EGU General Assembly 2021

Groundwater flow in Naturally Occurring Asbestos (NOA) rich settings: new findings on the relation among concentration, types and mobility of mineral fibres, and geological characteristics of aquifer formations.

UNIVERSITÀ DEGLI STUDI DI TORINO
ALMA UNIVERSITAS TAURINENSIS

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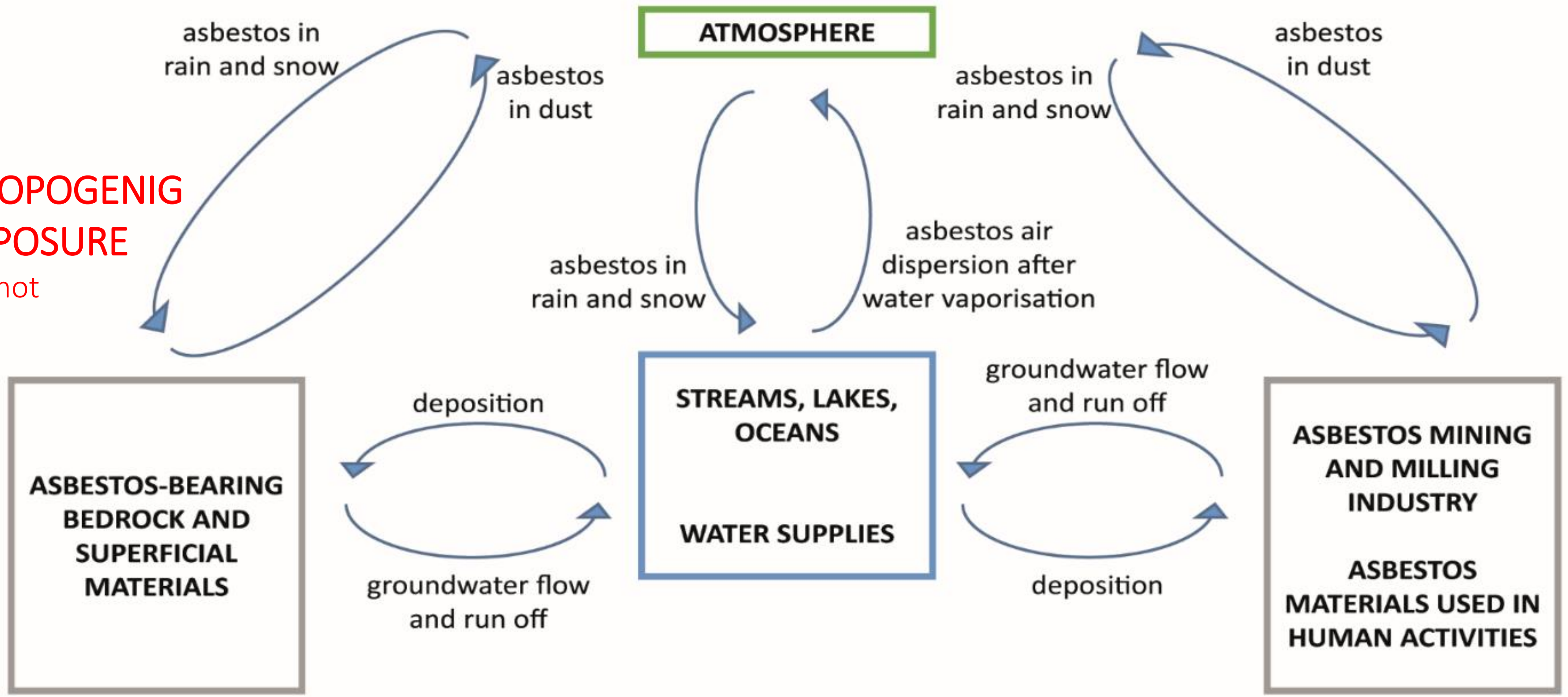
INTRODUCTION – Asbestos and human exposure

Asbestos circulation in the environment

NATURAL vs. ANTHROPOGENIG ENVIRONMENTAL EXPOSURE

*occupational exposure is not considered in this study.



INTRODUCTION – Waterborne asbestos

Water pollution by asbestos may occur as a consequence of **superficial and groundwater flow through natural rock formations containing NOA** (Naturally Occurring Asbestos), such as serpentinites and meta ophiolites.

Importance of water resources:

- primary source for drinking water
- agricultural activities
- industrial activities.

Could waterborne asbestos constitute a risk to human health?

It could be **source of airborne asbestos after water vaporisation →** noxiousness of respired asbestos is well known.

What is the relation between the amount of waterborne fibres and possible release in air?

Avataneo et alii, **LABORATORY TEST TO EVALUATE ASBESTOS RELEASE IN AIR FROM CONTAMINATED WATER.** *In preparation.*

It can reach the human body **via ingestion**, especially if it is present in drinking water.

Can asbestos ingestion cause pathological effects?

STILL DEBATED

INTRODUCTION – Waterborne asbestos

Few studies are available on possible asbestos occurrence in groundwater depending on the assumption that asbestos migration through soil and aquifers was negligible. Nowadays, emerging studies highlight that the **mechanism of asbestos movement in sediments and aquifers is not completely understood** and **try to characterise aquifers correlating mineral fibres occurrence with hydrochemical data**, such as dispersed metals and pH**.**

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Mobility of asbestos fibers below ground is enhanced by dissolved organic matter from soil amendments

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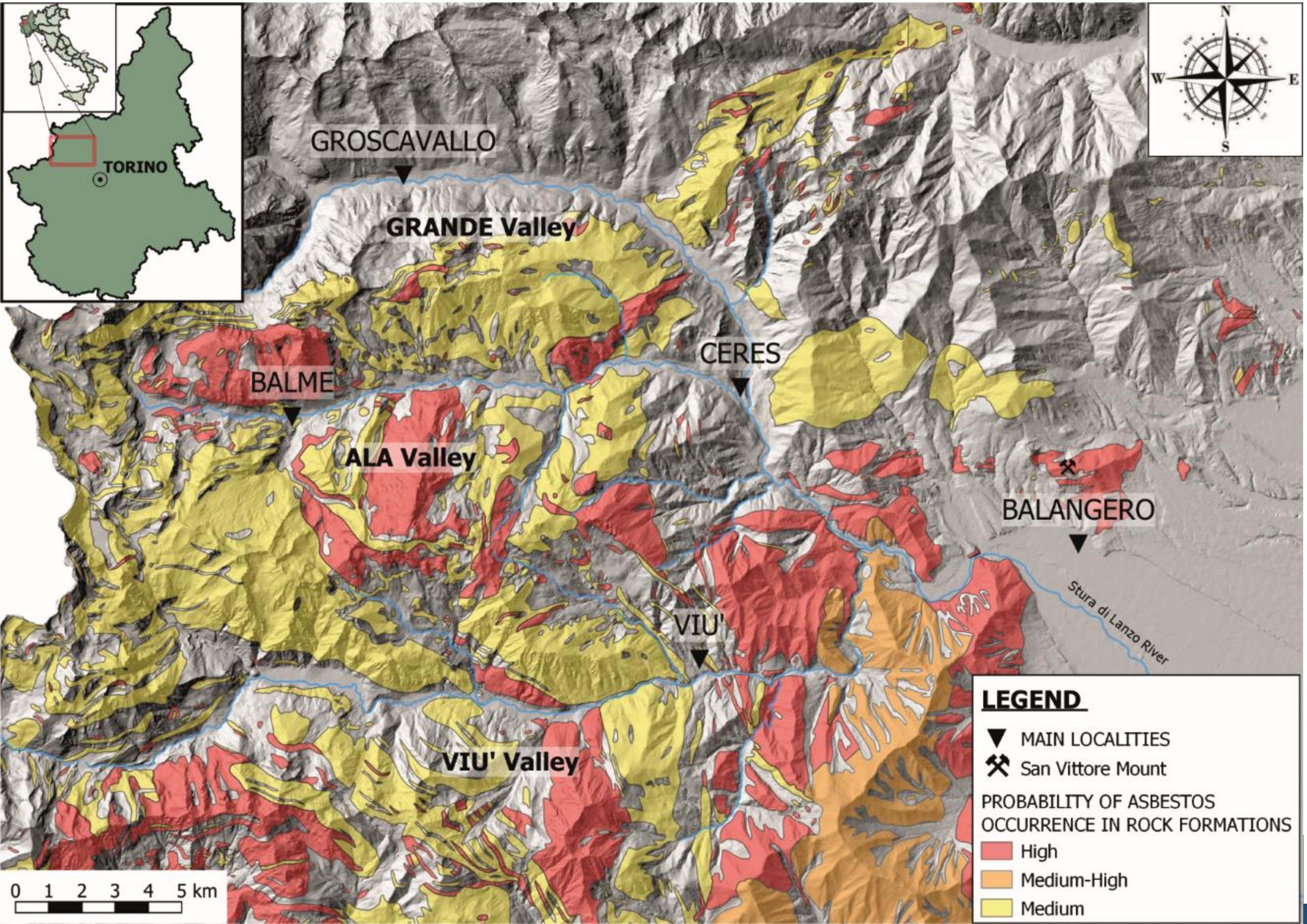
C. Avataneo, E. Belluso, S. Capella, D. Cocca, M. Lasagna, G. Pigozzi, D. A. De Luca (2021). **GROUNDWATER ASBESTOS POLLUTION FROM NATURALLY OCCURRING ASBESTOS (NOA): A PRELIMINARY STUDY ON THE LANZO VALLEYS AND BALANGERO PLAIN AREA, NW ITALY.** Italian Journal of Engineering Geology and Environment, *accepted.*

PRESENTED IN THE NEXT SLIDES

THE CASE STUDY – Introduction

The Lanzo Valleys and the Balangero Plain (North-West Italy)



The chosen study area is characterised by a widespread **occurrence of meta ophiolites** that are likely to contain **asbestos minerals**. The area includes a transition zone between mountain and plain in the surroundings of Lanzo and Balangero municipalities (NW of Torino). This area, called **Lanzo Valleys**, is formed by three valleys (Grande Valley, Ala Valley, Viù Valley) which merge at the basis of mountains in an alluvial plain called **Balangero Plain**: the valleys and plain system constitutes the Stura di Lanzo river basin. **Aquifers** are hosted by rocks in the mountainous area or by sediments in the plain, showing permeability by **fissuration or porosity** respectively.

In Balangero municipality the Lanzo Ultrabasic Massif, characterised by partially to deeply serpentinized peridotites, outcrops in the San Vittore Mount that was long exploited for **(chrysotile) asbestos extraction** (till the '90s) and constituted the larger asbestos mine in Europe.

Map modified from ARPA Piemonte (2016), Mappatura dell'amianto in natura. In: *Geoportale di ARPA Piemonte*, webgis.arpa.piemonte.it/geoportale

The aim of the study

The **objectives** of the study were:

1. to evaluate the possible occurrence of mineral fibres (asbestos and asbestiform minerals non-asbestos classified) in the water system of the study area
2. to correlate asbestos (and asbestiform minerals) occurrence to chemical parameters deriving from the geolithological and hydrogeological characteristics of the context
3. to explore the possible mobility of asbestos in aquifers (*deepened in the ongoing research*).

The **study developed** following two principal ways:

a. data collected from 2007 by RSA S.r.l. (society in charge of the remediation and the monitoring of the former asbestos mining site -air, soil and water- http://www.rsa-srl.it/) have been examined

b. a new sampling and analyses campaign regarding surface water and groundwater was carried out.

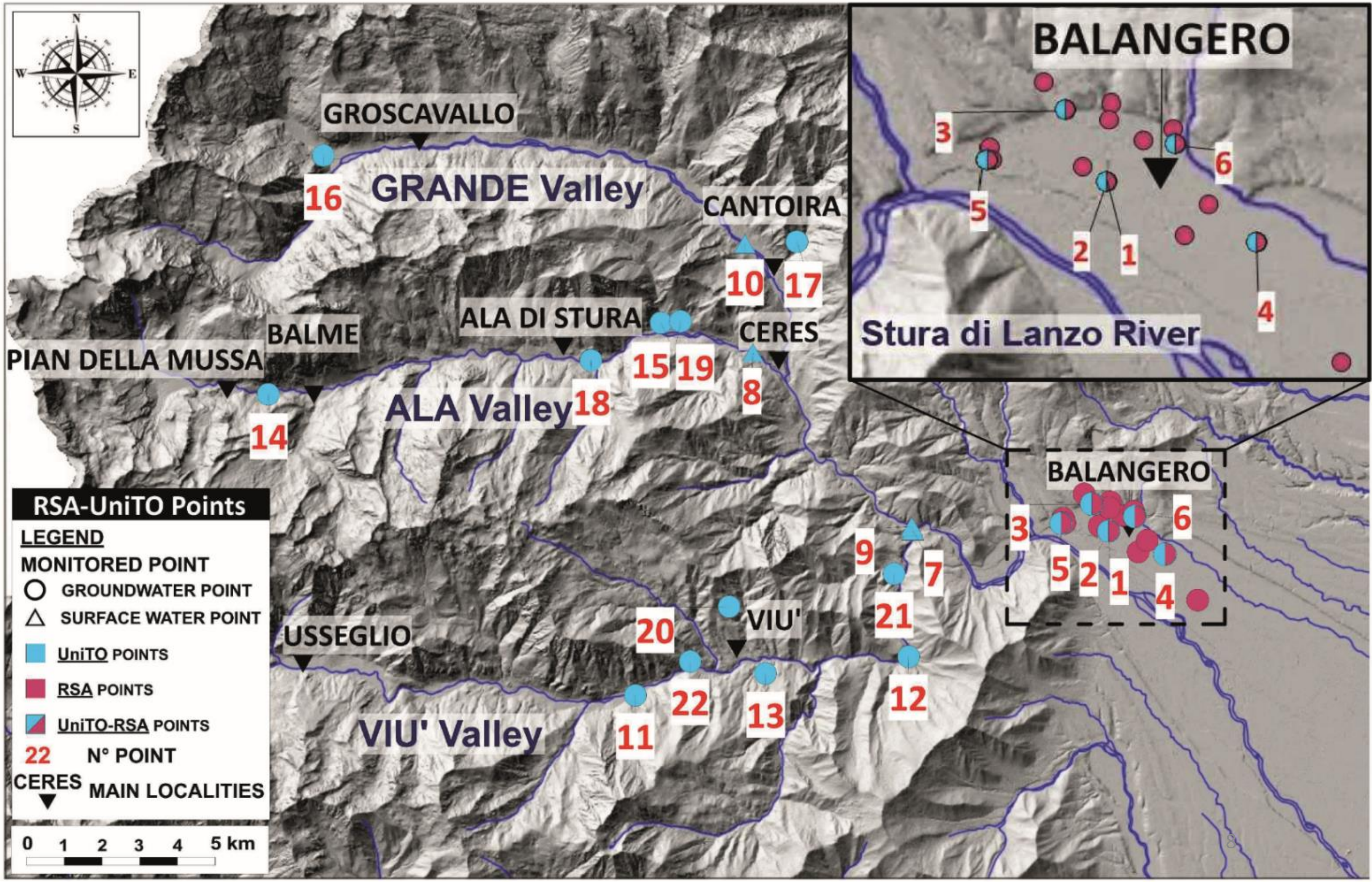
THE CASE STUDY – Sampling campaign

Water sampled in Lanzo Valleys and Balangero Plain in 2020 by **UniTO.**
22 samples in total:

- surface waters from Stura river or its tributaries
- groundwater from springs, wells and piezometers (sampled in static mode)

✚

data collected by RSA on asbestos occurrence in groundwater in the Balangero Plain (since 2007) – wells and piezometer sampled in dynamic mode



THE CASE STUDY – Method and analysis

Hydrochemical analyses

In situ:

- Electrolytic conductivity
- Temperature

In laboratory*:

- Electrolytic conductivity
- pH
- Water alkalinity
- Cations/anions in solution through ionic chromatography
- Dispersed metals by ICP-MS

* Following CNR-IRSA analytical methods (National Researches Council-Institute for Researches on Waters, www.irsa.cnr.it/Metodi)

Asbestos occurrence analyses

In situ:

/

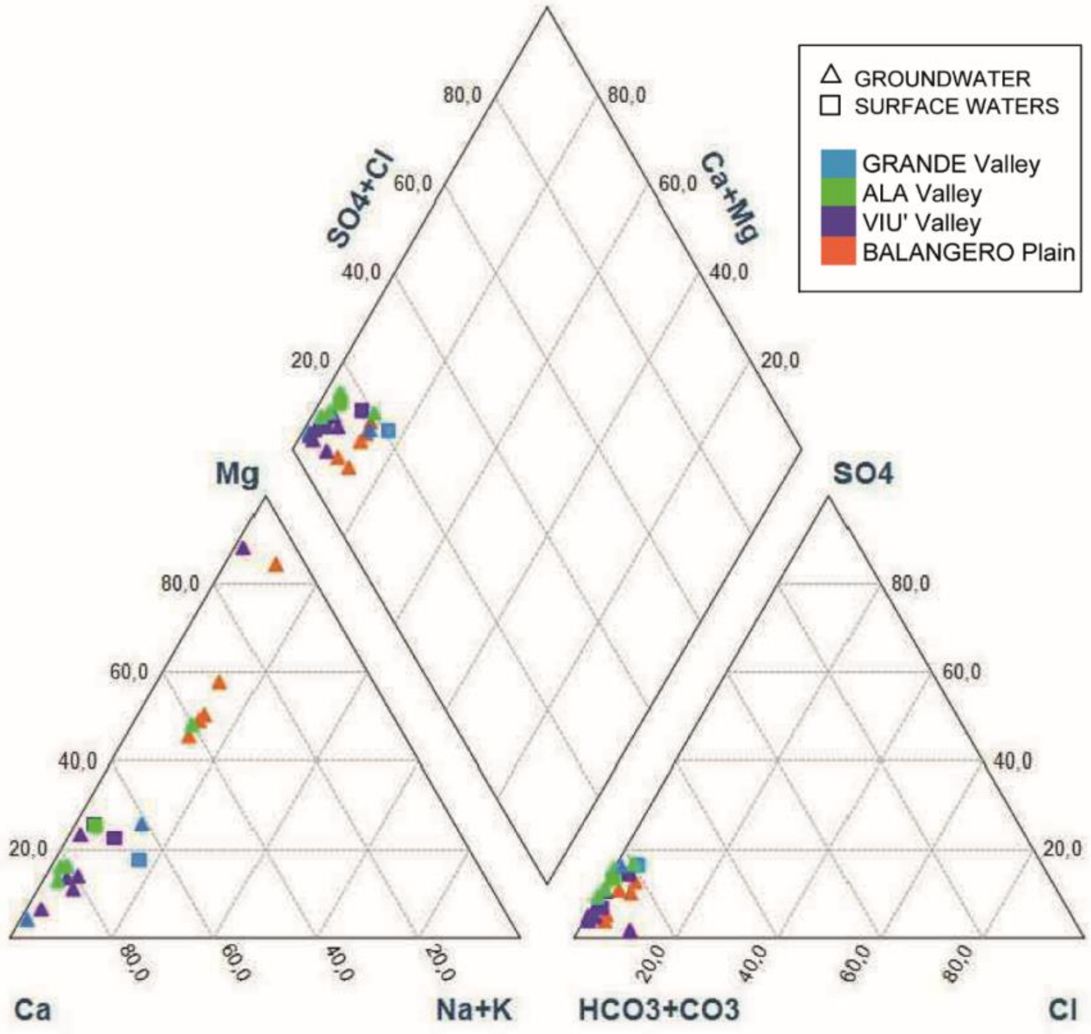
In laboratory:

- SEM-EDS analysis on all groundwater samples[1]
- TEM-EDS-SAED on a selected groundwater sample[2]

[1] Following U.RP M842 operating protocol rev.3 from ARPA Piemonte

[2] Following EPA method 100.1 for drinking water

Hydrochemical data/1

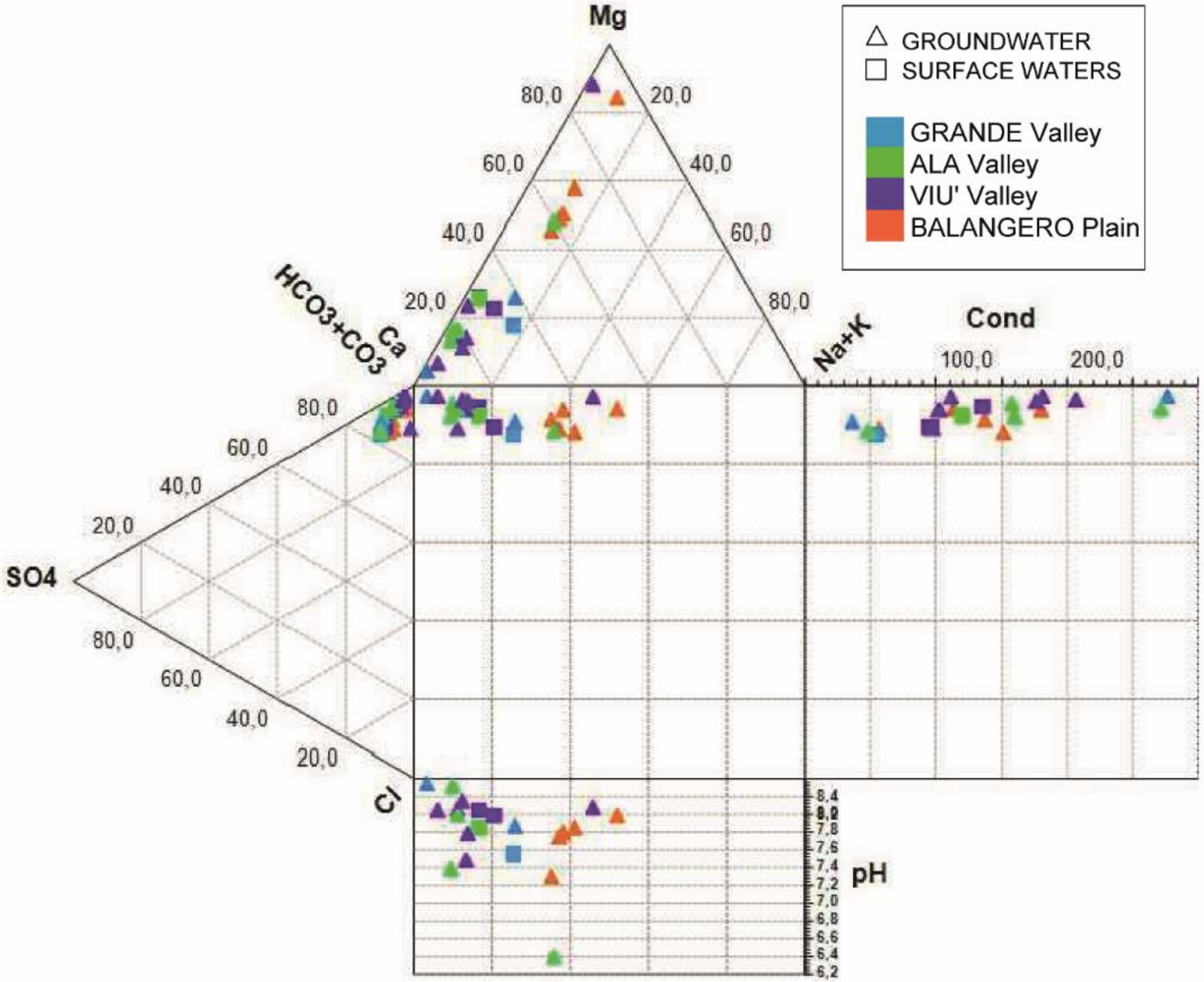


The analysed samples belong to the **bicarbonate-alkaline earth facies**, as shown by the Piper diagram, with variability in cations distribution. In particular, samples from the Balangero Plain have a percentage of **Mg** higher than 60%, while samples from the Lanzo Valleys have a higher presence of **Ca**. Groundwater and surface water in the different valleys show an almost hydrochemical similarity.

The presence of high level in Ca and Mg is likely due to the presence of **Ca and Mg minerals** (e.g. calcite, olivine, serpentine) in the rocks of oceanic origin (serpentinites, calcschists). Mg concentration shows a progressive increase starting from groundwater of the valleys to surface waters in the valleys up to groundwater of the Balangero Plain. The higher Mg content in the samples of the Balangero Plain compared to the valley sectors could be connected to a greater interaction of the water with the lithological matrix.

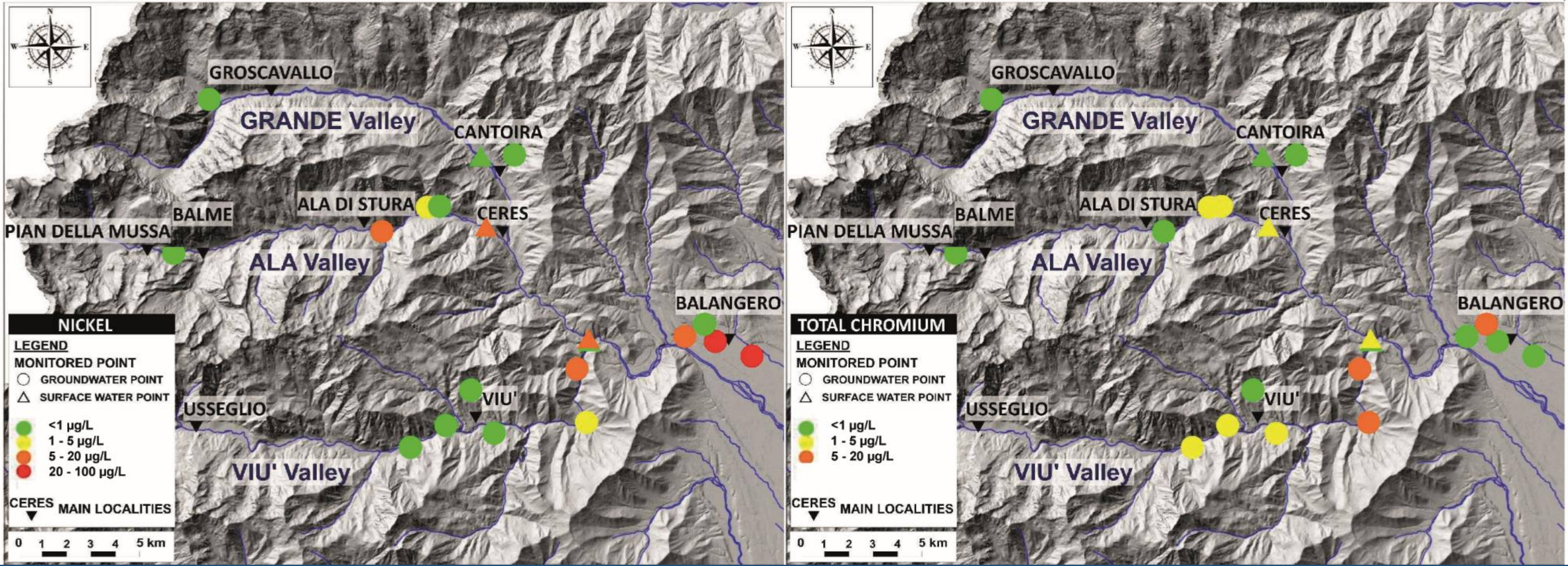
Hydrochemical data/2

The Durov diagram shows a general **basic pH**.
The variability among values reflects the different nature of the lithologies in the area, with high values related to calcschists and low values influenced by gneiss and granites.



Hydrochemical data/3

Nickel is always lower than the Italian legislation limit (20 µg/L) and locally lower than the detection limit (1 µg/L) in the Lanzo Valleys groundwater and shows higher concentrations, locally superior than the legislation limit, in the Balangero Plain. The high concentrations in this sector could be correlated to a major interaction of the waters with the lithological matrix, thus depending on natural origin. **Total chromium** never exceed the Italian legislation limit (50 µg/L) with numerous samples having concentrations below the detection limit (1 µg/L), both in the Lanzo Valleys and in the Balangero Plain.

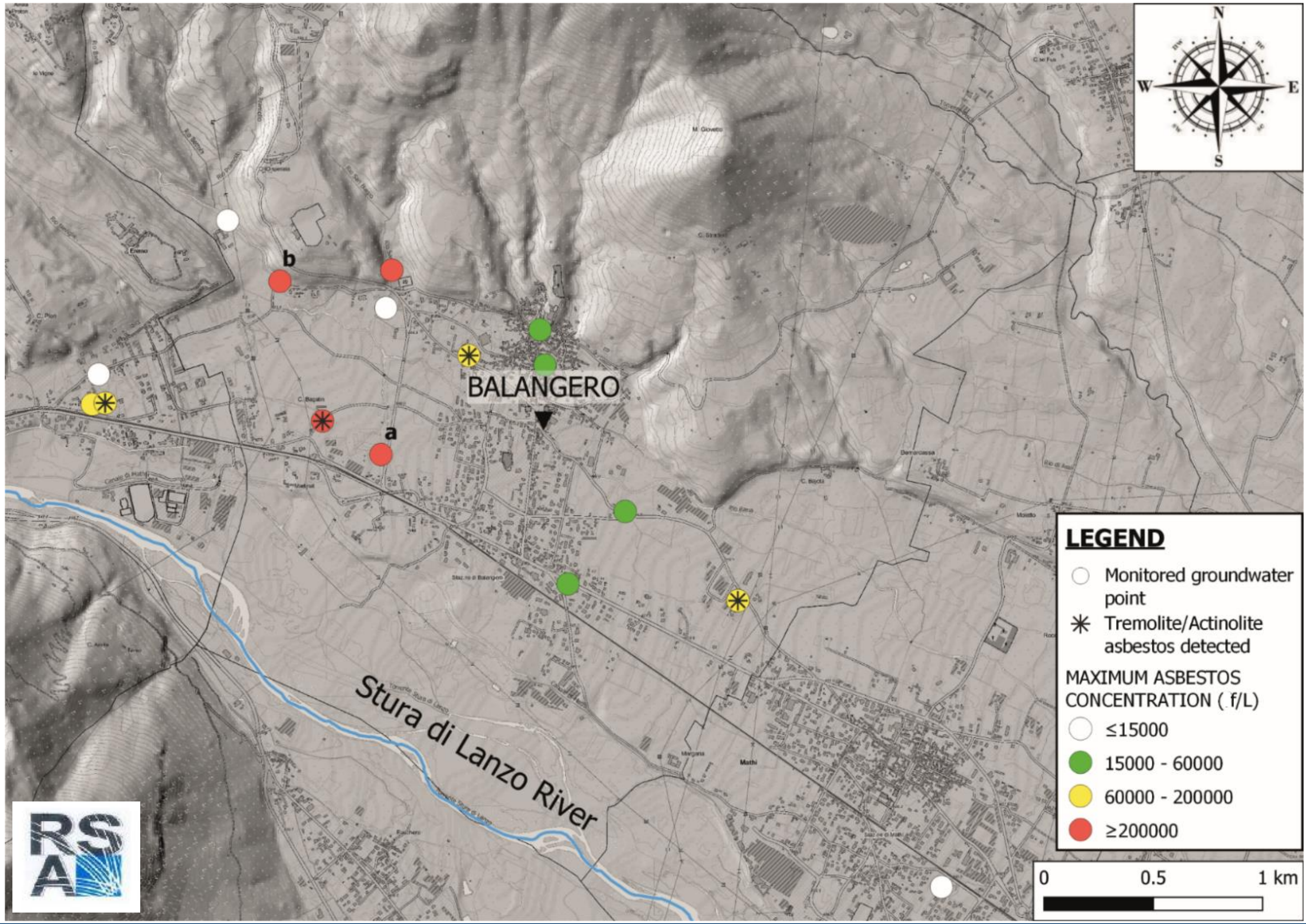


Asbestos occurrence data/1

The map shows **RSA data** on groundwater (acquired in the period 2007-2017) deriving from dynamic samplings in the Balangero Plain. Samples were analysed by means of SEM-EDS. The colours represent different **concentration ranges** and should be considered as a qualitative description of the study area.

Several points were sampled just once, therefore data don't have a statistical significance.

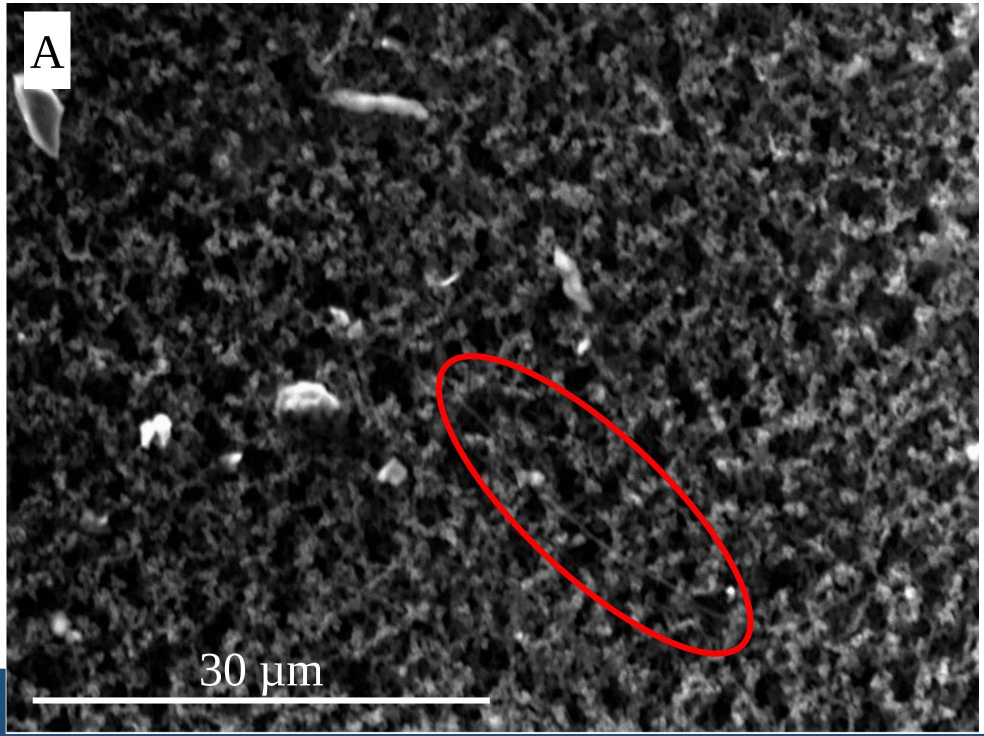
Mainly **chrysotile** was found in investigated samples. **Tremolite/actinolite asbestos** was revealed in low % only in samples with asbestos concentration >60˙000 f/L (fibres per litre) and located in the plain area, farther from the former chrysotile mine. This could indicate that **tremolite/actinolite contribution depends on rock formations located in the Lanzo Valleys and fibres possibly migrates through groundwater.** All the points with higher concentration are located at the basis of the former mine, suggesting that chrysotile coming from the San Vittore Mount outcrop influences the concentration in term of number. Two points ([a] and [b]), which were sampled several times, show a fluctuating asbestos content trend which goes from concentration below the limit of detection to over 200˙000 f/L: this could depend on the **precipitation pattern**, as demonstrated for other parameters in groundwater.

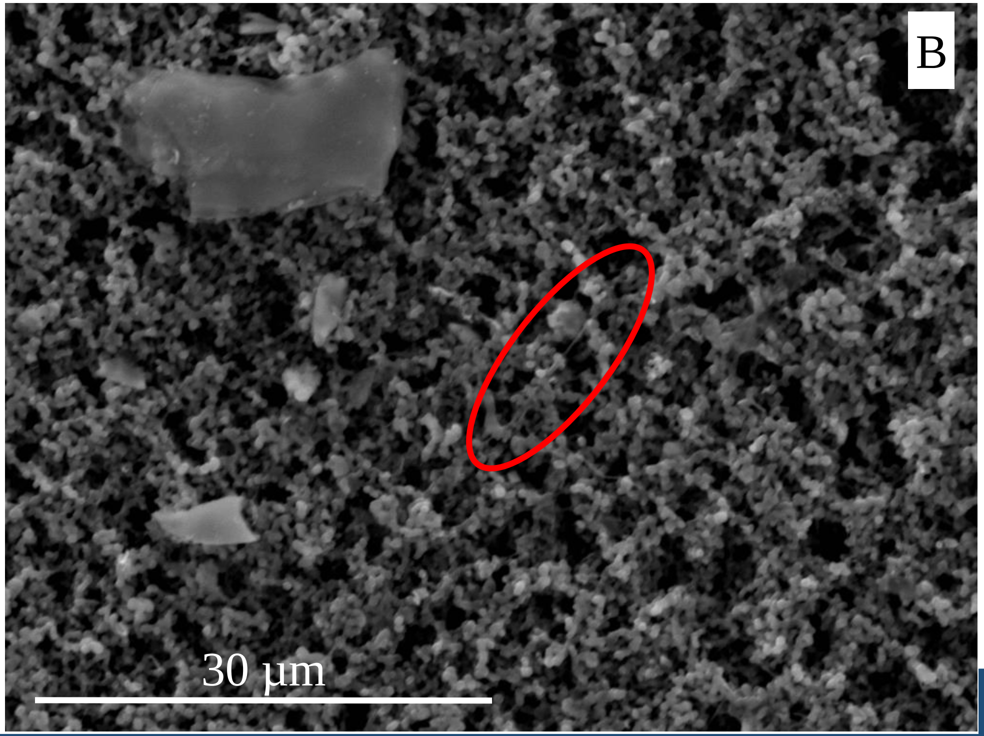


Asbestos occurrence data/2

UniTO's samples covered the whole study area, including the three Lanzo Valleys. Samples coming from the mountainous area appeared clean at a preliminary eye observation while a little amount of coarse particle was generally visible in samples collected in the Plain; a difference in particulate abundance was also seen by Electron Microscopy (both SEM and TEM) observations.

The most of the fibrous particles detected by **SEM-EDS analysis** showed a width < 0.2 µm (as shown in the images A and B below) and the resolution of the SEM was not enough to obtain clear EDS spectra and neither to define the morphology of the supposed elongated particles. Consequently, just a **qualitative sample characterisation** was performed by SEM-EDS. Detection problems were found particularly with fibres suspected to be chrysotile, because they are generally very thin and flexible and could get stuck in the filter surface. Amphiboles are easier to identify as a consequence of their stiffer shapes and greater width.

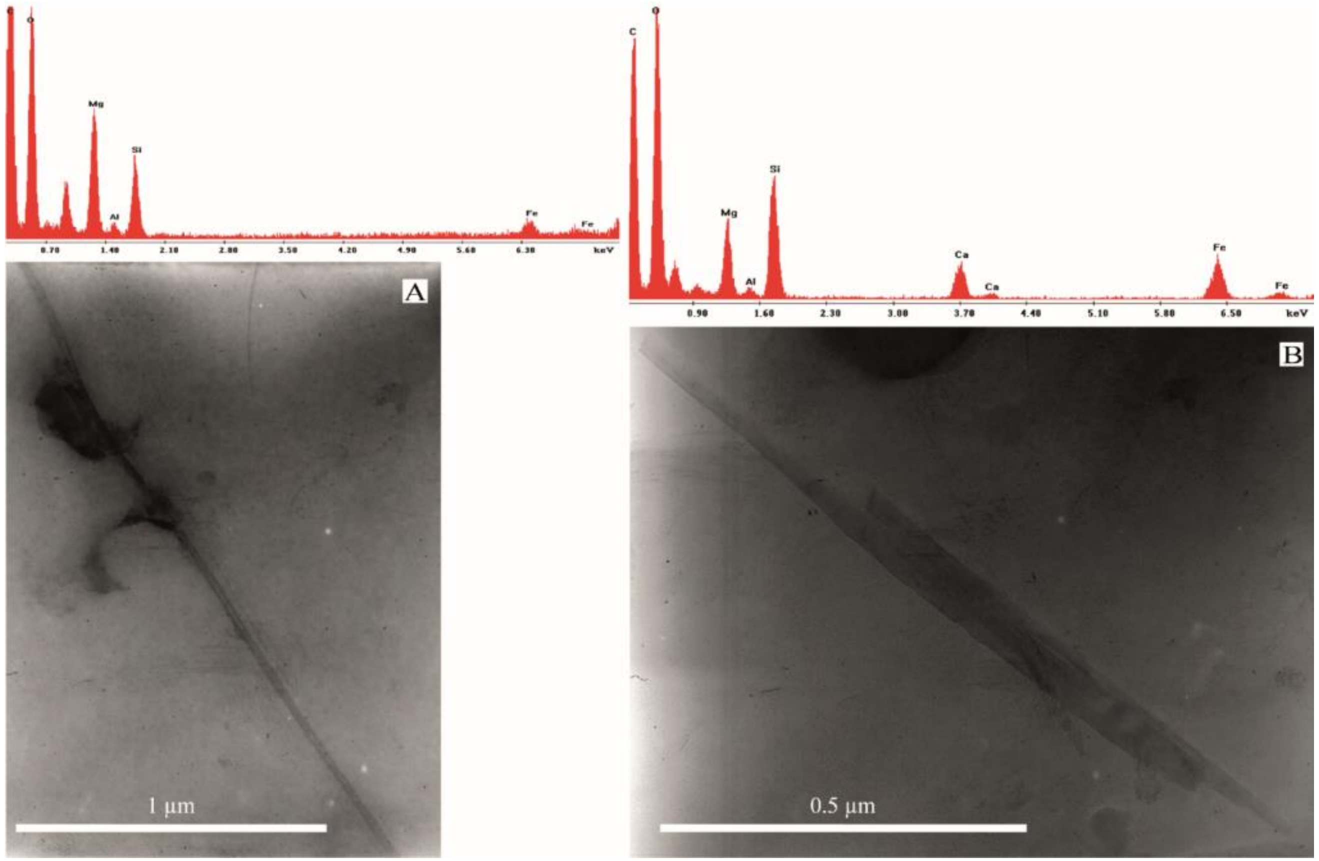




SEM images of very thin chrysotile fibres (inside red circles) on mixed-cellulose esters membranes.

THE CASE STUDY – Results

Asbestos occurrence data/3



Chrysotile/asbestiform antigorite fibre with relative EDS spectra (A), tremolite/actinolite asbestos fibre with relative EDS spectra (B), acquired by TEM-EDS.

To overcome detection problems found during SEM analysis, **TEM-EDS-SAED analyses** have been tested on a selected sample from Balangero Plain.

The investigation showed an abundant particles deposition on the grid, not equally distributed on all grid openings, thus making the sample observation not always easy.

The TEM-EDS analysis permitted to recognise a great amount of mineral fibres in the samples including asbestos ones (both **chrysotile** -image A- and **tremolite/actinolite asbestos** -image B), other phyllosilicates (chlorite and muscovite), various amphiboles (hornblende, glaucophane), clay minerals (kaolinite, palygorskite) and two asbestiform balangeroite particles (mineral characteristic of the area).

The **presence of tremolite/actinolite asbestos was not revealed by RSA past analyses.**

Selected Area Electron Diffraction (SAED) was not used for crystals characterisation because of difficulty to obtain readable patterns on very thin fibres (probably due to instaneous amorphisation of the crystal lattice induced by the electron beam). Therefore, it was not possible to discriminate between chrysotile and asbestiform antigorite.

Asbestos occurrence data/4

TEM analysis permitted to get details about **minimum, maximum and average size** of all mineral fibres observed.
From data reported in Table 1, it is clear that an **instrument with high magnification and resolution power**, such as TEM, is needed for the study of raw water, because all the fibrous particles detected had a sub micrometric width, down to few tens of nm for thinner ones.

TABLE 1	Length [μm]	Width [μm]
Max	13.23	0.4
Min	0.35	0.014
Average	2.74	0.077

TABLE 2	Concentration [f/L]	Concentration [μg/L]
All asbestiform particles	27˙195˙185	2.2
Asbestos	6˙731˙482	2.0

Table 2 reports **asbestos and asbestiform particles concentration** calculated in **fibres per litre (f/L)** and in **mass per litre (μg/L)**, quantified calculating the volume of each observed fibre and then the mass (multiplying the volume by the density). The calculated concentration is intended considering all fibres or just asbestos ones alternatively. Considering just asbestos, the total number is composed by **88% of chrysotile/asbestiform antigorite and 12% of amphiboles**.
The number of f/L detected, **exceeding $27 \cdot 10^6$ f/L**, is much higher than RSA concentration value for the same sampling point (indicated with [b] in the map at slide 13), obtained by SEM-EDS analysis: this difference should be linked to seasonal fluctuations in groundwater particulate content but could also depend on the analytical technique. In addition, the difference between the count considering just asbestos or all asbestiform particles highlights the **necessity to evaluate the chemical composition** of observed particulate in order to discriminate what is asbestos.

THE CASE STUDY – Conclusions

In this pioneering study, hydrochemical data were cross-referenced with asbestos concentration data in the water system of a selected study area. Main **results obtained** are:

- the **occurrence of different species of mineral fibres** (either asbestos and non-asbestos classified) in groundwater is verified with a not negligible presence of asbestos
- tremolite/actinolite asbestos presence in the Plain water suggests fibres **migration through groundwater**
- asbestos content variability in groundwater could be linked to the **precipitation pattern**
- **chemical parameters** in both surface waters and groundwater reflect the composition of **local occurring lithologies**, with higher Ca in the Lanzo Valleys and Mg in the Balangero Plain
- **weakly alkaline pH** seems to be linked to groundwater circulation in **serpentinites and metabasites host rocks**
- **Ni** shows a behaviour **in line with NOA occurrence** with concentrations increasing towards the Balangero Plain.

In addition, main **sampling and analysis problems** faced during the study were underlined. In particular:

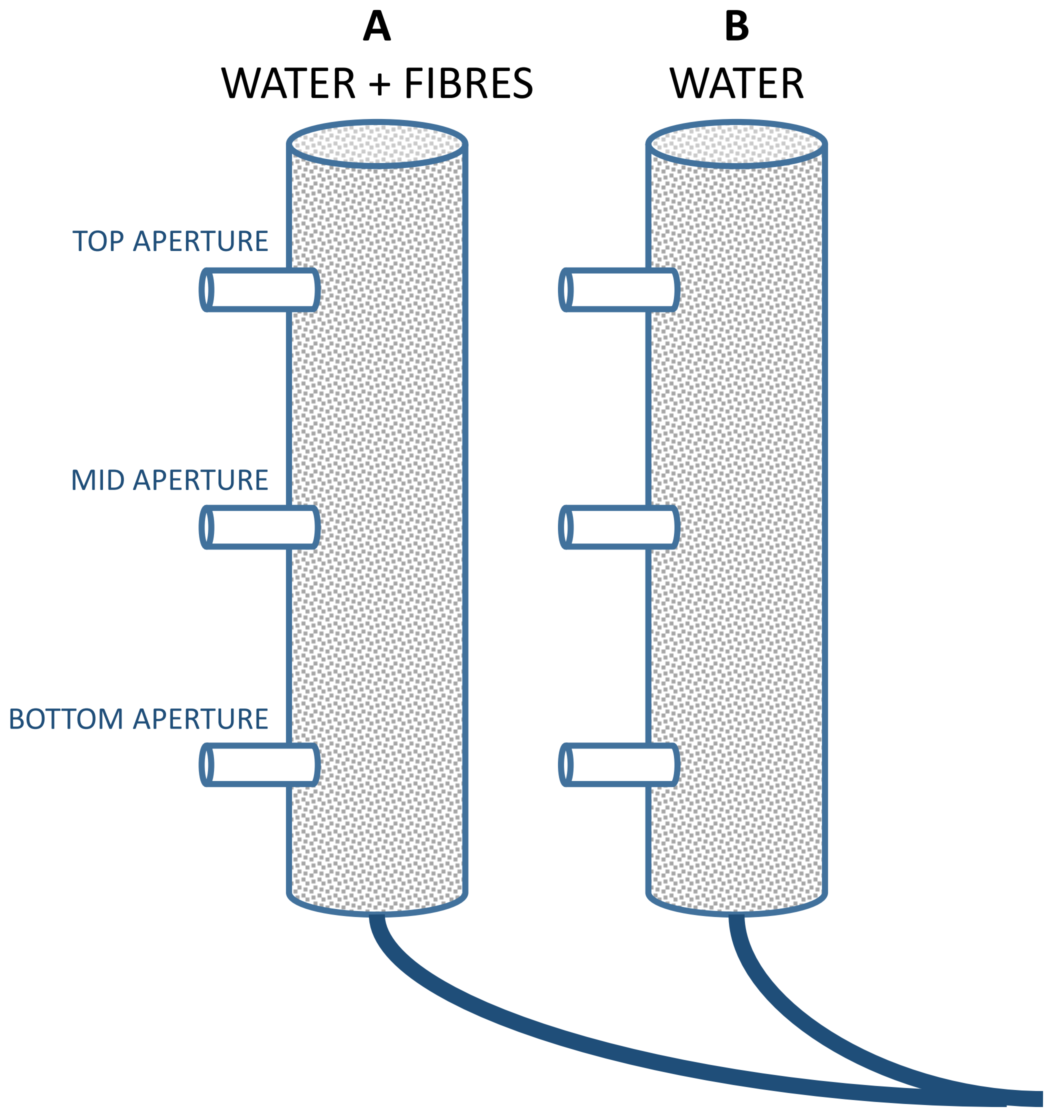
- the relation between **asbestos concentration and the sampling mode** → static or dynamic sampling could affect the fibres content, especially in case of sampling from wells and piezometers
- the lack of a really suitable **analytical method for groundwater samples** → in our experience, SEM-EDS analysis resulted not suitable for groundwater analysis but TEM-EDS analysis are extremely expensive and time consuming and just few laboratories in Italy can afford this technique, which could lead to difficulties in inter-laboratories validations.

Further sampling and analysis campaigns will be settled to evaluate the seasonal variability and to standardise the sampling and analysis procedure. Once defined a reliable sampling and analysis strategy, the variability of samples collected in different areas will reflect differences in the aquifer itself. This will allow to better **investigate possible fibrous mineral particles movement in porous media through water circulation**.

Laboratory studies on fibres mobility/1

To deepen our knowledge on mineral fibres mobility in porous media through water circulation, we set a laboratory experiment based on **columns study**.

Six columns of 30 cm length and 6.3 cm external diameter will be created with closed ends in order to force **water passage**.
Columns will be filled with 3 **different particle-sized materials** and water will be pumped from the basis to avoid the formation of percolating routes due to gravity. We will **sample the effluent** through **3 lateral doors** at top/mid/bottom of the column to verify the possible differences in fibres concentration at different heights and, therefore, to better represent fibres migration along the column.
Experimental **test** will be run **in parallel** on two twin columns: in A, water suspension of fibres will be fluxed, while in B just water will be used to define the background effluent.
Absorbance at a defined λ will be measured through a Spectrophotometer on all sampled effluents and obtained values will represent an **indirect quantification of fibres concentration**.
Representative effluent samples will be filtered on porous membranes and analysed by **SEM-EDS to characterise fibres morphology**.



Laboratory studies on fibres mobility/2

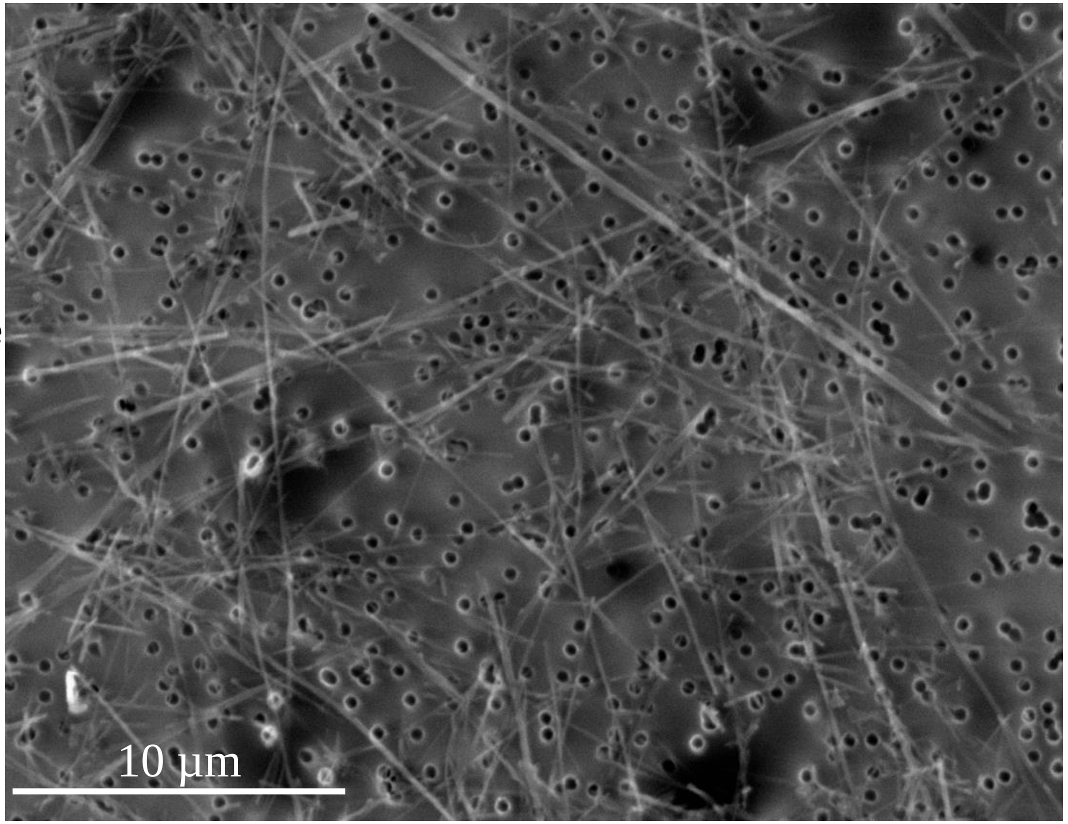
To avoid asbestos inhalation risks for operators linked to possible fibres passage in air after water vaporisation, the experimental test will be run using an **asbestiform sepiolite** water dispersion. At present, sepiolite is defined *non classifiable as to its carcinogenicity to humans* (Group 3) by IARC. Possible health risks linked to asbestiform morphology are currently under study.

The asbestiform sepiolite used for this study is a natural sample coming from NW Italy characterised by **very long fibres**, up to hundreds of µm. To obtain mineral fibres with dimensions comparable with natural samples (see slide 16) that could move in porous media, the asbestiform sepiolite has been gently **crushed** in agate mortar for 5 minutes adding isopropyl-alcohol.

Then, known concentration suspensions would be created and fluxed through the column.

At first just **geometric interactions** will be considered and evaluated.

In the future we will vary several **parameters** (such as pH, temperature etc.) and evaluate if **different behaviours** occur in mineral fibres diffusion through water movement in porous media.



SEM image of asbestiform sepiolite (after 5 minutes crushing) on polycarbonate membrane filter with 0.4 µm pores (black dots).

Many thanks to all the people who contributed to this study!

In particular:

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