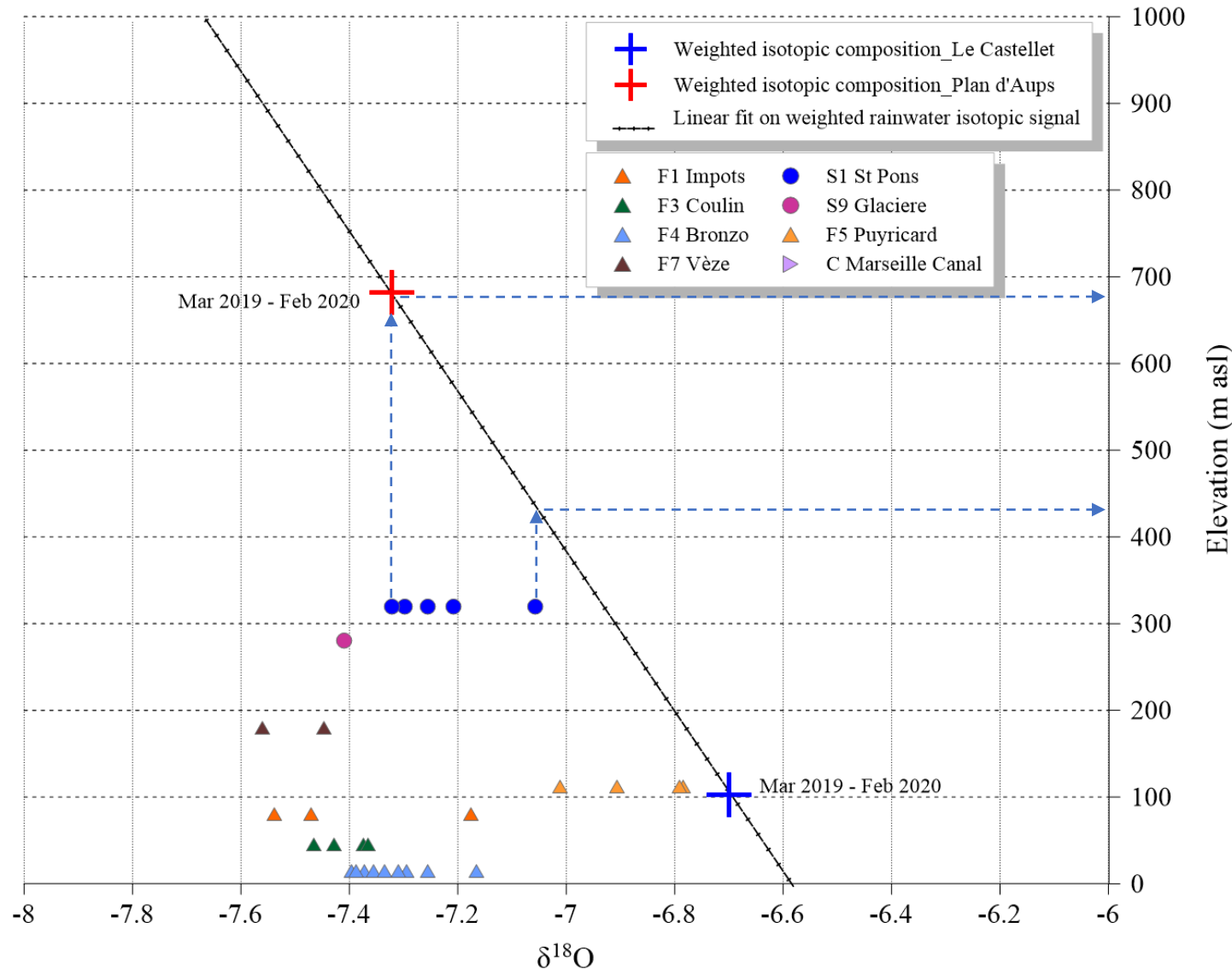
- **Qualification of rainwater isotopic composition in two contrasted sampling sites**
- **Monthly stable isotopic composition of rainwater ($\delta^{18}\text{O}/\delta^2\text{H}$) (blue and red dot)**
- **Enrichment in stable isotope in summer and impoverishment in winter with strong rainfall**
- (1) Use of ESPERE tool (Lanini et al, 2016) to calculate the effective rain and (2) calculation of a weighted effective rain isotopic signal on two stations (March 2019 – February 2020)
 - Plan d'Aups → $P_{\text{eff}} = 787 \text{ mm}$; $\delta^{18}\text{O} = -7.3 \text{ ‰}$; $\delta^2\text{H} = -44 \text{ ‰}$
 - Le Castellet → $P_{\text{eff}} = 406 \text{ mm}$; $\delta^{18}\text{O} = -6.7 \text{ ‰}$; $\delta^2\text{H} = -41 \text{ ‰}$

GW isotopic composition related to rainwater



- S4 (Port-Miou) enrichment link to the influence of SW (*dark dotted line*)
- F1 situated on the alluvial plain is on the GMWL
- ➔ Influence from irrigation open channel (Marseille canal)
- GW link to high elevation recharge

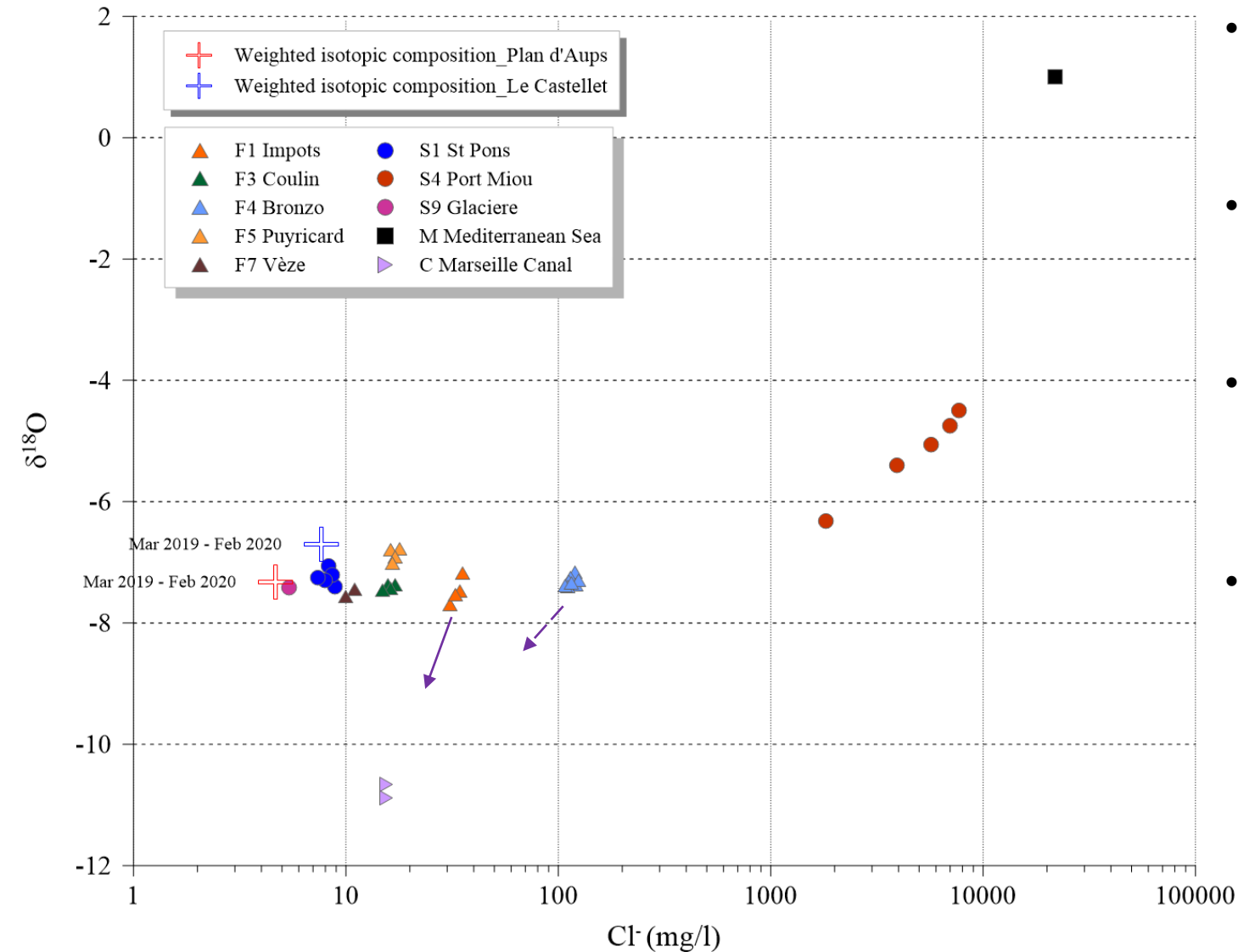
GW isotopic composition with elevation



- GW affected by high elevation recharge impluvium (S1, S9, F3, F4, F7)
- Elevation gradient for weighted effective rain for oxygen 18 = -0.11 ‰ / 100 m
- Utilization of $\delta^{18}\text{O}$ vs elevation to estimate the altitude of the recharge zone of the water sample (borehole/spring)
 - Example with S1 St Pons → 430-670 m asl

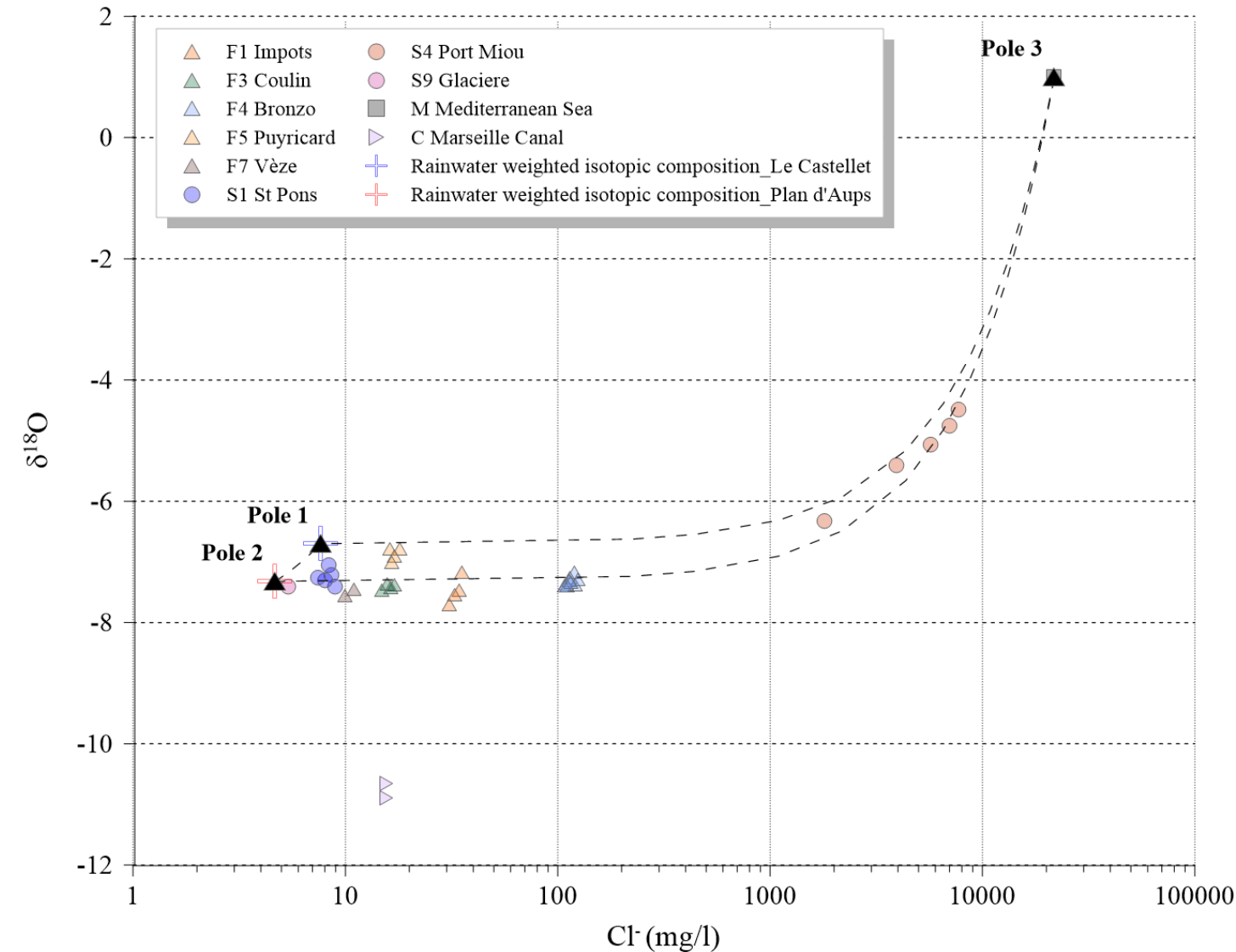


Mixing process between rainwater and seawater



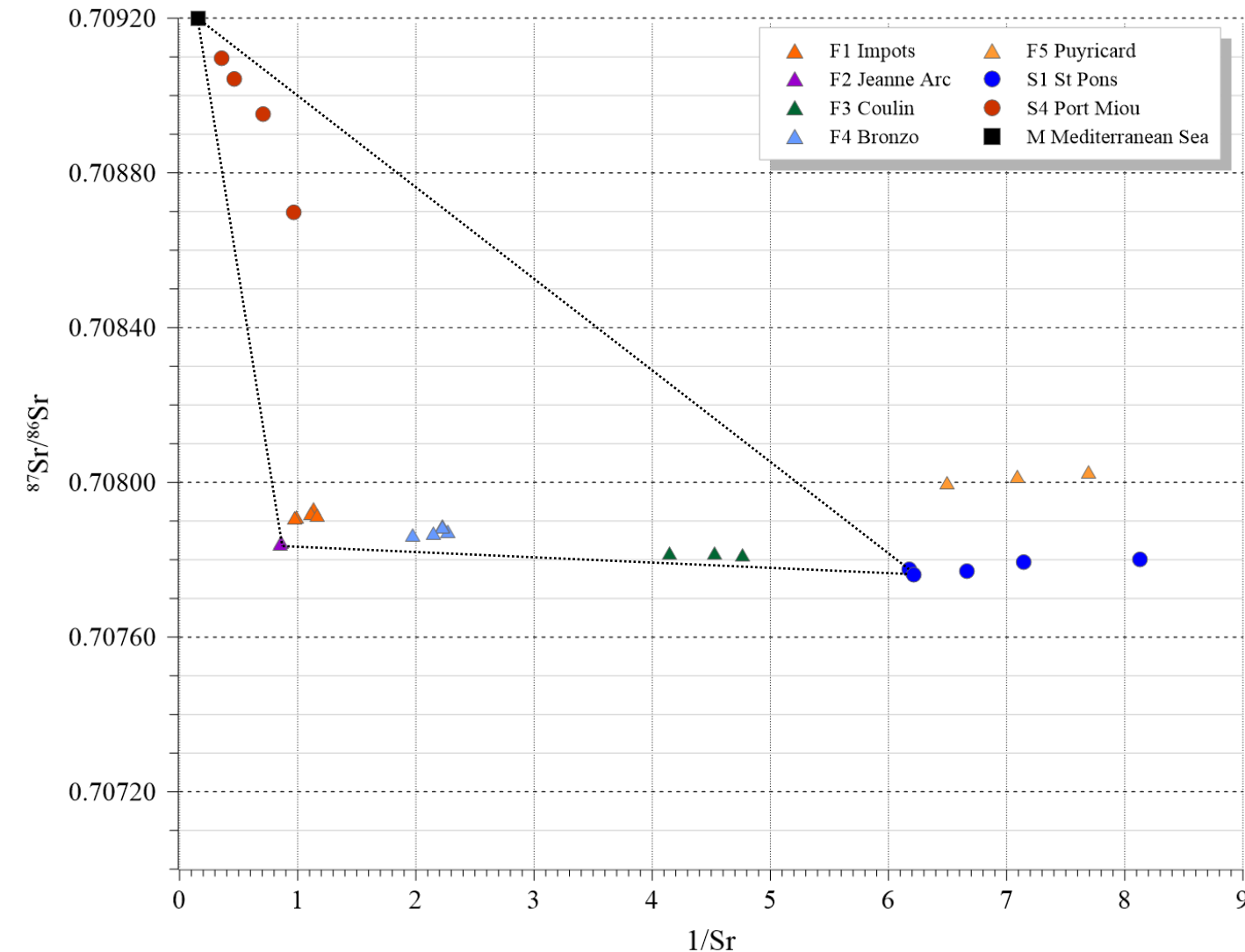
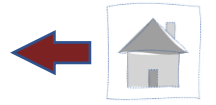
- **GW isotopic composition associated with chloride**
- F5 Puyricard seems influenced by rainwater slightly enriched, from lower recharge area
- Isotopic signature of F1 Impots seem to be influenced by irrigation water from the Marseille Canal – through agricultural practices on the alluvial plain (*purple line*)
- F4 Bronzo, probable influence by irrigation water (*dash purple line*)

Mixing process between rainwater and seawater



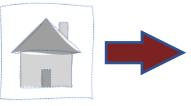
- The stable isotopic composition measured at the outlet (S4-Port-Miou) can be explained with mixing process between rainwater and Mediterranean seawater
- Two rainwater endmember are considered from the two specific sampling sites and representing the elevation variation on a regional scale
 - endmember 1 – rainwater from “Le Castellet” – representative of low elevation rainfall in the south of the study area
 - endmember 2 – rainwater from “Plan d’Aups” – representative of high elevation rainfall on the carbonate deposits located in the north of the study area

Strontium isotope in GW and SW

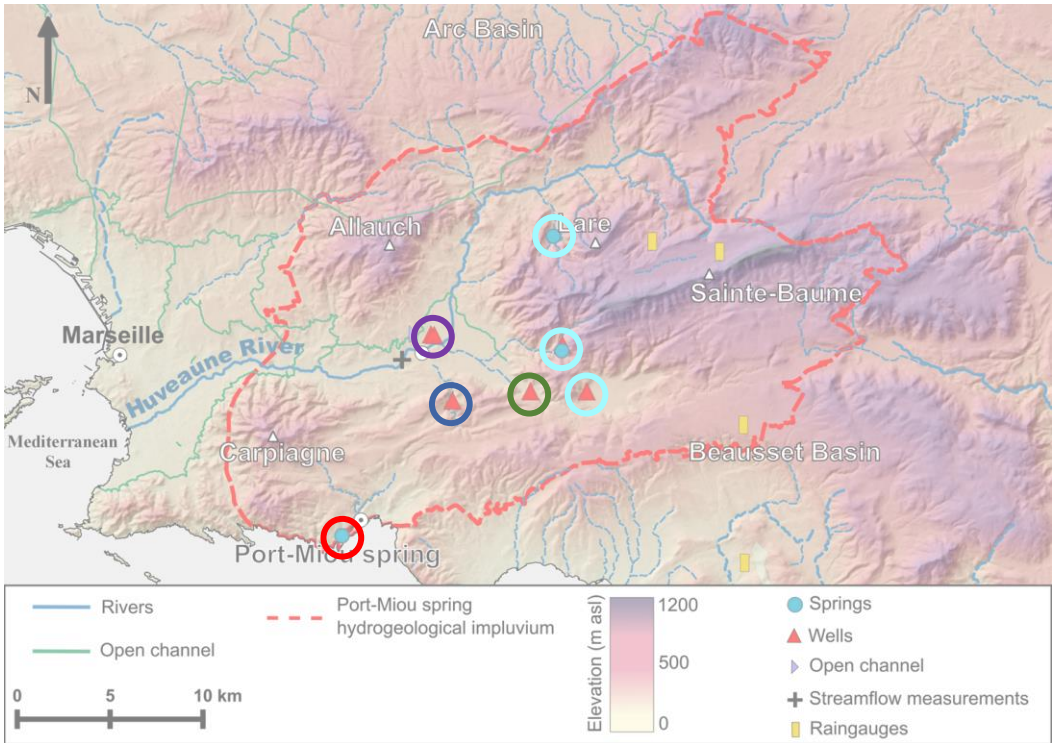
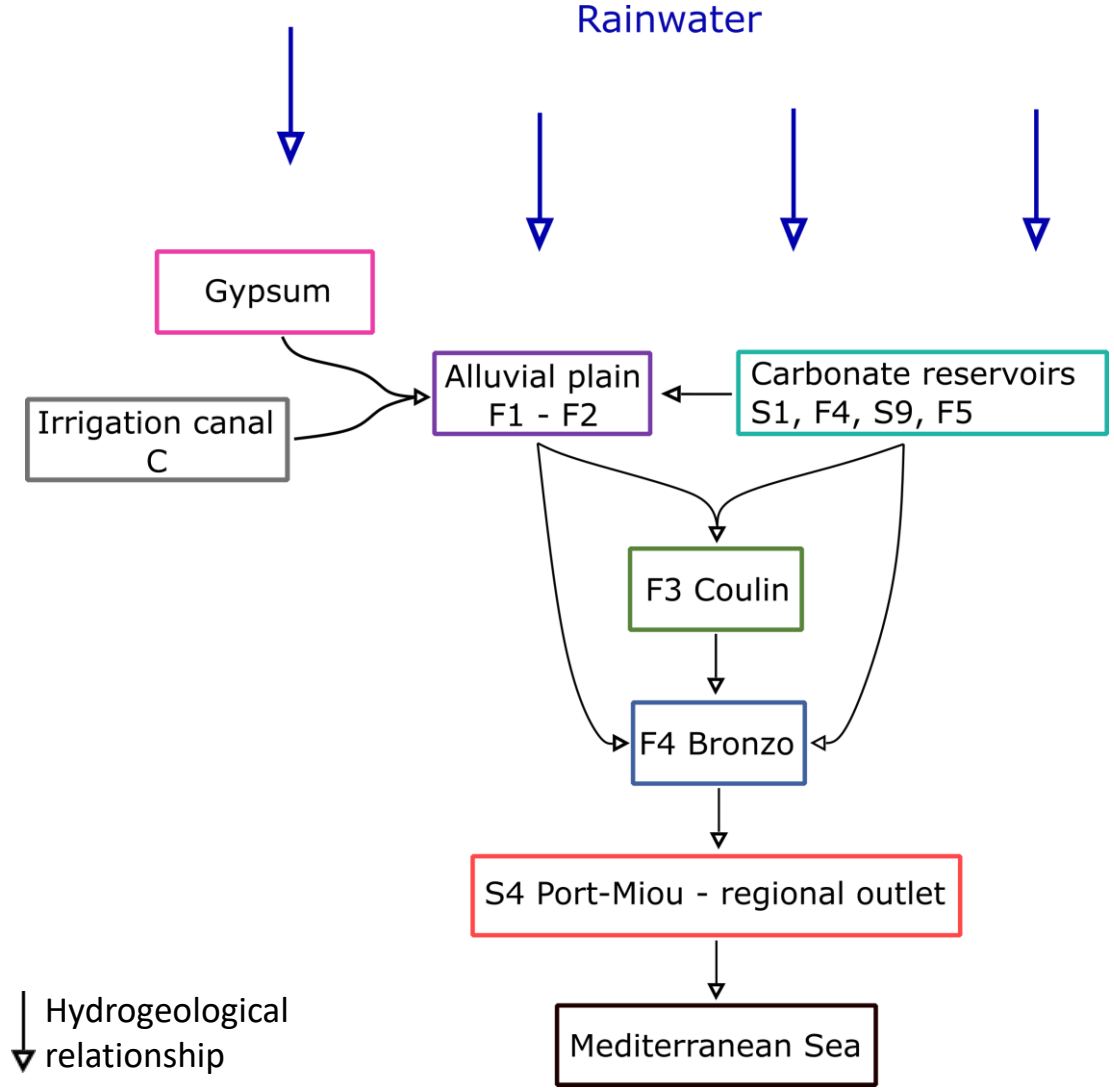


- $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic composition of GW to characterize the reservoirs
- Theoretically groundwater would present disparate isotopic composition acquires from the different reservoir
- Individualization of GW from 1/Sr ratio and $^{87}\text{Sr}/^{86}\text{Sr}$ isotopic ratio
- F4 Bronzo at an intermediate place between carbonate samples (1/Sr > 4) and samples from the alluvial plain (F1 and F2)
- Mixing process possible at three endmember between carbonate sample, alluvial plain and SW to define F4 Bronzo (*in dark dotted line*)



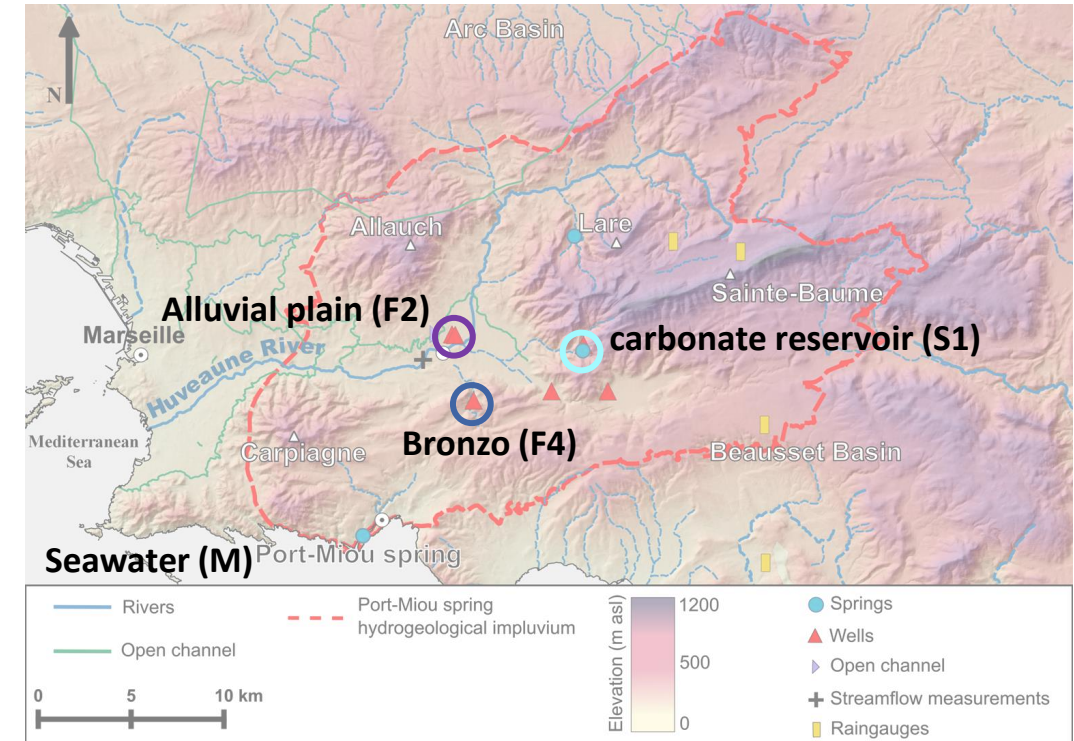
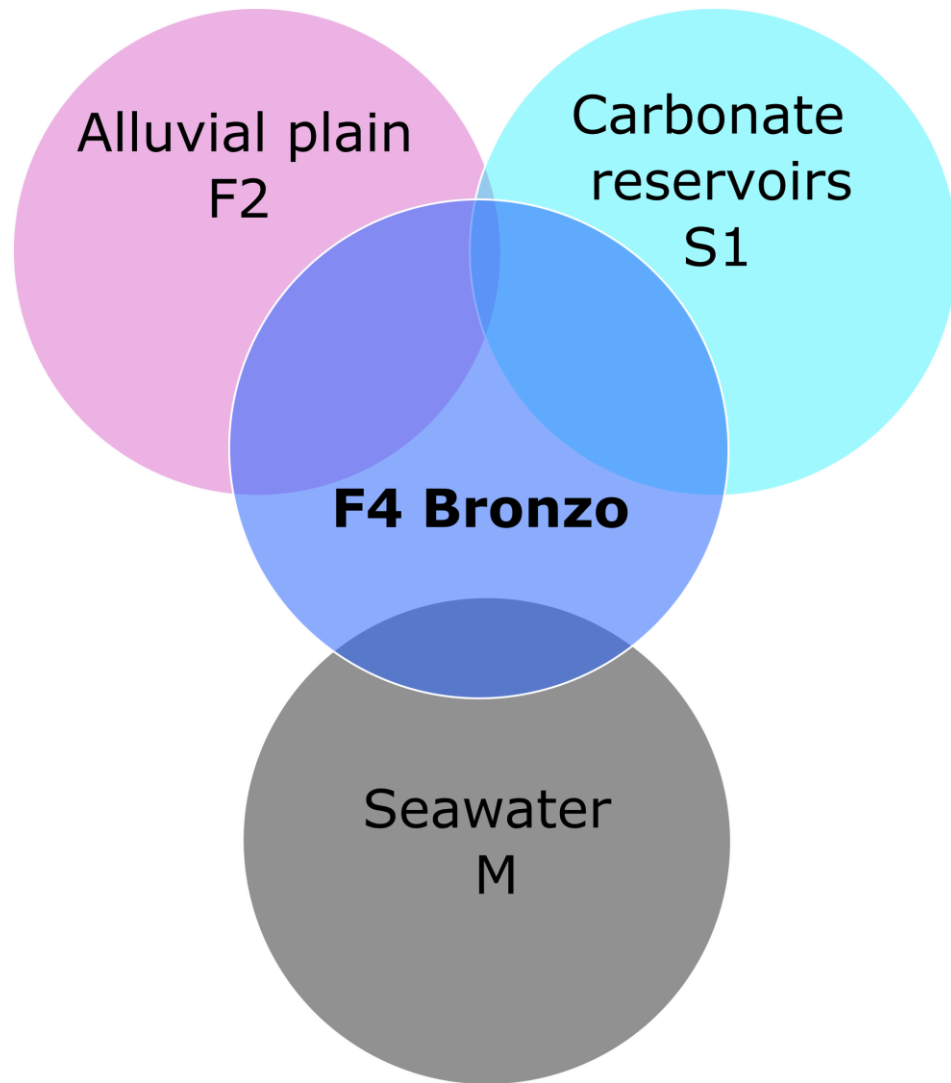


Conceptual model of regional hydrogeological functioning



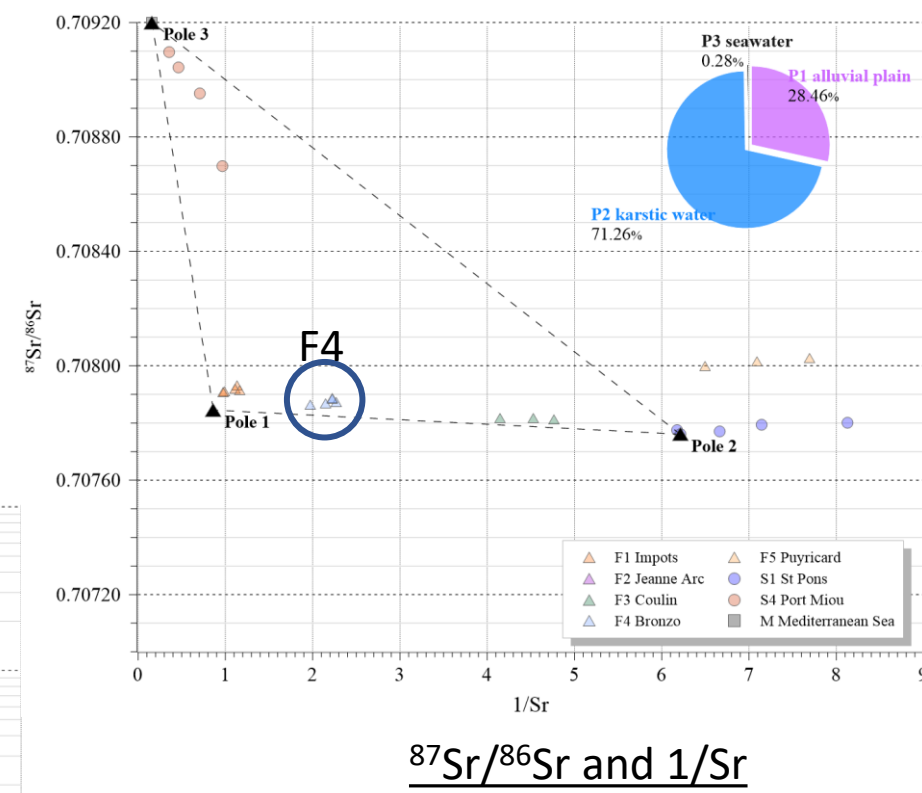
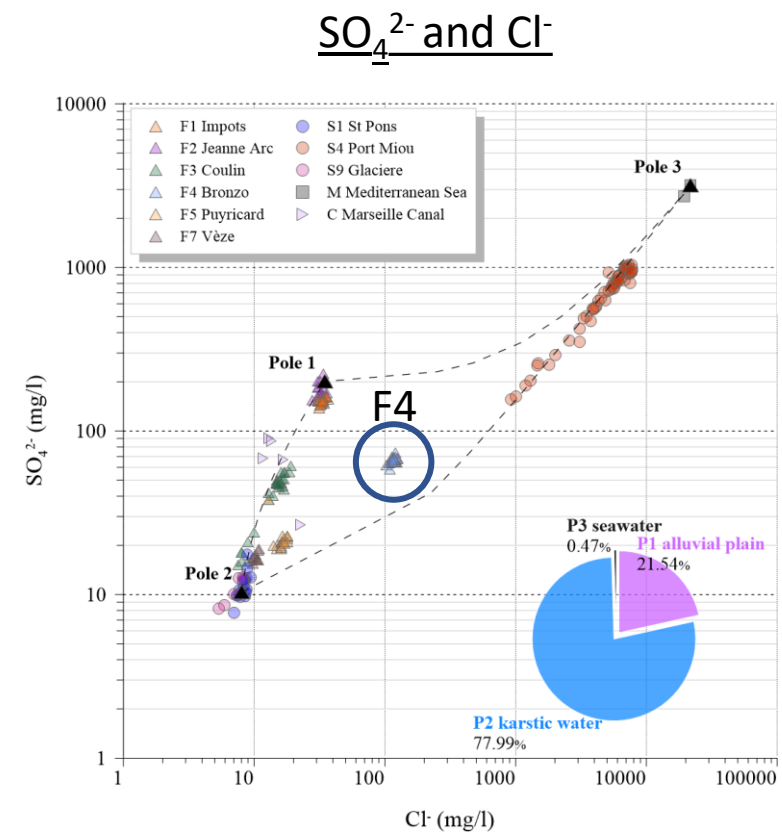
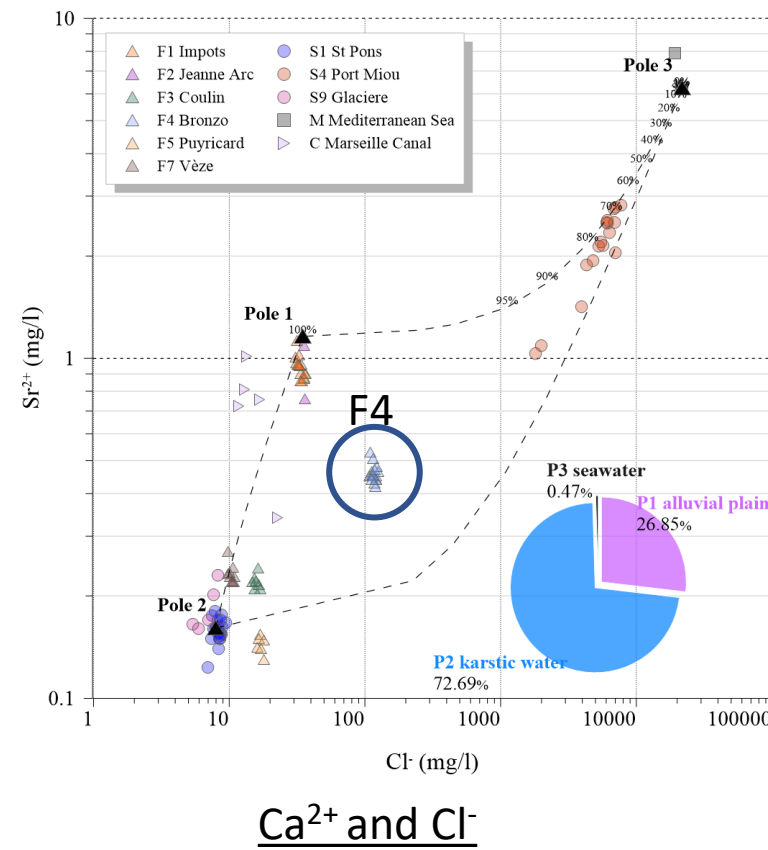
- **Conceptual model of regional hydrogeological functioning**
- **Definition of the endmember characterizing the main reservoirs**
- **Might have few values depending on the hydrological conditions**

Mixing process to characterize F4 Bronzo chemical composition

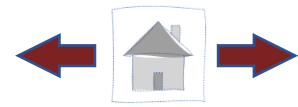


- **Conceptual model regarding mixing process in the borehole F4 Bronzo**
- **Three components**
 - endmember 1 - Sulfated water from the alluvial plain
 - endmember 2 - Karstic water from the Sainte Baume range
 - endmember 3 - Seawater

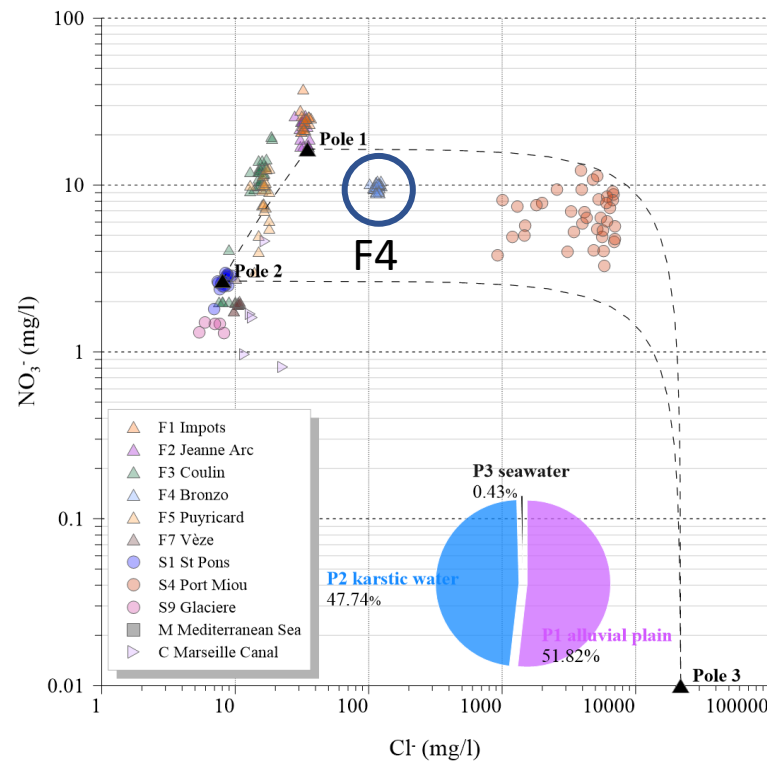
Quantification of mixing process in F4



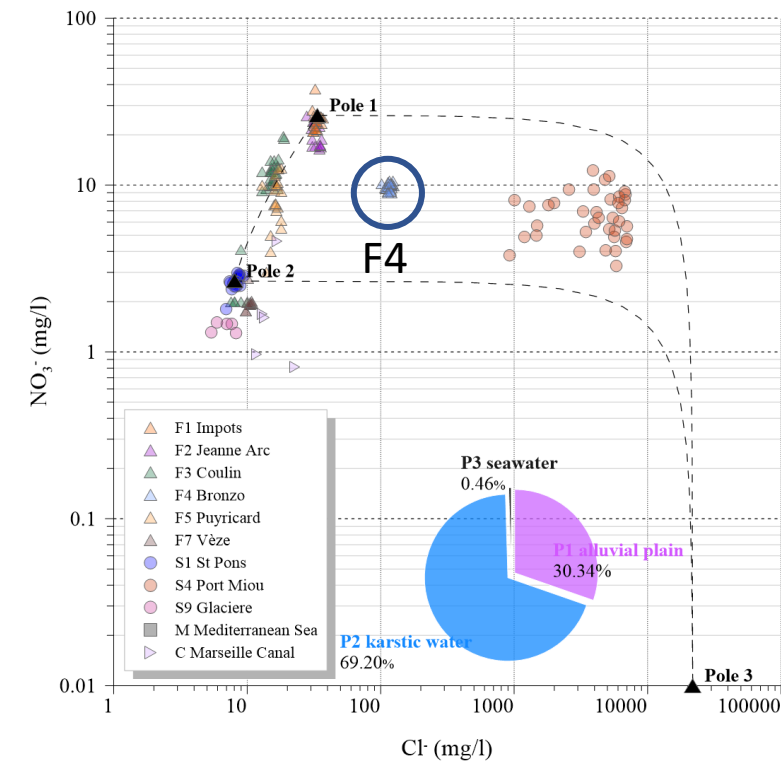
Quantification of mixing process in F4 with nitrate ion



- High variability of $[\text{NO}_3^-]$ in the alluvial plain



NO_3^- and Cl^-



- Considering the same endmember as the previous tracers, the mixing calculation show more than 50% of water coming from the alluvial plain

➔ These results suggest that the alluvial plain contribution to the karst functioning is significantly concentrated in NO_3 (estimate to 30 mg/l).

These results also makes it possible to underline that there is significant spatial variability of the NO_3 contents in the alluvial plain [characterized by multi-layer aquifer, with anthropogenic effect more visible on the upper layer (10 m depth) compare with the deeper groundwater (20-30 m depth)]

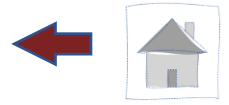
- Selecting an endmember with higher concentration $[\text{NO}_3^-]$ close to 30 mg/l], the percentage of water coming from the alluvial plain is about 30% (same magnitude with other tracers Cl , SO_4 and Sr)

Conclusion and perspective

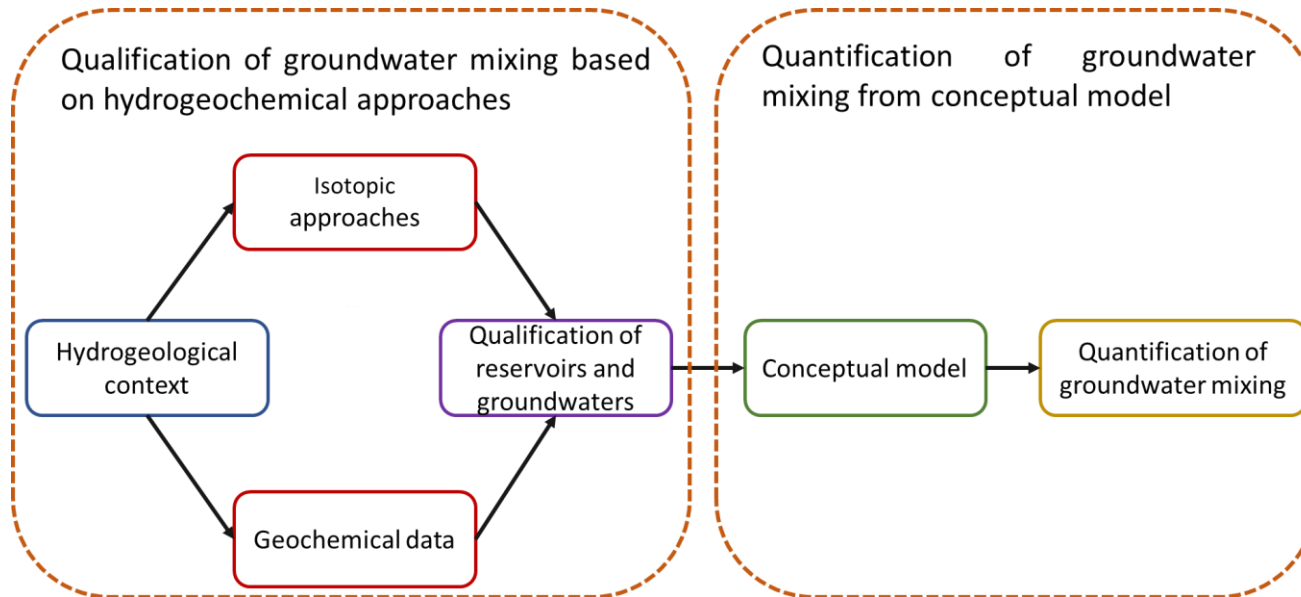


- **Consistency of quantification calculation** from the others representative tracers (Cl^- ; Sr^{2+} , SO_4^{2-} , $^{87}\text{Sr}/^{86}\text{Sr}$)
- **Nitrate ion**, as a proxy of anthropogenic activities, should be associated with local GW flows to identify a representing endmember
- **Quantification of GWs mixing bring some constraining information and allow us to ascertain the conceptual model** with :
 - Proportion of GWs
 - Impluvium elevation
 - Role of the alluvial plain in the regional GW flows

Conclusion and perspective



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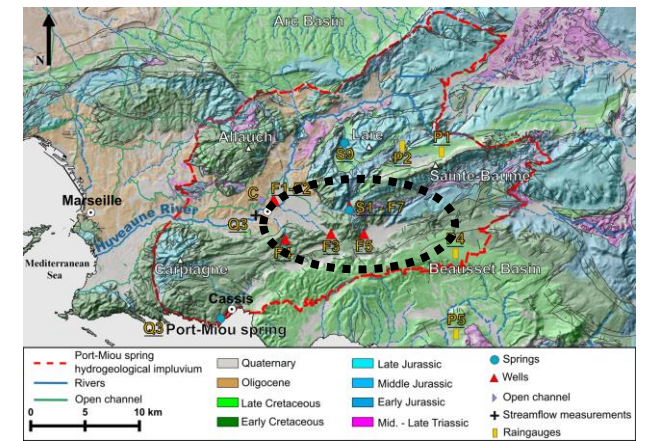


- **Water stable isotopes** ($\delta^{18}\text{O}/\delta^2\text{H}$) as a useful tool to **identify elevation of the impluvium** in fresh GW mixing area (F4 Bronzo) and the regional outlet (S4 Port-Miou spring)
- **Application on water resource management**
 - Highlight the origins of nitrates contamination with hydrogeological relationship between the alluvial plain and the karstic reservoir downstream



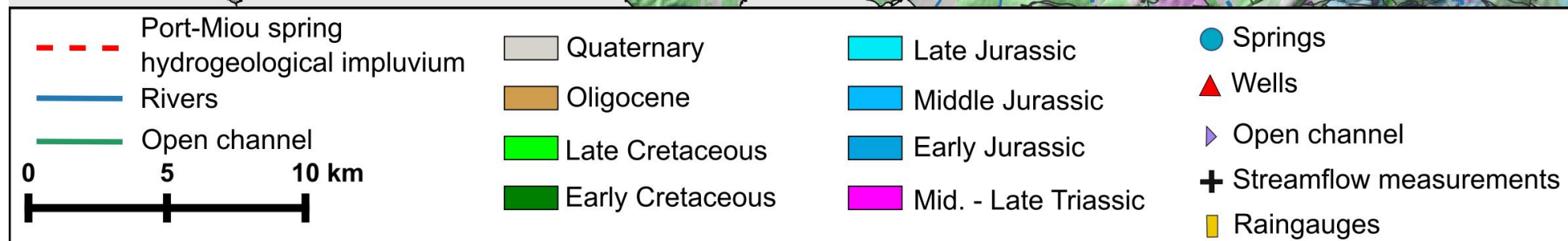
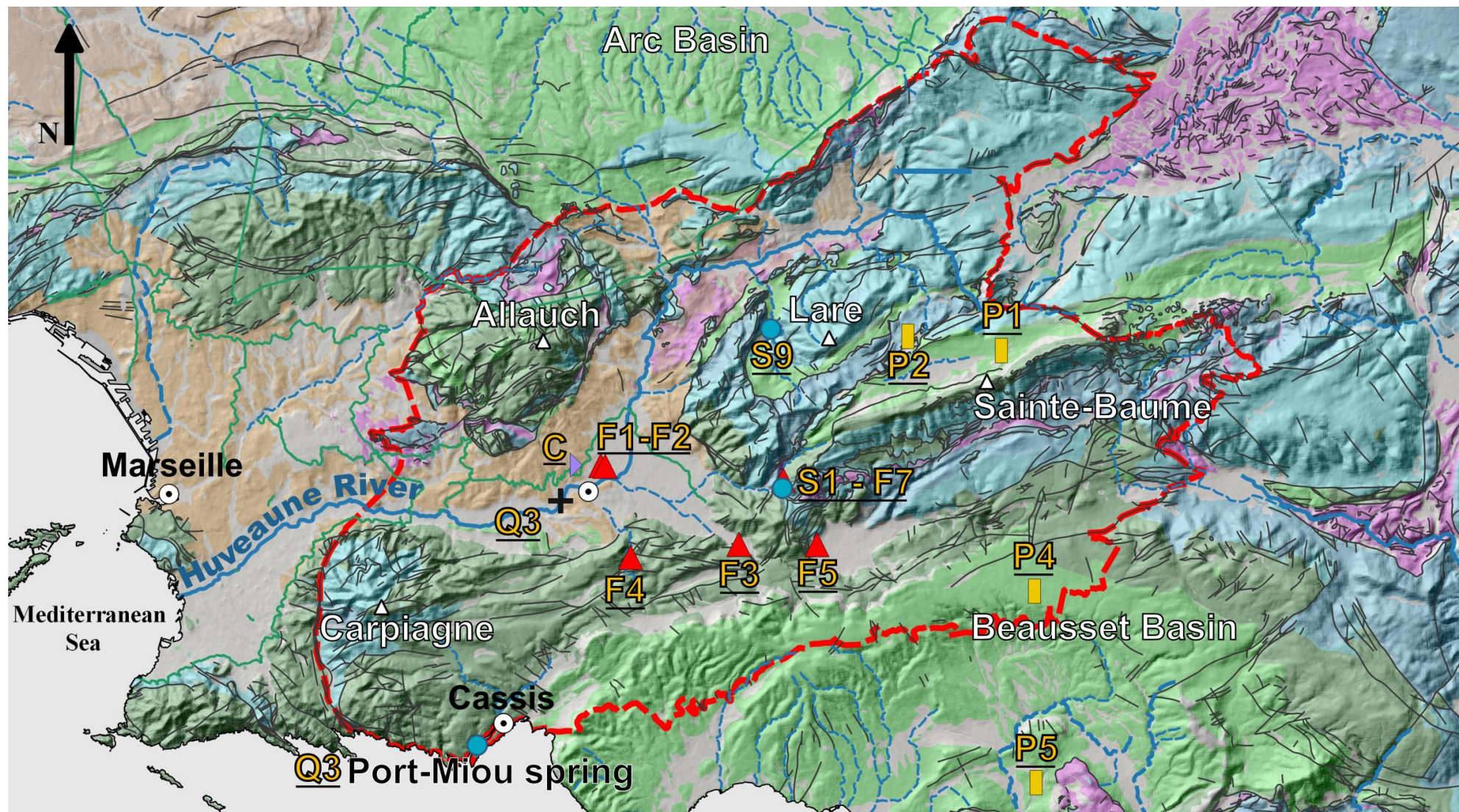
S1 Saint Pons Springs

F1 Impôts borehole



Sainte Baume panorama







Location of the rain gauge P1 « Plan d'Aups Les Béguines »



Rain collector for
qualification of
rainwater stable
isotopic composition

Tipping bucket
rain gauge





T. Garin
(16/03/2021)



Strontium isotopes – chemistry preparation in clean room