



# **The VIOLA project: geochemical characterization and natural background levels in a coastal groundwater body of the Apulia Region (southern Italy)**

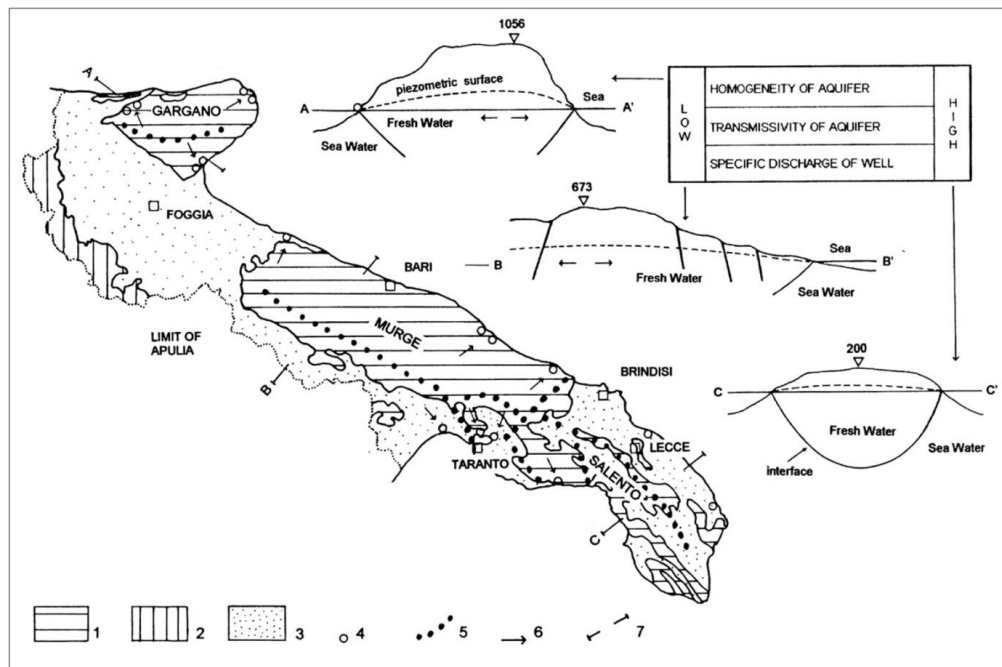
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Melita M., Passarella G., Vurro M., Zoppini A., Preziosi E.*

# Research and objectives

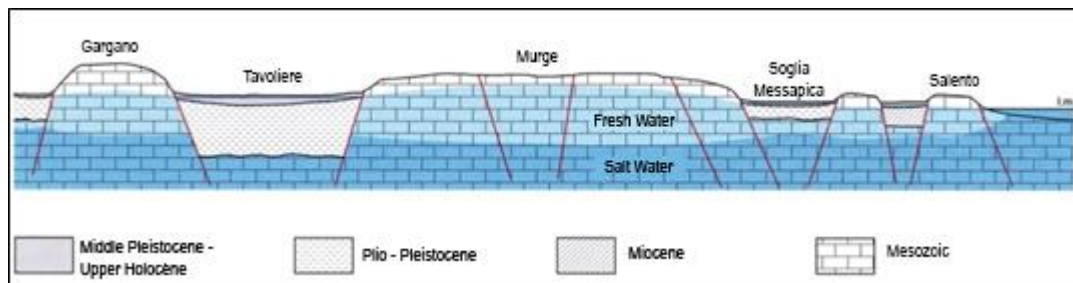
- Coastal areas worldwide are often highly impacted due to the concurrence of aquifer exploitation for irrigation, human consumption exacerbated during touristic seasons and industrial activities.
- In order to meet the objectives of the GWD, European groundwater bodies' status (chemical and quantitative) is evaluated every 6 years. Criteria for good status include chemicals exceeding standards and threshold values, saline intrusion and others.
- Apulian region features a very high ratio coastline/area (44 m/km<sup>2</sup>, for Italy is 25 m/km<sup>2</sup>) thus seawater intrusion is a very common phenomenon, due to both natural and anthropogenic drivers.
- In this contribution, the first results of the VIOLA project (Natural Background Values in Apulian groundwater bodies) are presented, supplying a preliminary geochemical characterization of the coastal Murgia groundwater body.
- The main objective is to assess the natural background levels for some critical parameters and discriminate between the natural and anthropogenic origin of saline intrusion.

# Geological settings of Coastal Murgia

The study area consists of the Jurassic-Cretaceous carbonate formations of the Apulian Platform, which emerge extensively on the Murge Plateau. In the Apulian carbonatic units freshwater floats on saltwater, both in the coastal area and inland, where salt groundwaters are found thousands of meters below sea level.



Hydrogeological scheme of the Apulia Region (Maggiore & Pagliarulo, 2003).



Hydrogeological section of the outcrop part of the Apulian platform (Maggiore & Pagliarulo, 2004)

The coastal Murgia groundwater body is part of a fractured and karstified calcareous-dolomitic aquifer with groundwater naturally flowing to the Adriatic sea. The aquifer is essentially superiorly confined, with an irregular geometric configuration and mostly artesian. The low permeability of limestones and dolomites due to poor and discontinuous cracking and karstization forces the aquifer to flow under high and extremely variable piezometric heads.



Hydrogeological Map with indication of salinity (Cotecchia, 2014)



# On field and lab activities

## Groundwater sampling

- 2 of the 4 planned sampling campaigns (spring and fall 2019)
- 47 wells (42 dynamic sampling, 5 static sampling)

## On field determinations

- Physical-chemical parameters: Temp, pH, ORP, DO, El. Cond.
- UV-Vis Spectrophotometry:  $\text{NH}_4$ ,  $\text{NO}_2$ , CN

## Laboratory analysis

- Within 48-72 hrs:
  - Alcalimetry:  $\text{HCO}_3$
  - Ion-Exchange Chromatography: F, Cl,  $\text{NO}_2$ , Br,  $\text{NO}_3$ ,  $\text{PO}_4$ ,  $\text{SO}_4$
- Within 1 month:
  - IR-Analyzer: DOC
  - ICP-OES: Ca, Mg, Na, K
  - ICP-MS: Al, V, Cr, Fe, Mn, As, Rb, Sr, Li, Ba, Pb, B, Se, Ni, Cu, Zn, U



Physical-Chemical  
parameters  
measurements in  
low flow cell



In-line filtration



Dionex Aquion  
IC System

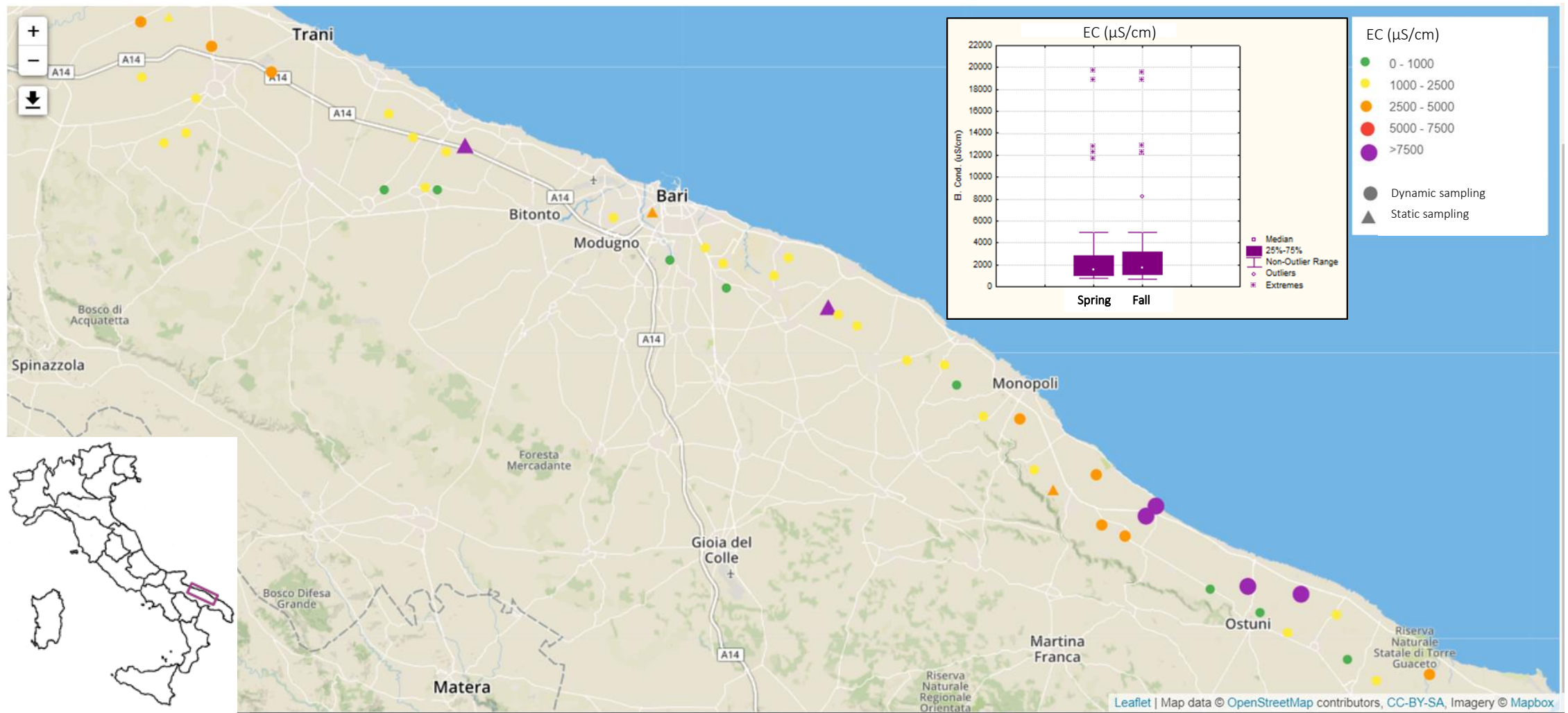


$\text{HNO}_3$  acidification  
for metal analysis

# Study area and sampling points

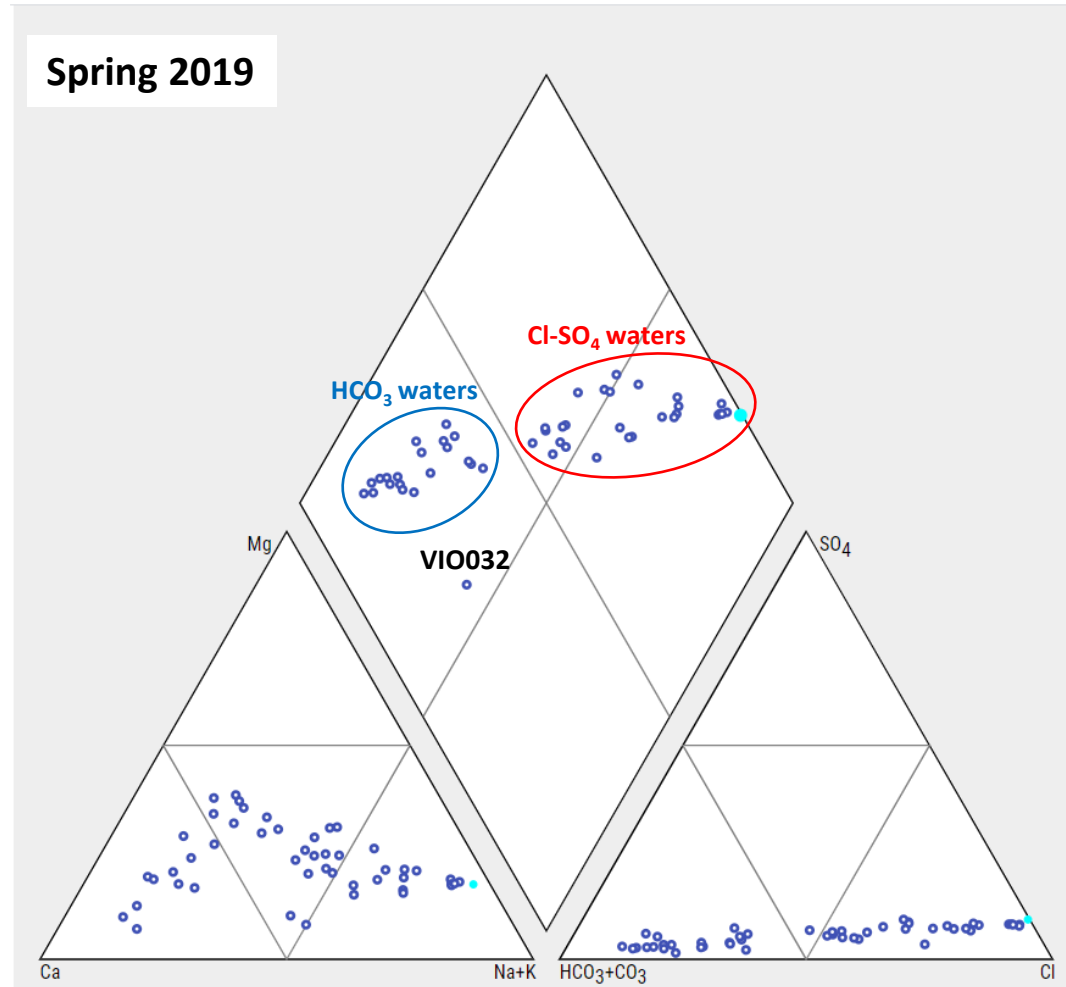


# Electrical Conductivity map

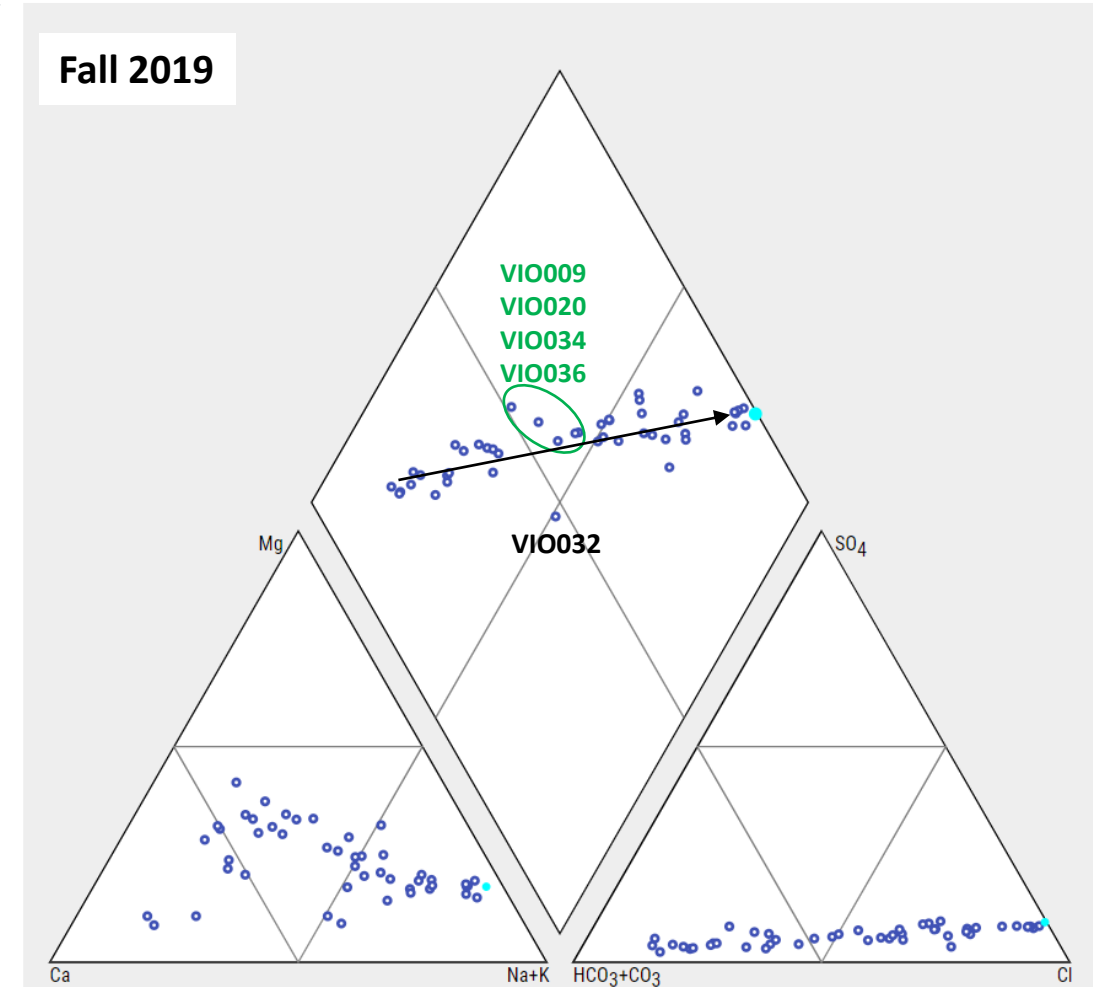




# Hydrochemical classification



● Seawater



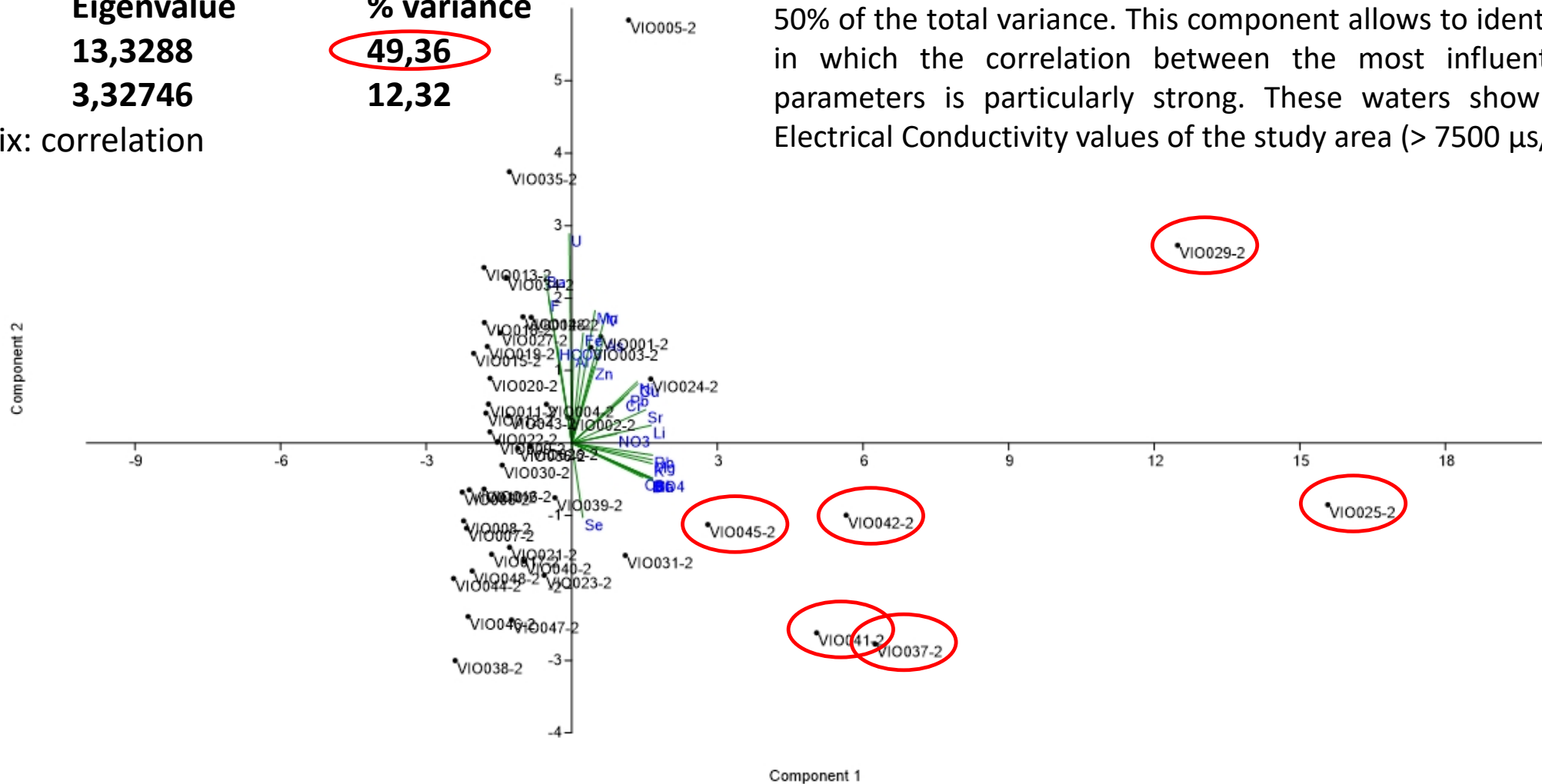
● Seawater

In the first campaign two groups are clearly distinguishable (HCO<sub>3</sub> and Cl-SO<sub>4</sub> waters), while in the second one there is an evolution from bicarbonate terms towards waters progressively closer to the seawater composition. 4 samples pass into the Cl-SO<sub>4</sub> water group in the second campaign. The only exception is the VIO032 sample which also shows anomalies for other parameters (eg. NH<sub>4</sub>), suggesting a possible anthropogenic contamination.

# Principal Component Analysis

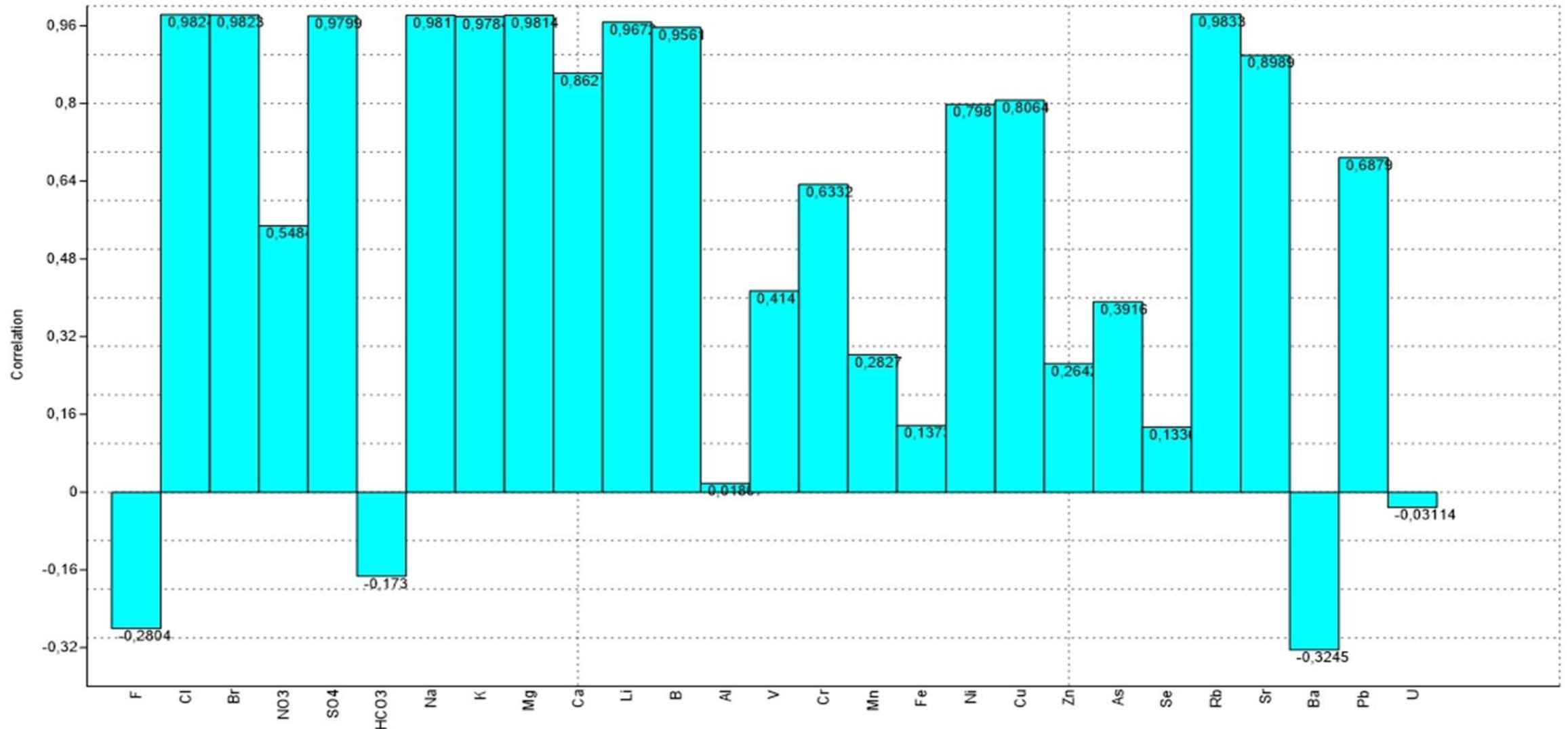
PC	Eigenvalue	% variance
1	13,3288	49,36
2	3,32746	12,32
Matrix: correlation		

The first component is by far the most important, explaining almost 50% of the total variance. This component allows to identify 6 samples in which the correlation between the most influential chemical parameters is particularly strong. These waters show the highest Electrical Conductivity values of the study area (> 7500  $\mu\text{s}/\text{cm}$ ).





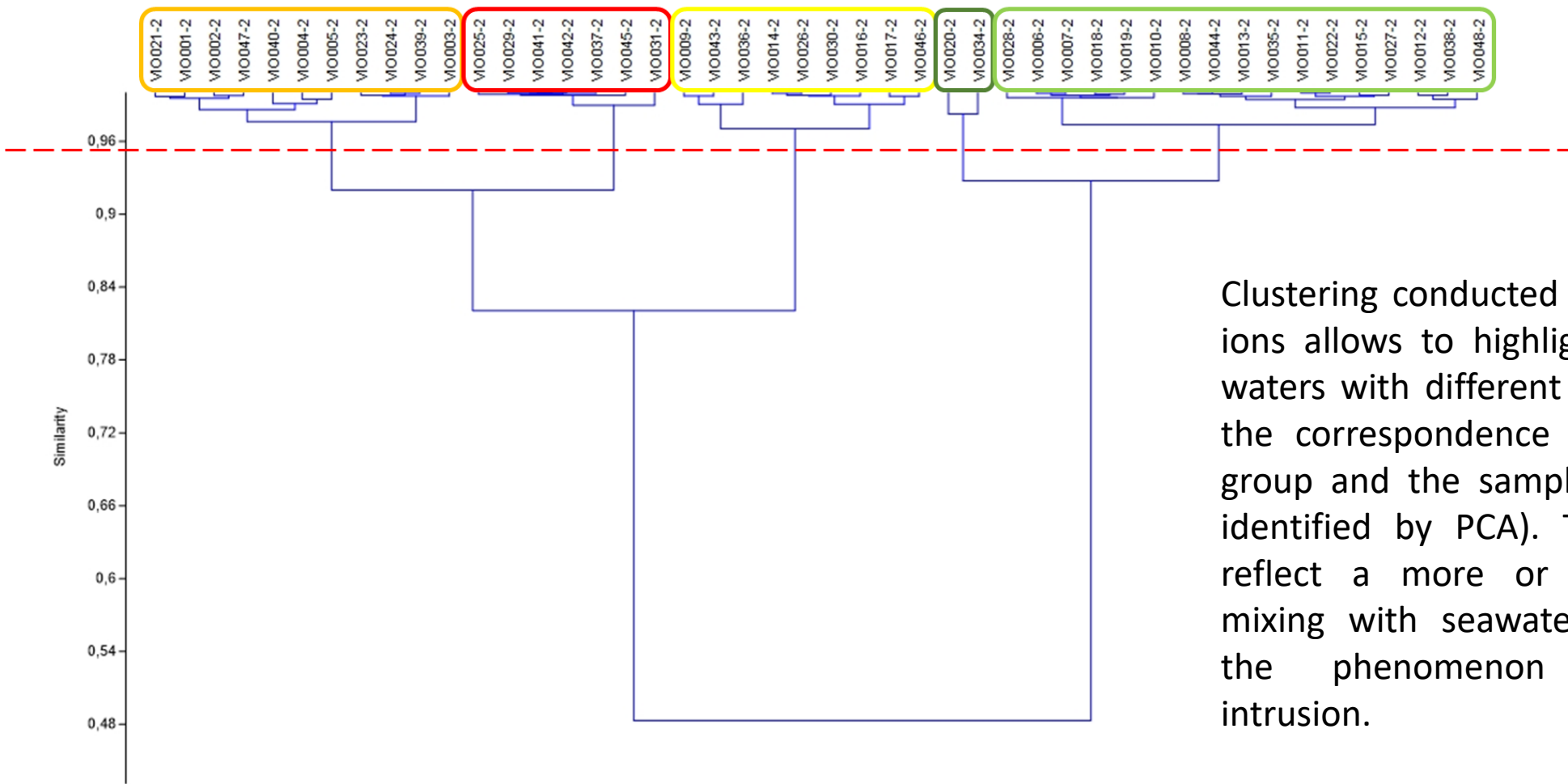
# PC1 (49,36%)



PC1 positive loadings highlight the important contribution of almost all major ions (with the exception of  $\text{HCO}_3$  and  $\text{NO}_3$ ), together with some minor elements with high residence times and normally more abundant in seawater (Li, B, Sr, Rb).

# Cluster Analysis

Algorithm: Paired group  
Similarity measure: correlation



Clustering conducted on the major ions allows to highlight groups of waters with different salinity (note the correspondence between red group and the samples previously identified by PCA). These groups reflect a more or less marked mixing with seawater, caused by the phenomenon of saline intrusion.

# Natural Background Levels (NBLs)

- An attempt was made to define the NBLs for the parameters showing at least one exceeding of threshold values:  $\text{SO}_4$ , B, As, Fe, Mn, Ni
- The procedure established by the italian guidelines (ISPRA, 2017) has been applied, which integrates the two main approaches for the definition of NBLs at the groundwater body scale (pre-selection and probabilistic method)
- The procedure is divided into two main parts:
  - 1<sup>st</sup> part (to be applied to the water points): aquifer conceptual model definition, sampling and analysis, preliminary evaluation of data, hydrochemical facies separation, pre-selection of uninfluenced samples
  - 2<sup>nd</sup> part (to be applied to each compound): temporal and spatial statistical analysis, evaluation of the consistency of residual datasets, definition of the NBLs, attribution of a confidence level to the defined NBLs

# NBLs: pre-selection by nitrates

NO<sub>3</sub> < 37.5 mg/L\*: **29 water points**

	SO <sub>4</sub> (mg/L)	B (µg/L)	Mn (µg/L)	Fe (µg/L)	Ni (µg/L)	As (µg/L)	Statistical test
Outliers	0	2	3	2	3	0	Rosner/Huber
Remaining data	29	27	26	27	26	29	-
Normality	No	No	Yes	Yes	Yes	Yes	Shapiro-Wilk
NBL	143.5	224.2	2.5	78.1	2.9	1.2	-
Confidence Level	M	M	M	M	M	M	-

\*75% of the threshold value for the good chemical status

Using only nitrates for pre-selection, the residual dataset allows the application of the complete procedure. The NBLs were therefore defined (max value for normal distributions, 95<sup>th</sup> percentile for non-normal distributions) and we attributed them a medium (M) confidence level, according to the number of monitoring sites, extension of the groundwater body and the aquifer type (confined).

Coastal Murgia GWB: 1227 km<sup>2</sup>

Aquifer type: confined

	N. total obs.	N. total MS	Size of GWB or portion of GWB represented by dataset (km <sup>2</sup> )							
			Aquifer type (unconf./conf.)							
			<10 km <sup>2</sup>		10-70 km <sup>2</sup>		70-700 km <sup>2</sup>		>700 km <sup>2</sup>	
			Unconf.	Conf.	Unconf.	Conf.	Unconf.	Conf.	Unconf.	Conf.
A		15-25	H	H	H	H	M	H	M	H
		>25	H	H	H	H	H	H	H	H
B		15-25	M	H	M	H	L	M	L	M
		>25	H	H	H	H	M	H	M	M
C	≤15		M	M	L	M	LL	L	LL	LL
	16-30		M	H	M	M	L	M	LL	L
	>30		H	H	M	H	M	A	M	M
D	<10		L	L	LL	LL	LL	LL	LL	LL
	≥10		L	L	L	L	LL	L	LL	LL

H: High; M: Medium; L: Low; LL: Very Low.



# NBLs: pre-selection by nitrates and chlorides

Coastal Murgia GWB: 1227 km<sup>2</sup>  
Aquifer type: confined

NO<sub>3</sub> < 37.5 mg/L\* and Cl < 187.5 mg/L\*: **14 water points**

	SO <sub>4</sub> (mg/L)	B (µg/L)	Mn (µg/L)	Fe (µg/L)	Ni (µg/L)	As (µg/L)
Data	14	14	14	14	14	14
Observations	28	28	28	28	28	28
Estimated NBL	33.7	226.9	2.5	87.7	5.0	0.6
Confidence Level	LL	LL	LL	LL	LL	LL

14x2 campaigns

\*75% of the threshold value for the good chemical status

Using also chlorides as pre-selection marker, the residual dataset is insufficient and the background values can only be estimated by a simplified procedure (90<sup>th</sup> percentile of the total observations). The confidence levels in this case are very low (LL) and new monitoring data are needed.

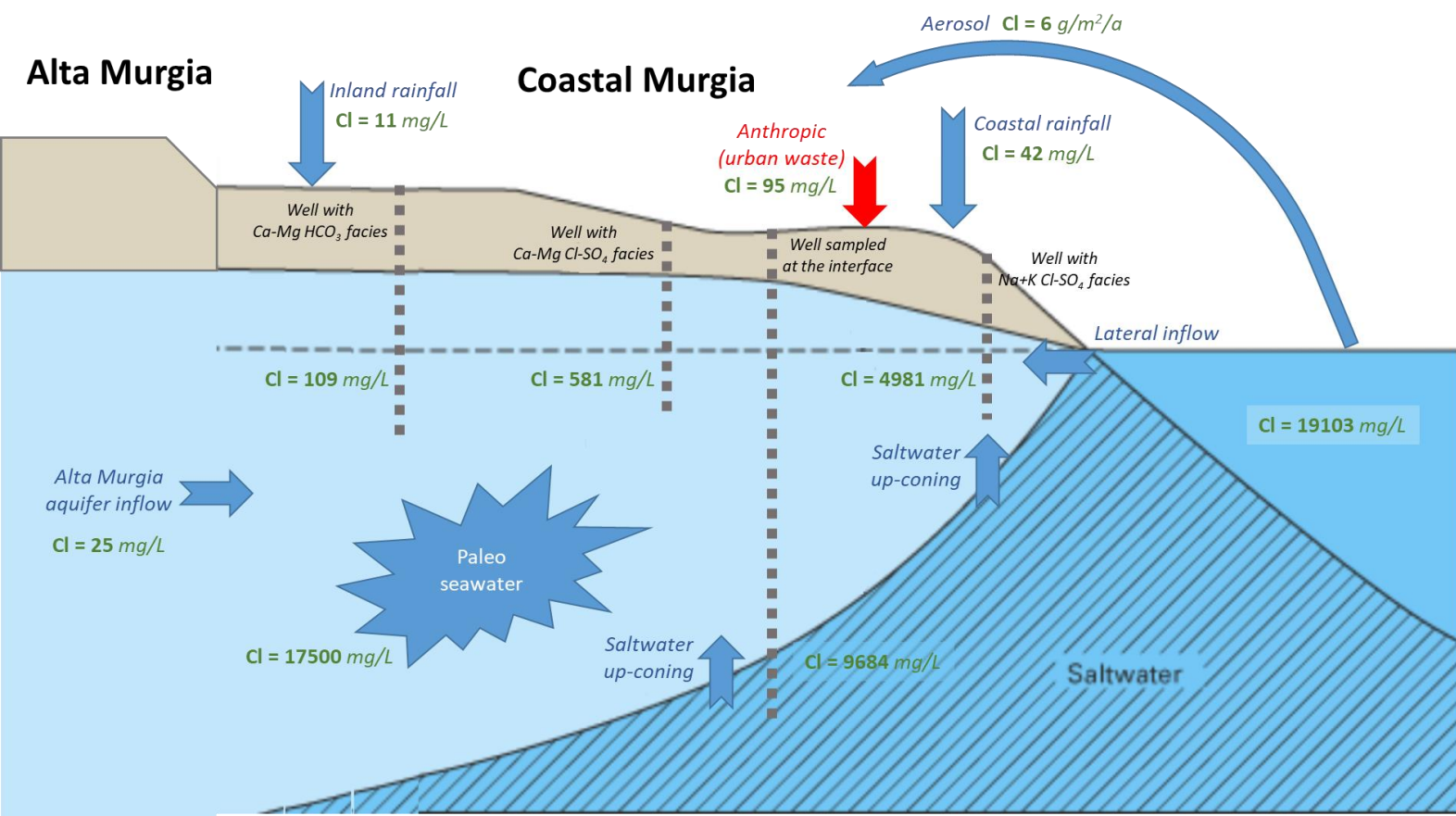
	N. total obs.	N. total MS	Size of GWB or portion of GWB represented by dataset (km <sup>2</sup> )							
			Aquifer type (unconf./conf.)							
			<10 km <sup>2</sup>		10-70 km <sup>2</sup>		70-700 km <sup>2</sup>		>700 km <sup>2</sup>	
			Unconf.	Conf.	Unconf.	Conf.	Unconf.	Conf.	Unconf.	Conf.
A		15-25	H	H	H	H	M	H	M	H
		>25	H	H	H	H	H	H	H	H
B		15-25	M	H	M	H	L	M	L	M
		>25	H	H	H	H	M	H	M	M
C	≤15		M	M	L	M	LL	L	LL	LL
	16-30		M	H	M	M	L	M	LL	L
	>30		H	H	M	H	M	A	M	M
D	<10		L	L	LL	LL	LL	LL	LL	LL
	≥10		L	L	L	L	LL	L	LL	LL

H: High; M: Medium; L: Low; LL: Very Low.

... but the question is: are the high levels of chlorides attributable to natural or anthropic causes?  
Which is the limit?

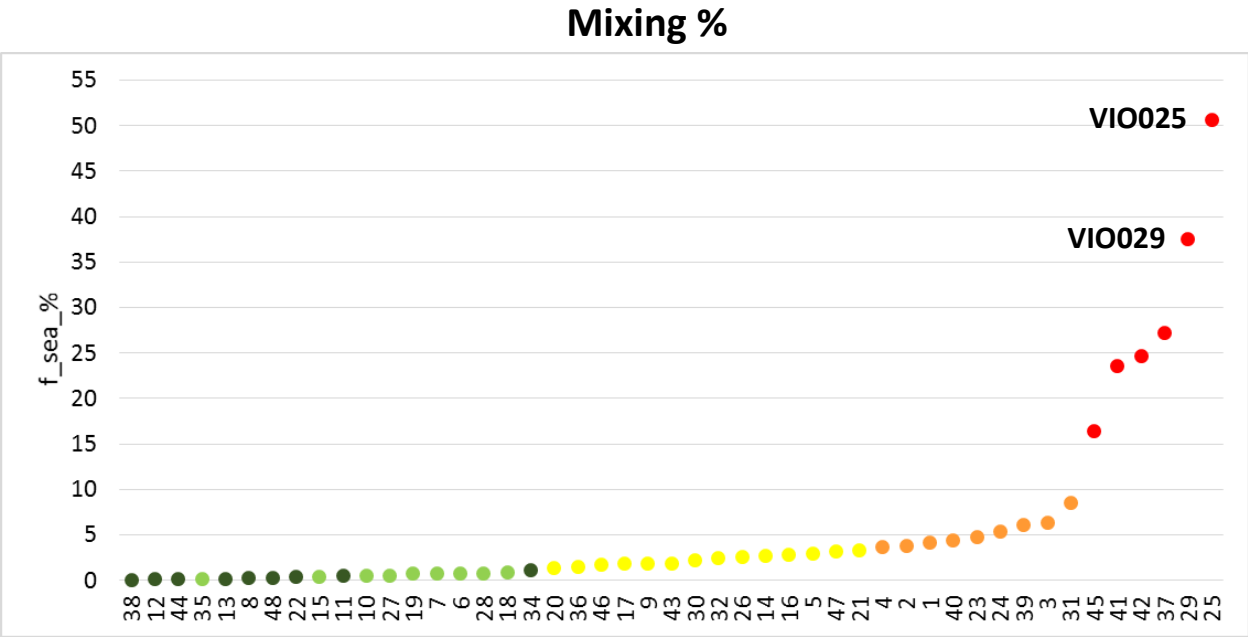
# Conceptual model

Conceptual model of the study area, with the possible chloride sources. Approaching the coastal zone, salt concentration in groundwater increases, in particular due to recent seawater intrusion. However, other contributions may have some influence, such as rainfall (note Cl difference between inland and coastal inputs), marine spray or the presence of paleo-seawater, in addition to possible anthropogenic inputs. Due to all these possible contributions, the Cl concentration in freshwater of the recharge area (25 mg/L) can progressively vary up to two orders of magnitude near the coast.



Source	Cl (mg/L)	Reference
Inland rainfall	11	Lucera pluviometric station (Cotecchia et al. 1971)
Coastal rainfall	42	Vieste pluviometric station (Cotecchia et al. 1971)
Aerosol	6 (g/m <sup>2</sup> /y)	Mediterranean coasts of Spain (Alcalà & Custodio 2008)
Urban waste	95	Bari and BAT provinces wastewater treatment plant effluent analysis 2018
Alta Murgia aquifer inflow	25	Monitoring points of the Alta Murgia GWB (present work)
Well Ca-Mg HCO <sub>3</sub> facies	109	Low Cl sampling points (present work)
Well Ca-Mg Cl-SO <sub>4</sub> facies	581	Medium Cl sampling points (present work)
Well Na+K Cl-SO <sub>4</sub> facies	4981	High Cl sampling points (present work)
Well Interface	9684	Sample VIO025 (present work)
Paleo-seawater	17500	Fidelibus & Tulipano 1996
Saltwater	19103	Sampling points of Adriatic Sea (present work)

# Seawater intrusion and mixing phenomena



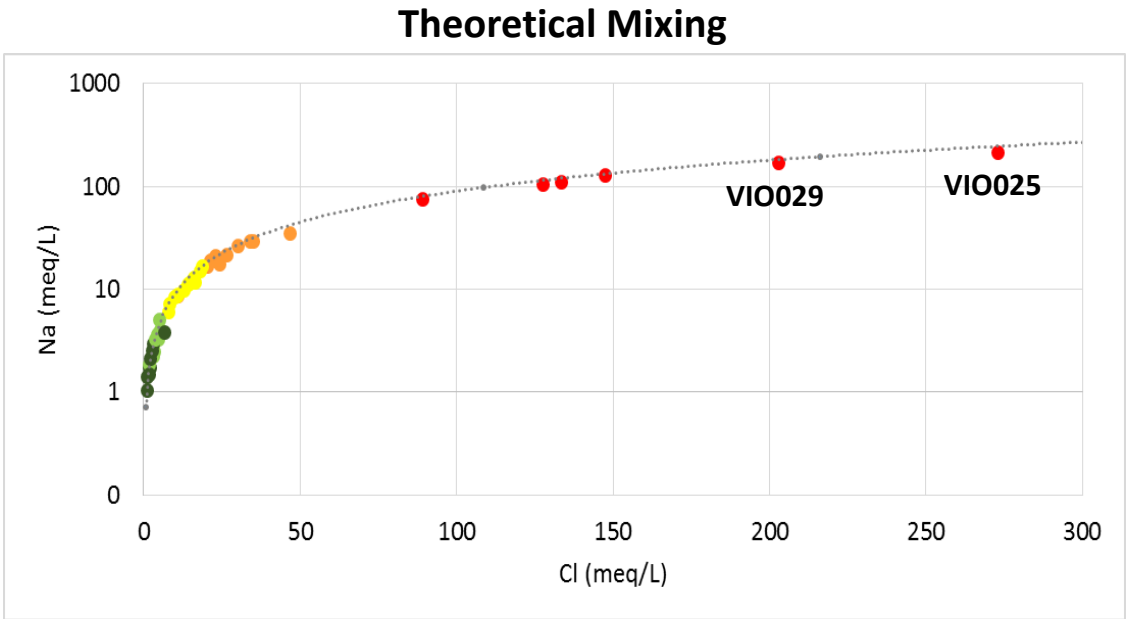
1a	Dark green	Cl < 250 mg/L (Mg/Ca < 0.7 meq/L)
1b	Light green	Cl < 250 mg/L (Mg/Ca ≥ 0.7 meq/L)
2	Yellow	250 mg/L ≤ Cl < 700 mg/L
3	Orange	700 ≤ Cl < 3000 mg/L
4	Red	Cl ≥ 3000 mg/L

The mixing % is calculated applying the equation 1:

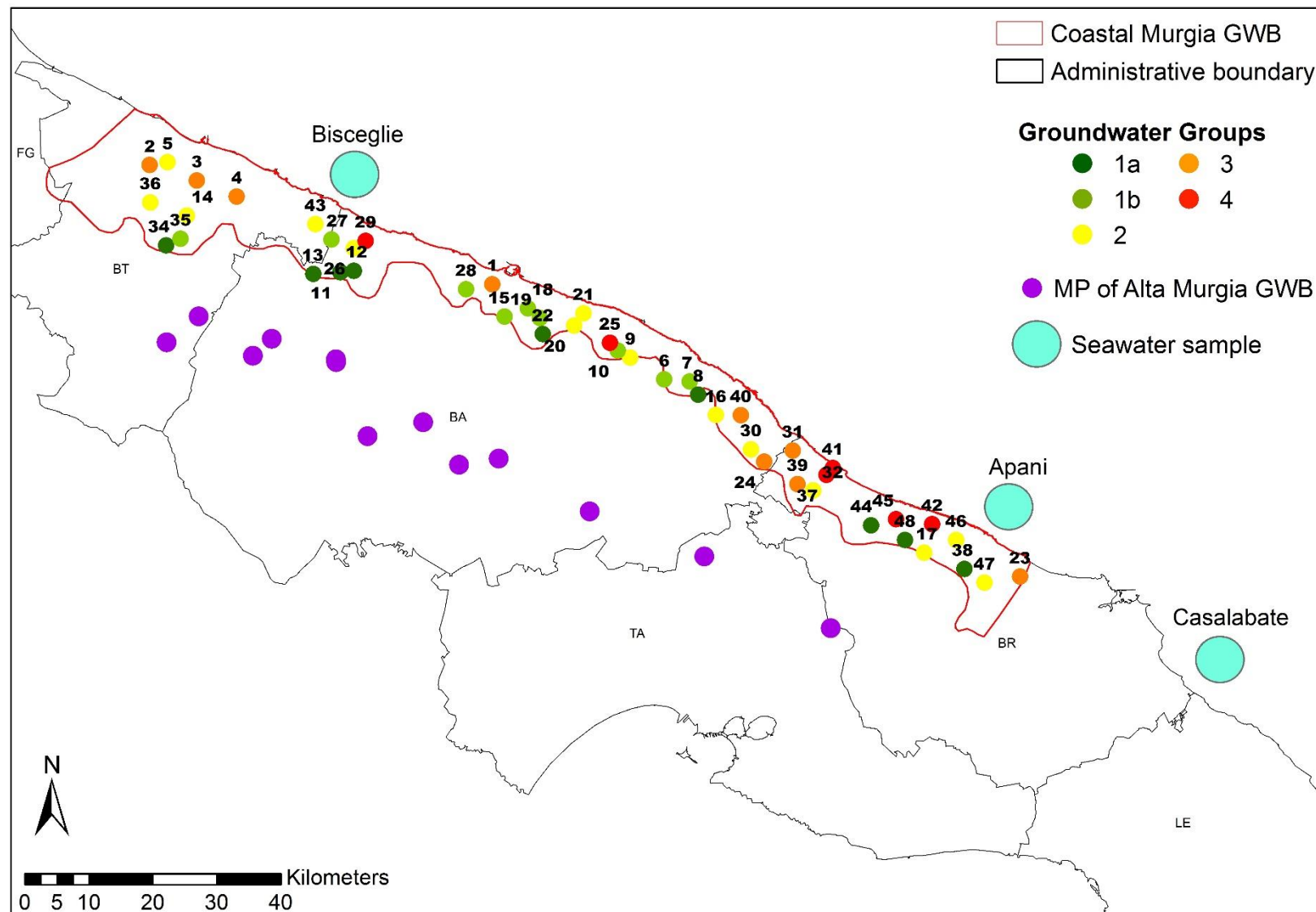
$$f_{\text{sea}}\% = (Cl - Cl_{\text{FW}}) / (Cl_{\text{SW}} - Cl_{\text{FW}}) * 100 \quad \text{Eq. 1}$$

In the graph, green dots show mixing % lower than 1, so the sampling points to be considered not affected by sea water intrusion. Table on the right show the group classification criteria, based on different limits of chlorides concentration.

In the Theoretical Mixing graph is shown the good alignment with the theoretical Na-Cl mixing line (obtained considering the Na and Cl concentration of FW and SW end-members), not only of sampling points with high f\_sea % (red dots), but also of those with lower f\_sea %.



# Seawater intrusion and mixing phenomena



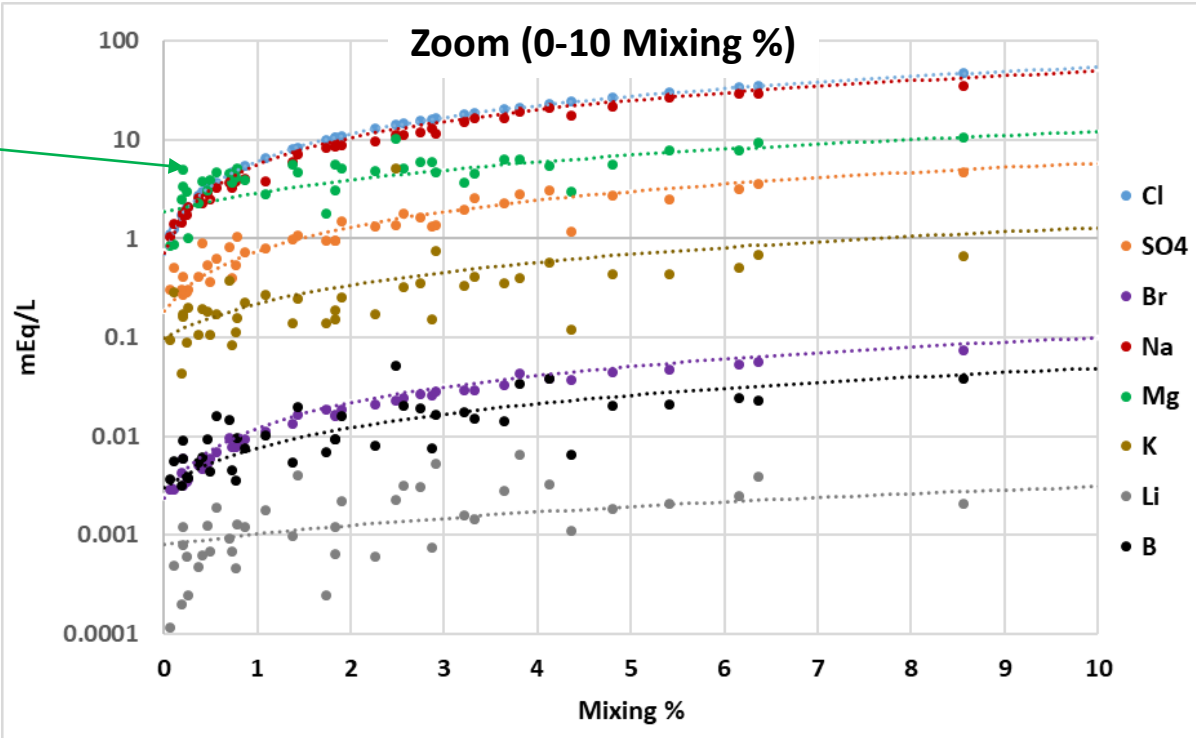
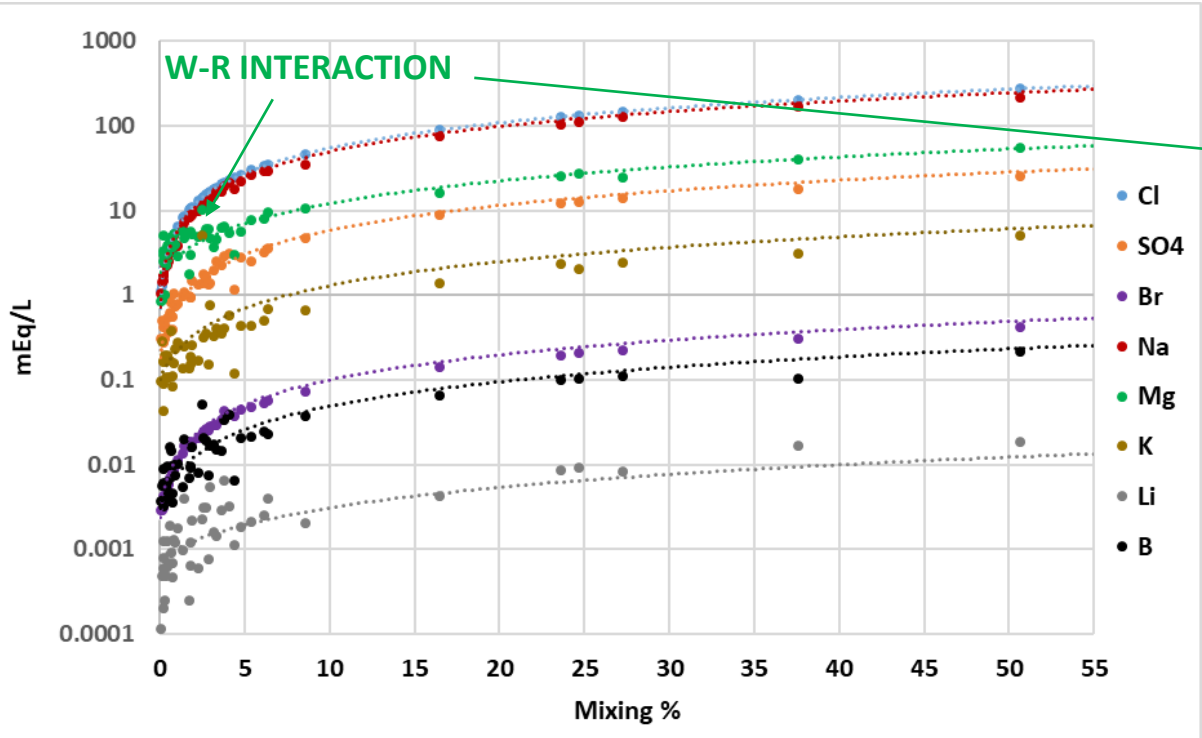
Map of the sampling points classified into groups with different mixing %. The good agreement with the Electrical Conductivity map is evident. The points used to define the two end-members are also indicated. **FW end-member** was defined starting from the monitoring points of the Alta Murgia groundwater body (recharge areas). The time series for the period 2007-2017 were first analyzed, defining a representative value for each MP. The mean of the obtained values was therefore calculated for each compound. **SW end-member** is instead given by the mean of the concentrations measured in three different points of the Adriatic Sea.



# Seawater intrusion and mixing phenomena

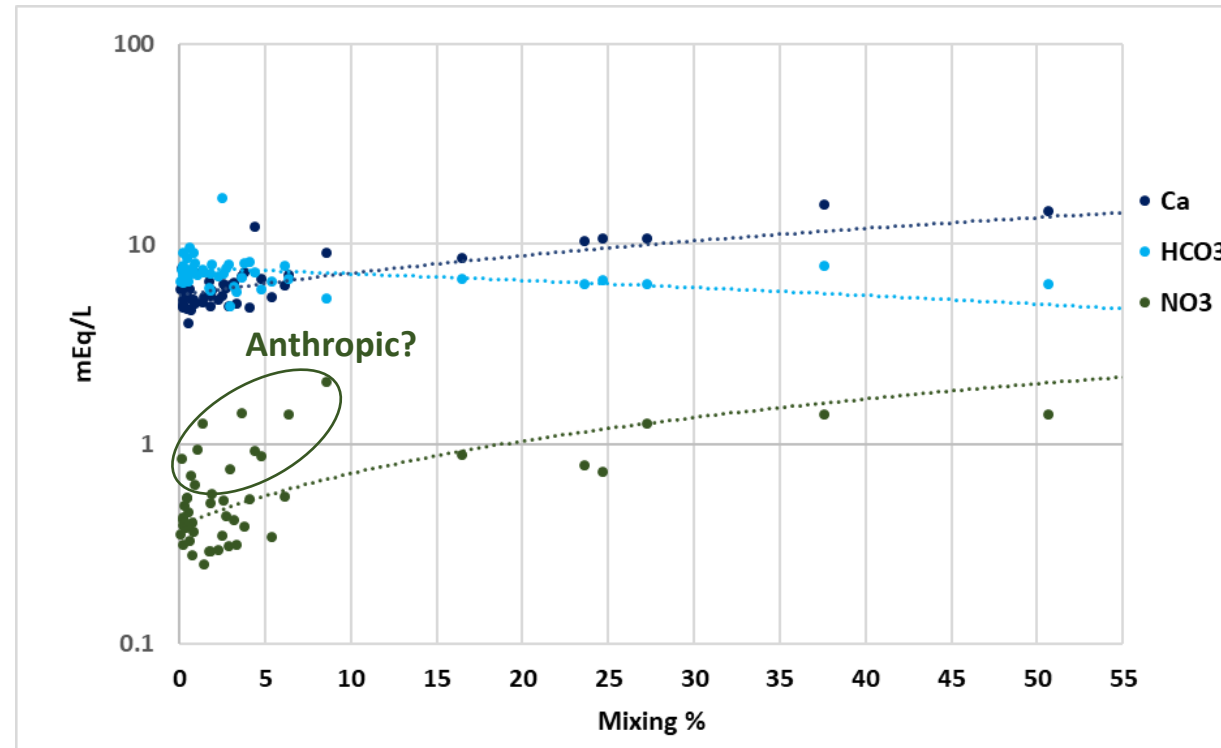
	Freshwater	Seawater	SW/FW
Cl (mEq/L)	0.71	539.20	764.2
Na (mEq/L)	0.72	488.10	679.6
Br (μEq/L)	2.38	974.30	409.5
SO <sub>4</sub> (mEq/L)	0.18	56.58	308.6
B (μEq/L)	3.03	461.30	152.4
K (mEq/L)	0.10	12.01	120.3
Mg (mEq/L)	1.86	104.38	56.1
Li (μEq/L)	0.79	23.70	30.0
NO <sub>3</sub> (mEq/L)	0.39	3.62	9.3
Ca (mEq/L)	5.56	21.66	3.9
HCO <sub>3</sub> (mEq/L)	7.63	2.32	0.3

The graphs show the concentration trends of the parameters more influenced by seawater intrusion (SW/FW≥30). Dotted lines represent the mixing (simulated by PHREEQC code version 3) of the two end-members, while points represent the concentrations detected at the sampling points (mixing % calculated by Eq.1). For relevant percentages (> 5%), mixing with SW is the most important process: the points, although slightly lower, follow the trend of the simulated mixing curves, in particular Mg, Na, Br and SO<sub>4</sub>. Lithium is the exception, showing concentrations generally above the theoretical curve (FW end-member too low?). The good linearity is gradually lost when the mixing % become lower (<5%, see graph zoom on the right). A good agreement of Na and Br values remains, while the other compounds show fluctuations linked to removal or enrichment processes overlapping the mixing with SW. Here Mg shows higher concentrations than the mixing curve, probably related to water-rock interaction (dolomites and dolomitic limestones).



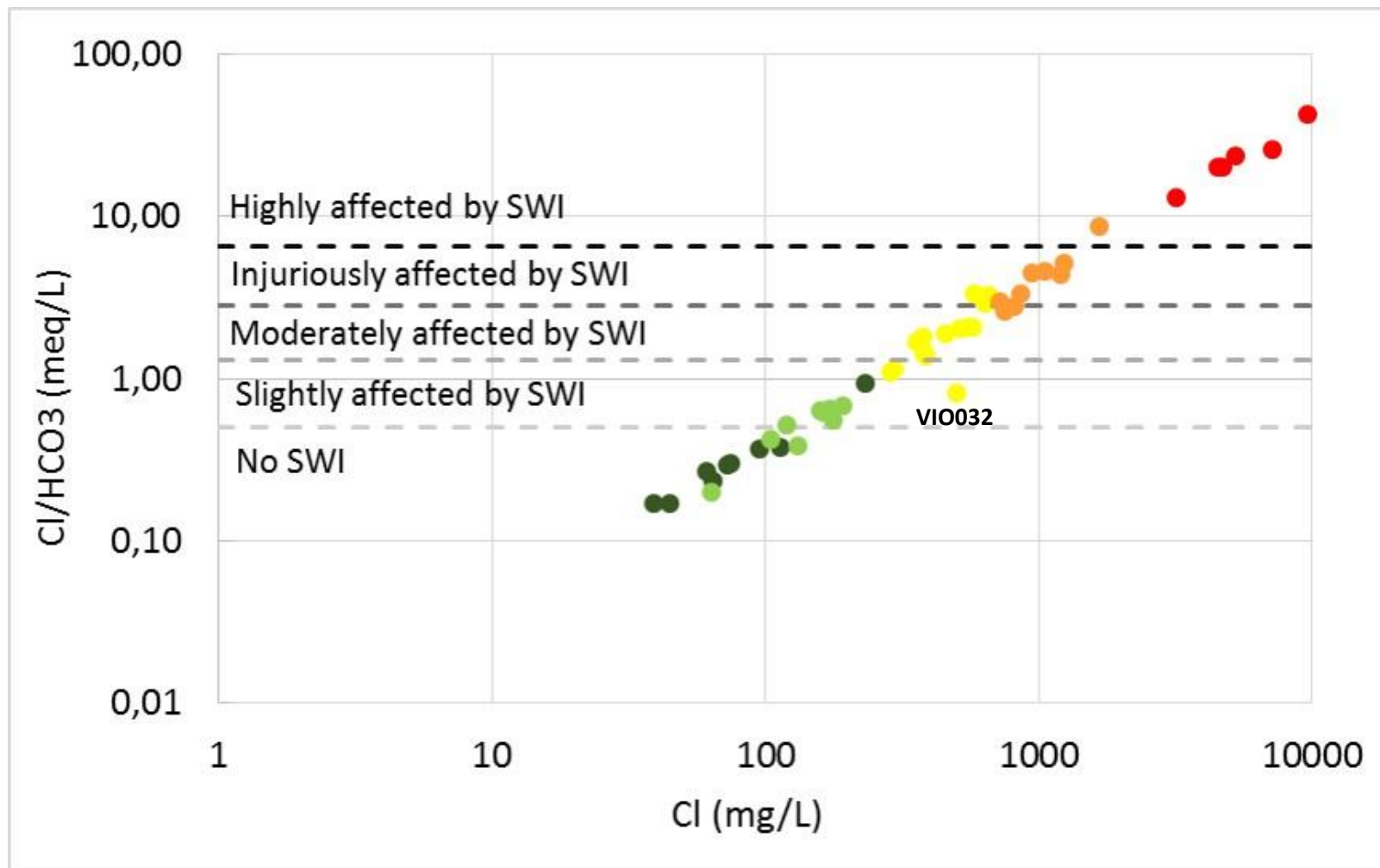
# Seawater intrusion and mixing phenomena

	Freshwater	Seawater	SW/FW
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Regarding the elements less linked to seawater (SW/FW<10), the mixing processes in this case have less influence and only at particularly high mixing % there's a certain agreement with the theoretical curves (increase of concentration for Ca and NO<sub>3</sub>). As regards bicarbonates, the other overlapping processes determines a deviation from the theoretical curve also at mixing % which would indicate a dilution of the concentration values. Nitrates show great variability even in absence of mixing processes, with values even higher than 100 mg/L. They are widespread in the study area, as well as the agricultural pressures, probably the most important NO<sub>3</sub> source in the Coastal Murgia GWB.

# Chemical ratios: $\text{Cl}/\text{HCO}_3$

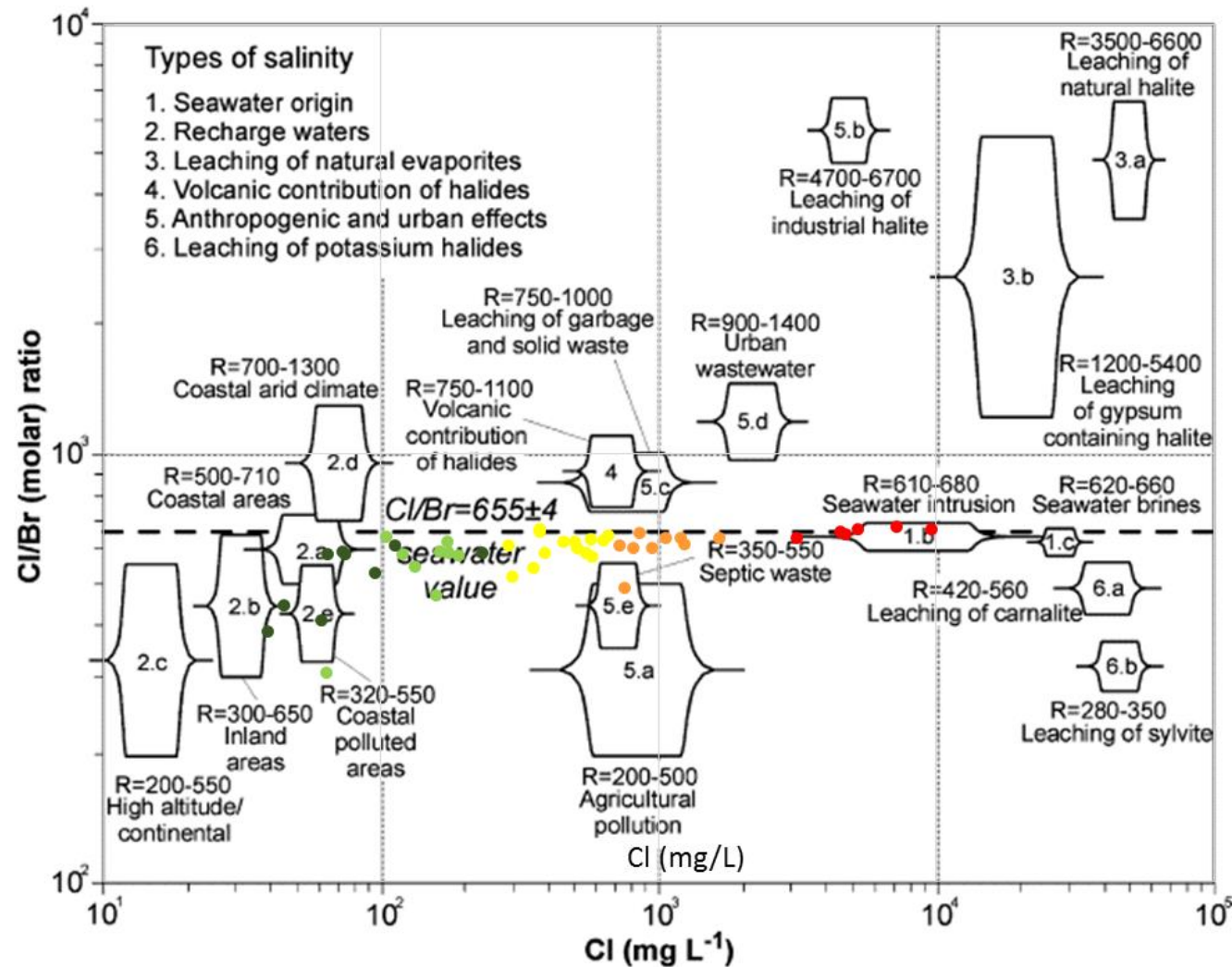


Groups: 1a - dark green dots; 1b – light green dots; 2 – yellow dots; 3 – orange dots; 4 - red dots

The Simpson ratio ( $\text{Cl}/\text{HCO}_3$ ) classification (Todd, 1959; Moujabber et al, 2006; Mtoni et al 2013) shows that 21 of 47 sampling points are not or slightly affected by seawater intrusion (SWI) (in general corresponding with green groups), 19 have from moderate to injurious SWI (yellow and orange groups), 7 are characterized by high SWI (mainly red group). This overlaps the results shown by the mixing percentage ( $f_{\text{sea}}\%$ ).

The point VIO032 belonging to the yellow group ( $250 \leq \text{Cl} < 700$  mg/L), is slightly affected by SWI, but it differs from the general trend of the entire data population: this is due to the high concentration of bicarbonates, which determines a lower value of the Simpson ratio ( $\text{Cl}/\text{HCO}_3 = 0.83$ ).

# Chemical ratios: Cl/Br

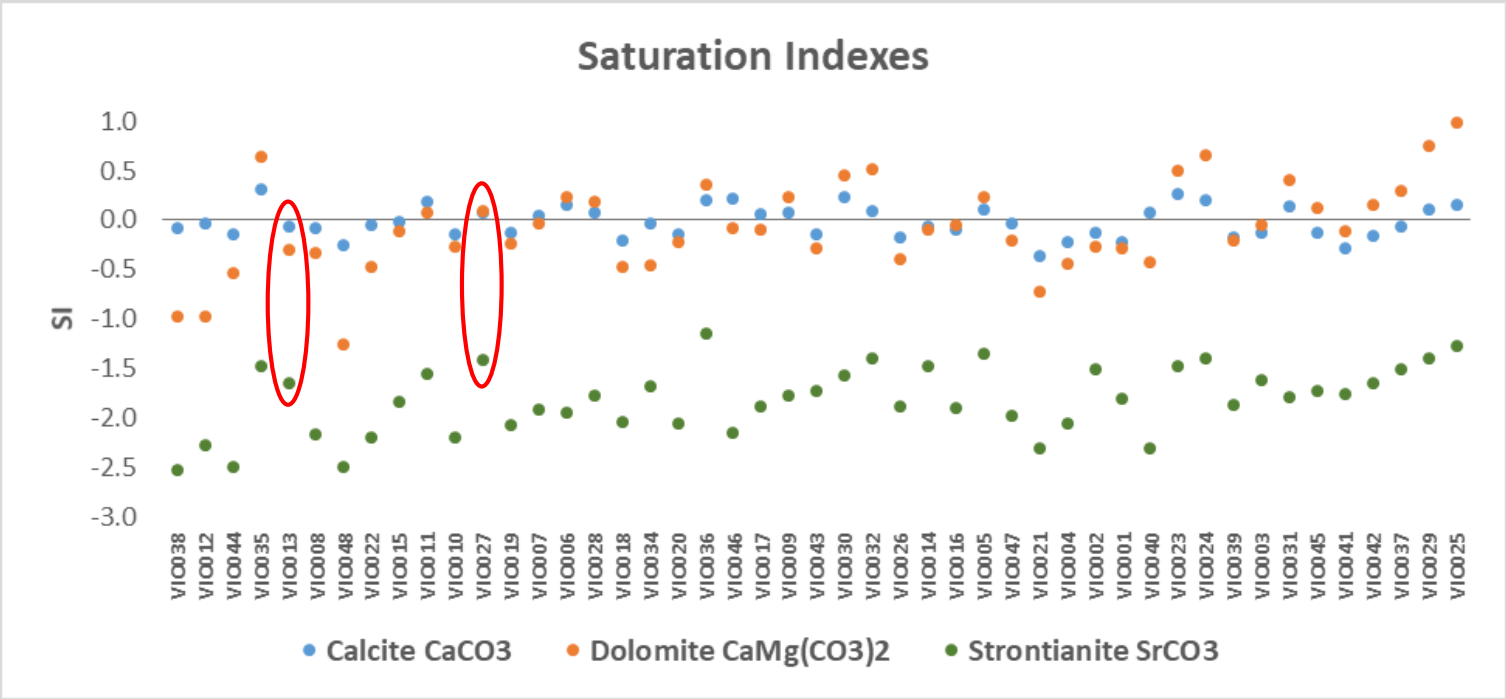


Groups: 1a - dark green dots; 1b – light green dots; 2 – yellow dots; 3 – orange dots; 4 - red dots

Cl and Br are ubiquitous and conservative solutes in all natural water, therefore their molar ratio (Cl/Br) can be used as tracer to identify the origin of salinity in ground water. Their ratio in seawater is around  $655 \pm 4$  (Alcala and Custodio, 2008). In the figure, Cl/Br ratio is plotted vs Cl concentration, overlapping the case study results to the Cl/Br vs Cl plot of Alcala and Custodio (2008). The recorded Cl/Br ratios align along the Cl/Br ratio of SW reported by Alcala and Custodio (2008). Red dots fall into the SWI range, indicating a clear and substantial influence of SWI to these points. Orange, yellow and green dots, instead, have Cl/Br comparable with the Cl/Br ratio of SWI, but also with the typical Cl/Br ratio of recharge waters of coastal areas. This and the lower Cl concentration, highlight that these points can be influenced by both a minor mixing with SW and by airborne marine aerosols from the nearby coast.



# Water-rock interaction



	Saturation Indexes			
	CO <sub>2</sub> (g)	Calcite	Dolomite	Strontianite
VIO013	-1.26	-0.06	-0.30	-1.64
VIO027	-1.16	0.07	0.10	-1.41

	VIO013	VIO027	VIO027 Simulated	Diff %
pH	6.86	6.87	6.87	-
HCO <sub>3</sub> (mg/L)	479.0	588.4	621.1	5.26
Mg (mg/L)	40.4	56.9	61.1	6.87
Ca (mg/L)	106.1	120.1	118.8	-1.09
Sr (µg/L)	908.0	1342.0	1269.6	-5.70

Saturation indexes (SI) for mineralogical pure phases likely to be present in the carbonate aquifer were calculated, such as Calcite, Dolomite and Strontianite (Sr is a well-known vicariant of Ca). Groundwaters are at the saturation limit with respect to Calcite and Dolomite, instead showing undersaturation in Strontianite. However, rather than a pure Strontianite, the existence of an impure Calcite (CaSrCO<sub>3</sub>), equally close to equilibrium, is more likely.

The SIs and the geographical position suggest that VIO027 water could represent the natural evolution of VIO013 water, located upstream and undersaturated in the mineralogical phases. The SIs of VIO013 were therefore adapted to those of VIO027, simulating the resulting solution. The simulation results show a good agreement with the concentration values of VIO027, indicating that water-carbonate rocks interaction processes govern groundwater geochemistry in absence of mixing with seawater.

# Preliminary conclusions

- We presented the results of the first two sampling campaigns planned in the VIOLA project.
- Geochemical characterization and statistical analysis have highlighted at least two main processes responsible for the groundwater chemistry in the study area: the water-rock interaction within the carbonate aquifer and the mixing with seawater caused by saline intrusion.
- Other possible sources of chlorides include rainfall, marine spray, presence of paleo seawater and anthropogenic inputs. However, no evidences of human impact emerged from these first investigations.
- As for the NBLs derivation, classic indicators of anthropogenic contamination (e.g.  $\text{NO}_3$ , Cl) for the pre-selection of uninfluenced samples failed due to the extensive distribution of saline groundwaters in the Coastal Murgia GWB, which prevents their joint use.
- New solutions, including environmental isotope analysis, for discriminating the anthropogenic and natural origin of the salinity are under evaluation.

# Other displays on the VIOLA project

EGU2020-7716

## **The VIOLA Project: Natural background levels for the groundwater bodies of Apulia Region (Southern Italy)**

Masciale R., Amalfitano S., Frollini E., Ghergo S., Melita M., Parrone D., Preziosi E., Vurro M., Zoppini A., and Passarella G.

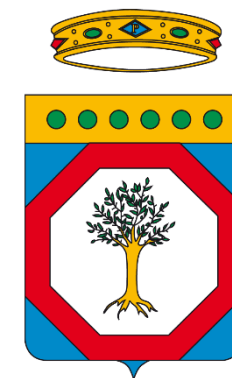
EGU2020-7630

## **The VIOLA Project: Functional responses of groundwater microbial community across the salinity gradient in a coastal karst aquifer**

Melita M., Amalfitano S., Frollini E., Ghergo S., Masciale R., Parrone D., Passarella G., Preziosi E., Vurro M., and Zoppini A.

# Acknowledgements

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# Bibliography

- Alcalá F. J., Custodio E. (2008) - Using the Cl/Br ratio as a tracer to identify the origin of salinity in aquifers in Spain and Portugal, *Journal of Hydrology*, 359, 189-207
- Cotecchia V., Tadolini T., Tittozzi P. (1971) - Influenza del chimismo delle piogge sulle acque sotterranee della Puglia. *Geologia Applicata e Idrogeologia*, 6, 175-196, Bari
- Cotecchia V. (2014) - Acque sotterranee e l'intrusione marina in Puglia: dalla ricerca all'emergenza nella salvaguardia della risorsa. *Memorie descrittive della carta geologica d'Italia*, vol. 92. Editore: ISPRA Serv. Geologico d'Italia. ISBN-13: 9788893110037
- El Moujabber M., Bou Samra B., Darwish T., Atallah T. (2006) – Comparison of different indicators for groundwater contamination by seawater intrusion on the Lebanese coast. *Water Resources Management*, 20, 161- 180, doi 10.1007/s11269-006-7376-4
- Fidelibus M.D., Tulipano L. (1996) - Regional flow of intruding sea water in the carbonate aquifers of Apulia (Southern Italy). 14th SaltWater Intrusion Meeting, Malmo, Sweden
- ISPRA (2017) – Linee guida recanti la procedura da seguire per il calcolo dei valori di fondo per i corpi idrici sotterranei (DM 6 luglio 2016). *Manuali e Linee Guida dell'Istituto Superiore per la Protezione e la Ricerca Ambientale (ISPRA)*, 155, 2017
- Maggiore M., Pagliarulo P. (2003) - Groundwater vulnerability and pollution sources in the Apulian region (Southern Italy). *Proceedings of 2<sup>nd</sup> Symposium "Protection of Groundwater from Pollution and Seawater Intrusion"*, pp. 9-20; Bari, September 27 – October 1999
- Maggiore M., Pagliarulo P. (2004) - Circolazione idrica ed equilibri idrogeologici negli acquiferi della Puglia. Conference «Uso E Tutela Dei Corpi Idrici Sotterranei Pugliesi», Bari 21 Giugno 2002. In *Geologi e Territorio – Suppl. n. 1-2004*, pp.13-35
- Mtoni Y., Chikira Mjemah I., Bakundukize C., Van Camp M., Martens K., Walraevens K. (2013) – Saltwater intrusion and nitrate pollution in the coastal aquifer of Dar es Salaam, Tanzania. *Environmental Earth Science*, 70, 1091-1111, doi 10.1007/s12665-012-2197-7
- Todd D. K. (1959) – *Ground Water Hydrology*, John Wiley and Sons. Inc.