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# CHARACTERIZATION OF THE MAIN KARST AQUIFERS OF THE MIDDLE VALSERIANA (NORTHERN ITALY) BASED ON ISOTOPIC AND HYDROGEOCHEMICAL DATA: NOSSANA AND PONTE DEL COSTONE SPRINGS

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HYDROGEOCHEMISTRY, GROUNDWATER AGE,  
PALEOGROUNDWATER AND ISOTOPES IN HYDROGEOLOGY

X SEPTEMBER 2021

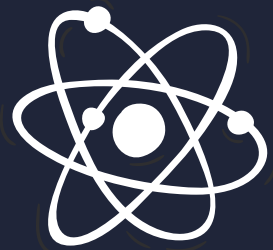


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# Study Goals



Chemical-physical characterization



Isotopic  
characterization



Residence time  
estimation



Definition of the internal dynamics  
of the two water systems



# Study Area

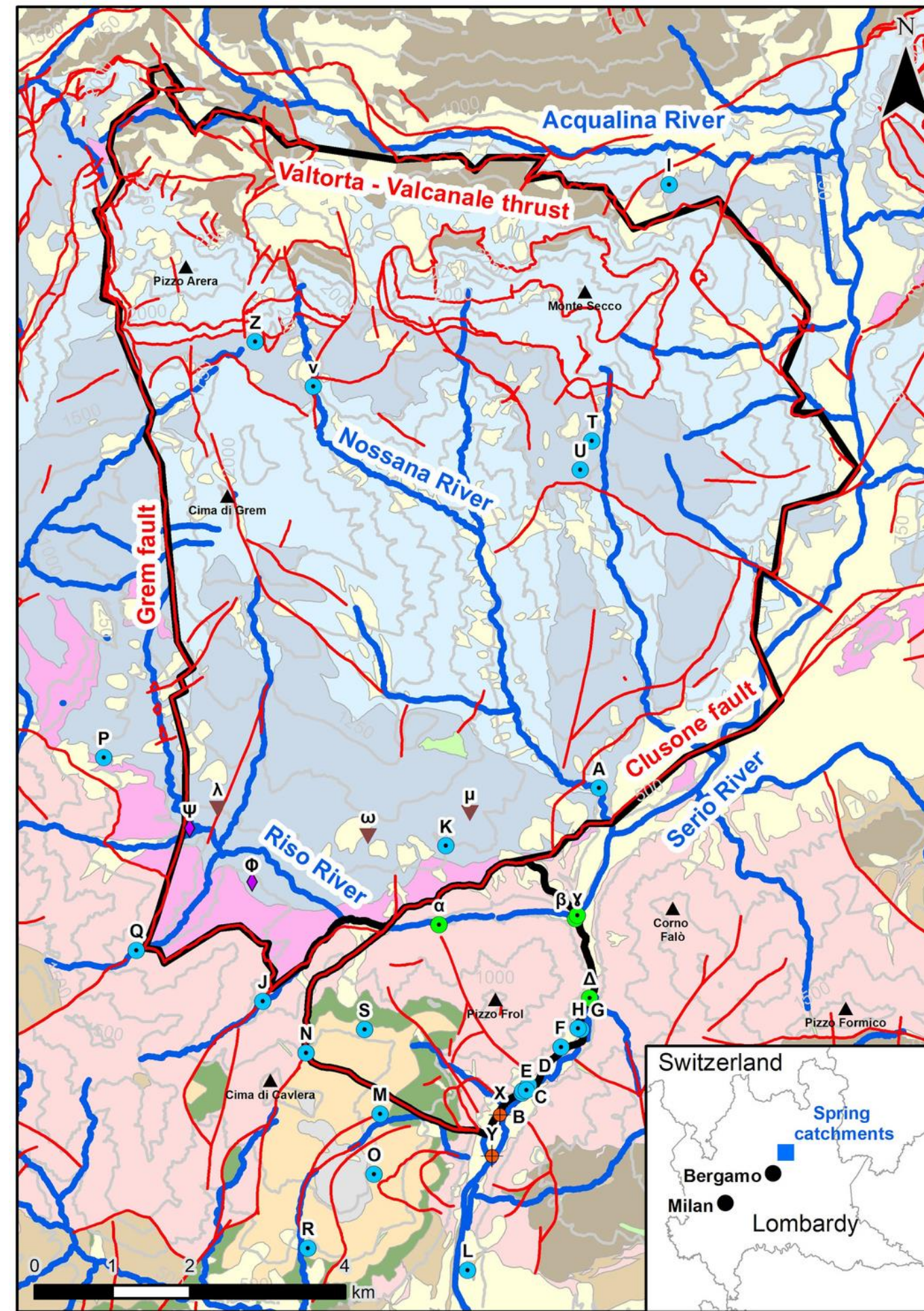
- The springs are located in Northern Italy, in the **Central Pre-Alps** within the Province of Bergamo, Lombardy Region
- **Nossana** catchment: **80 km<sup>2</sup>**
- **Ponte del Costone** catchment: **10 km<sup>2</sup>**
- **High differences in altitude**, from 427 m a.s.l. (Ponte del Costone Springs) to 2512 m a.s.l. (Pizzo Arera mountain).



Characterization of the main karst aquifers of the middle Valseriana (Northern Italy) based on isotopic and hydrogeochemical data: Nossana and Ponte del Costone springs

# Study Area

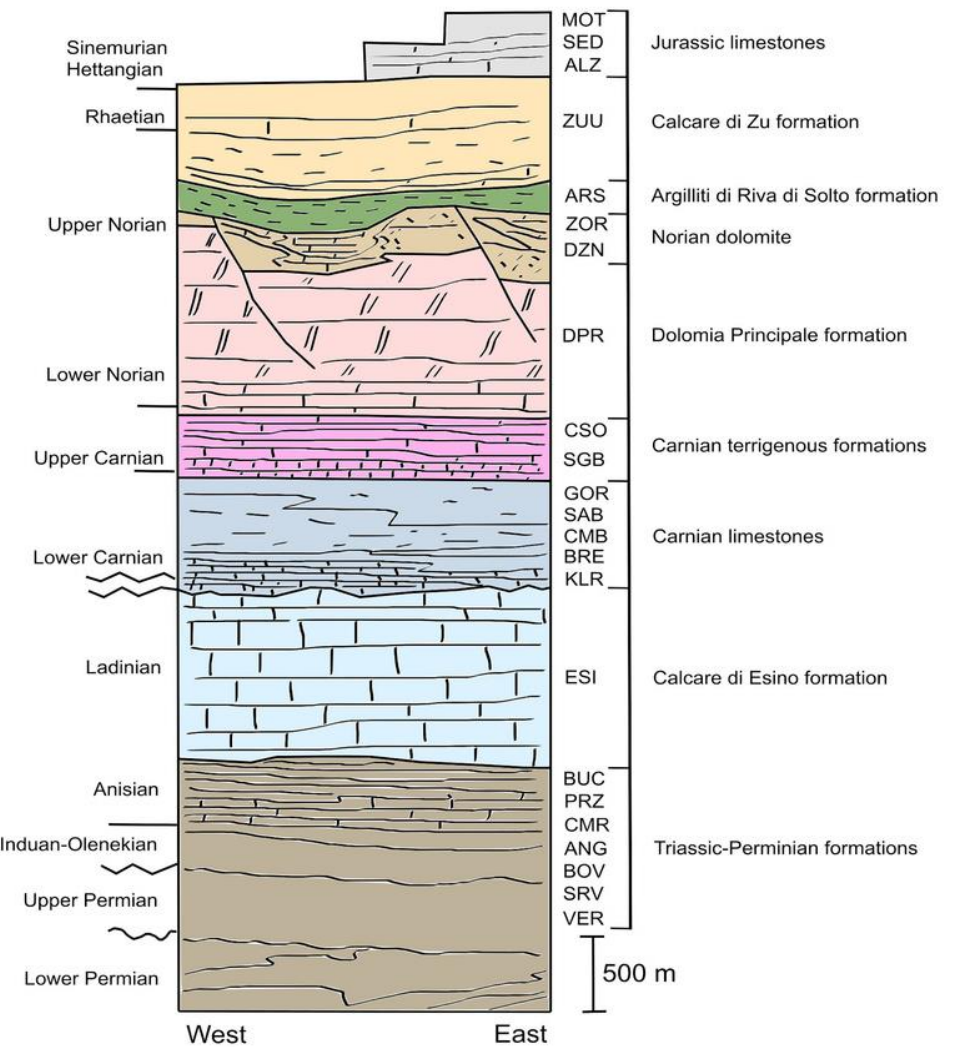
- The whole environment is dominated by **calcareous-dolomitic carbonate series**
- The **Nossana** aquifer is set in the **Calcare di Esino formation** (Ladin - Carnic age)
- The water system of **Ponte del Costone** is formed by 13 springs distributed in about 1 km along the Serio river and it has the **Dolomia Principale Formation** (Noric age) as reservoir rock
- The average **precipitation** is close to **2000 mm/year** with peaks of about **3000 mm/year** (Ceriani et al., 2000)



## Legend

- Sampling points**
- Spring water
  - River water
  - Well water
  - Cave water
  - Mine water
  - ▲ Main mountain peaks
  - Main tectonic structures
  - Main rivers
  - ⊕ Spring catchments
- Geology**
- Quaternary deposits
  - Andesitic vein
  - Jurassic limestones
  - Calcare di Zu formation
  - Argillite di Riva di Solto formation
  - Norian dolomite
  - Dolomia Principale formation
  - Carnian terrigenous formations
  - Carnian limestones
  - Calcare di Esino formation
  - Triassic-Permian formations

## Stratigraphic scheme

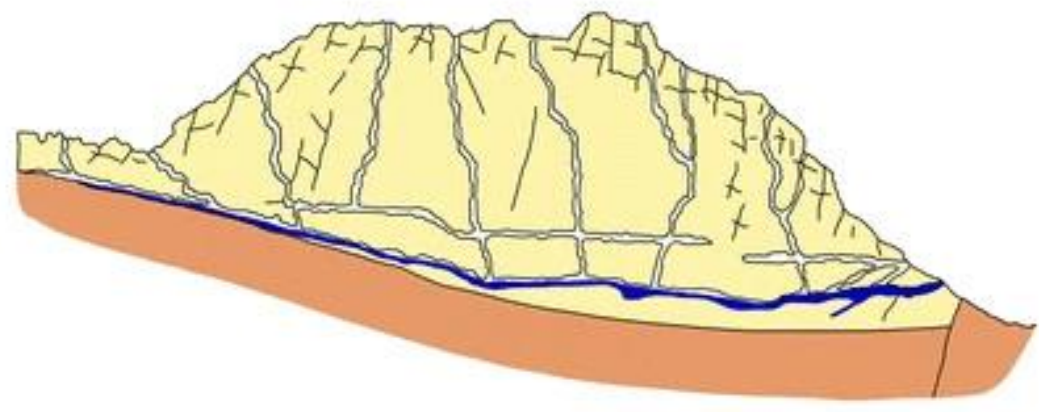
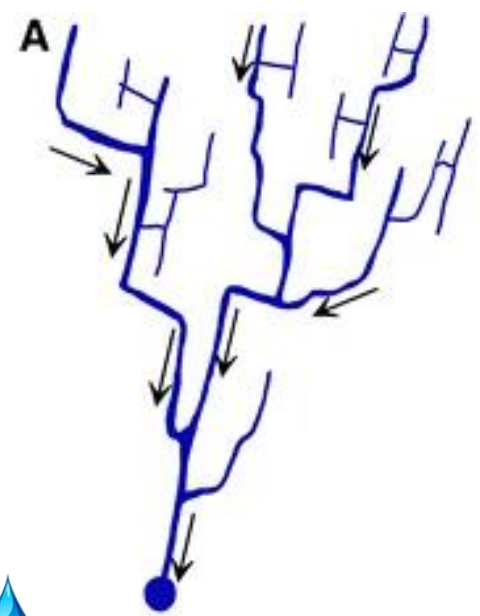
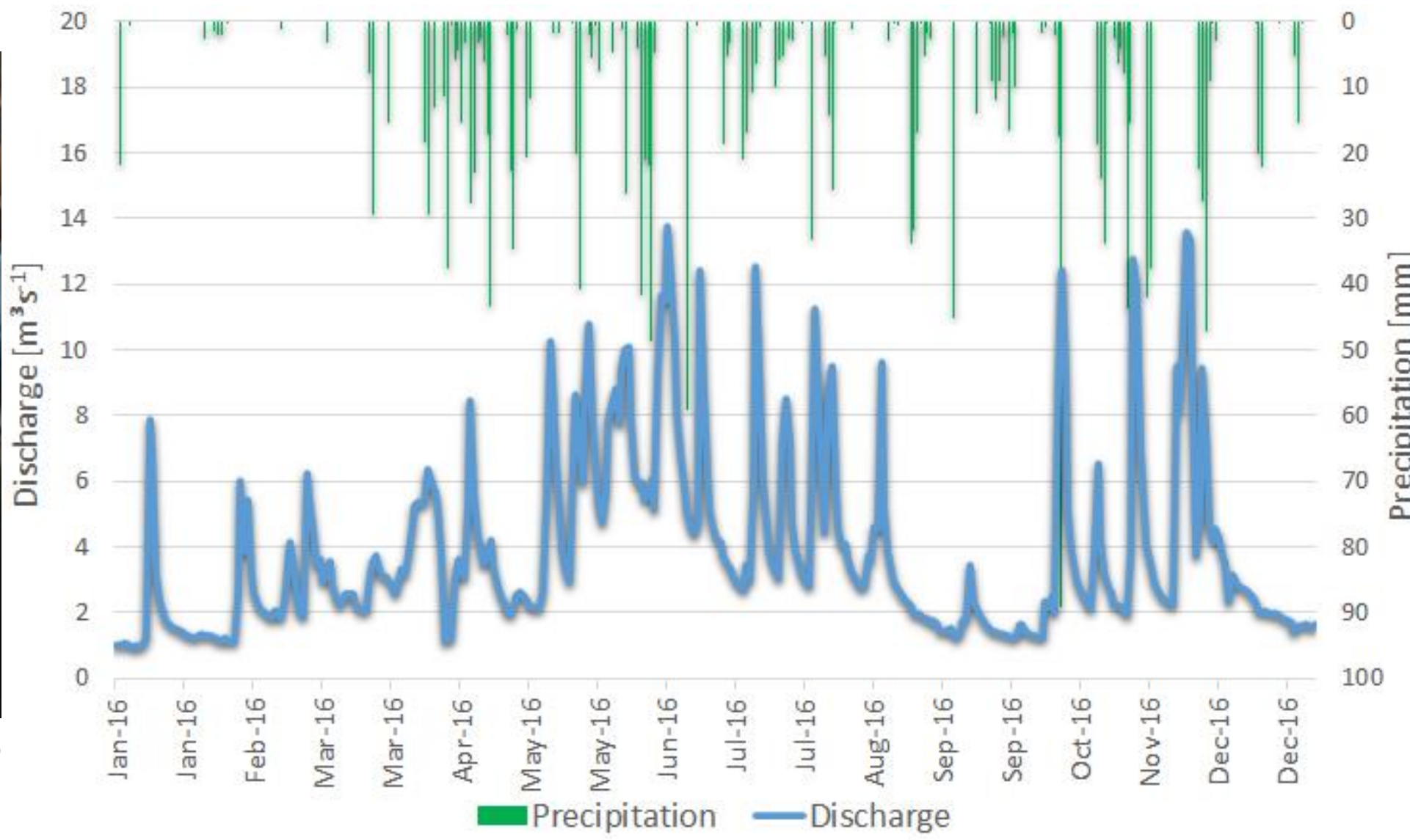


Characterization of the main karst aquifers of the middle Valseriana (Northern Italy) based on isotopic and hydrogeochemical data: Nossana and Ponte del Costone springs

# Study Area



Credits: Eco di Bergamo



From Vigna & Banzato, 2015

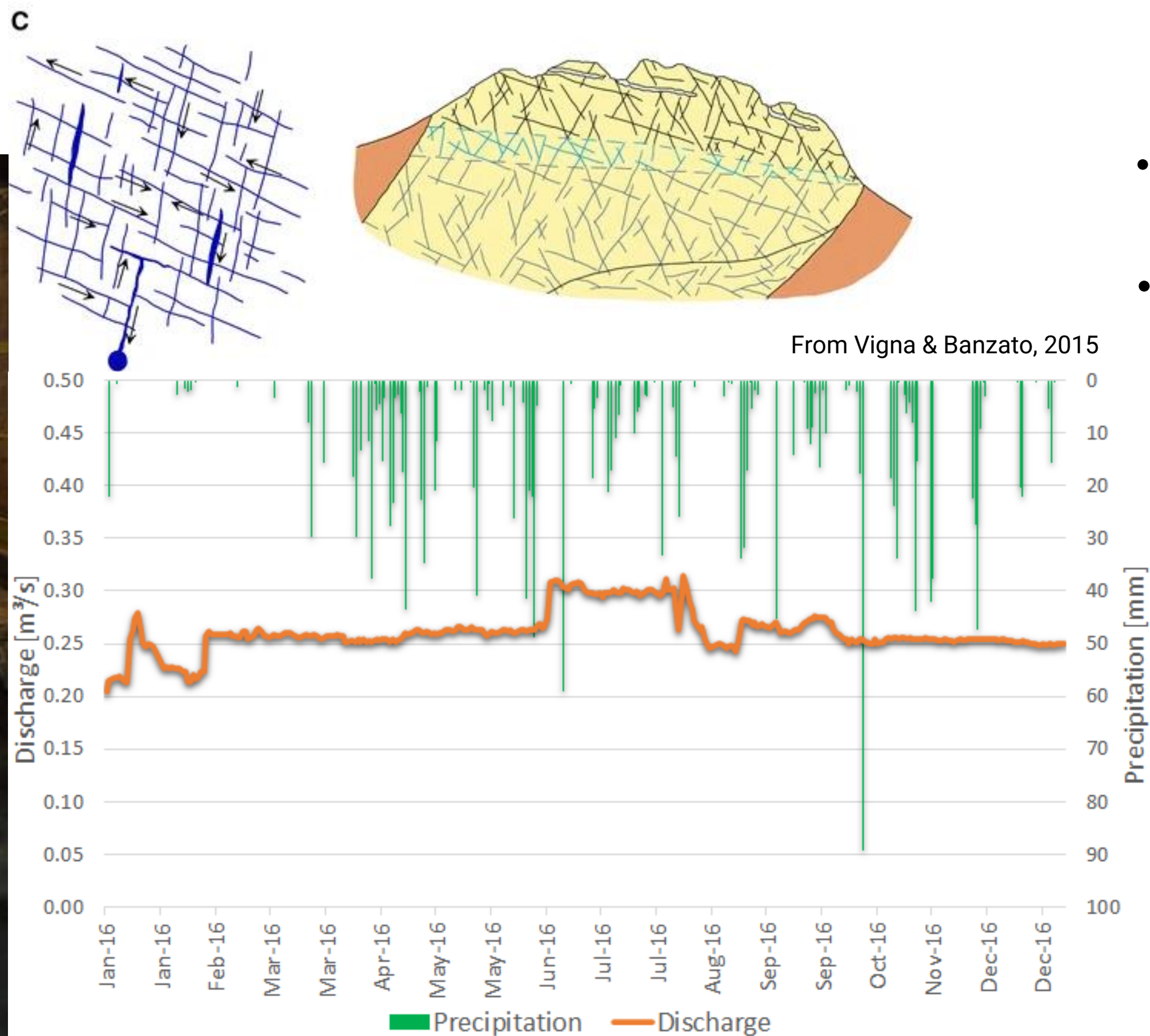
- The **springs** are managed by the public company UniAcque S.p.A. and **feed more than 315,000 people**
- **Nossana spring discharge  $0.5 - 18 m^3 s^{-1}$**

## Nossana spring

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# Study Area

Credits: UniAcque S.p.A.



- The **Ponte del Costone** cumulative discharge **0.15 - 0.45  $m^3s^{-1}$**
- System with **dispersive circulation**
- **Three main group** distributed along Serio river: Galleria del Costone, Merlo, and Bosco (from South to North)

## Ponte del Costone springs

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# Methodology



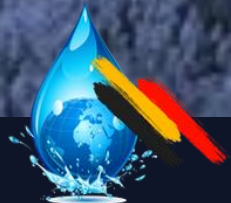
## 1 - SAMPLING CAMPAIGN (MAY 2018 - JULY 2019)

34 sampling points were set up. 23 points are related to **natural spring** waters, 4 points to **surface waters**, 2 points to **wells**, 3 points to waters from **karst caves**, and 2 points to the Val del Riso mine



## 2 - HYDROCHEMICAL AND ISOTOPIC ANALYSIS

- **Chemical analyses** were performed at UniAcque S.p.A. laboratories via ion chromatography (IC) and inductively coupled plasma mass spectrometry (ICP-MS)
- **Stable isotopes analyses** ( $^{18}\text{O}$ ,  $^2\text{H}$ , and  $^{13}\text{C}$ ) were performed in the laboratory of the Université d'Avignon et des Pays de Vaucluse (France) using an isotope ratio mass spectrometer (IRMS).
- the  $^3\text{H}/^3\text{He}$  **analysis** was performed in the laboratories of the Institute of Environmental Physics and Oceanography at the University of Bremen (Germany) (Sültenfuß et al., 2009).





### 3 - HYDROCHEMICAL CHARACTERIZATION

- Through the use of PHREEQC (Parkhurst & Appelo, 2013),  $p\text{CO}_2$  and Saturation Indices were calculated with respect to calcite (**Slc**) and dolomite (**Sld**)
- Using Instant Clue software (Nolte et al., 2018), a **Hierarchical Cluster analysis** was performed considering major cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$ ), major anions ( $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ ), alkalinity ( $\text{CaCO}_3$ ), temperature,  $\text{CO}_2$  partial pressure, Slc and Sld, and electrical conductivity [ $\mu\text{S}/\text{cm}$ ]



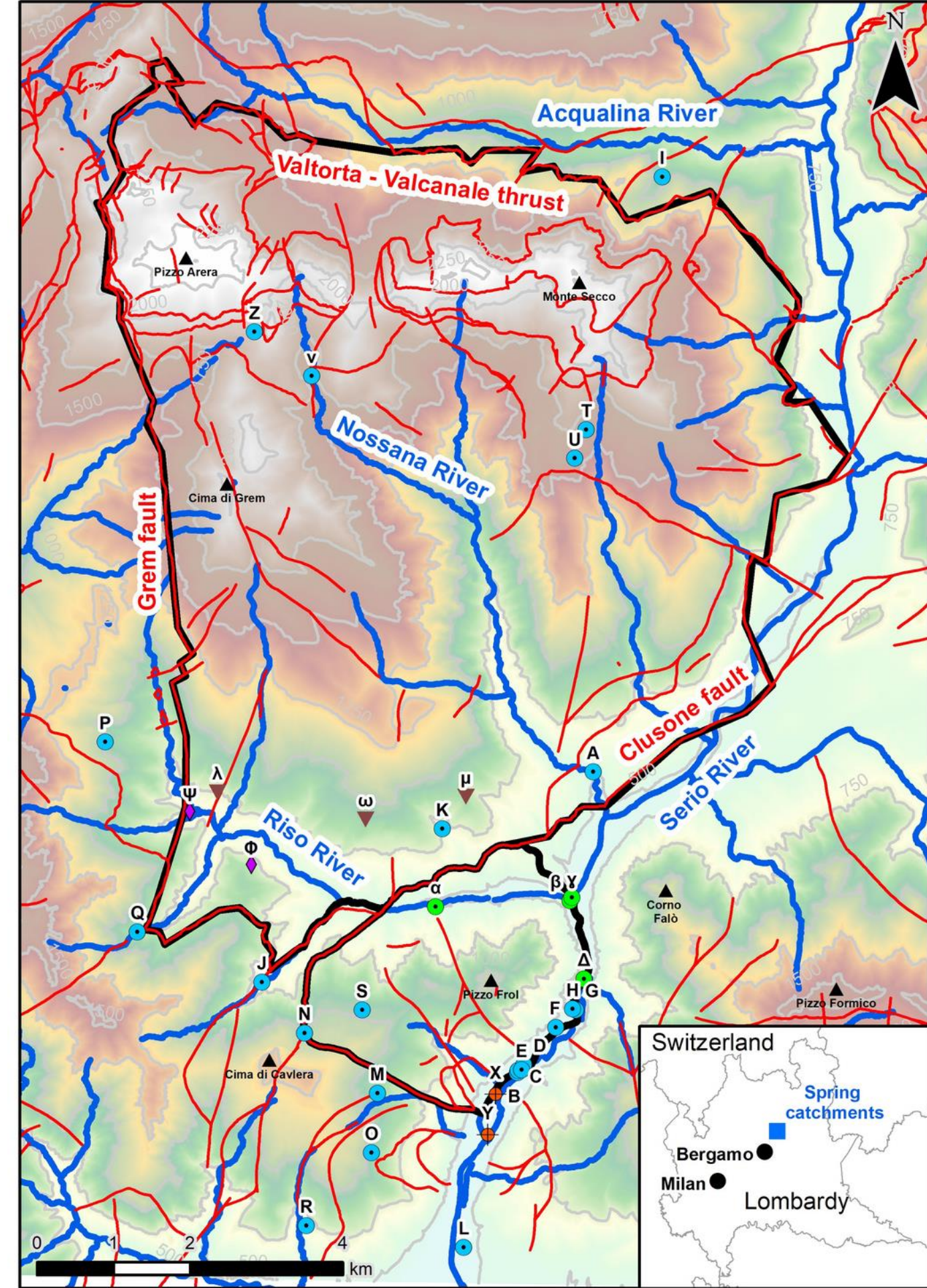
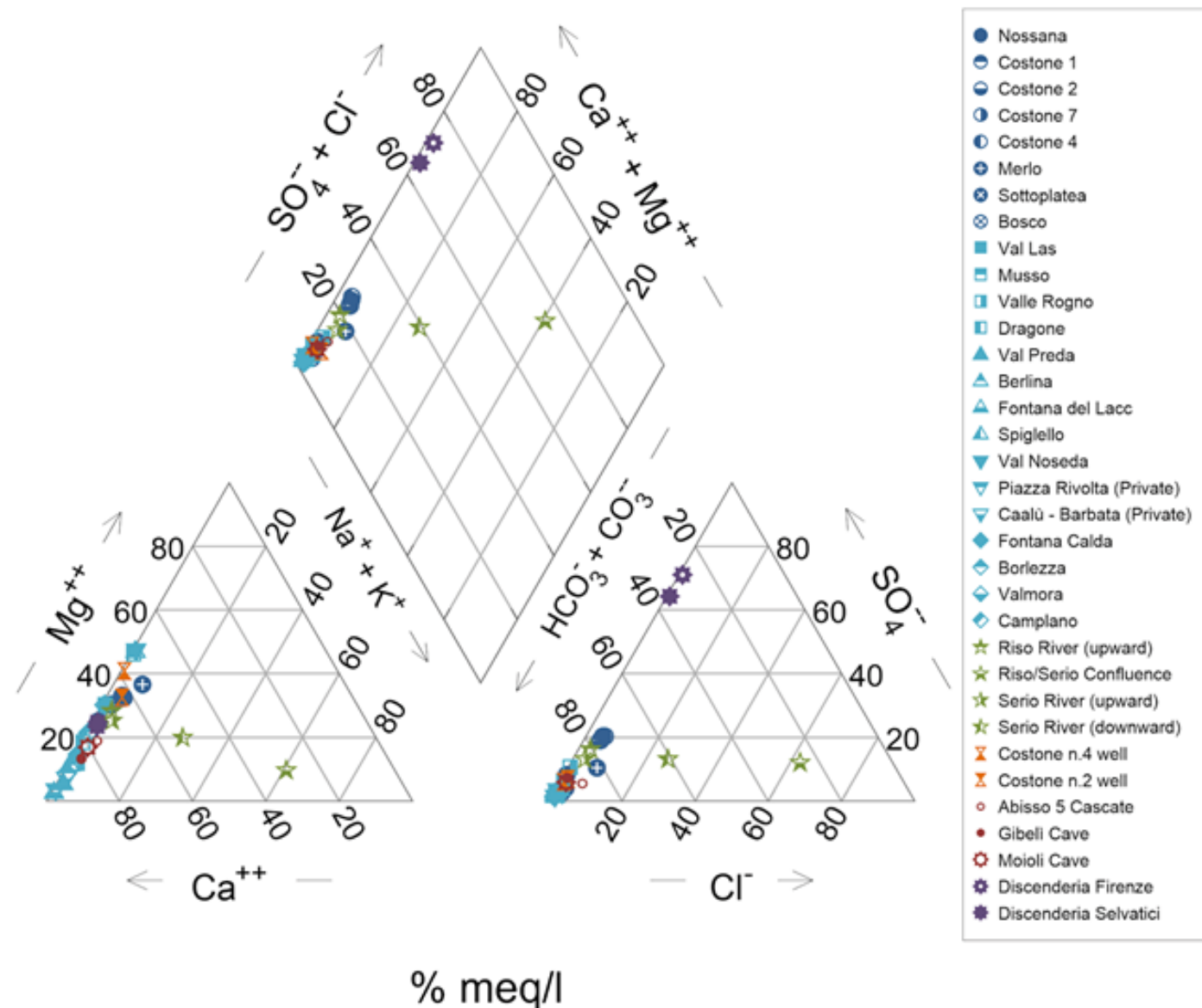
### 4 - FLOW DYNAMICS FEATURES WITHIN THE WATER SYSTEMS

Through comparison of the results of chemical and isotopic analysis, a **hypothesis** was proposed about **how the flow dynamics** within the two water systems **work**



# Sampling phase

- from **May 2018 to July 2019**
- focused primarily on the main spring systems: **Nossana and Ponte del Costone**
- The waters belong the **magnesium - bicarbonate hydrochemical facies**



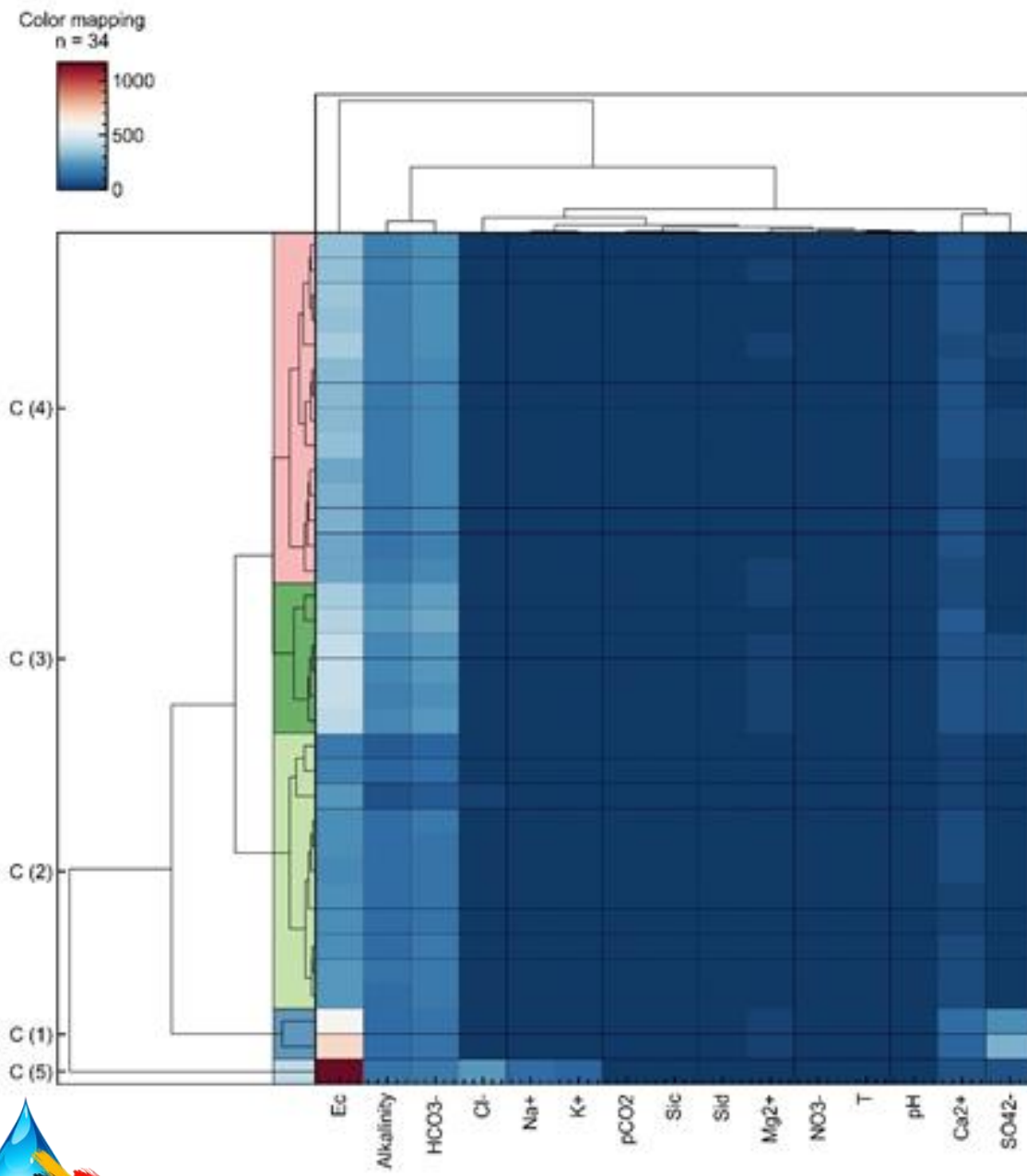
### Legend

Sampling points

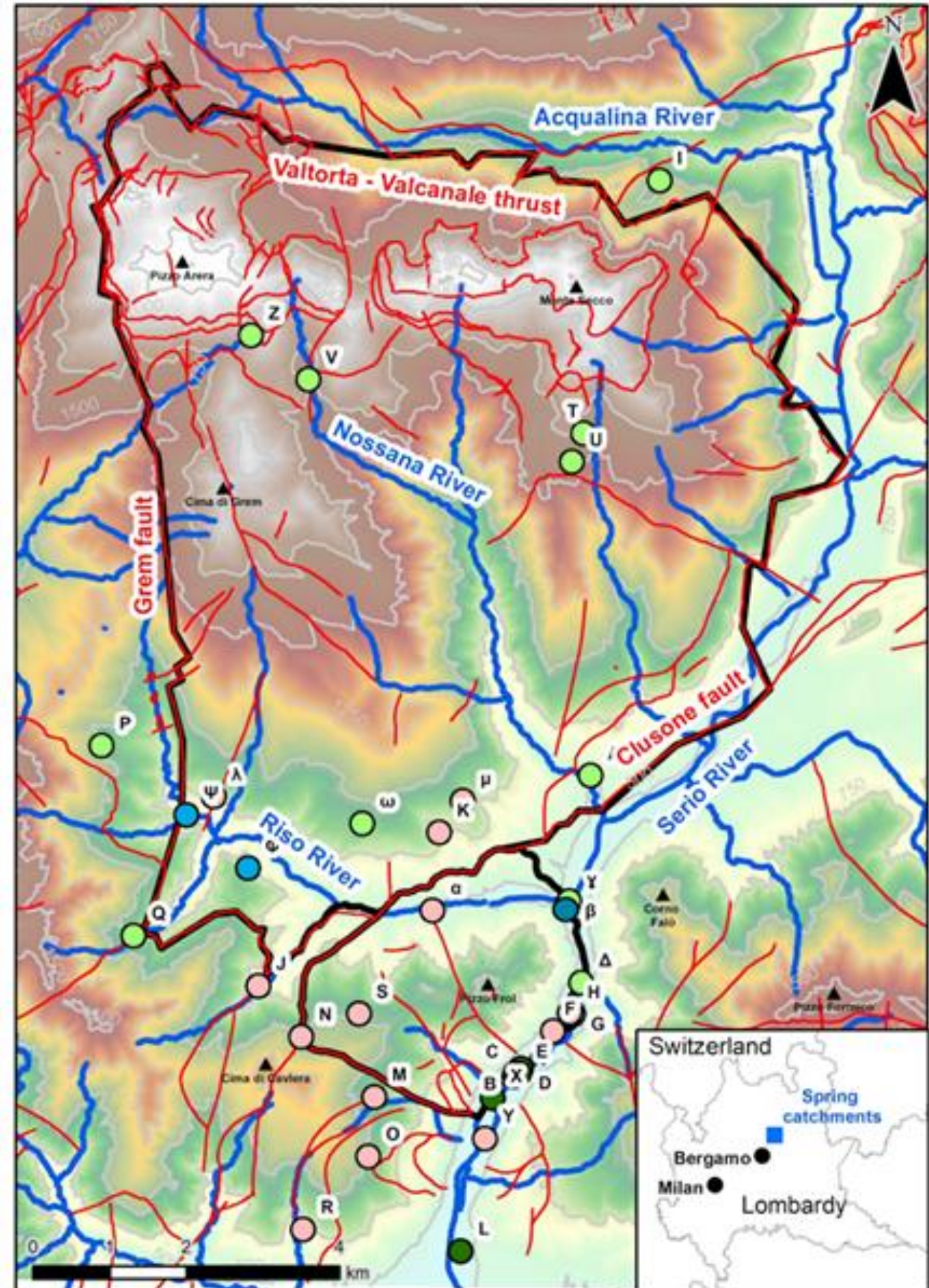
- Spring water
- River water
- Well water
- Cave water
- Mine water
- Main mountain peaks
- Main tectonic structures
- Main rivers
- Spring catchments

# Hierarchical clustering analysis

	T	pH	pCO <sub>2</sub>	Alkalinity	Ca <sup>2+</sup>	Mg <sup>2+</sup>	Na <sup>+</sup>	K <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>	Cl <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>
	[°C]		log(atm)	CaCO <sub>3</sub> [mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]	[mg/l]
<b>C(1)</b>	9.2	8.0	-2.1	120.8	114.2	22.4	3.3	1.0	146.3	3.3	2.5	253.8
<b>C(2)</b>	7.9	8.0	-2.5	116.7	37.0	8.3	1.8	1.1	140.5	3.2	4.1	5.8
<b>C(3)</b>	11.0	7.5	-1.9	207.5	64.4	18.9	3.6	1.0	251.7	7.0	5.0	35.5
<b>C(4)</b>	10.2	7.8	-2.0	171.3	61.2	9.7	2.3	0.8	207.1	3.5	5.5	10.1
<b>C(5)</b>	15.2	8.6	-3.2	142.0	73.9	14.1	116.2	98.2	165.7	249.2	5.7	63.0



- λ - Abisso 5 Cascate
- Y - Costone n.2 well
- S - Caalù - Barbata (Private)
- N - Berlina
- F - Merlo
- O - Fontana del Lacc
- M - Val Preda
- K - Valle Rogno
- α - Riso River (upward)
- H - Bosco
- G - Sottoplatea
- R - Piazza Rivolta (Private)
- μ - Gibeli Cave
- J - Musso
- X - Costone n.4 well
- L - Dragone
- D - Costone 7
- B - Costone 1
- E - Costone 4
- C - Costone 2
- γ - Serio River (upward)
- I - Val Las
- Δ - Serio River (downward)
- V - Valmora
- A - Nossana
- T - Fontana Calda
- Q - Val Nosedà
- P - Spigello
- Z - Camplano
- U - Borlezza
- ω - Moiola Cave
- ♣ - Discenderia Selvatici
- ψ - Discenderia Firenze
- β - Riso/Serio Confluence



**Legend**

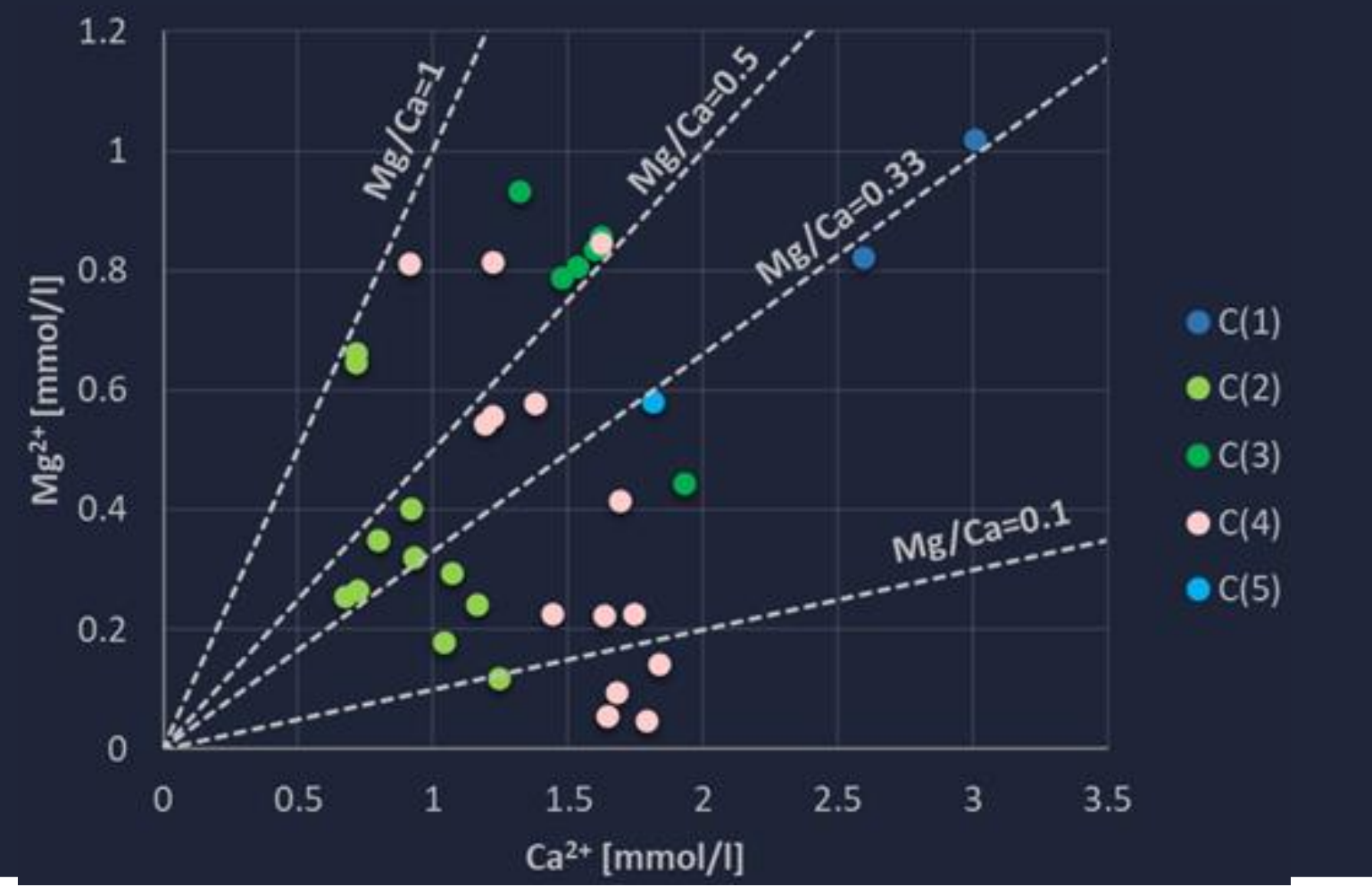
Class

- C1 (light blue circle)
- C2 (light green circle)
- C3 (dark green circle)
- C4 (pink circle)
- C5 (dark blue circle)

- ▲ Main mountain peaks
- Main tectonic structures
- Main rivers
- ⊕ Spring catchments

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# Hydrochemical features

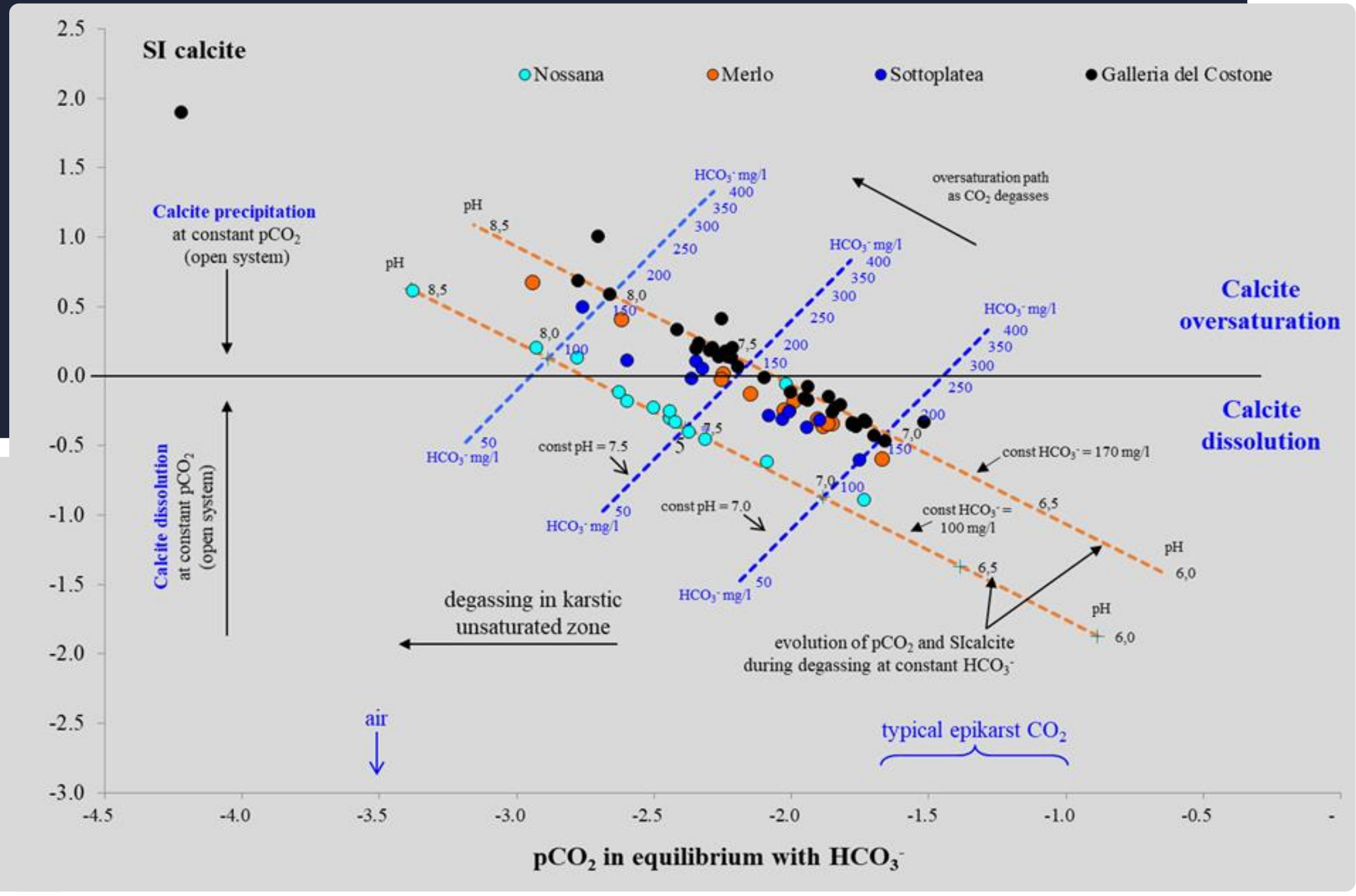


## Mg<sup>2+</sup>/Ca<sup>2+</sup> graph

- 58% of the values lie below the Mg/Ca = 0.5 line
- **Dissolution dominated by calcite**
- Mean value = 0.38, ranging from 0.03 to 0.93

- The relationship between the partial pressure of CO<sub>2</sub> and the calcite saturation index.
- The pH variation keeping constant the bicarbonate ion content (orange lines)
- The bicarbonate ion variation keeping constant the pH value (blue lines)

Nossana and Ponte del Costone are characterized by two different families of water in terms of bicarbonate contents



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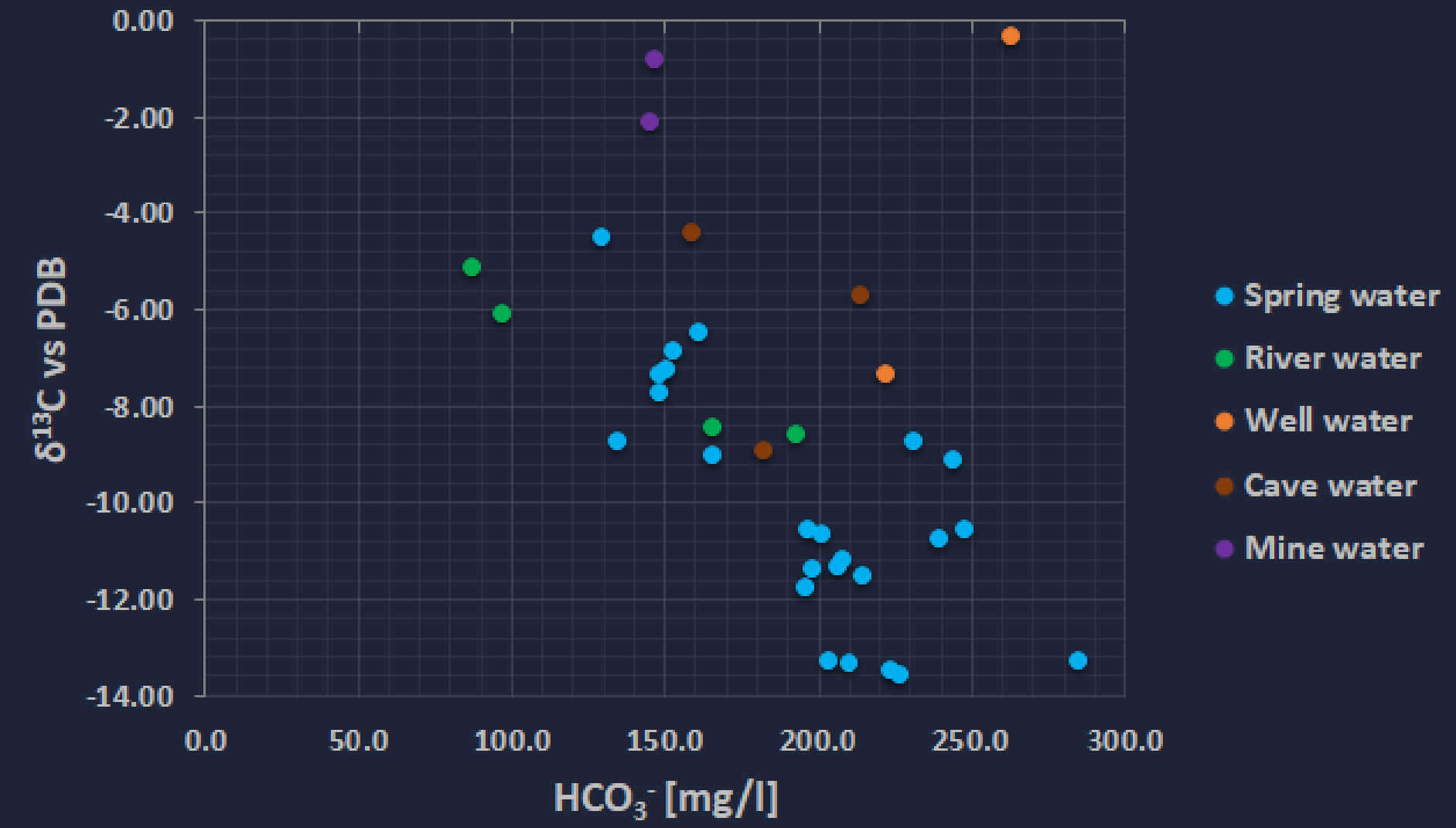
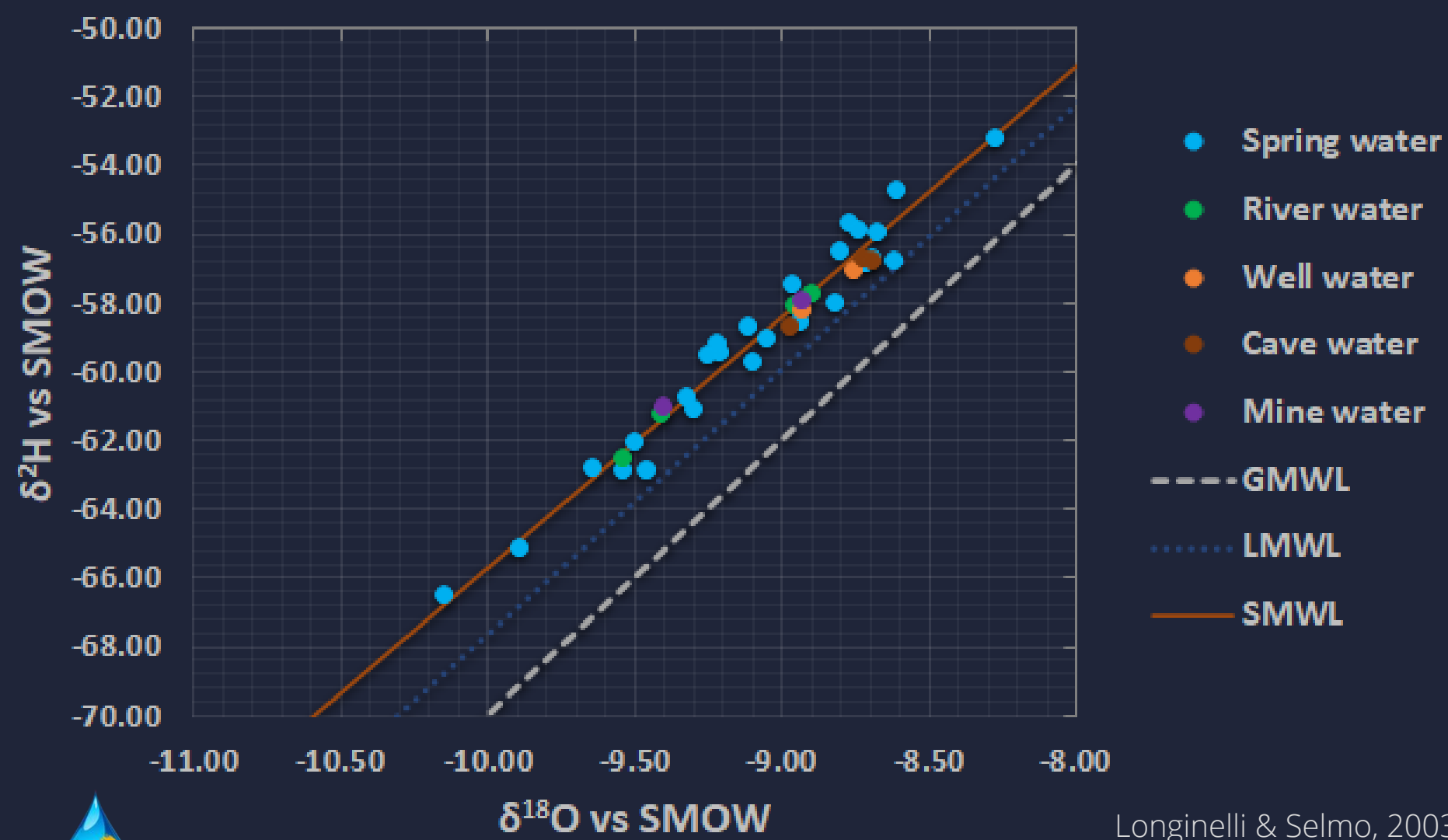
# Isotopic features

Type of water	n°	δ <sup>18</sup> O vs SMOW	δ <sup>2</sup> H vs SMOW	δ <sup>13</sup> C vs PDB
		Range	Range	Range
Spring	23	-10.15 to -8.27	-66.54 to -53.22	-13.56 to -4.49
River	4	-9.54 to -8.90	-62.54 to -57.74	-8.59 to -5.14
Well	2	-8.93 to -8.75	-58.22 to -57.07	-7.36 to -0.34
Cave	3	-8.97 to -8.69	-58.67 to -56.70	-8.91 to -4.40
Mine	2	-9.40 to -8.93	-61.02 to -57.97	-2.11 to -0.79

• Study area Meteoric Water Line:

$$\delta^2\text{H} = 7.71\delta^{18}\text{O} + 9.40$$

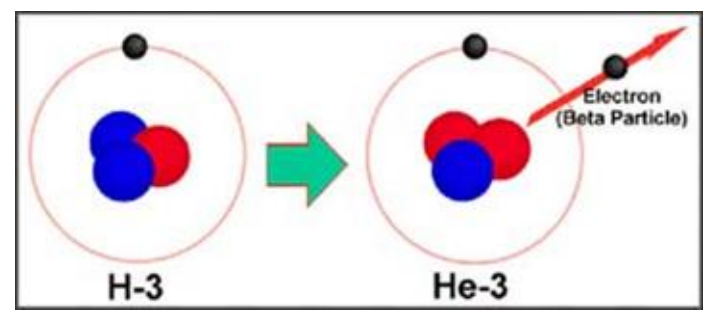
- **Deuterium enrichment** given by re-evaporation due to effect of secondary valleys (Riso Valley)
- **<sup>13</sup>C** suggests an **isotopic composition** of spring waters attributable to **different contributions**



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# Residence time estimation

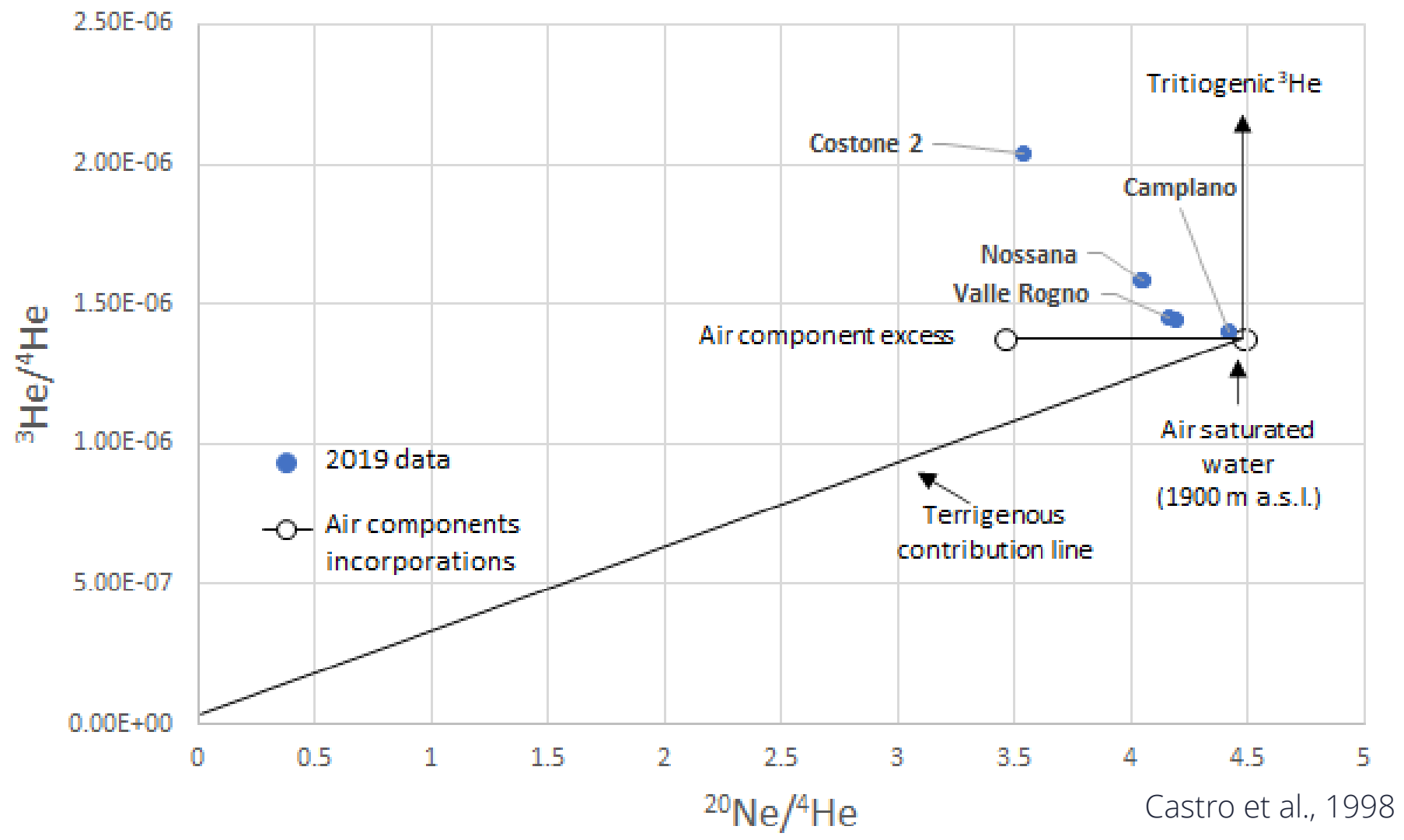
Spring name	Sampling 2015		Sampling 2019	
	Age (years)	Recharge year	Age (years)	Recharge year
Camplano	1.50	2014	0.96	2018
Valle Rogno	8.10	2007	5.24	2014
Nossana	7.90	2008	13.10	2006
Costone 2	29.30	1986	32.48	1987



$$t[\text{years}] = \frac{1}{\lambda} \ln \left( \frac{{}^3\text{He}_{\text{tritogenic}}}{{}^3\text{H}} + 1 \right)$$

$$\lambda = 0.056/\text{years}$$

- 10 years for Nossana, 30 years for Ponte del Costone
- For the main springs **cyclical renewal** of the resource is **not clear**
- The results can be explained as an effect of the incorporation of air components (**turbulent flow**, typical in karst phenomena) and the decay of  ${}^3\text{H}$  into  ${}^3\text{He}$ .



Castro et al., 1998

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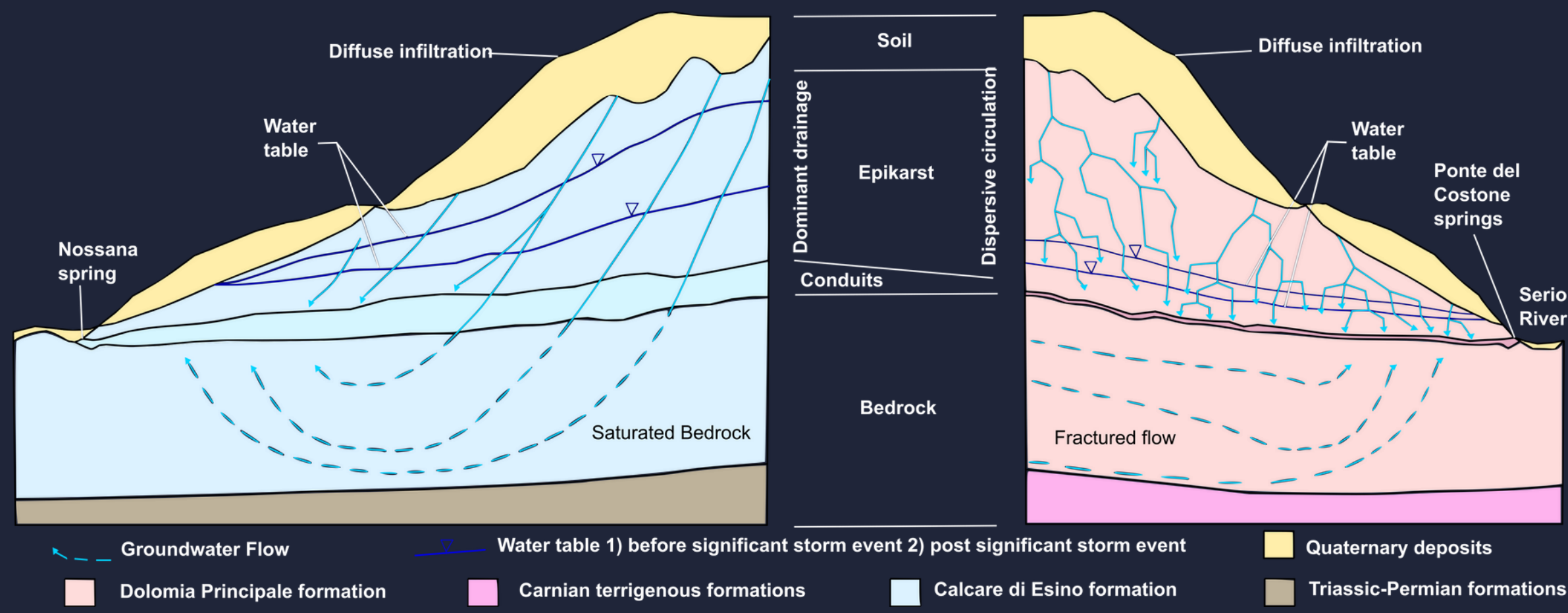
# Concluding remarks

- The chemical composition of the waters reflects the carbonate context and is completely controlled by the **spatial distribution** of the different geological formations, by the **different degree of susceptibility to karst dissolution** of the rocks that characterize the study area, and by the **altitude**.

- It was estimated the age of the reserve (or **residence time**) for **Nossana** of about **10 years**, while for the **Ponte del Costone** springs of about **30 years**
- For these main springs, the **cyclical renewal of the resource is not evident**; rather, the water reserve ages in the 2015 - 2018 comparison.

Nossana and Ponte del Costone can be simplified with **hierarchical models** (Asante et al., 2018, White, 2002):

- Piston effect controlled by the amount of precipitation
- Diffuse infiltration in very different timing due to the different response to karst dissolution of the encasing rocks



modified from Asante et al. (2018) and re-elaborated from White (2002)

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# Thank you for attention



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# References

- Asante, J., Dotson, S., Hart, E., & Kremer, D. K. (2018). Water circulation in karst systems: Comparing physicochemical and environmental isotopic data interpretation. *Environmental Earth Sciences*, 77(11), 421. <https://doi.org/10.1007/s12665-018-7596-y>
- Castro, M. C., Goblet, P., Ledoux, E., Violette, S., & de Marsily, G. (1998). Noble gases as natural tracers of water circulation in the Paris Basin: 2. Calibration of a groundwater flow model using noble gas isotope data. *Water Resources Research*, 34(10), 2467–2483. <https://doi.org/10.1029/98WR01957>
- Ceriani, M., Carelli, M., Agnelli, U., Bodio, N., Colombo, S., Lauzi, S., & Martelli, M. (2000). Carta delle precipitazioni medie, massime e minime annue del territorio alpino della Regione Lombardia (registrate nel periodo 1891 – 1990). *Professione geologo*, 10, 12-27
- Longinelli, A., & Selmo, E. (2003). Isotopic composition of precipitation in Italy: A first overall map. *Journal of Hydrology*, 270(1–2), 75–88. [https://doi.org/10.1016/S0022-1694\(02\)00281-0](https://doi.org/10.1016/S0022-1694(02)00281-0)
- Nolte, H., MacVicar, T. D., Tellkamp, F., & Krüger, M. (2018). Instant Clue: A Software Suite for Interactive Data Visualization and Analysis. *Scientific Reports*, 8(1), 12648. <https://doi.org/10.1038/s41598-018-31154-6>
- Parkhurst, D., & Appelo, C. (2013). Description of input and examples for PHREEQC version 3: A computer program for speciation, batchreaction, one-dimensional transport, and inverse geochemical calculations. *US Geological Survey Techniques and Methods*, 6(A43).
- Sültenfuß, J., Roether, W., & Rhein, M. (2009). The Bremen mass spectrometric facility for the measurement of helium isotopes, neon, and tritium in water. *Isotopes in Environmental and Health Studies*, 45(2), 83–95. <https://doi.org/10.1080/10256010902871929>
- Vigna, B., & Banzato, C. (2015). The hydrogeology of high-mountain carbonate areas: An example of some Alpine systems in southern Piedmont (Italy). *Environmental Earth Sciences*, 74(1), 267–280. <https://doi.org/10.1007/s12665-015-4308-8>
- White, W. B. (2002). Karst hydrology: Recent developments and open questions. *Engineering Geology*, 65(2–3), 85–105. [https://doi.org/10.1016/S0013-7952\(01\)00116-8](https://doi.org/10.1016/S0013-7952(01)00116-8)

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