VIOLA
natural background levels
in Apulian groundwater bodies

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., Passarella G.*

EGU General Assembly 2020
Online | 4–8 May 2020
HS8.2.9 - Groundwater flow and geofluids system understanding with regard to environmental problems and resource management

IRSA CNR

Introduction

- The Natural Background Levels (NBL) can be defined as the concentration of a substance or the value of an indicator in a groundwater body corresponding to the absence or extremely limited anthropogenic modifications.
- NBLs are the result of various processes of geochemical, chemical, and biological origin that occur in the unsaturated and saturated area.
- The Daughter Directives on Groundwater (GWDD 2006/118/EC) specifies that the chemical status of groundwater is assessed on the basis of standards defined at the European scale for some contaminants, while the Member States can derive their own threshold values, for the other contaminants, even considering the NBLs, if necessary.
- The GWD does not provide rules on how to derive these values, however, some technical suggestions are provided by the guidelines of the European Commission.
- This study presents the first results of the VIOLA Project related to the assessment of the NBLs in the 29 groundwater bodies in the Apulia region (South Italy), which is characterized by serious problems of salinization of coastal aquifers.

The VIOLA project
Main objectives

- To define and verify on field, methods, and specific protocols for groundwater sampling and for groundwater NBLs assessment in accordance with the guidelines defined by the Italian Institute for Environmental Protection and Research (ISPRA) in collaboration with IRSA-CNR and the Ministry of the Environment.
- To test innovative approaches in the groundwater quality assessment to verify whether chemical quality can affect resident microbial community and their role in the biogeochemical cycling

VIOLA project

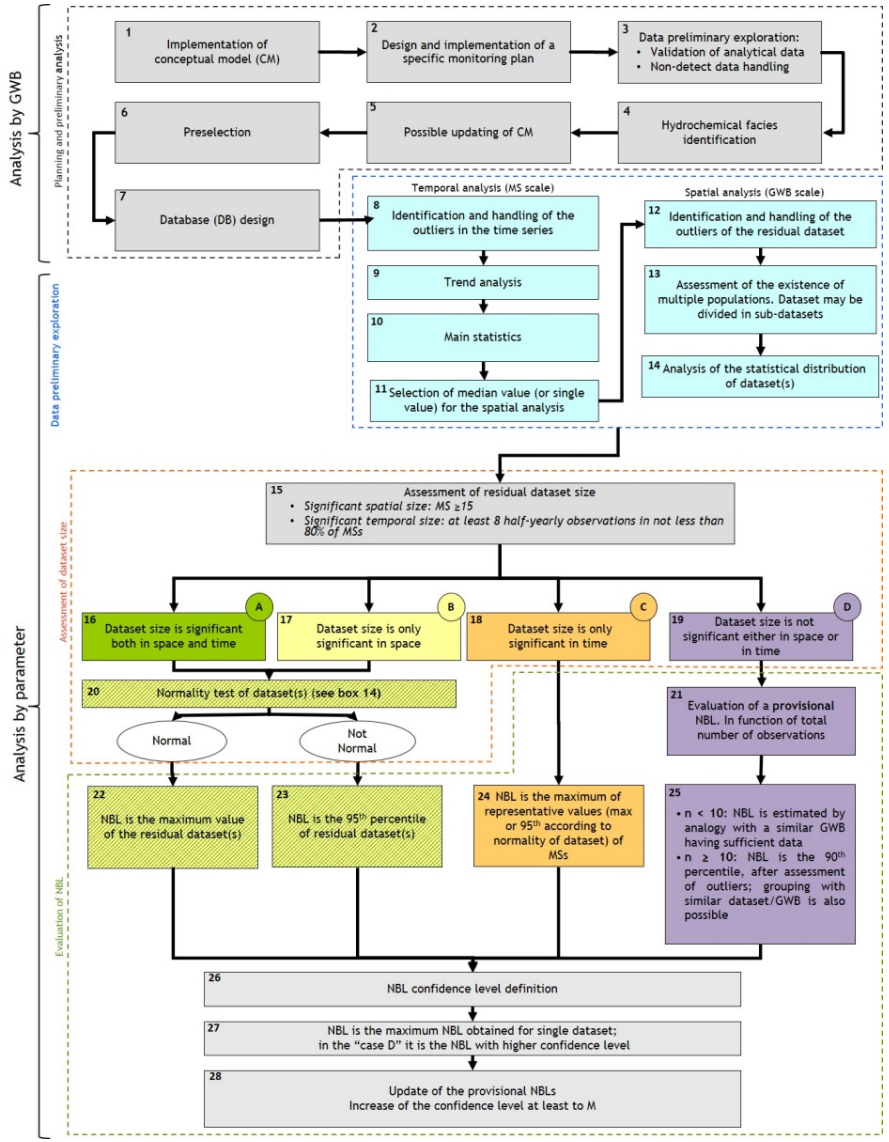
The VIOLA project
Specific objectives

- To determine, in agreement with the Regional Department of Water Resources Management, the inorganic substances in groundwater for which the knowledge of the NBLs need to be deepened
- To study the NBLs with reference to the specific issues of Apulia groundwater bodies
- To test, in a study area of Apulia Region, innovative approaches to assess how changes in groundwater quality can affect resident microbial communities which play an important role in the biogeochemical cycling
- To edit reports and cartographic representations of the study results useful for the regional water management authority and for the development of future water basin plans

Guidelines for the NBLs assessment

- GWDD 2006/118/EC require the Member States to establish threshold values (TVs) for each pollutant, or indicator of pollution, characterizing groundwater bodies (GWBs) at risk of failing to achieve good chemical status. The establishment of TVs must take into account the NBLs.
- The Italian guidelines, implemented in 2017 (ISPRA, 2017), integrates two main approaches for the definition of NBLs at the GWB scale:
  - the probabilistic methods – based on the assumption that different water genetic processes can give rise to different types of population distinguishable by statistical methods
  - the pre-selection – based on the preselection of water samples unaffected, or poorly affected, by human activities. A marker, such as nitrates, ammonia, or chlorides, is chosen and a threshold value fixed. Samples exceeding the threshold value are excluded in advance. On the preselected dataset, a value is chosen as NBL (e.g. 95 percentile)

Guidelines for the NBLs assessment



The procedure is divided into four main steps:

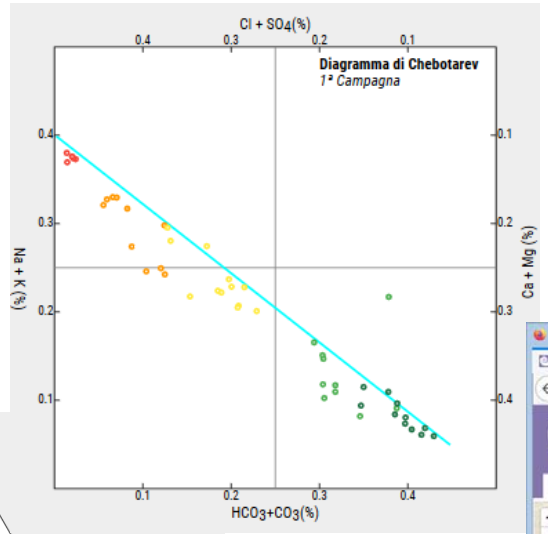
1. Data validation, redox facies separation, preselection of uninfluenced samples (to be applied to the water points)
2. Statistical analysis - temporal and spatial analysis (to be applied to each parameter)
3. Evaluation of the consistency of the dataset
4. Definition of the NBLs and attribution of a level of reliability (high, medium, low, very low) to the defined NBLs

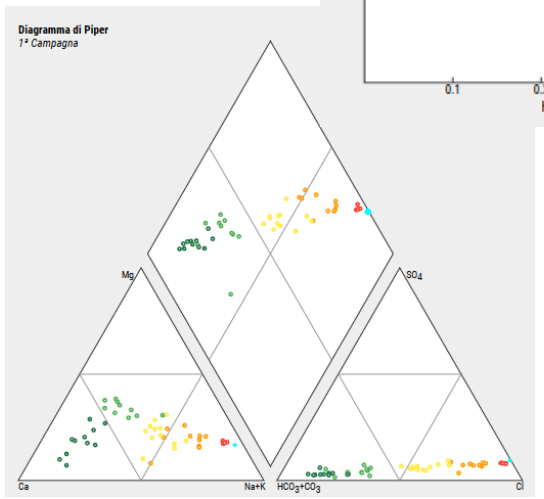
Procedure for the NBLs assessment in the GWBs (ISPRA, 2017)

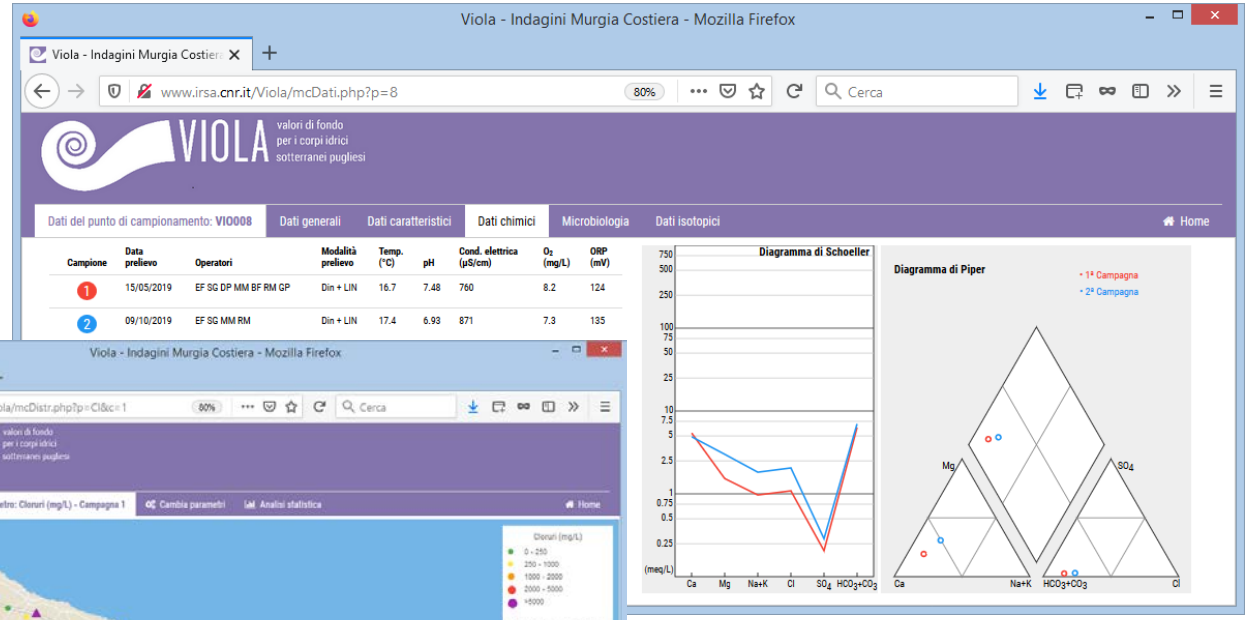
Tools to support the NBLs management

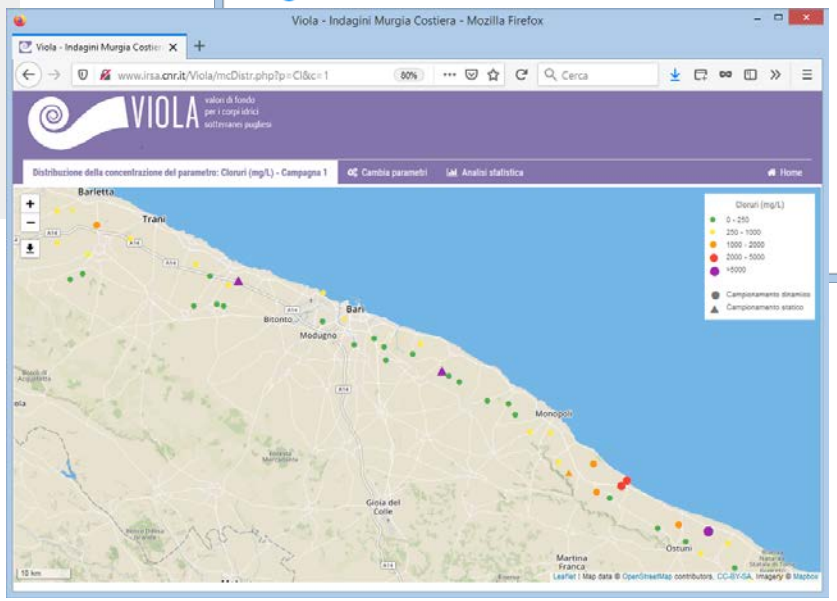
VIOLA website

- Currently, VIOLA website acts mainly as an operative tool for the staff involved in the Project. Monitoring data are organized in a database and easily displayed and processed to obtain maps and charts.

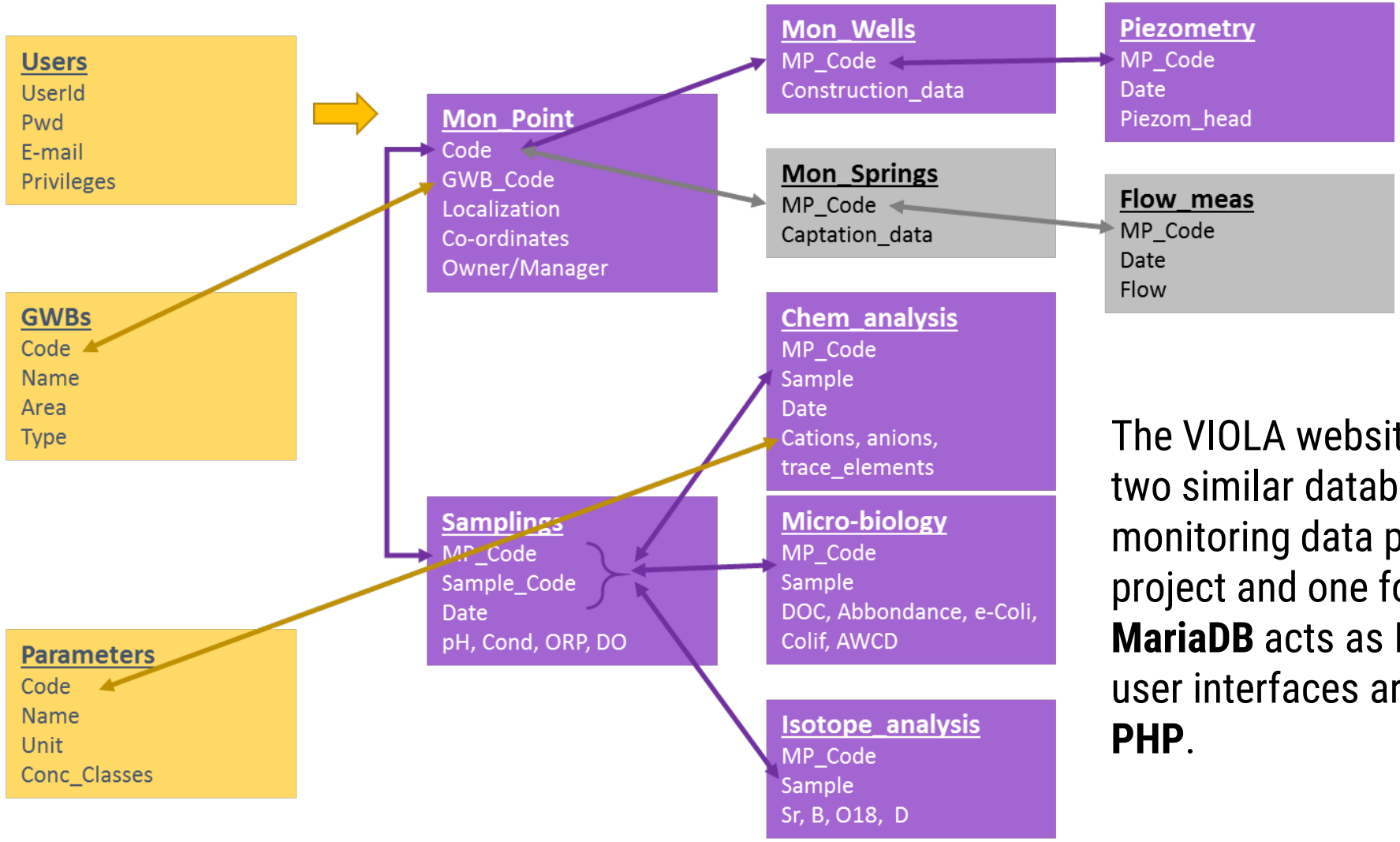








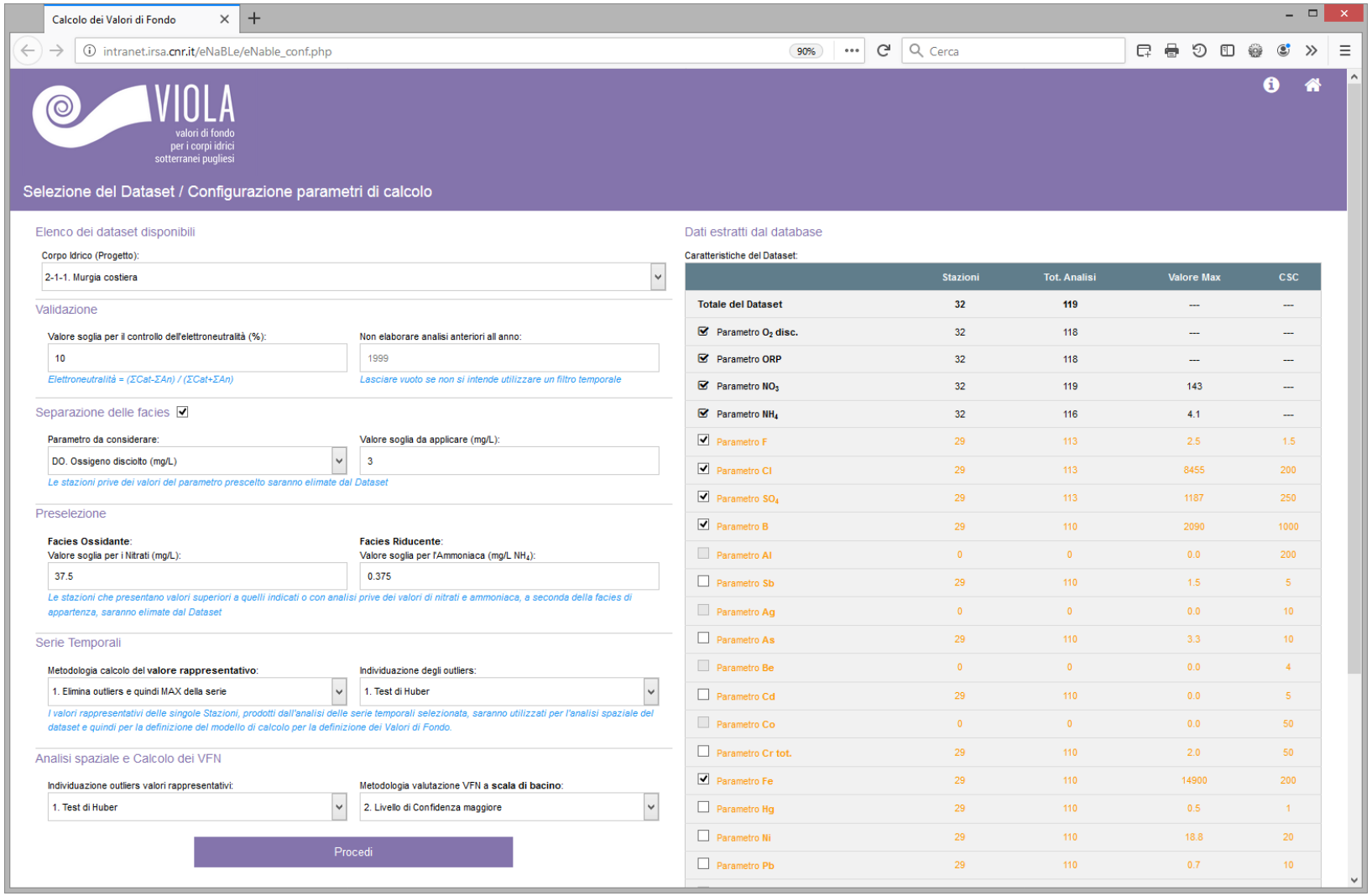
Tools to support the NBLs management
VIOLA database



The VIOLA website procedures rely on two similar databases, one for the new monitoring data produced within the project and one for the previous ones. **MariaDB** acts as DBMS, data access, and user interfaces are implemented with **PHP**.

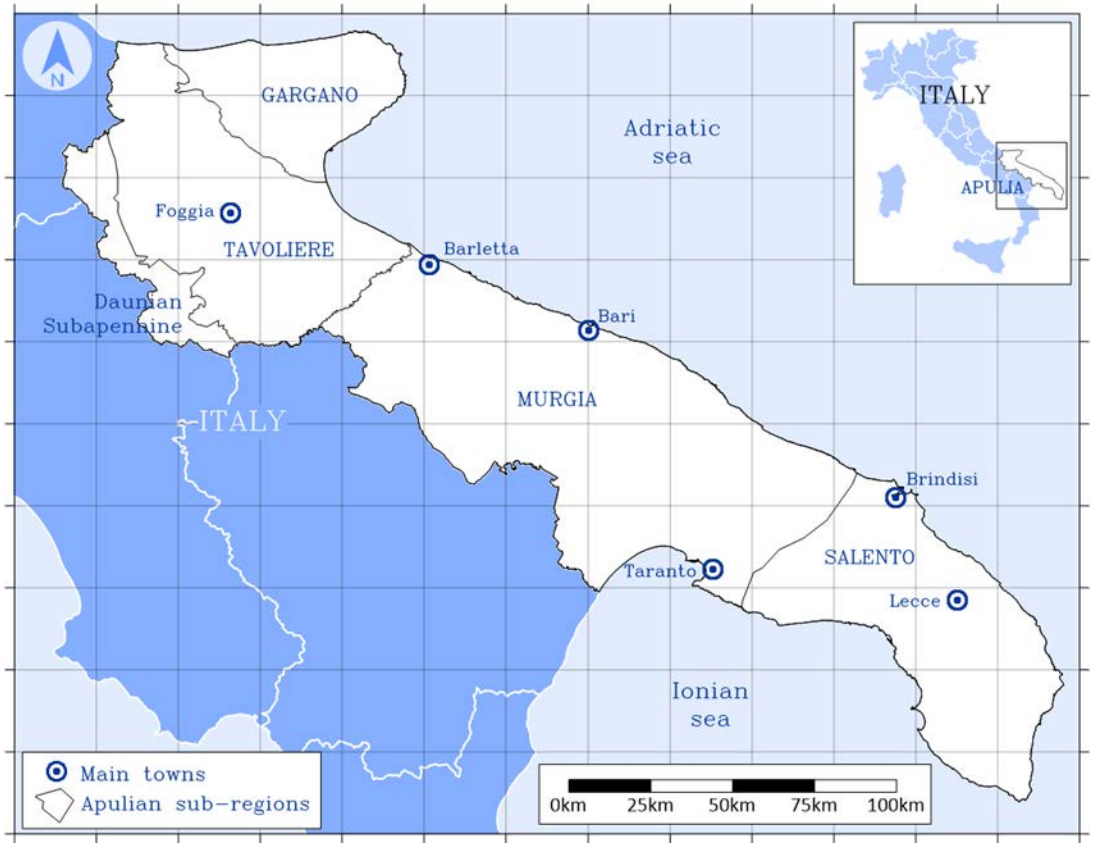
Tools to support the NBLs management

VIOLA website tools



VIOLA NBL evaluation tool allows the choice of all the parameters for the assessment (redox facies separation parameter and relative threshold, marker threshold, time series analysis method, confidence level assignment method) and supplies general information on the dataset.

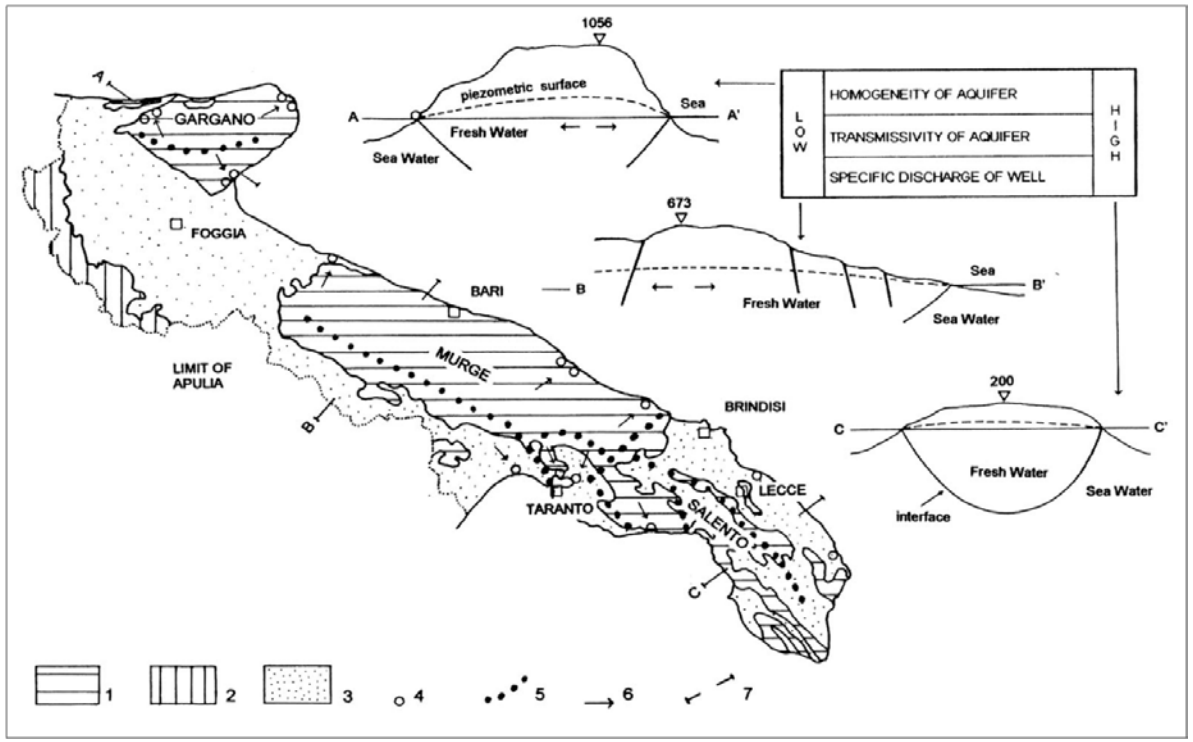
Study area
The Apulia region



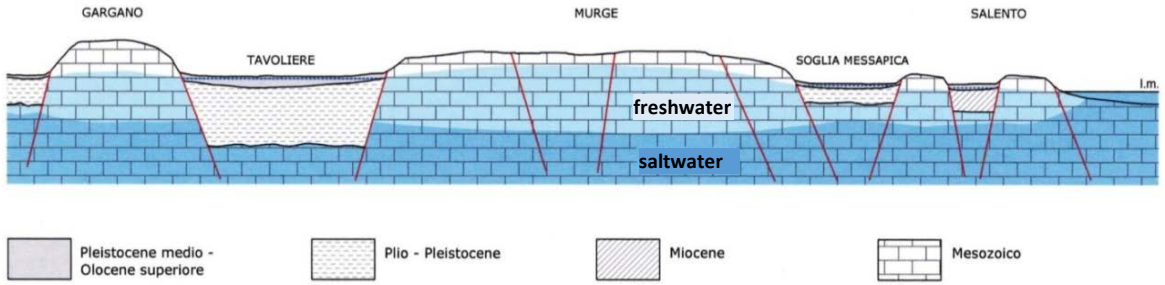
The Apulia region is located on the southeastern side of Italy

- Located on the southeastern side of Italy
- Area: ~ 19.400 km2 (6,5 % of the country) Lowlands 53% - Hills 45% - Mountains 2%
- Extensive coastal development (about 900 km)
- Mediterranean climate (mean annual rainfall: 600mm)
- Karst landscape (caves, sinkholes, springs, fluvial - karstic valley)
- Almost totally absence of surface water (intermittent and ephemeral streams)
- Notable groundwater resources (~80% of the total irrigation needs and ~16% of the total drinking water needs are provided by groundwater)
- Population: ~4 mln – density : 210 inhabitants/km2
- Economy: predominant agricultural vocation

Geological and hydrogeological framework



Hydrogeological scheme of Apulia : 1) Mesozoic carbonate succession ; 2) Apennine allochthonous units; 3) Plio-Pleistocene deposits ; 4) main coastal springs; 5) hydrogeological watershed; 6) groundwater flow direction; 7) trace of sections (after Maggiore e Pagliarulo, 2003).



Schematic NW-SE section accross the outcropping Mesozoic succession [after Maggiore e Pagliarulo, 2004]

Apulia Region mostly corresponds to the exposed area of the southern Apennines foreland.

It is characterized by a thick Mesozoic carbonate succession (limestone, dolomitic-limestones, and dolostones), overlain by discontinuous Plio-Pleistocene deposits.

Different fields of tectonic stresses have acted on the carbonate bedrock, producing bland deformations and ruptures (joints and normal faults).

The main groundwater Apulian reservoirs, fed by autumn-winter rainfalls, are hosted in the carbonate successions outcropping in the Gargano, Murge, and Salento.

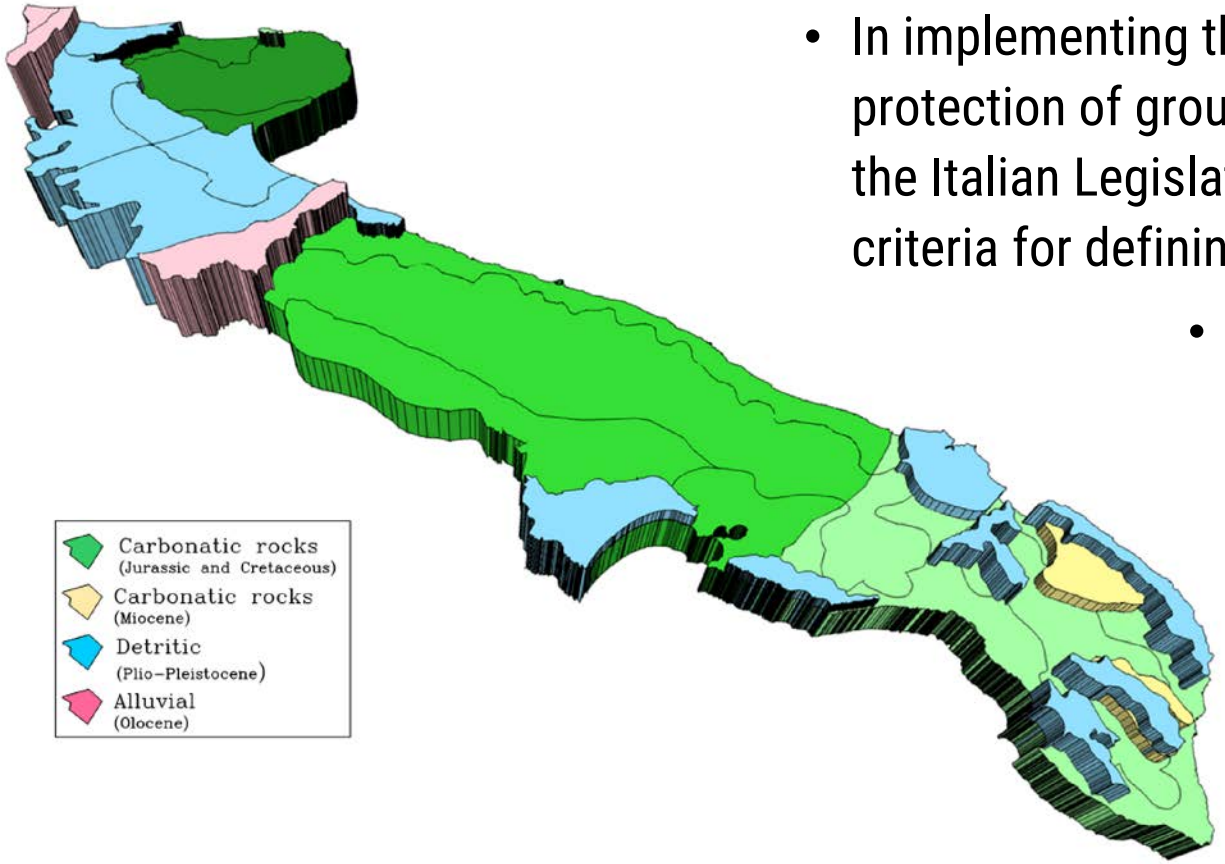
The three hydrogeological structures, due to particular structural setup, are closely connected regarding the deep groundwater circulation.

Hydrogeological features (permeability, depth of water, specific discharge of wells, water quality), are strongly influenced by stratigraphic and structural factors and by the irregular distribution of karst phenomena affecting the carbonates.

Generally, groundwater flows toward the sea, often under pressure, and fractionated into distinct levels separated by dry layers.

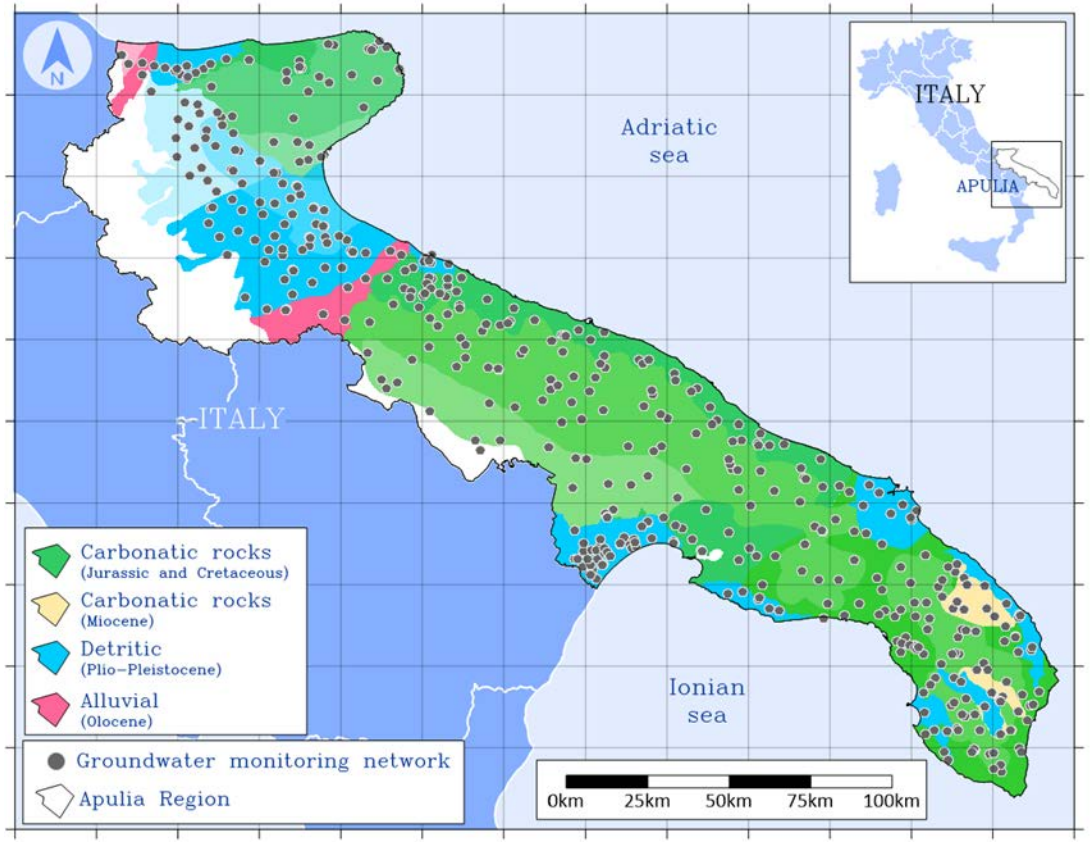
All carbonate groundwater systems in Apulia are governed by the fresh – saltwater equilibria, which may be altered by a progressive decrease of rainfall alimentation and uncontrolled withdrawals.

Regional groundwater bodies (GWBs)



- In implementing the provisions of the EU GWD on the protection of groundwater against pollution and deterioration, the Italian Legislative decree no. 30/2009 establishes uniform criteria for defining the GBWs and characterizing their status.
  - Following the established criteria, the Regional Department of Water Resources Management delineated 29 GWBs grouped in 3 types of hydrogeological complexes: carbonatic, detrital, and alluvial (Passarella et al., 2013; 2015).

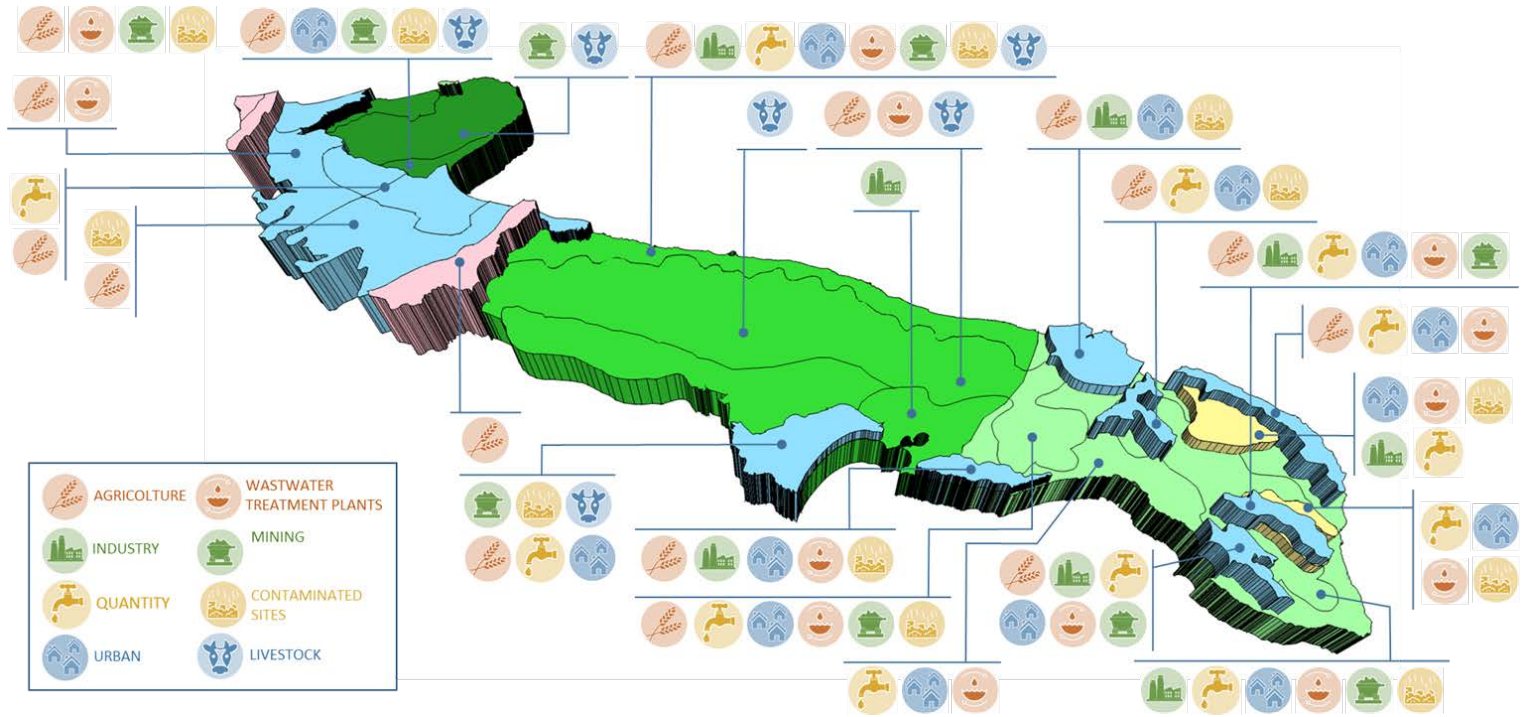
Regional GW monitoring network



The regional groundwater monitoring network consists of 487 sites and in particular of 470 wells and 17 springs clustered in the following sub-networks:

Sub-network	N. of sites	Measurements
Quantitative	227 wells	Static water level
	17 springs	Flow rate
Qualitative	427 wells	Physico-chemical and microbiological parameters
	17 springs	

GWBs characterization
Significant pressures



As a result of the different human activities, the GWBs are affected by various pressures that impact both the qualitative and quantitative status.

The pressures affecting the qualitative status can be grouped into diffuse sources and point sources of contamination.

Among the point sources of contamination, the most common are landfills, contaminated sites of national interest, wastewater treatment plants, petrol stations, oil mills, and tourism settlements, the latter mainly located near the coast.

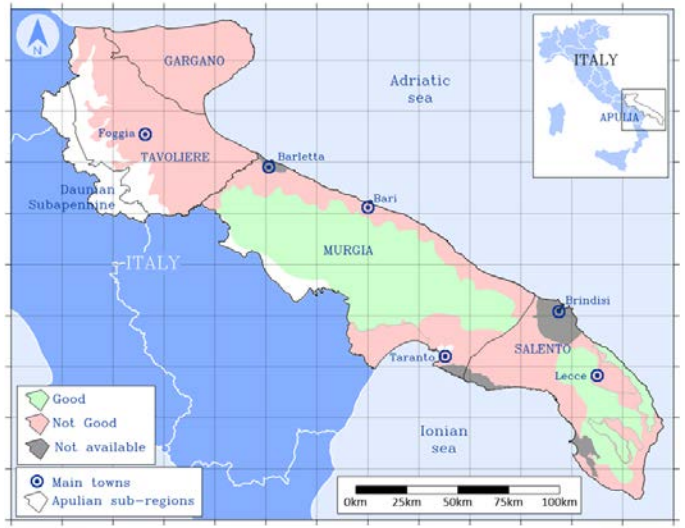
The most important sources of diffuse contamination are agriculture, livestock, urbanized, industrial, and mineral areas.

These pressures, in turn, cause overexploitation of the groundwater resources to meet domestic, agricultural, and industrial demand.

GWBs Status

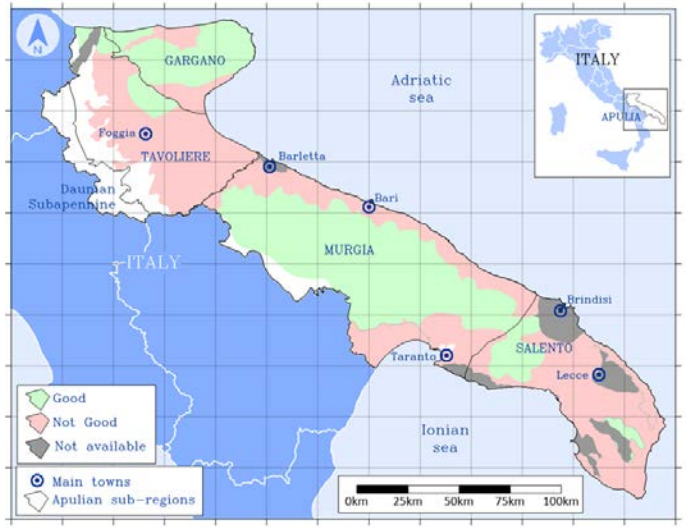
According to the procedure defined in the «Guidance Document n.18 – Guidance on Groundwater Status and Trend Assessment (2009)», GBWs status was assessed considering a series of classification tests, for both quantitative and chemical status. Due to the low significance of the available data, the status could not be assessed for some GWBs. These are shown as not available.

- Chemical status



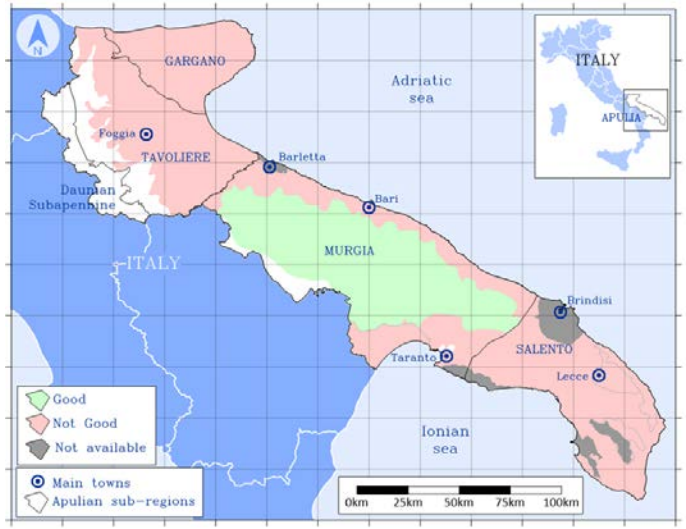
	N. of GWBs
good	5
not good	18
not available	6

- Quantitative status



	N. of GWBs
good	8
not good	12
not available	9

- GWB overall classification



	N. of GWBs
good	2
not good	20
not available	7

NBLs for Apulian GWBs
Preliminary results

Corpo Idrico: 2-1-2. Alta Murgia | Riconfigurazione Parametri | CIS 2-1-2

Dati Generali

Superficie CIS: **3842 km²**
Tipologia: **Confinato**
Stazioni con dati: **42**

Gestione valori inferiori al LOQ

Sono stati modificati **261** record

Validazione

Valore soglia per l'elettroneutralità (%): **10**
Sono stati individuati **3** record

Separazione delle Facies

Parametro per la separazione facies: **ORP** - Valore soglia: **0**
Dataset Ossidante: **37** Stazioni di campionamento
Dataset Riducente: **5** Stazioni di campionamento

Preselezione

Valore soglia facies oss. (NO_3): **37.5** - Valore soglia facies rid. (NH_4): **0.375**
Dataset Preselezionato Ossidante: **33** Stazioni di campionamento
Dataset Preselezionato Riducente: **4** Stazioni di campionamento

Analisi delle serie temporali e spaziali

Modello di calcolo per le serie temporali: **2** (1 = outliers+MAX; 2 = Mediana)
Dataset dei valori rappresentativi facies ossidante
Dataset dei valori rappresentativi facies riducente

Calcolo dei valori di Fondo e dei relativi Livelli di Confidenza

Test per eliminazione outliers dei valori rappresentativi: **Test di Huber**
Modello di valutazione per la scala di bacino: **LdC** maggiore

Facies Ossidante	Fe µg/L	Mn µg/L
CSC	200	50
Valori rappresentativi	21	17
Minimo (val. rappresentativi)	2.5	2.5
Massimo (val. rappresentativi)	150	76
Modello di calcolo	B	B
Distribuzione normale	no	no
Valore di Fondo	*13*	**60**
Livello di Confidenza	*M*	**M**

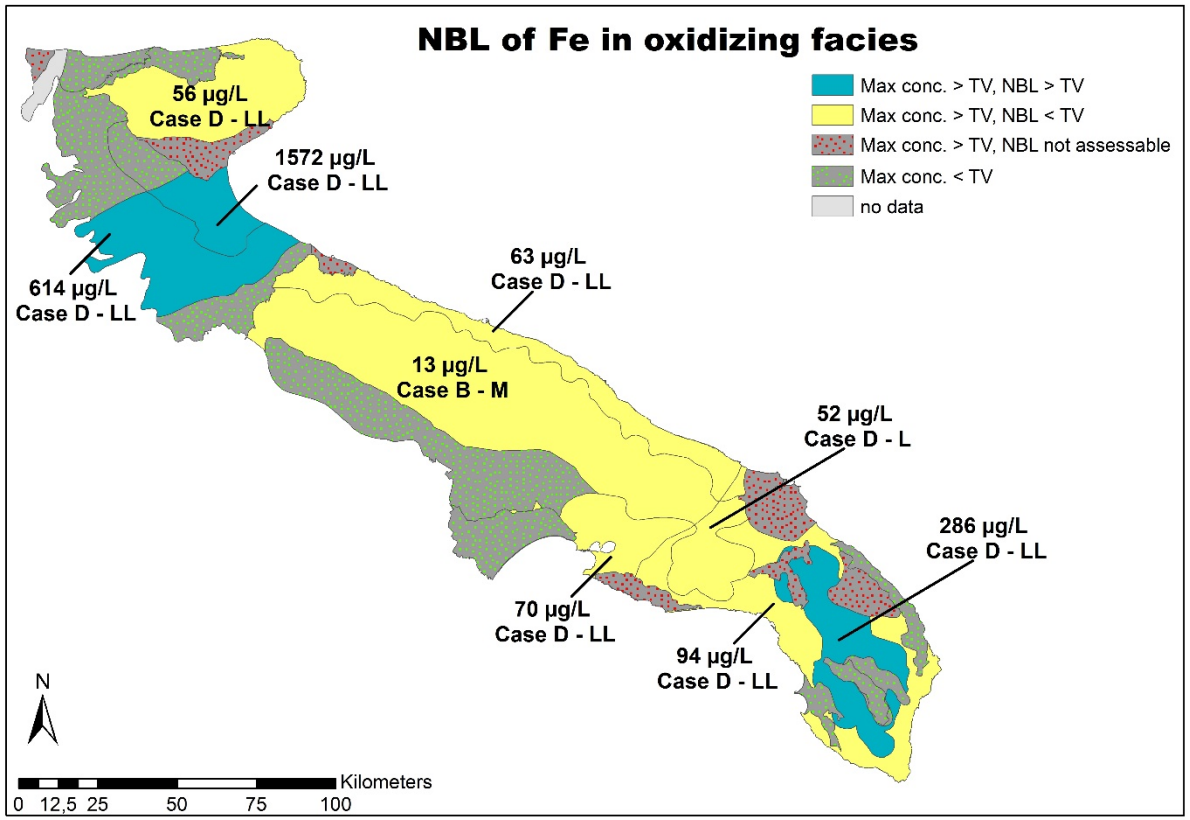
Facies Riducente	Fe µg/L	Mn µg/L
CSC	200	50
Valori rappresentativi	4	3
Minimo (val. rappresentativi)	15.5	23
Massimo (val. rappresentativi)	338	52.5
Modello di calcolo	D	D
Distribuzione normale	-	-
Valore di Fondo	**604**	**273**
Livello di Confidenza	**BB**	**BB**

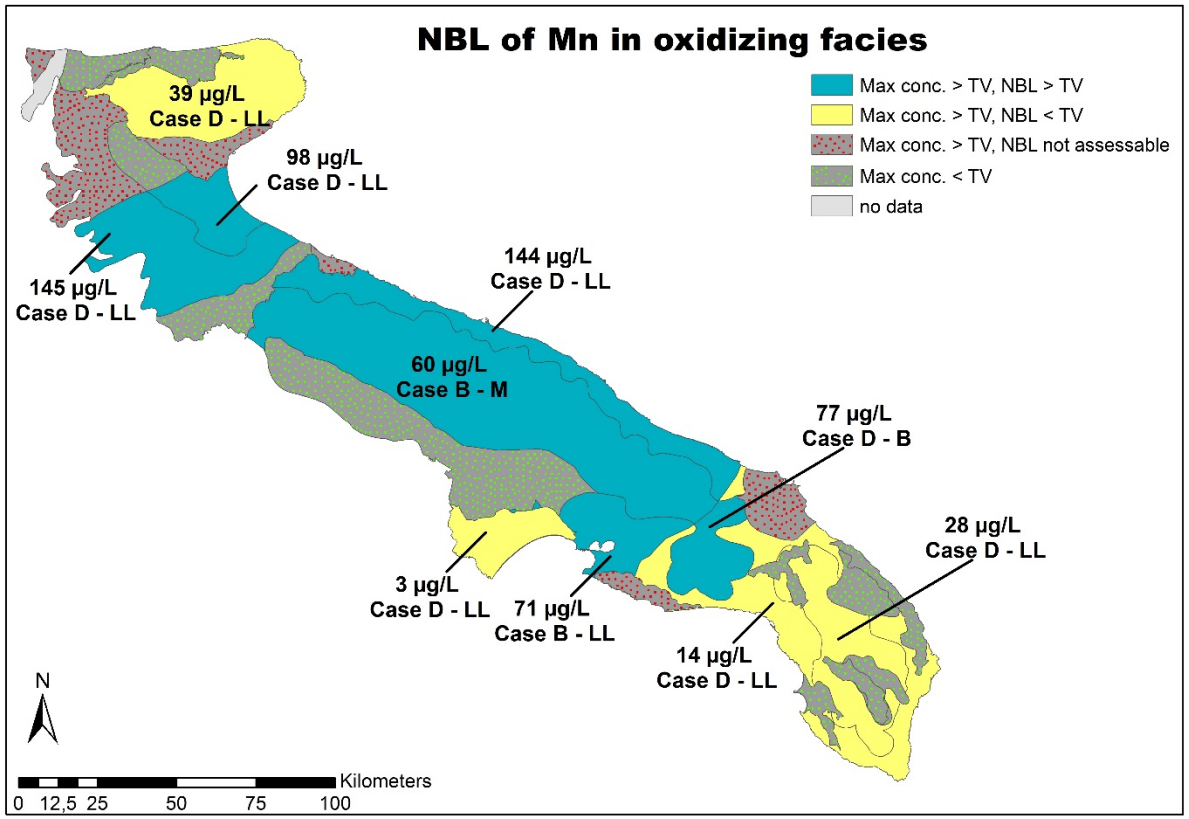
VIOLA NBL tool has been used for a preliminary assessment using some of the existing Regional monitoring datasets (4 campaigns, years 2016-2017), and selecting the following calculation parameters:

- redox facies separation parameter: ORP (0 mV as a threshold)
- preselection markers threshold: 37.5 mg/L for nitrates – 0.375 mg/L for ammonia
- time series analysis method: median
- spatial outliers exclusion: Huber test.

NBLs of Fe and Mn

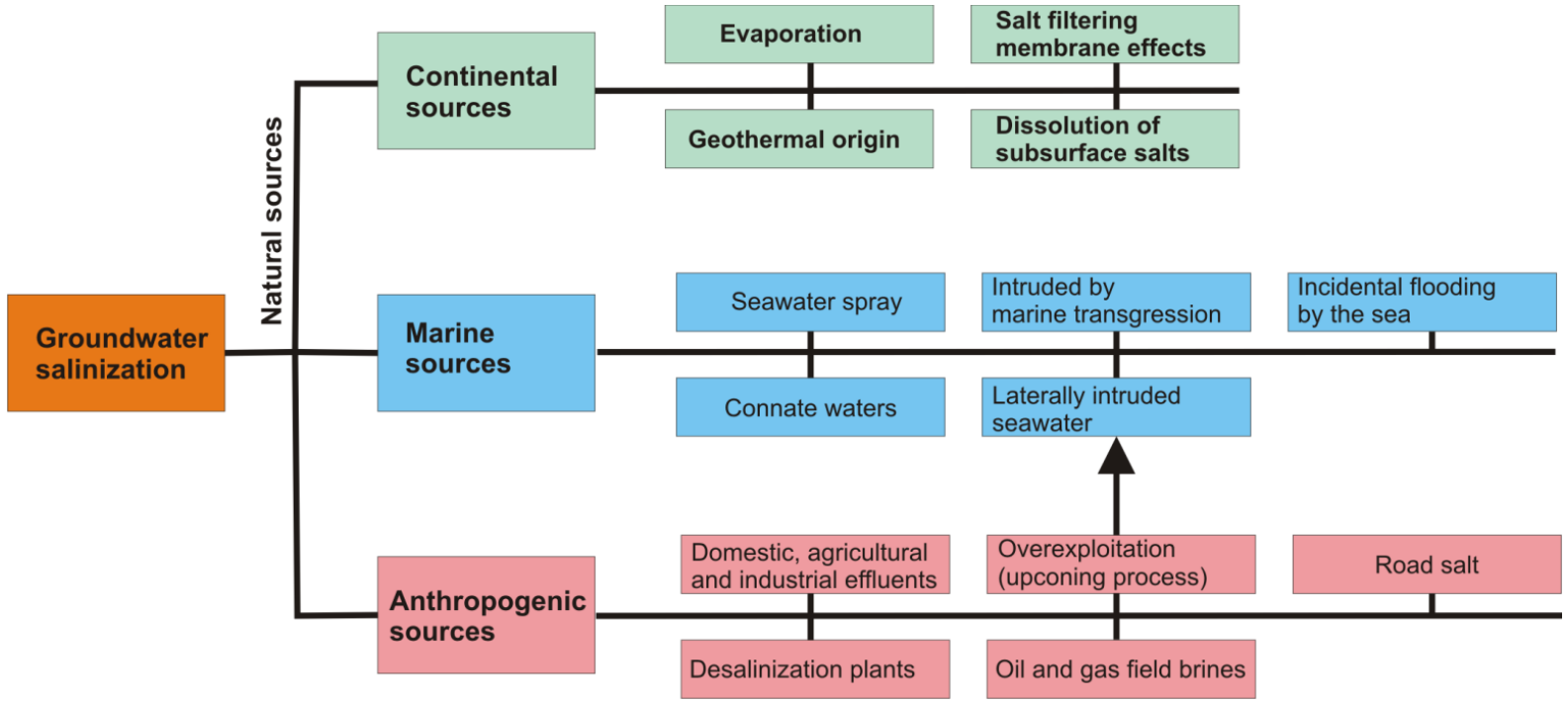
In the maps, NBL values for Fe and Mn are shown relative to all the Apulian GWB, as well as the assessment paths used (B: the dataset is spatially significant, D: the dataset is not significant spatially and temporally) and the corresponding confidence levels (M: medium, L: low, LL: very low). Threshold concentration values (TV) for Fe and Mn in groundwater are respectively 200 **µ**g/L and 50 **µ**g/L. "*Max conc.*" refers to the highest value found in the GWB dataset.





Coastal aquifers salinization

- A wide area of the Apulia Region hosts coastal GWBs
- The use of Cl as pre-selection marker in these GWBs makes the residual dataset insufficient and the estimation of the background values possible only by a simplified procedure with very low confidence levels.
- The study of groundwater salinization in coastal aquifers is only apparently simple, being in most cases the modern seawater intrusion the most obvious saline source.



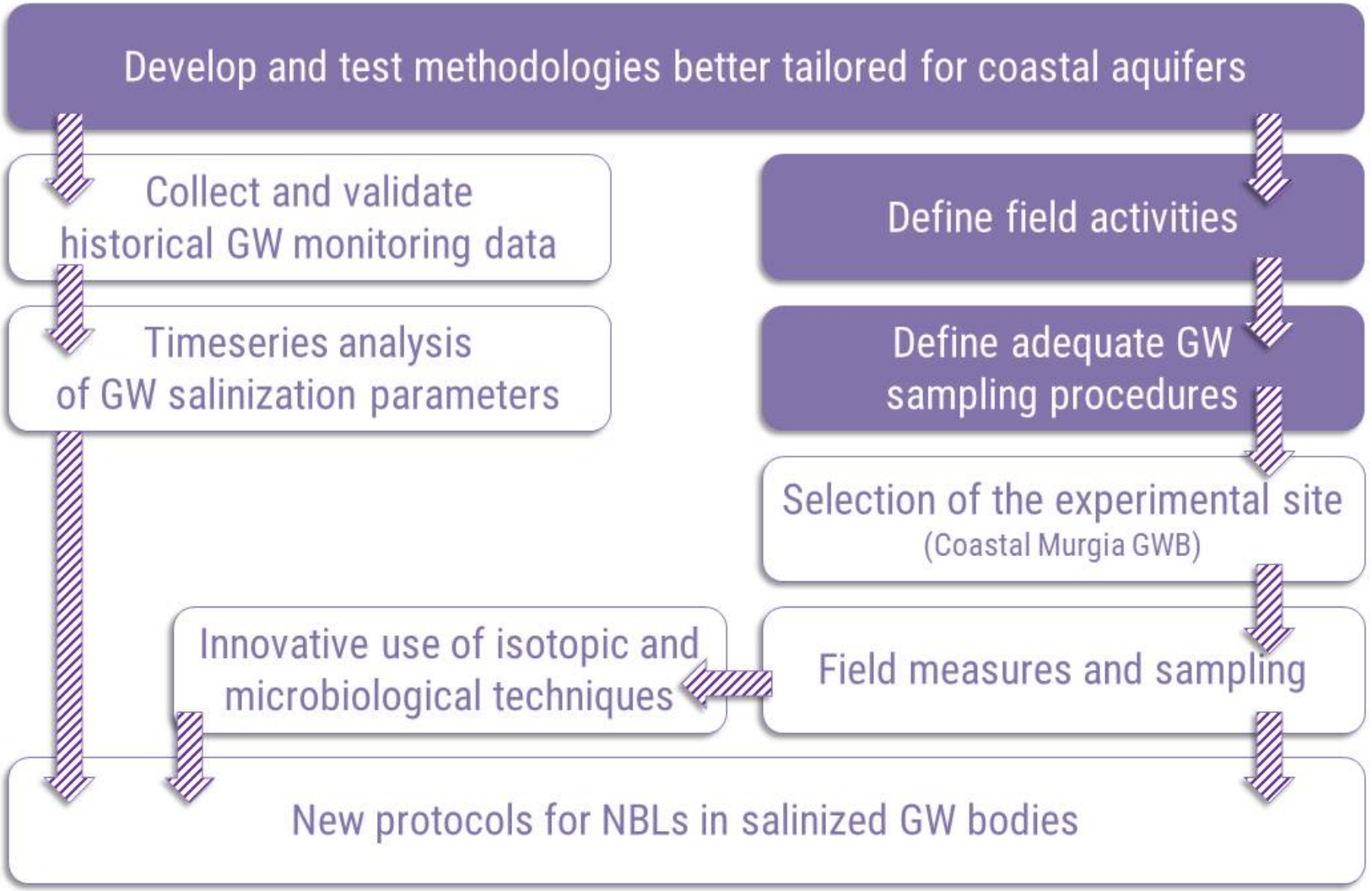
Potential sources of groundwater salinization (modified after Mirzavand et al, 2020)

Coastal aquifers salinization

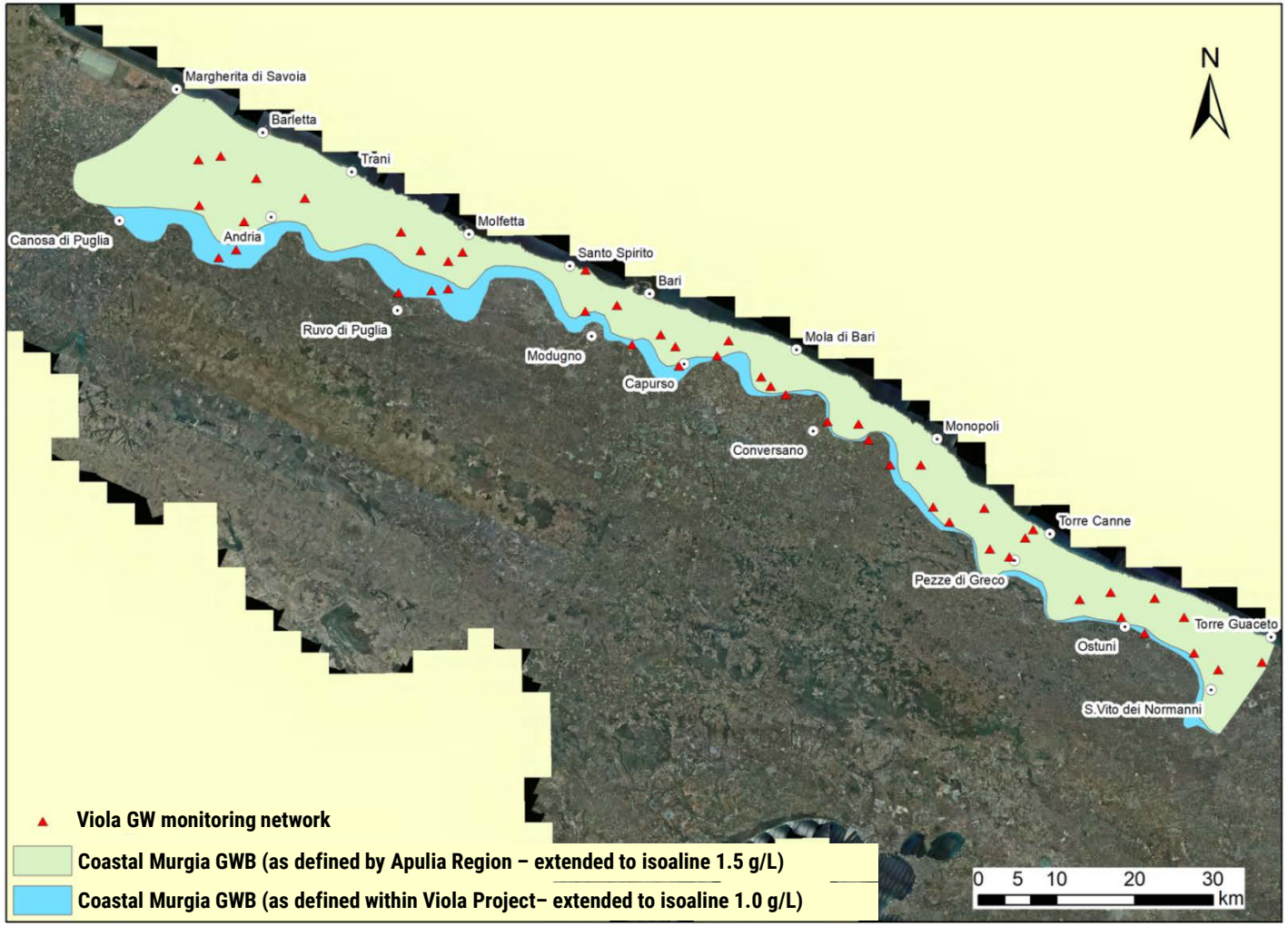
- Is the modern lateral seawater intrusion the main source of high levels of chlorides?
  - Can we prove that other sources exist?
- How much the phenomenon is attributable to natural or anthropogenic causes?

Let's experiment with an alternative approach

Coastal aquifers salinization



Coastal aquifers salinization
Field activities



Groundwater sampling at the experimental site

47 Monitoring wells
- 5 Static sampling wells (*seawater intrusion observation*)
- 43 dynamic sampling wells

Distance of wells to the coastline
127÷16,800 m

4 monitoring campaigns

I May 13 - Jun 21, 2019
II Sep 17 - Oct 29, 2019
~~III spring 2020~~ *(Postponed due to COVID-19)*
III scheduled in autumn 2020
IV scheduled in spring 2021

Coastal aquifers salinization
Monitoring parameter

In situ chemical-physical parameters:

Multiparametric probe with low flow cell

- Electrical Conductivity (EC)
- Temperature (T)
- pH
- Dissolved oxygen (DO)
- Oxidation-reduction potential (ORP)

In situ ions concentration:

Portable UV-Vis Spectrophotometer

- Ammonium (NH_4^+)
- Nitrite (NO_2^-)
- Cyanides (CN^-)

Laboratory analyses

Ion-exchange chromatography (within 48-72 hrs)

- F - Cl - Br - NO_3 - PO_4 - SO_4

Alkalimetry

- $HCO3^-$

Organic carbon analyzer

- DOC

(ICP-OES) (within 1 month)

- Na K Mg Ca

(ICP-MS)

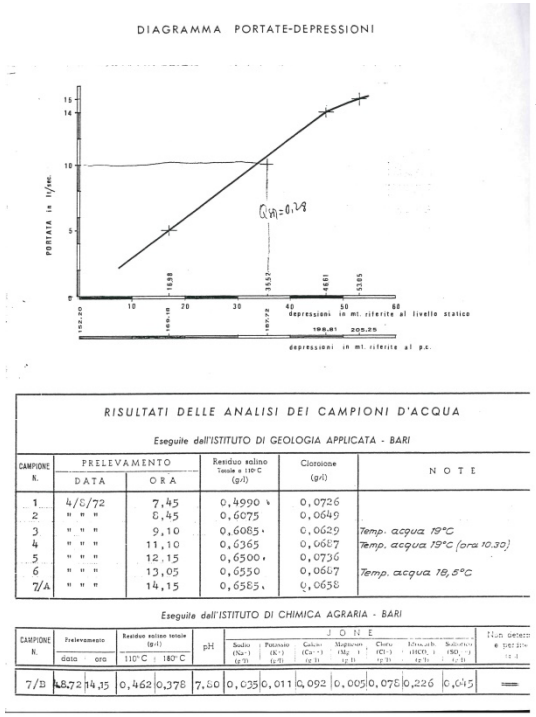
- Li - B - Al - V - Cr_{tot} - Mn - Fe - Ni - Cu - Zn - As_{tot} - Rb - Sr - Ba - Pb - U

First results of the two monitoring campaigns are in [Parrone et al., 2020 (D408 EGU2020-7561)]

Coastal aquifers salinization

Historical data of groundwater salinization

All the background knowledge related to the hydro-geo-chemical characteristics of the Murgia's aquifer have been collected and ordered.
These data, starting from the fifties-sixties of the last century, refer to a period when withdrawals for agricultural purposes were not yet intensive.
Consequently, they could provide precious information about the study groundwater system salinization status in an almost total absence of anthropic pressures.
Up today, about 4400 sets of analyses, related to 432 wells, have been found and digitized into a database.



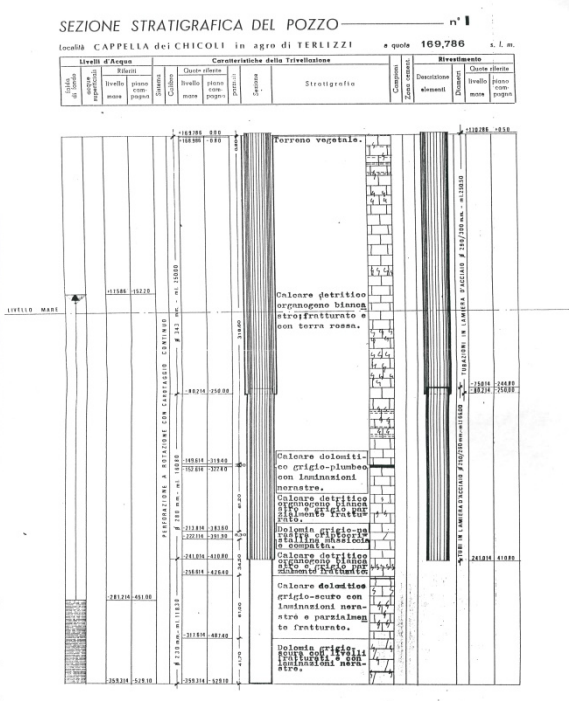
RISULTATI DELLE ANALISI DEI CAMPIONI D'ACQUA

Eseguite dall'ISTITUTO DI GEOLOGIA APPLICATA - BARI

CAMPIONE N.	PRELEVAMENTO DATA	PRELEVAMENTO ORA	Residuo salino Totale a 110°C (g/l)	Clorazione (g/l)	NOTE
1	4/8/72	7,45	0,4990	0,0726	
2	" " "	8,45	0,6075	0,0649	
3	" " "	9,10	0,6085	0,0629	Temp. acqua 19°C
4	" " "	11,10	0,6365	0,0687	Temp. acqua 19°C (ora 10.30)
5	" " "	12,15	0,6500	0,0736	
6	" " "	13,05	0,6550	0,0667	Temp. acqua 18,5°C
7/A	" " "	14,15	0,6585	0,0658	

Eseguite dall'ISTITUTO DI CHIMICA AGRARIA - BARI

CAMPIONE N.	Prelevamento data	Prelevamento ora	Residuo salino totale (g/l) 110°C	Residuo salino totale (g/l) 180°C	pH	IONE Sodio (Na^+) (g/l)	IONE Potassio (K^+) (g/l)	IONE Calcio (Ca^{++}) (g/l)	IONE Magnesio (Mg^{++}) (g/l)	IONE Cloro (Cl^-) (g/l)	IONE Idrocarb. (HCO_3^-) (g/l)	IONE Solfati (SO_4^{--}) (g/l)	Non determ. e per mg/l
7/B	4	14,15	0,462	0,378	7,80	0,035	0,011	0,092	0,005	0,075	0,226	0,045	—



Examples of sixties well stratigraphy and related analyses

Coastal aquifers salinization
Innovative isotopic approach

The use of isotopic parameters, as environmental tracers, in the study of seawater intrusion is relatively recent. Combined with physical and chemical parameters, they can play an important role in answering many crucial questions like these:

- What are the fluids involved in salinization? Is seawater the only one?
- What is the origin of saline fluids found in coastal aquifers? How old are they?

The following isotopic ratios were chosen in this study to focus on the assessment of possible process responsible for the observed chemical GW features:

$^{87}Sr/^{86}Sr$ - $^{11}B/^{10}B$	Plasma-source mass spectrometry (PSMS)
$^{2}H/^{1}H$	Laser spectroscopy
$^{18}O/^{16}O$	Isotope ratio mass spectrometry (IRMS)

The isotopic analyses, performed by the Institute of Geosciences and Earth Resources (IGG) of the Italian National Research Council (CNR), are still ongoing.

Up today, water samples for isotopic analyses were collected only in the 2nd monitoring campaign.

Coastal aquifers salinization
Innovative microbiological approach

Up today, the biological communities populating the GW are largely ignored, although a wide range of organisms is adapted to live under the limiting conditions of this kind of environment.

The environmental factors that influence the physiological profiling and functional diversity of GW microbial communities are increasingly attracting the research interest.

Within the Viola Project, the link between the changes in water physical-chemical characteristics (e.g salinization) and the functional responses of the resident microbial communities related to C-cycle are explored.

The following parameters were chosen :

- total microbial cells counts and nucleic acid content - Flow-cytometer
- microbial metabolic potential and functional diversity - BIOLOG™ EcoPlates,
- respiration rates - BIOLOG™ MT2 MicroPlates
- extracellular enzymatic activities - APYZYM® assay
- total coliforms and *E. coli* - Colilert-18® test

First results of the two monitoring campaigns are in Melita et al., 2020 (D409 EGU2020-7630)

Other displays on the VIOLA Project

EGU2020-7561

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

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

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.

References

- 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), pp. 155
- Maggiore M., Pagliarulo P. (2003) - Groundwater vulnerability and pollution sources in the Apulian region (Southern Italy). Proceedings of 2nd Symposium "Protection of Groundwater from Pollution and Seawater Intrusion", Bari September 27 – October 1999, pp. 9-20
- 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
- Passarella G., Vurro M., Barca E., Sollitto D., Pedalino M., Iannarelli M.A. , Campana C., Casale V. (2013) - Identificazione e Caratterizzazione dei Corpi Idrici della Puglia ai sensi del D.Lgs.30/2009, pp. 94
- Passarella G., Vurro M., Barca E., Bruno D.E. (2015) - Attività complementari ed integrative della caratterizzazione dei corpi idrici sotterranei., pp. 117
- Mirzavand M., Ghasemieh H., Sadatinejad· S. J., Bagheri R. (2020) - An overview on source, mechanism and investigation approaches in groundwater salinization studies. International Journal of Environmental Science and Technology, 17, pp. 2463–2476.

Acknowledgements

The **VIOLA project** has been funded by **Apulia Region** within the frame of the P.O. F.E.S.R. Puglia 2014-2020
asse VI, azione 6.4, sub-azione 6.4.a.