NATURAL BACKGROUND IN GROUNDWATER: EXPERIENCES FROM ITALY

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ITALY

Outline of the presentation

1. Concepts and definitions: natural background levels (NBL) and threshold values (TV) in the European and Italian legislation
2. Determination of NBL: methods and critical issues
3. A case study : waste disposals in Latium (central Italy). Anthropogenic contamination or natural background?
4. Key issues

Introduction

The **EU Water Framework Directive (WFD) and Groundwater "daughter" Directive (GWD)** require that EU member states assess the chemical status of groundwater bodies based on the groundwater quality standards defined in Annex I of the GWD for NO_3 and pesticides. **Threshold values** (**TVs**) must be established for other substances, following the guidelines set out in Annex II, taking into account **natural background levels (NBLs)** if needed.

But what are NBLs and TVs according to the GWD?

- **natural background level** is "*the concentration of a substance or the value of an indicator in a groundwater body corresponding to no anthropogenic alterations, or to the presence of extremely limited alterations, compared to undisturbed conditions*" (GWD, 2006/118/EC)
- **threshold value** means a (national) groundwater quality standard set by Member States in accordance with Article 3

NBL and TV: critical issues at EU level

- **Threshold values established in Europe are hardly comparable** due to the different criteria, approaches and methodologies applied by Member States.
- **Wide ranges and high values of TVs throughout Europe are mainly caused by the Natural Background Levels**. Currently, each Member State is free to apply any methodology in deriving NBLs. But the TV establishment strongly depends on the NBLs.
- The fact that the NBLs are established at **different geographical levels** also influences variability and comparability (at the level of groundwater bodies, river basin districts or at national level)

(Form: "Background paper to the Public Consultation on the revision of the Annexes of the Groundwater Directive", Scheidleder & Bogaert 2013)

Key messages from the Conference on the review of Annexes I and II of GWD

- "In order to enhance comparability, it might be advisable to come to an EU-wide agreement on the methodologies to be used for setting TVs and for deriving NBLs."

- "CIS guidance could be developed to ensure a common approach. This should be aimed at improving the comparability of results."

(Report of the Conference on the Review of the Annexes I and II of the Groundwater Directive, 9 October 2013, Brussels)

Natural Background Levels in the Italian legislation

GROUNDWATER STATUS ASSESSMENT (GROUNDWATER BODY SCALE)

TVs have been set for 52 substances/parameters at the national level (Nat. Decree 30/2009); TVs can be increased at the ground water body scale by Regions when local **NBLs** are found to be higher

PREVENTING AND LIMITING INPUT (LOCAL SCALE)

Additionally, the Nat. Decree 152/2006, has set specific national level Compliance Values (CVs) not to be exceeded when a groundwater body is threatened by potentially polluting activities such as a dump filling or an industrial site; the existence of **background levels** is also considered

In both cases TVs/CVs can be increased locally considering NBLs, at the groundwater body scale / local scale to distinguish between natural vs. anthropogenic contamination

What happens if the concentration is found to be higher than TVs?

- GROUNDWATER STATUS ASSESSMENT (GWD Art. 4 ; Dlgs 30/2009) → 20% exceedances is admitted although an appropriate investigation is then required. More flexible assessment

- "PREVENT OR LIMIT" objective (GWD Art. 6; Nat.Decree 152/2006) → one sample out = pollution. More stringent threshold, no flexibility

(CIS guidances n.18 "Status and Trend" and n. 17 "Preventing and limiting inputs")

How to assess background levels (1)

Reference documents:

1) FP6 BRIDGE project, D18: Final Proposal For A Methodology To Set Up Groundwater Treshold Values In Europe (Muller et al. 2006)
2) CIS Guidance n.18 “Status and Trend”, European Communities 2009
3) In Italy: National Guidance “*Protocollo per la Definizione dei Valori di Fondo per le Sostanze Inorganiche nelle Acque Sotterrane» (ISPRA, 2009)*

How to assess background levels (2)

- **Pre-selection of samples** → based on *markers* of human activities such as nitrates or syntethic contaminants

  (FP6 project «BRIDGE»; CIS guidance n.18)

→ The samples affected by human activities are excluded

→ On the «pristine» water samples a value is chosen as NBL (e.g. 90th, 95th or 97.7th percentile)

PROS: Easy to use (APPARENTLY…) and objective . It can be used with small datasets

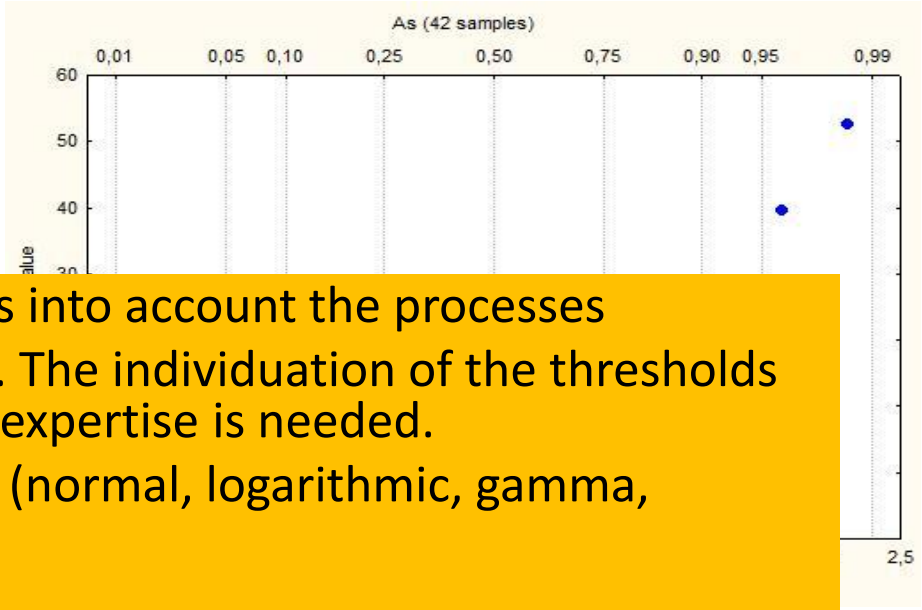
CONS: selection criteria could be too stringent, The ultimate selected data-set can be very tiny. It relies on simple statistics, does not consider the processes

KEY ISSUES: Results are very sensitive to the chosen percentile

How to assess background levels (3)

- **Probability distribution functions** (component separation)
  - Dates back to the geochemical exploration (Sinclair 1974)
  - Different sources (natural/anthropogenic) generate diverse statistical populations which overlap
  - Populations can be separated using e.g. probability graphs with arithmetic or log y axis

$$f_{obs}(c) = f_{nat}(c) + f_{inf}(c)$$



PROS: All data are used. It takes into account the processes

CONS: It needs a large data set. The individuation of the thresholds can be difficult and subjective, expertise is needed.

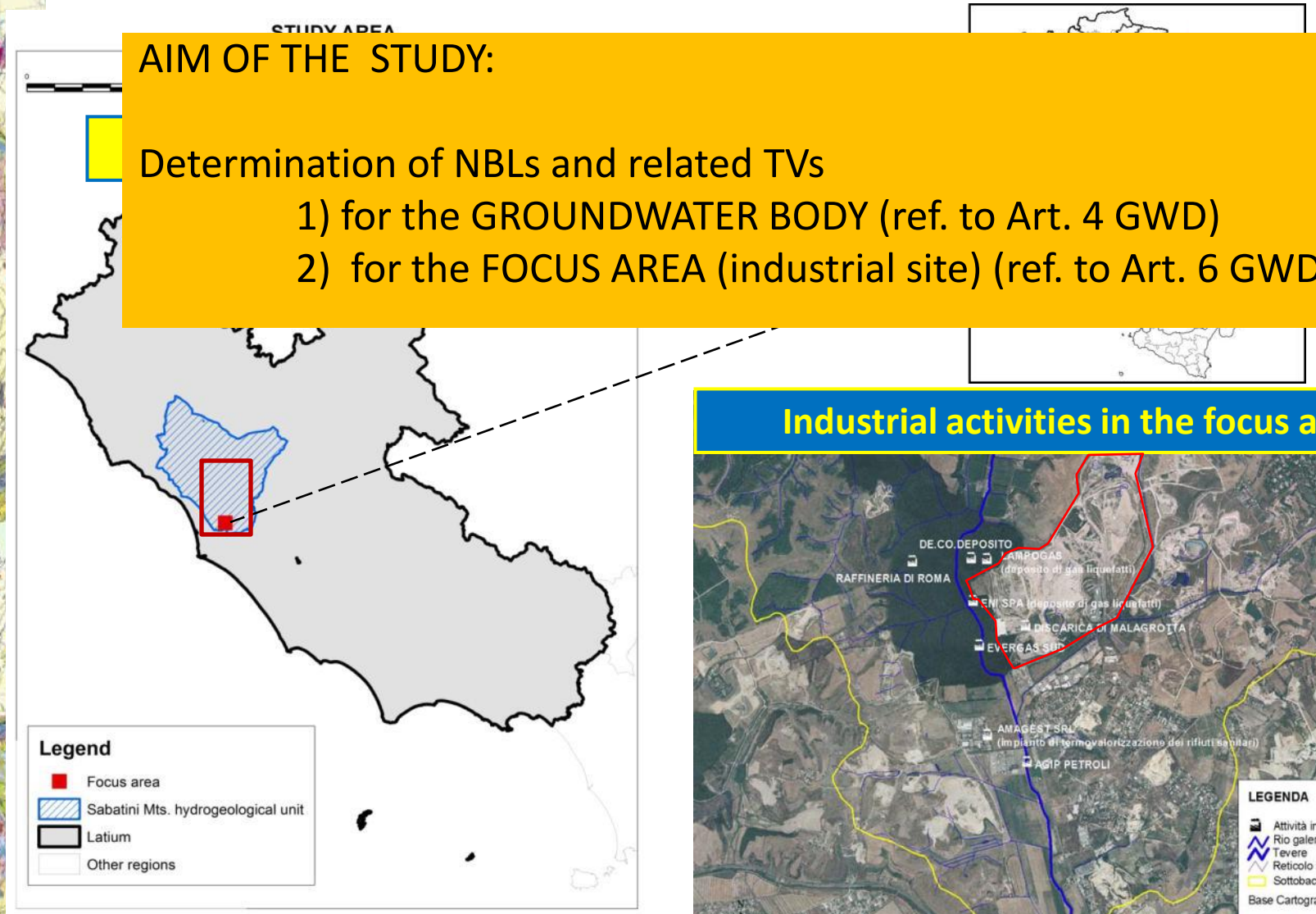
KEY ISSUES: Which distribution (normal, logarithmic, gamma, mixtures, …) should be used?

A case study in Italy

AIM OF THE STUDY:

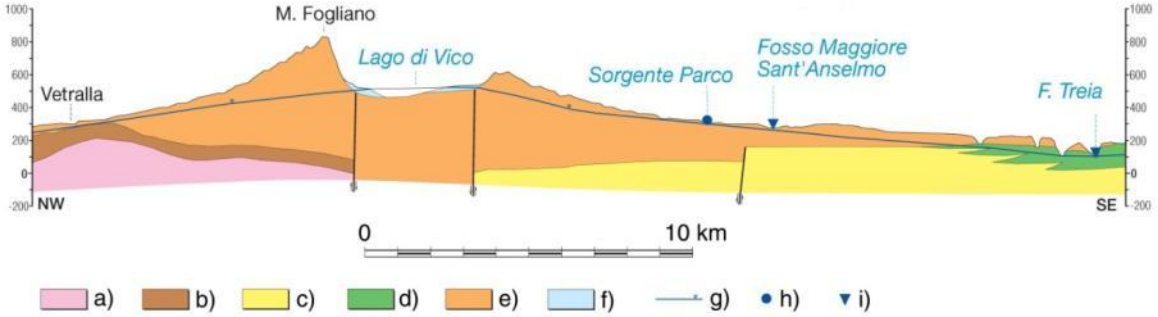
Determination of NBLs and related TVs

1) for the GROUNDWATER BODY (ref. to Art. 4 GWD)
2) for the FOCUS AREA (industrial site) (ref. to Art. 6 GWD)



Industrial activities in the focus area

The volcanic belt aquifers



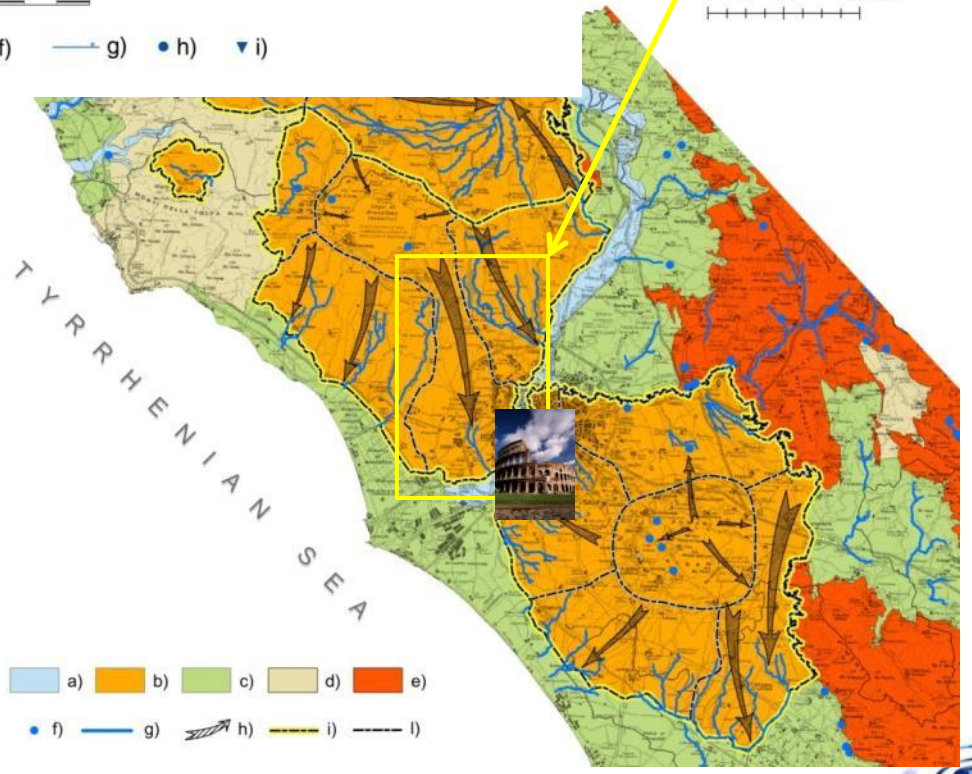
alluvial Units

volcanic Units

clastic-alluvial Units

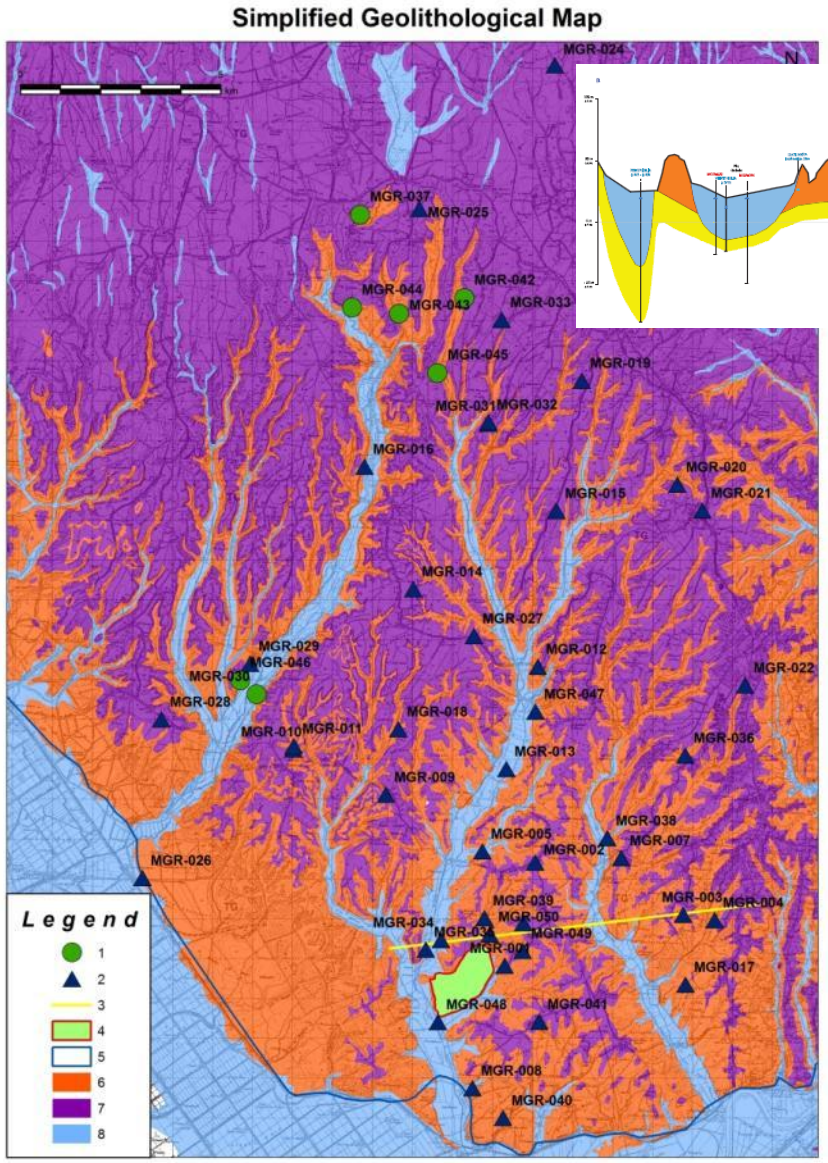
flysch Units

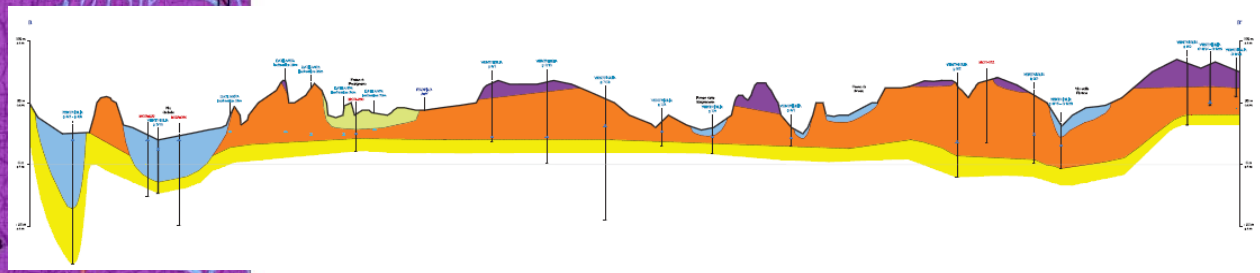
carbonate Units



(From: Mazza and Mastrorillo, in press,)

Hydrogeological set up





- 50 samples (february-june 2011)
- All analyzed for anions and As
- 42 analyzed for metals

Legend

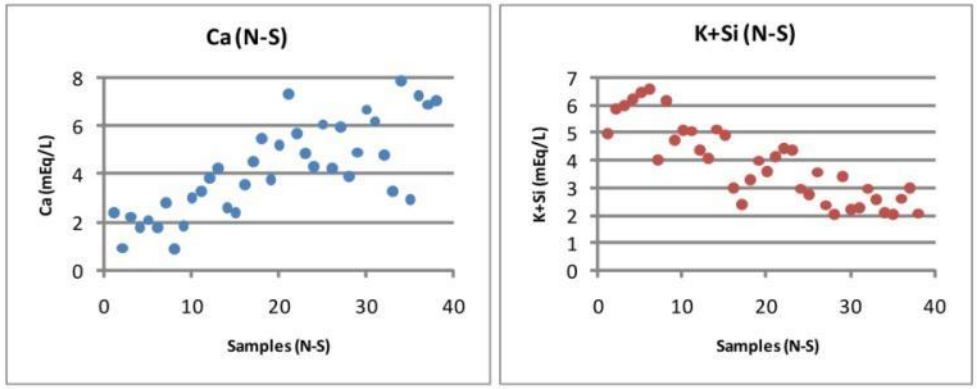
- Springs
- Wells
- Trace of hydrogeological section
- Malagrotta landfill
- Sabatin Mts. hydrogeological unit
- Sedimentary deposits (Plio-Pleistocene - Holocene)
- Volcanic deposits (Pleistocene)
- Alluvial deposits (Holocene)

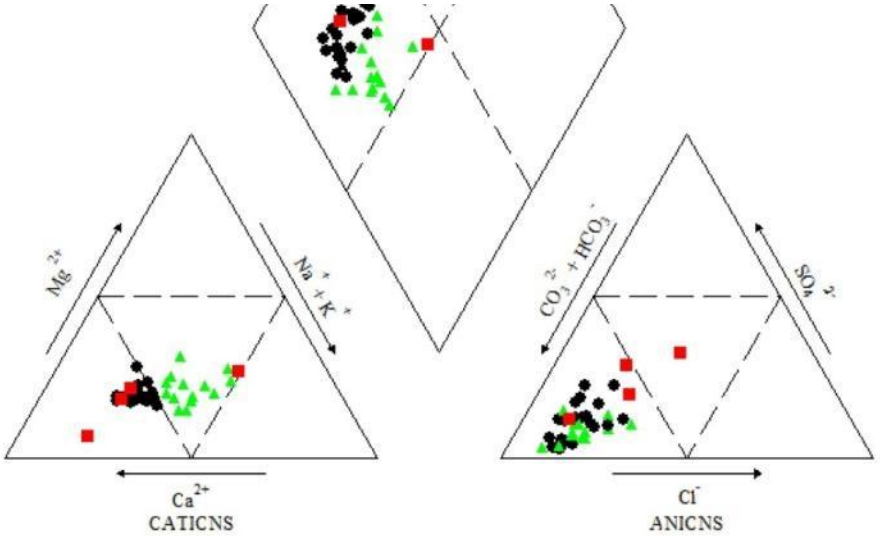
Field sampling protocol

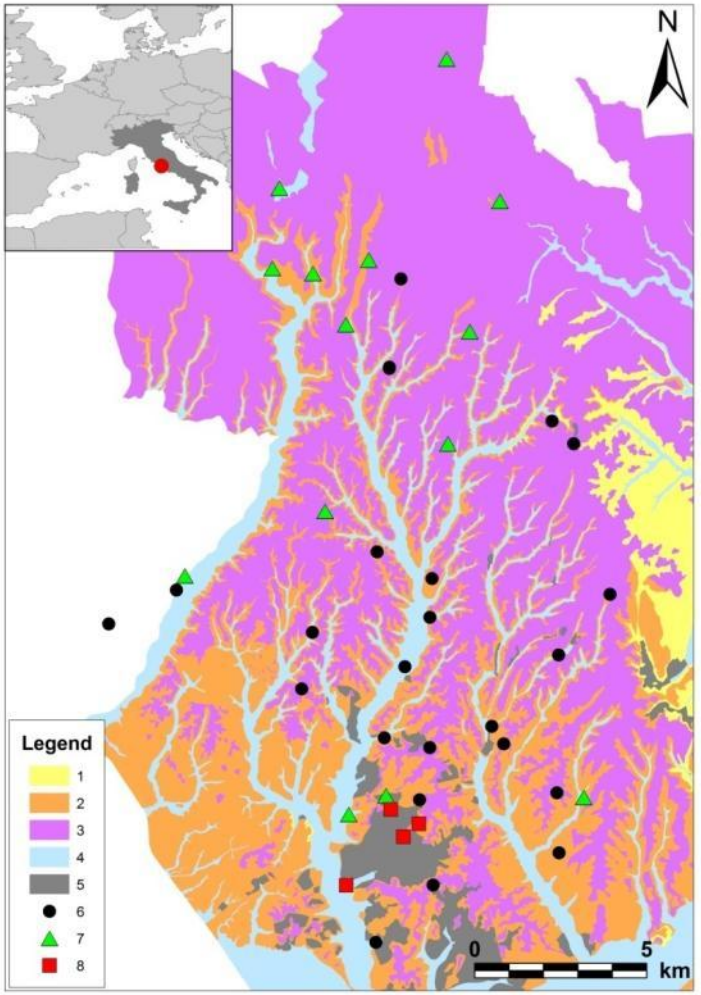
Laboratory analysis

Technique	Analyzed parameters	Instrument
Alcalimetry	HCO_3	
Ionic Cromatography	F, Cl, Br, NO_2, NO_3, SO_4, PO_4	
Optical Emission Spectroscopy (ICP-OES)	Ca, Mg, Na, K, Si	
Inductively Coupled Plasma Mass Spectrometry (ICP-MS)	Al, As, B, Ba, Be, Cd, Cr, Cu, Fe, Hg, Li, Mn, Ni, Pb, Rb, Se, Sb, Sr, U, V, Zn	
UV-Visible Spectrophotometry	NO_2, NH_4, PO_4	

Hydrogeochemical characterization

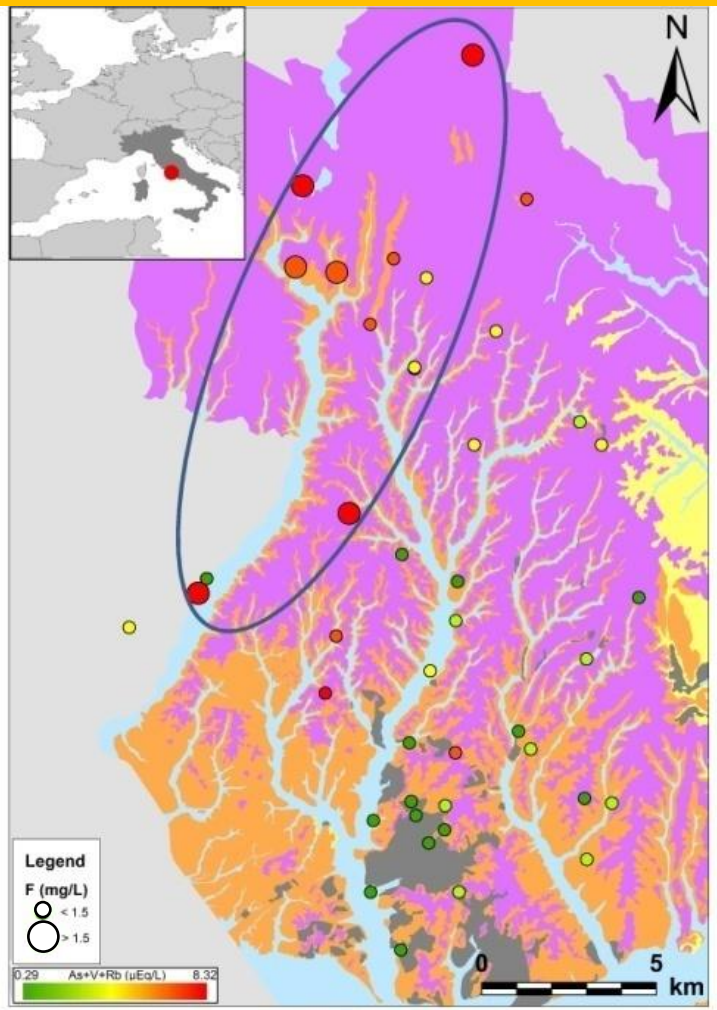






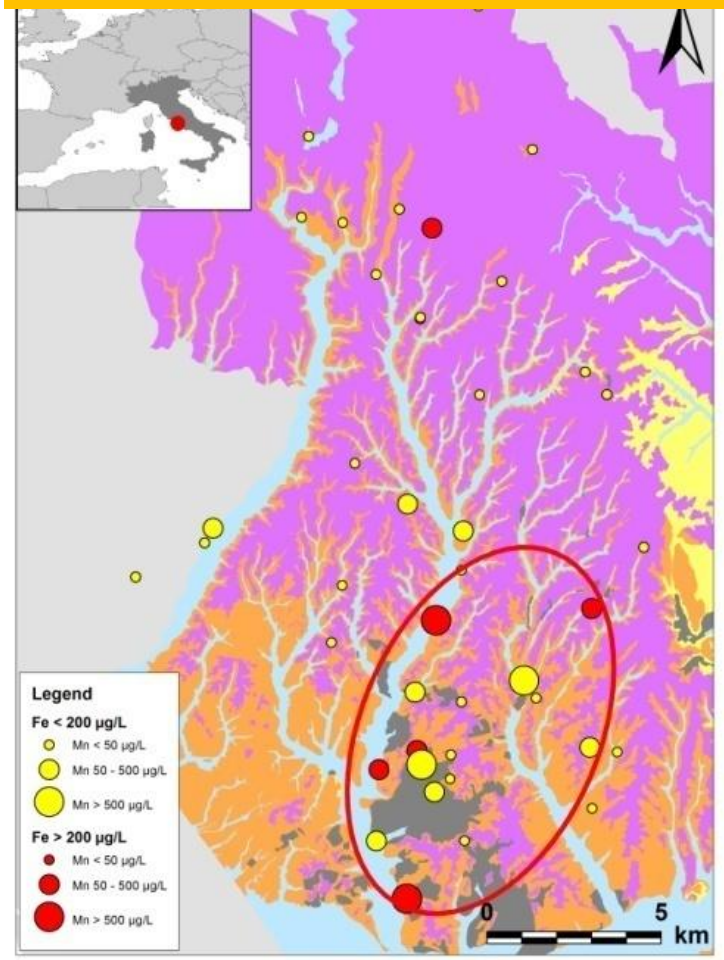
Hydrogeochemical characterization

Arsenic and fluoride higher values in NW sector (GEOCHEMICAL ANOMALY)



a

Iron and Manganese higher values in industrial area, (MAINLY ANOXIC WATERS)



b

Pre-Selection exclusion criteria

INITIAL DATA SET : 42 SAMPLES

- Electroneutrality ≥ 10%
- NO_3 > 50 mg/L (10 mg/L suggested by BRIDGE) → 12 points
- Eh <100 mV
- DO < 3 mg/L

} anoxic waters → 14 samples

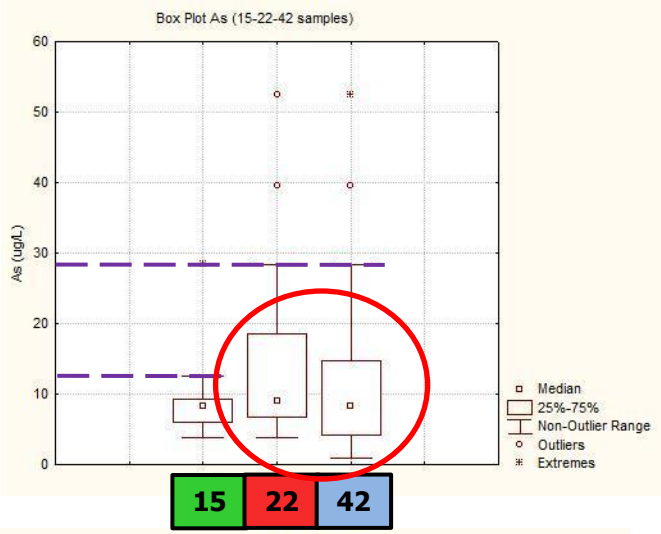
- Proximity to the focus area → 4 samples
- Geochemical anomaly (only for As and F) → 7 samples
- 95th percentile chosen as NBL (Italian protocol)

TO SUM UP: 2 different pre-selected data sets

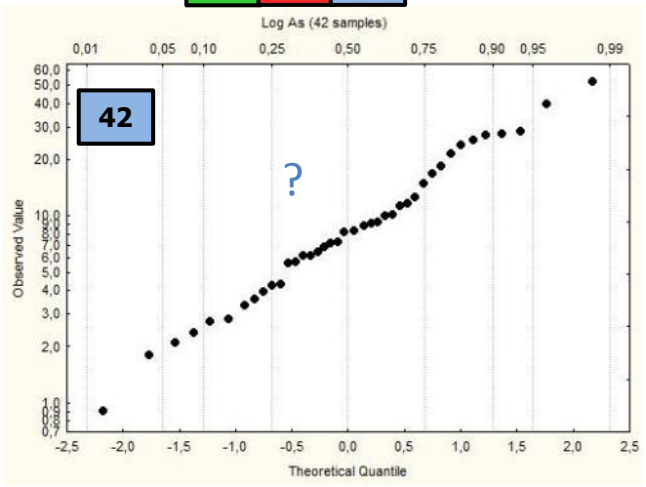
1. 22 samples (<u>only oxidizing waters</u>) for NBL assessment at the GWB scale
2. 15 samples for NBL assessment IN THE FOCUS AREA to avoid an overestimation of arsenic and fluoride

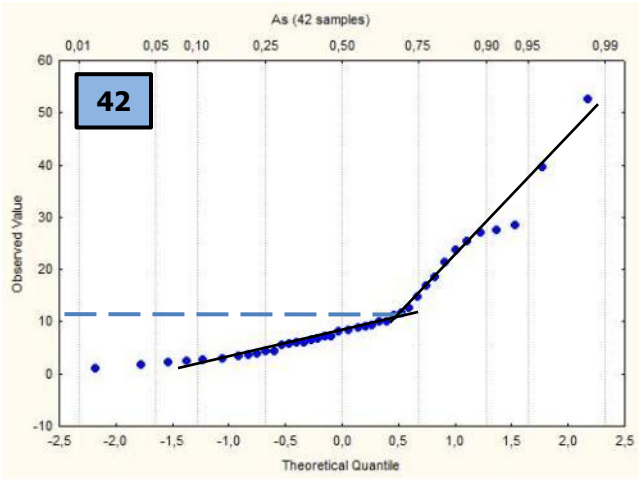
Application of methods: arsenic

Total dataset: 42 samples; PS dataset: 22 samples (15 for As-F in focus area)



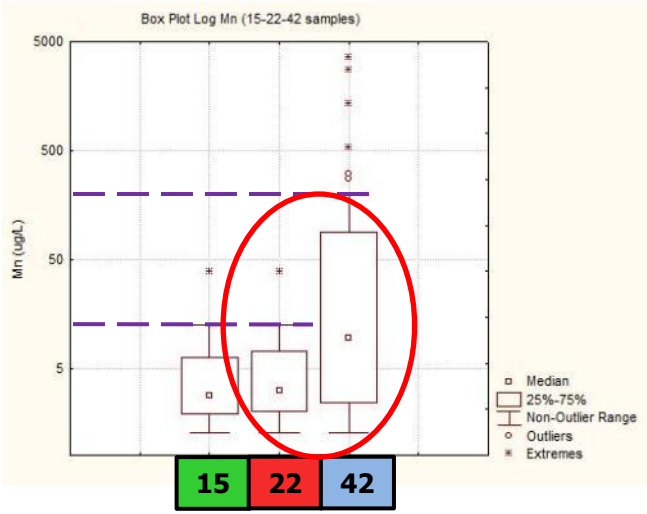
ELEMENT	As (ug/L)		
N. SAMPLES	15	22	42
NORMAL STATISTICALTEST	no	no	no
LOGNORMAL STATISTICALTEST	yes	yes	yes
90th PERCENTILE	12.2	28.3	26.9
95th PERCENTILE	16.6	39.0	28.4
98th PERCENTILE	24.0	47.1	41.9
MEAN+2 STD DEV	20,8	39.3	33.6
MEDIAN+ 2 MAD	12.1	14.7	17.0
UPPER WHISKER	12.6	28.4	28.4
QQ PLOT (normal)	11		
QQ PLOT (lognormal)	?		



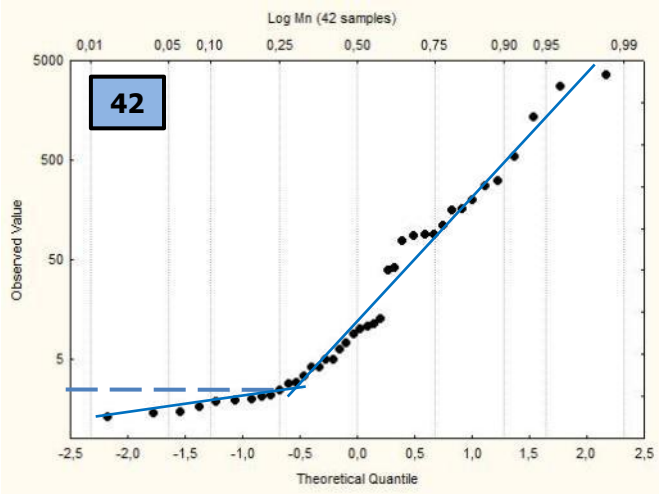


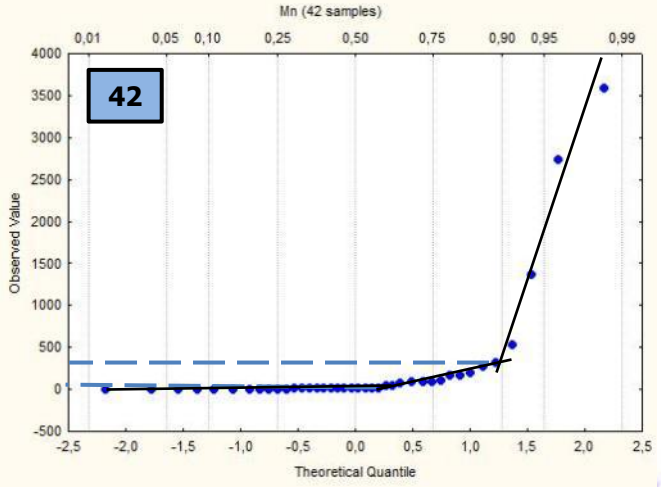
Application of methods: manganese

Total dataset: 42 samples; PS dataset: 22 samples (15 for As-F in focus area)



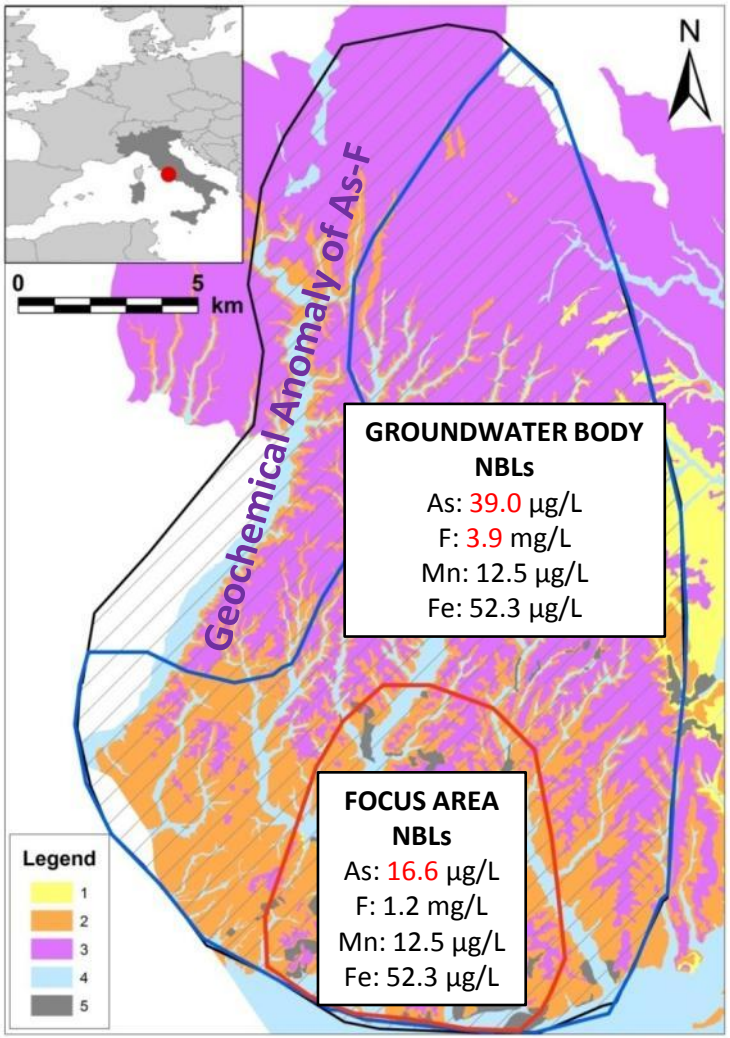
ELEMENT	Mn (ug/L)		
N. SAMPLES	15	22	42
NORMAL STATISTICALTEST	no	no	no
LOGNORMAL STATISTICAL TEST	yes	yes	No
90th PERCENTILE	11.1	11.1	306.5
95th PERCENTILE	20.3	12.5	1323
98th PERCENTILE	31.2	27.6	2888
MEAN+2 STD DEV	25.2	22.1	1648
MEDIAN+ 2 MAD	5.5	5.7	25.0
UPPER WHISKER	12.5	12.5	195.2
QQ PLOT (normal)	13/ 300		
QQ PLOT (lognormal)	3		





RESULTS: GW body and focus area

Pre-selection method (95th perc)



Probability Plot method

ELEMENT	As (µg/L)	F (µg/L)	Mn (ug/L)	Fe (µg/L)
NORMAL LOWER THRESHOLD	**11**	**0.8**	**13**	20
NORMAL UPPER THRESHOLD	/	**1.5**	300	**70**
LOGNORMAL LOWER THRESHOLD	/	**0.8**	3	20
LOGNORMAL UPPER THRESHOLD	/	**1.5**	/	300

National level TVs	
Mn (µg/L)	**50**
Fe (µg/L)	**200**
F (mg/L)	**1.5**
As (µg/L)	**10**

Key issues: the percentile choice

- If the TV is set equal to the NBL concentration (when NBL > TV), whatever percentile will be chosen, part of the samples are expected to show exceedances. This would inevitably lead to an 'appropriate investigation' for all groundwater bodies, which needs to be considered.
- For this reason the use of a «high» percentile (eventually the 100th perc) could be appropriate, when only pristine waters are selected. In every case the conceptual model of the study area must be properly considered

Key issues: on the number of data

- The number of data should ensure statistical significance. The identification of an adequate number of sites with little or no impact can be an issue. The number of sites to be sampled is a compromise between the logistics and an effective evaluation.
- The choice of the spatial scale is critical in relation to the objective, i.e. where TVs will be applied
- Whatever the number of the sampling points, the aquifer conceptual model is the pillar on which a sound determination of the NBLs is based. It must be formulated considering the hydrogeological set up and the natural as well as the human processes

Key issues: on the methods

- Different methods provide (very) different results
- Different percentiles correspond to (very) different values
- There is a need for an harmonized procedure at EU level for NBLs assessment and TV derivation to enhance comparability among theTVs set by the Member States
- Both pre-selection and probability plot methods have a certain degree of subjectivity. However the integration of multiple methods strengthen the evaluation and identifies the limitations of individual approaches
- The pre-selection method seems to provide a rough but robust estimation of the NBLs, when integrated with a sound hydrogeochemical conceptual model and compared to other estimation methods

Thanks for the attention

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