GROUNDWATER ASBESTOS POLLUTION FROM NATURALLY OCCURRING ASBESTOS (NOA): A PRELIMINARY STUDY ON THE LANZO VALLEYS AND BALANGERO PLAIN AREA, NW ITALY

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EXTENDED ABSTRACT

I processi di dilavamento di rocce contenenti amianto (naturally occurring asbestos-NOA) costituiscono la principale fonte di contaminazione naturale da amianto delle acque. L'amianto idrodisperso costituisce un rischio per la salute umana poiché può disperdersi in aria, veicolato dal vapore acqueo, ed essere quindi inalato; inoltre, le fibre potrebbero essere ingerite, specialmente nel caso in cui si trovino in acqua potabile: ad oggi, non è chiaro se questa seconda modalità di esposizione costituisca un rischio per la salute umana per la difficoltà di condurre studi epidemiologici che non risentano di fattori confondenti.

Considerando il rischio per la salute umana derivante dall'inalazione di fibre di amianto e, in via precauzionale, dall'ingestione, risulta particolarmente importante valutare la presenza di amianto nelle risorse idriche, visto il loro utilizzo nell'agricoltura, per attività industriali e come sorgente d'acqua potabile.

Il presente progetto di ricerca ha quindi come obiettivo lo studio della presenza di amianto e altre fibre minerali nelle acque sotterranee delle Valli di Lanzo e nella Piana di Balangero (Piemonte, Italia nord-occidentale) dovuta a sorgenti naturali, vista l'attestata presenza di NOA in quest'area.

A questo scopo, una campagna di campionamento e analisi è stata condotta su 21 punti di monitoraggio di acque superficiali e sotterranee delle Valli di Lanzo e Piana di Balangero, campionati nell'autunno 2020: questi campioni sono stati sottoposti ad analisi in Microscopia Elettronica a Scansione e Trasmissione (SEM e TEM) per la valutazione della concentrazione di amianto e, inoltre, sono stati valutati i parametri chimico-fisici principali (conducibilità elettrolitica, pH, ioni fondamentali ed elementi metallici in traccia). A completamento, sono stati analizzati e rielaborati dati riguardanti la concentrazione di amianto in pozzi e piezometri della Piana di Balangero, raccolti dal 2007 ad oggi da RSA S.r.l. nell'ambito del Piano di Caratterizzazione del Sito di bonifica di Interesse Nazionale della ex miniera di amianto di Balangero e Corio.

I risultati di questo studio mettono in luce la presenza pressoché ubiquitaria di fibre nelle acque sotterranee della zona, in particolare nella Piana di Balangero: i dati raccolti dal 2007 da RSA denotano, però, notevoli fluttuazioni nella concentrazione di amianto che potrebbero essere legate a variazioni stagionali e all'influenza delle precipitazioni. Per quanto riguarda i campioni della campagna 2020, risultano difficilmente caratterizzabili tramite il SEM-EDS, strumento previsto dalla normativa italiana per lo studio degli amianti aerodispersi, per la presenza di fibre molto sottili (larghezza <0.2 micrometri) non caratterizzabili a livello chimico. Si è quindi scelto di procedere con l'analisi TEM-EDS di un campione selezionato, secondo il metodo 100.1 proposto da U.S.-EPA per le acque potabili. La concentrazione risulta essere $6.7*10^6$ ff/L considerando esclusivamente le fibre di amianto, mentre si otterrebbe un valore di $27.2*10^6$ ff/L considerando tutte le fibre minerali presenti, rafforzando ancor più la necessità di una buona caratterizzazione chimica delle fibre minerali riscontrate nei campioni d'acqua.

I dati chimici, in particolare i cationi in soluzione, rispecchiano le differenti litologie affioranti nelle varie parti dell'area di studio: l'abbondanza di Ca e Mg sembrerebbe legata alla presenza di rocce quali serpentiniti e ofioliti nelle zone vallive; l'arricchimento delle acque in Mg nella zona della Piana di Balangero potrebbe essere legata ad una maggiore interazione delle acque con la matrice rocciosa. Il pH debolmente basico sembrerebbe essere anch'esso legato alla tipologia di rocce ospitanti l'acquifero. Il nichel, che presenta valori di concentrazione generalmente bassi nelle valli e si arricchisce via via verso la Piana (raggiungendo valori >20 µg/L), è il solo metallo in traccia che sembrerebbe in stretta connessione con la presenza di NOA.

Infine, vengono presentate e discusse una serie di problematiche metodologiche relative al campionamento, alla preparazione ed alla successiva analisi dei campioni: la scelta di eseguire un campionamento statico o dinamico nei pozzi o piezometri, la quantità di acqua filtrata per la preparazione del campione e la stessa metodica analitica utilizzata possono influenzare notevolmente il risultato finale, rendendo difficoltosa, ad oggi, la valutazione della concentrazione di amianto nelle acque sotterranee e, più in generale, in quelle non potabili. Risulta quindi fortemente necessaria una mobilitazione della comunità scientifica su questo tema che porti a stilare una metodica ad hoc riguardante le acque non potabili.

ABSTRACT

Groundwater or surface water flow into natural rock formations containing asbestos (NOA), e.g. serpentinites and metabasites, may result in water asbestos pollution. In fact, asbestos-bearing rocks weathering is the principal natural cause of fibres water-dispersion.

As asbestos constitute a risk to human health, it is crucial, into NOA contexts, to verify the occurrence of mineral fibres in water resources, given their importance for agricultural and industrial activities and as a primary source for drinking water.

For this purpose, the Lanzo Valleys and Balangero Plain (NW Italy) were selected as study area where to evaluate the possible occurrence of asbestos in groundwater, to correlate it to the geolithological and hydrogeological characteristics of the context and therefore to evaluate the possible mobility of asbestos in aquifers.

The results of this preliminary study show the presence of asbestos in groundwater, generally occurring in very thin fibres which require TEM-EDS analysis. Water chemical characters, particularly dissolved cations, reflect the lithologies which occur in the area; concerning trace metals, only Ni shows a relation with NOA occurrence. In addition, several problems on sampling and analysis procedures are highlighted and discussed.

INTRODUCTION

The asbestos commercial term refers to a group of six minerals (chrysotile, tremolite asbestos, actinolite asbestos, anthophyllite asbestos, amosite and crocidolite) which have fibrous habit and are characterised by regulated dimensions making them respirable. Those minerals were known for their technological properties and accordingly four of them were commercially exploited (e.g. FLANAGAN, 2020). Nowadays, asbestos extraction and processing is banned in many countries (e.g. RICCHIUTI *et alii*, 2020), as a consequence of the definition of asbestos carcinogenicity via respiration (IARC, 2012).

In fact, asbestos was recognised as one of the most important occupational risk factor for respiratory apparatus pathologies, but in recent years, after the bans, the focus shifted on environmental exposure, both natural and anthropogenic, related to low dose exposure which could lead to dose-independent malignancies (e.g. CASE *et alii*, 2011; DONGEL *et alii*, 2013).

Regarding natural environmental exposure, one of the principal dispersion sources are rock formations containing asbestos (natural occurring asbestos, NOA), e.g. serpentinites and metabasites, which are spread in meta ophiolites rich areas where the oceanic crust and the upper mantle were tectonically emplaced into continental margins (e.g. DILEK & FURNES, 2014).

As rocks can undergo weathering and erosion and be subjected to anthropogenic activities, asbestos minerals could be release in air and also dispersed in surface water and groundwater, become part of sediments and again be released in air from water or soil according to an unlimited cycle (e.g. VIGNAROLI *et alii*, 2014), as shown in Fig. 1. Thus, studying natural environmental exposure, the three matrixes air, water and soil/rocks have to be considered in mutual connection.

Focussing on the water matrix, it is fundamental to define how asbestos pollution can constitute a risk to human health, given the importance of water resources for both agricultural and industrial activities and especially as a primary source for drinking water. Even if it is always difficult to evaluate environmental exposure due to many confounding factors which can occur simultaneously, two main exposure paths could be defined regarding waterborne asbestos.

Firstly, waterborne fibres could be source of airborne ones after water vaporisation. As reported before, the noxiousness of respired asbestos is well known but the relation between the amount of waterborne and, consequently, airborne fibres has to be deepened. Few articles have been published on the subject because of difficulties to correlate waterborne fibres to the number of those that can eventually be released in air, minimising confounding factors (WEBBER *et alii*, 1988; ROCCARO & VAGLIASINDI, 2018). Recently, a research project has developed at the University of Torino (Italy), on waterborne-airborne asbestos relation by means of a laboratory test (AVATANEO *et alii*, Chrysotile asbestos dispersion in air from contaminated water: an experimental simulation, in preparation). In addition to this exposure path, waterborne asbestos can reach the human body via ingestion, especially if it is present in drinking water. It is not yet understood if the ingestion of asbestos can cause pathological effects owing to limited critical studies (CHENG *et alii*, 2020; WHO, 2020). The IARC claim (2012), not yet changed, is that data on cancer due to the ingestion of asbestos are not conclusive.

Concerning water asbestos occurrence in NOA rich settings, several studies focussed on superficial water and water supplies (e.g. MILLETTE *et alii*, 1980; BALES *et alii*, 1984) while groundwater was very little studied (e.g. HAYWARD *et alii*, 1984). This lack of interest depended on the assumption that asbestos migration through soil is negligible (FULLER, 1977) but, nowadays, emerging studies highlight that the mechanism of asbestos movement in sediments and aquifers is not completely understood (MOHANTY *et alii*, 2021).

In view of this, it was considered important to select a pilot area where to evaluate the possible occurrence of asbestos in groundwater, to correlate it to the geolithological and hydrogeological characteristics of the context and therefore to evaluate the possible mobility of asbestos in aquifers.

The study area chosen to conduct this research is located in Piedmont (North western Italy) where the occurrence of
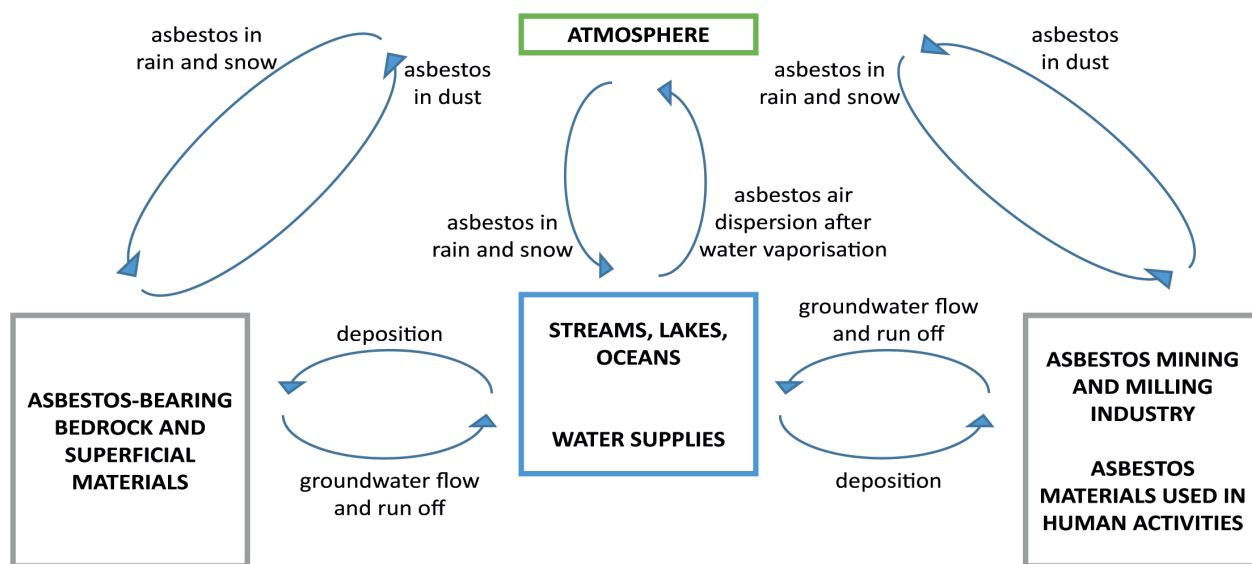
Fig. 1 - Scheme of asbestos circulation in the environment

meta ophiolites is widespread: in particular, the area includes a transition zone between mountain and plain in the surroundings of Lanzo and Balangero municipalities located in the NW of Torino, the capital city of the region. This area, called Lanzo Valleys, is formed by a system of three valleys 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. Here, the Lanzo Ultrabasic Massif, characterised by partially serpentinized peridotites, outcrops in the San Vittore Mount serpentinitic outcrop. The San Vittore Mount outcrop in Balangero municipality was long exploited for chrysotile asbestos extraction (till the '90s) and constituted the larger (chrysotile) asbestos mine in western Europe. The mining area is nowadays characterised by an open pit which is filled by a lake and whose terraces are subjected to constant weathering; it is monitored by RSA S.r.l. (from now on indicated as RSA), the public company in charge of the remediation and environmental development of the former asbestos mine site of Balangero and Corio municipalities. Several studies on the mining area and its surroundings revealed the occurrence of asbestos in the water system, particularly surface waters (Buzio *et alii*, 2000; Turci *et alii*, 2016).

The present research project is a preliminary study on the mineral fibres (asbestos and asbestiform non-asbestos classified fibres) occurrence in the water system of the Lanzo Valleys and Balangero Plain area. Data collected from 2007 by RSA have been examined and a new sampling campaign has been settled

recently by the Earth Sciences Department, University of Torino (UniTO), regarding surface water and groundwater. A water hydrochemical characterisation was performed and analysis procedures for asbestos detection were developed.

More specifically, a great quantity of water samples was subjected to asbestos and asbestiform fibres count and analysis by Scanning and Transmission Electron Microscopy techniques (SEM and TEM, coupled with Energy Dispersive Spectroscopy - EDS), to dissolved ions analysis through chromatography and to metals quantification by Inductively Coupled Plasma-Mass Spectrometry (ICP-MS).

THE GEOLOGY AND HYDROGEOLOGY OF THE STUDY AREA
Geological framework

Lanzo Valleys, located in the southern part of Graian Alps (NW Italy), include three different valleys with parallel elongation (East-West direction): Grande Valley, Ala Valley and Viù Valley. These three valleys constitute the upper part of the Stura di Lanzo river basin, which has a total extension of approximately 745 km², also considering the plain area.

The Lanzo Valleys geology (Fig. 2) reflects a complex geological history; the pre-quaternary testimony is represented mainly by three lithological units resulting from continental collision, preceded by the subduction of the European Paleomargin and the Piedmont-Ligurian Basin below the Adriatic Paleomargin (Platt *et alii*, 1989; Piana *et alii*, 2017). The three
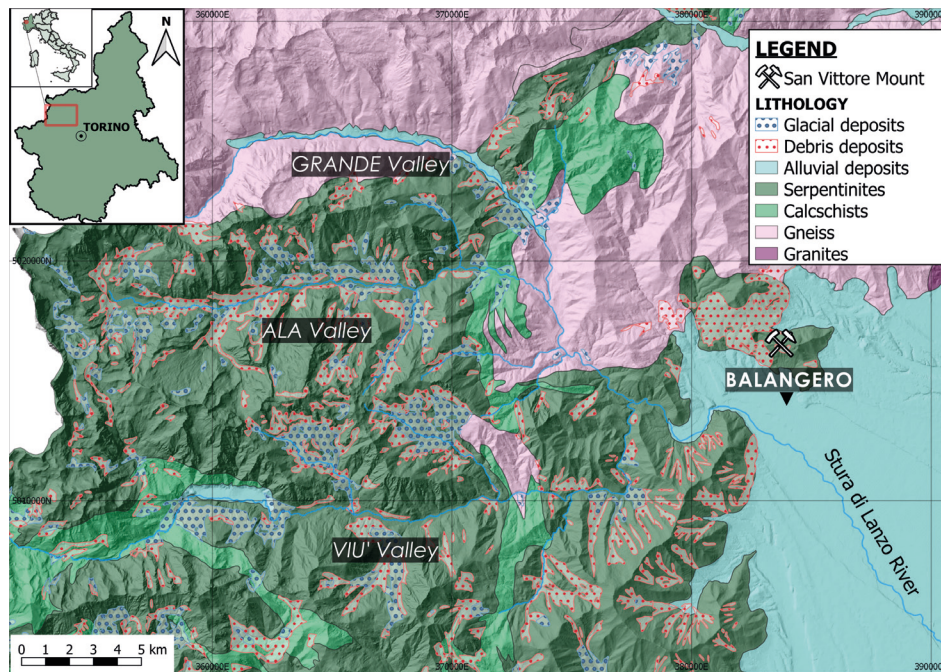
Fig. 2 - Simplified lithological map of the area (WGS 84 32 N). Modified from ARPA PIEMONTE (2011)

pre-quaternary lithologies observed are the units of the Gran Paradiso Crystalline Massif (Upper Pennidic Domain), the Piemonte Zone of Calcschist with meta-ophiolites and the Sesia-Lanzo Zone (Australpine Domain).

Particularly, the Piemonte Zone, composed by metaophiolitic units with peak in eclogitic facies and blueschists facies, is tectonically sandwiched between the European and Adriatic continental margin units (Bigi *et alii* 1990; DAL Piaz *et alii,* 2003; Balestro *et alii*, 2015). In the innermost part of the Piemonte Zone it is located the Lanzo Ultrabasic Massif, an extensive portion of the mantle consisting mainly of lherzolites converted to serpentinites at the rim and along the shear zones (Compagnoni *et alii*, 1980; Groppo *et alii,* 2007). The entire massif is composed of a central part of slightly serpentinized lherzolites surrounded by 3-5 km thick envelope of foliates serpentinites with, sometimes, a thin intermediate zone of massive serpentinites (Debret *et alii*, 2013). The Balangero Ultramafic Complex is a satellite body and an important part of the Lanzo Massif. It consists in serpentinites derived from spinel-plagioclase lherzolite, partially preserved only in certain places (Compagnoni *et alii,*1980). Asbestiform minerals were found in all investigated serpentinites of the internal Piemonte Zone, where the primary ophiolitic mineral assemblages show early-alpine eclogite facies and meso alpine greenschist facies metamorphic overprints; the asbestiform minerals occur in serpentinites deformed under brittle conditions and, much less frequently, in sheared serpentinites (Belluso *et alii,* 1994).

In the study area the occurrence of three asbestos minerals was detected, in connection with described lithology: chrysotile, the only phyllosilicate asbestos $[Mg_3[Si_2O_5](OH)_4]$, actinolite asbestos $[Ca_2(Mg,Fe^{2+})_5[Si_8O_{22}](OH,F)_2]$ and tremolite asbestos$[Ca_2Mg_5[Si_8O_{22}](OH)_2]$, both amphiboles. In addition, other minerals with asbestiform habit (but non-asbestos classified) were found in the area: asbestiform antigorite (a mineral of the serpentine group), asbestiform balangeroite (hydrate silicate of Mg, Fe and Mn), asbestiform carlosturanite (hydrate silicate of Mg, Fe, Ti, Mn and Al), asbestiform diopside $[CaMgSi_2O_6]$, asbestiform brucite $[Mg(OH)_2]$ and asbestiform brugnatellite (a rare carbonate of Mg and Fe) (Belluso *et alii*, 1994; Compagnoni & Groppo, 2006).
Figure 3 shows the different probability of asbestos occurrence in rock formations of the study area (ARPA PIEMONTE, 2016).

Hydrogeological framework
The plain hydrogeological structure consists of two main superimposed complexes represented by, from the top to the bottom, the Alluvial deposits complex (lower Pleistocene-Holocene) and the 'Villafranchiano' transitional complex (late Pliocene–early Pleistocene). A shallow unconfined aquifer is hosted in the Alluvial deposits complex, consisting of coarse gravel. 'Villafranchiano' transitional complex consists of both permeable deposits (pebble, gravel, sand) and low-permeability deposits (silt and clay). It hosts an unconfined aquifer in the area closest to the Alps, where sediments are undifferentiated, and in
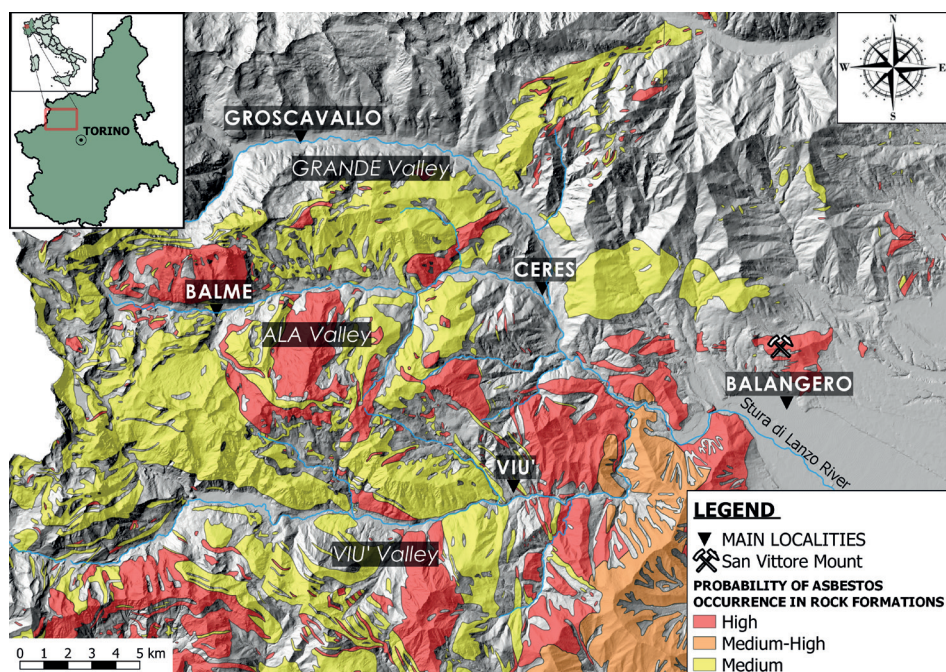
Fig. 3 - Probability of asbestos occurrence in the rock formations of the study area. Modified from ARPA PIEMONTE (2016)

coarse facies; on the contrary, a multi-aquifer system is present where the deposits are in alternating facies (fine grained deposits and coarse deposits). The groundwater flow direction of shallow and deep confined aquifers is NW-SE flowing towards the Po River.

The plain is bordered by the crystalline rocks of the Alps. They are mostly impermeable or slightly permeable by fissuration. In the mountain area, water resources are mainly located in the valley-floor aquifers, in intensely fractured rocks or in sedimentary non-cohesive bodies (e.g., glacial deposits, debris, and landslide) (De Luca *et alii*, 2020). Springs with low discharge (smaller than 1 L/s or few L/s) are generally connected to thin and discontinuous Quaternary deposits. Springs with higher discharge are, instead, linked to significant aquifers corresponding to large and thick landslide bodies (De Luca *et alii*, 2015; De Luca *et alii*, 2019).

Hydrochemical framework

Previous researches mainly focused on the Balangero mining site, that is characterized by numerous data, while a low number of studies was conducted in the remaining part of the study area.

Surface water in the Lanzo Valleys belongs in general to the bicarbonate-alkaline earthy facies. However, each valley has different features. Grande Valley surface water shows higher concentrations for alkaline ions, while in the Ala Valley a predominance of alkaline earth ions over alkaline ones is observed. Furthermore, water at the confluence of the Grande Valley and Ala Valley rivers shows greater affinity with the

samples of the Grande Valley, while water in Lanzo Torinese municipality shows an intermediate value (Berardi, 2020).

Detailed analyses carried out within and near the former mine site by RSA, to define the metals concentration in surface waters and groundwater, highlighted the legislative limits compliance (Repubblica Italiana, 2006), with the exception of nickel and, secondarily, manganese, iron, chromium VI in some groundwater monitoring points. They were attributed to natural origin, compatible with the local geological conditions (www.rsa-srl.it).

Greater availability of studies is present for the plain sector. An hydrochemical characterisation of Balangero plain surface water detected the exceeding of the legislation limit values (Repubblica Italiana, 2006) for nickel and sulphate (Porrera, 2010).

Surface waters and groundwater in the Lanzo conoid highlighted the belonging to the bicarbonate-alkaline earthy facies with an enrichment in Ca in surface waters and Mg in groundwater. Nickel exceeds the legislative limits in almost all groundwater samples. A direct proportionality between electrolytic conductivity and nickel is confirmed in groundwater and surface waters with a significant values increase from upstream to downstream. The high nickel concentrations in shallow groundwater are attributed to the interaction between shallow groundwater and the unsaturated zone, site of important reactions between the matrix and water, that do not occur in surface waters. This confirms the natural origin of nickel (De Stefanis, 2012).

Several studies also reported hydrochemical characteristics of waters in ophiolitic context, possibly connected to asbestos occurrence in water.

In acidic conditions mineral fibres, particularly chrysotile, could deteriorate releasing in water several elements: Mg and trace elements which are present in the crystal structure in isomorphic substitution of Mg, as Mn, Ni, Cr, Co, Fe (SCHREIER, 1987; SCHREIER et alii, 1987; SCHREIER, 1989). More recently, SCHREIER and LAVKULIK (2015) postulated that chrysotile Mg could even be leached and precipitated as Mg carbonate at high pH. Cr and Ni high levels in sediments have been found to be indicators of asbestos occurrence caused by a landslide of serpentinitic material in Sumas River, on the border between Washington State (USA) and British Columbia (Canada) (SMITH et alii, 2007). WEI et alii (2013) detected significant quantity of asbestos in surface and well water linked to crocidolite mineral in soil and rocks; the concentrations of Ni, Fe, Ca, Mg and Na were also higher in those sampling points than in the water from a control area.

MATERIALS AND METHODS
RSA Sampling campaigns

Sampling and analysis campaigns on surface water and groundwater have already been settled in the Balangero Plain by RSA since 2007 (www.rsa-srl.it). Several groundwater samples were collected over time in dynamic mode, using a low flow pump (5-8 L/min), from different wells and piezometers located in the Balangero Plain. All groundwater samples were stored in 1L glass bottles with hermetic closure in fridge at 4°C. On these samples, asbestos count and analysis were conducted following the operating protocol from the regional environmental

protection agency, the ARPA Piemonte U.RP M842 rev.1 (2007): water is filtered through a porous membrane (poly-carbonate filters with 0.8 μm diameter pores), the filter is then covered by a thin conductive layer and analysed by means of SEM-EDS. After observing 1 mm^2 of the filter surface with a magnification of 4000x, the asbestos concentration is calculated in number of fibres per 1 litre of water (ff/L).

For selected samples the amount of chrysotile and tremolite asbestos was evaluated verifying chemical composition. SEM-EDS analyses have been carried out by the SEM ZEISS model EVO 50 xvp, coupled with EDS INCA microanalysis suite 2003 at the 2i3T Incubator of the Chemistry Department, University of Torino, and at the RSA laboratory using a TESCAN VEGA 3 SBH Vega TC ver. 4.2.25.1 SEM, coupled with a INCA microanalysis suite EDS Oxford Instruments.

After the first more extensive campaign (2007/2008), few points selected as control ones were sampled again in 2015 and 2016/2017 for asbestos content evaluation (see Fig. 4 for sampling points location).

UniTo sampling campaign

As it is shown in Fig. 4, surface water and groundwater were sampled in Lanzo Valleys and Balangero Plain in 2020. 21 samples (4 surface waters and 17 groundwaters) were collected in October in a rather dry period, while 1 groundwater point had been sampled in February. Surface water samples were collected along the Stura river (and its tributaries) using polyethylene bottles (1 L or 0.5 L) with sealing discs: bottles were directly filled by stream water (in case of accessible riverbank) or using a bucket (sampling done from bridges). Concerning groundwater samples, in the mountainous area bottles were filled with spring
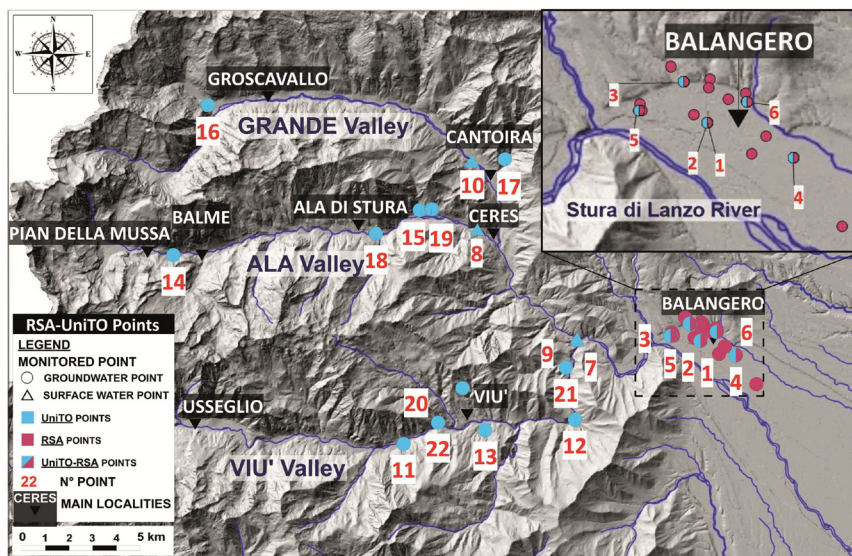

Fig. 4 - Sampling points location in the Lanzo Valleys and Balangero Plain regarding RSA (since 2007) and UniTO (2020) sampling campaigns

water, selecting those not included in the drinking water system. Groundwater samples from the plain were collected by static sampling using bailers in piezometers or wells, while bottles were directly filled in case of private wells which were equipped with pump and tap system (after waiting few minutes to allow water parameters stabilisation). All bottles were filled until reaching the sealing disc, avoiding air presence inside the bottle, and stored in fridge at 4°C.

SAMPLES PREPARATION AND ANALYSIS

Chemical analyses

Electrolytic conductivity (EC) and temperature were measured in situ with a conductivity meter by Hanna instruments. Hydrochemical analyses were performed in the laboratory of the Earth Sciences Department (UniTO), except for the ICP-MS analysis that was performed in collaboration with the Chemistry Department.

The pH value was measured following the 2060 method by CNR-IRSA (NATIONAL RESEARCHES COUNCIL-INSTITUTE FOR RESEARCHES ON WATERS, www.irsa.cnr.it/Metodi), using a Hanna HI2211 pH/ORP meter; measurements have been done at room temperature (16.8-17.7°C). EC was measured again in laboratory using a Hanna HI8820N instrument following the 2030 protocol by CNR-IRSA. Water alkalinity was measured following the 2010 method by CNR-IRSA using a Metrohm Dosimat 655: the method consists of a two-step acid-base volumetric titration using 0.1 M HCl and phenolphthalein and methyl orange indicators. Cations and anions quantity in solution was measured through ionic chromatography techniques: a Metrohm 883 Basic IC plus ionic chromatographic system equipped with autosampler was used following the CNR-IRSA methods n.3030 (Li^+, Na^+, NH_4^+, K^+, Mg_2^+, Ca_2^+) and n.4020 (F^-, Cl^-, NO_2^-, Br^-, NO_3^-, PO_4^{3-}, SO_4^{2-}).

Then each water sample was prepared for dispersed metals analysis (method derived from 3020 protocol by CNR-IRSA): an aliquot of 50 mL was filtered on a 0.45 µm syringe filter to remove coarse particulate matter and the resulting water was acidified with few drops of HNO_3 (HP quality) to obtain a pH<2. The analysis has been performed using a ICP Agilent 7500 to measure the quantity of B, Ba, Cd, Co, Cr, Fe, Mn, Ni, Pb, Sr, Zn.

Asbestos analyses

Just groundwater samples have been analysed for asbestos content. For each sample, stored in bottles in fridge, an aliquot was used to prepare the electron microscopy sample. This aliquot was put in ultrasonic bath for 16 minutes to allow the disaggregation of possible fibres bundles and aggregates; then water was filtered through a 25 mm diameter Mixed Cellulose Esters (MCE, 0.45 µm pores diameter) or, alternatively, Poly-Carbonate filters (PC, 0.4 µm pores diameter) using a vacuum filtration system. For

samples coming from the Lanzo Valleys 200 mL were filtered, while an aliquot of 100 or 50 mL was filtered for plain samples to avoid the clogging up of the filtration system. After letting the filter dry, half of it was placed on an Al stub and covered by a thin graphite layer to make it conductive and then suitable for SEM-EDS analysis. It was not possible to prepare samples n.1 and n.2 because of an excessive particulate presence.

For one selected sample, a 10 mL aliquot was filtered on a PC membrane and one eighth of the filter was dissolved with Chloroform in Jaffe Washer producing a filter replica on a 200 mesh copper TEM grid with carbon layer (FEW & MILLETTE, 2008).

SEM analyses were performed following the U.RP M842 operating protocol rev.3 (2016) from ARPA Piemonte with few modifications: after covering the filter with a thin graphite layer, a portion of less than 1 mm^2 of the membrane was observed at 4000x magnification and particulate was chemically characterised by Energy Dispersive Spectroscopy. For reasons detailed below (see the Results and Discussion section), just a qualitative samples characterisation was possible with SEM-EDS. The JEOL JSM IT300LV SEM (with W filament) coupled with EDS detector Oxford INCA Energy 200, INCA X-act SDD thin window available at the Earth Sciences Department (UniTO) was used for analyses.

At the best of the authors knowledge, the U.RP. M482 method is the only that is designed for water samples in general (thus also raw ones), while other possible methods refer to drinking water.

TEM-EDS investigations were performed on one selected sample using the Philips CM12 instrument (operating at 120 kV, LaB_6 cathode) equipped with an EDAX Genesis EDS system, available at the Earth Sciences Department, following the EPA method 100.1 for drinking water (EPA, 1983) considering all elongated particles, even those shorter than 0.5 µm, but having aspect ratio (length/width) >3 and parallel elongated sides. Grid openings were examined at 15000x, while interesting elongated particles were observed at higher magnifications (up to 230000x). Particles with aspect ratio ≥10 and parallel elongated sides where considered as fibres. The analysis stops when 20 grid openings are examined or 100 fibres counted, whichever comes first.

Mineral fibres can be defined by morphology, chemical characteristics and diffraction pattern. The asbestos content in ff/L is calculated as follows:

$$C = \frac{n_{ff} \times A_{tot}}{A_{grid} \times n_{grid} \times V}$$

where:

n_{ff}: number of fibres observed

A_{tot}: total area of the membrane on which filtration was performed [mm^2]

A_{grid}: area of a grid opening [mm^2]

n_{grid}: number of grid openings examined

V: original sample filtered on the membrane [L].

For the procedure followed in this research project, the analytical sensitivity of the method is approximately 1.5×10^5 ff/L.

RESULTS AND DISCUSSION

Hydrochemical data

The Piper diagram (Fig. 5) shows the analysed samples belonging to the bicarbonate-alkaline earth facies. The distribution of the anions shows that samples are located at the HCO_3 vertex, while the distribution of the cations shows greater variability. More specifically, all the samples have a percentage of Na+K lower than 20% but different Ca and Mg concentrations. Samples from the Balangero Plain have a percentage of Mg higher than 60%, while samples from the 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. olivine, serpentine) in the rocks of oceanic origin (serpentinites, calcschists). The presence of alkaline ions is linked to the occurrence of sodium-potassium minerals (e.g. sodium plagioclase, potassium feldspar, micas) in the lithologies of the Gran Paradiso (gneiss) units. Mg concentration shows a progressive increase starting from groundwater of the valleys to surface waters in the valleys up
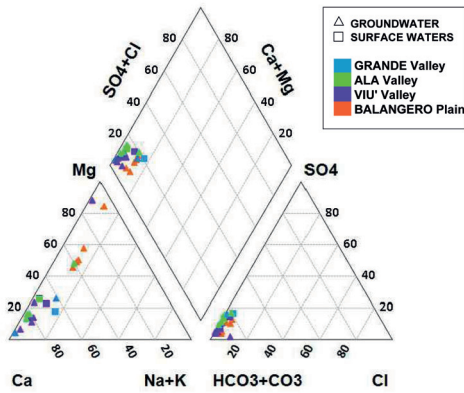

Fig. 5 -   *Piper classification diagram for different water types in the investigated area*

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. The almost hydrochemical similarity in Lanzo Valleys is connected to the geological homogeneity due to the large outcrop of ophiolitic units.

The Durov diagram (Fig. 6) shows, with only one exception, a general basic pH between 7.2 and 8.4. This variability reflects the different nature of the lithologies in the area, with high values

related to calcschists and low values influenced by gneiss and granites (SMEDLEY, 1991). The arrangement of the points within the central square suggests the process of the Ca-Na ion exchange for the samples of the Balangero Plain, potentially connected to the presence of clay minerals.

The nickel and total chromium concentrations of groundwater samples show a different spatial distribution (Fig. 7). Nickel is always lower than the legislation limit (20 µg/L) (REPUBBLICA ITALIANA, 2006) and locally lower than the detection limit (1 µg/L) in the 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
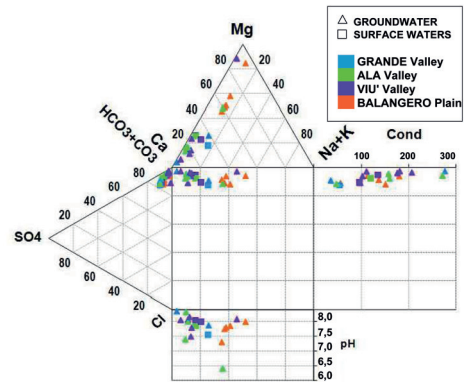

Fig. 6 - *Durov diagram for different water types in the investigated area*

major interaction of the waters with the lithological matrix, as found in the remaining portion of the Lanzo conoid (DESTEFANIS, 2012), confirming the local natural origin of the concentrations.

The concentrations of total chromium parameter never exceed the legislation limit (50 µg/L) (REPUBBLICA ITALIANA, 2006), with numerous samples having concentrations below the detection limit (1 µg/L), both in the valleys and in the Balangero Plain.

The surface waters concentrations of the analysed metals show no differences compared to groundwater concentrations. Sample n.6, located in the Balangero Plain, is not reported in maps and diagrams in relation to the high values of Na, Cl, NO_3 and EC which suggest a relevant anthropogenic influence.

ASBESTOS OCCURRENCE DATA

Asbestos content situation emerging from RSA data

The data set acquired by RSA during the past years (2007-2017) regarding asbestos occurrence in groundwater in the Balangero Plain is here discussed.

In general, RSA data show great variability in asbestos concentration values. One of the most impacting factors of this variability was considered the sampling mode (static vs. dynamic): as a consequence, just data derived from dynamic
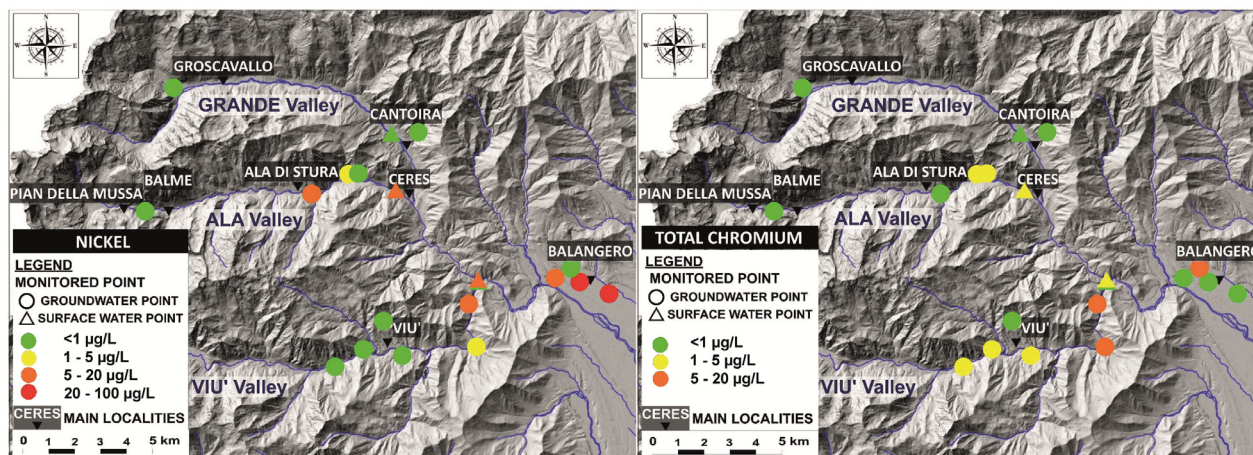
Fig. 7 - *Nickel and total chromium distribution in the monitored points of the study area*

samplings were considered for this study. In addition, even the analytical method could affect the results: in fact, it was demonstrated by RSA tests that concentration values calculated in case of SEM 2000x observations, following the Italian regulation to quantify airborne asbestos (REPUBBLICA ITALIANA, 1994, All. 2B), were always lower than the corresponding values obtained with higher magnification observations (4000x). Therefore, just concentrations calculated after SEM-EDS analysis at higher magnification (4000x) are considered. Besides, since the asbestos content in number of fibres per litre is the result of a calculation that amplifies the situation detected in a very small area to a larger scale value, it is clear that one more fibre leads to a great difference in the final result. With these premises, the following map (Fig. 8) reports the asbestos maximum quantity revealed in groundwater by RSA in the period 2007/2017.

The colours in the map represent different concentration ranges that have to be considered descriptive of the study area only and don't indicate a risk evaluation, as a maximum contaminant level for asbestos in raw water doesn't exist. In addition, considering that several points were sampled just once, data don't have a statistical significance.

Mainly chrysotile was found in investigated samples. Tremolite/actinolite asbestos was revealed with an amount up to 12% of the total number of fibres detected just in sample with medium to high asbestos content 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 asbestos mine, which suggests that the chrysotile coming from the San Vittore Mount outcrop influences the concentration in term of number. Two points (a and b in Fig. 8) were sampled in 2007/2008, 2015 and 2016/2017: they show great variability in asbestos concentration measured in different

sampling campaigns and even in different samplings during a single campaign, resulting in a fluctuating asbestos content trend which goes from concentration below the limit of detection to over 200000 ff/L. This could depend on the precipitation pattern: in fact, strong precipitations very likely influence groundwater asbestos content, such as demonstrated for other parameters (LASAGNA *et alii*, 2020), which shows an increase within few weeks from the meteorological event.
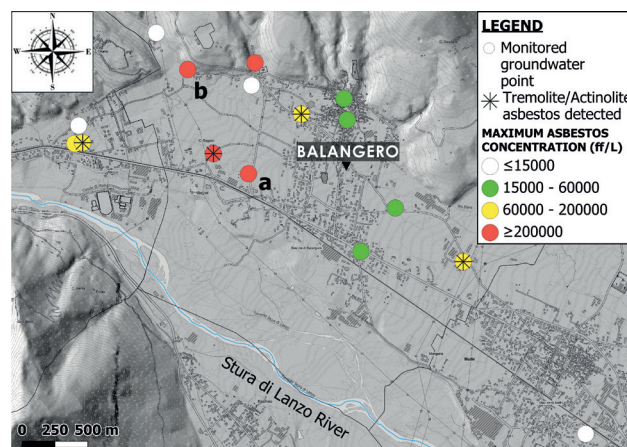

Fig. 8 - *Maximum asbestos concentration revealed in the RSA groundwater monitoring points since 2007. Chrysotile was found in every points, while tremolite/actinolite asbestos was detected just in 4 points (marked with *). The points a and b, monitored over time, show a fluctuating concentration trend which reaches maximum concentration over 200000 ff/L for both*

New data on asbestos occurrence in Lanzo Valleys and Balangero Plain area

Concerning samples collected during the sampling campaign in autumn 2020, the study area is much wider than the RSA one and comprehends the three Lanzo Valleys. It should be noted that a great difference is observable between samples collected

in the Lanzo Valleys and the plain area: those coming from the mountainous area appear clean at a preliminary eye observation while a little amount of coarse particle is generally visible in samples collected in the plain. This difference resulted in a different amount of water required to prepare samples for electron microscopy: for valleys samples, a water aliquot of 0.2 L was filtered, while for plain samples a filtration of 0.1-0.05 L was required to get membranes readable for SEM-EDS (see Tab. 1).

particles. Consequently, the analyses were stopped before observing 1 mm^2 of the membrane surface and 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 diameters (SCHREIER, 1989).

Sample	Sampling point position	Filtration amount [L]	Filter area scanned [mm^2]	Observations
3	Balangero Plain	0.05	0.17	Filter is overloaded, SEM analysis is not possible. Several very thin elongated particles observed.
4	Balangero Plain	0.1	0.17	Filter is overloaded, SEM analysis is not possible. Very few thin elongated particles observed.
5	Balangero Plain	0.1	0.17	Filter is overloaded, SEM analysis is not possible. Several thin fibres (W<0.2 μm), chemical data not achievable (just Si detected in some cases). Few acicular particles containing Ca.
6	Balangero Plain	0.05	0.17	Filter is overloaded, SEM analysis is difficult. Diatoms are visible. Several thin fibres (W<0.2 μm), chemical data not achievable.
11	Lanzo Valleys	0.2	0.5	Several very thin fibres (W<0.2 μm), chemical data not achievable (just Si detected in some cases). Few acicular particles.
12	Lanzo Valleys	0.2	0.5	1 TiO$_2$ fibre. No other fibres detected.
13	Lanzo Valleys	0.2	0.15	Several very thin elongated particles.
14	Lanzo Valleys	0.2	0.09	Several very thin fibres (W<0.2 μm), chemical data not achievable (just Si detected in some cases).
15	Lanzo Valleys	0.2	0.5	1 actinolite asbestos L≈4.77μm, W≈0.35μm. Several very thin fibres (W<0.2 μm), chemical data not achievable.
16	Lanzo Valleys	0.2	0.5	1 tremolite asbestos L≈3.9μm, W≈0.3μm. No other fibres detected.
17	Lanzo Valleys	0.2	0.12	Several very thin fibres (W<0.2 μm), chemical data not achievable (just Si detected in some cases).
18	Lanzo Valleys	0.2	0.18	Several very thin elongated particles.
19	Lanzo Valleys	0.2	0.5	Several thicker fibres (W≈0.2μm), chemical data not achievable.
20	Lanzo Valleys	0.2	0.12	Several very thin elongated particles.
21	Lanzo Valleys	0.2	0.15	Several very thin elongated particles.
22	Lanzo Valleys	0.2	0.12	Many very thin fibres (W<0.2 μm), chemical data not achievable. Few acicular particles.

Tab. 1 - Brief description of SEM-EDS observations on groundwater samples of the UniTO campaign. L=length, W=width

Again, the U.RP M842 analytical method was used for samples examination by SEM-EDS. The most of the particles detected showed a width < 0.2 μm (see Fig. 9) and the resolution of the SEM was not enough to obtain clear EDS spectra and neither to define the morphology of the supposed elongated

Table 1 briefly shows the main observations emerged from SEM examination.

It is clear how the process of identification and quantification of asbestos in water is strongly influenced by the small size of fibres (Buzio et alii, 2000). Consequently, it is preferable to
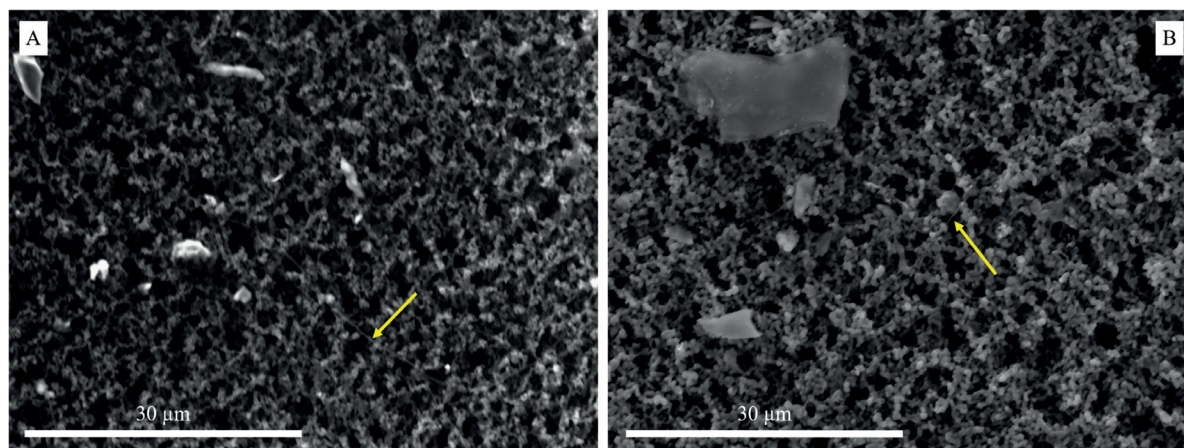

Fig. 9 - Two examples of very thin fibres (indicated by yellow arrows) observed on a MCE filter during SEM analyses, from which it is not possible to collect chemical data. A: fibre width≈0.2 μm, B: fibre width≈0.15 μm

operate with higher magnification to detect even very thin fibres that are common in water samples (e.g. Millette *et alii*, 1980). For this reason, the US regulation foresees a protocol which involves TEM analyses for water samples (EPA 100.1). The method is suitable for drinking water and involves counting just fibres longer than 0.5 µm: however, it should be noted that is not so uncommon to find shorter fibres in raw water (Millette *et alii, 1980).*

Therefore, TEM analysis has been tested on the sample n.3 (from Balangero Plain) which showed a great amount of particles at SEM observation. The same sampling point was monitored by RSA since 2007 and revealed great asbestos concentration variability over time (see Fig. 8, point b). The sample has been prepared filtering a lower quantity of water, in accordance with higher sensitivity of the analytical technique, and TEM-EDS analysis was performed following the EPA 100.1 method for drinking water with few modifications, as reported in the Materials and Methods session. The TEM observation permits to detect and define the morphology of very thin fibres (few tens of nm) thanks to the higher magnification and resolution power of the instrument. In addition, it is possible to obtain clear EDS spectra and therefore to define the chemistry of particles.

TEM-EDS analysis on sample 3 showed an abundant particles deposition on the grid. The particulate was not equally distributed on all grid openings but tends to accumulate and possibly overlap in certain part of the grid, thus making the sample observation not always easy.

As the sample was rich in particulate, the analysis stopped with the observation of 13 grid openings, having counted more than 100 elongated particles. Clearly the small surface observed and the irregular particles distribution could pose representativeness problems, which have to be deepened in further researches.

The TEM-EDS analysis permitted to recognise a great amount of mineral fibres in the samples, considering morphological information and chemical data. Regarding asbestos, both chrysotile and tremolite/actinolite asbestos were detected. In addition, phyllosilicates (other than the minerals of the serpentine group, such as chlorite and muscovite), various amphiboles (hornblende, glaucophane), clay minerals (kaolinite, palygorskite) with fibrous morphology were observed. Two asbestiform balangeroite particles, a mineral characteristic of the area, have been detected in the sample. The detection of clay minerals seems to confirm what have been hypothesised considering chemical data; on the contrary, the presence of tremolite/actinolite asbestos was not revealed by RSA past analyses.

Selected Area Electron Diffraction (SAED) patterns were difficult to obtain on very thin fibres because the beam seemed to cause instantaneous amorphisation of the crystal lattice. Alternatively, we could speculate that very thin fibres were already amorphous before the analysis, as a consequence of

possible crystal structure alteration caused by water action, which could be a possible result of particles leaching in water in acidic or strong alkaline conditions (Schreier, 1989). This aspect needs to be deepened in further studies.

Therefore, SAED was not used for crystals characterisation and it was not possible to discriminate between chrysotile and asbestiform antigorite (a mineral of the serpentine group) particles when the hollow core was not evident. Then, we will refer to them as chrysotile/asbestiform antigorite particles from now on.

Regarding relative minerals abundance, chrysotile/asbestiform antigorite fibres were approximately 22% of the total number of fibres detected, while tremolite/actinolite asbestos constituted the 3% of the total: thus, asbestos constitute the 25% of the total number of asbestiform particles observed. Considering just asbestos, the total number is composed by 88% of chrysotile/asbestiform antigorite and 12% is made by amphiboles asbestos. Table 2 shows details about minimum, maximum and average size of all mineral fibres observed.

	Length [µm]	Width [µm]
Max	13.23	0.4
Min	0.35	0.014
Average	2.74	0.077
Mode	0.55	0.045

Tab. 2 - Particles size distribution observed by TEM analysis, considering all asbestiform particles detected despite their chemical composition

From data reported in Tab. 2, 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 nanometres for thinner ones.

In addition, the range of measured length is very wide, from 13.23 to 0.35 µm, indicating that it is not possible to rigorously follow the EPA 100.1 method counting just fibres longer than 0.5 µm. As an example, a chrysotile fibre and a short tremolite/actinolite asbestos bundle images are reported (Fig. 10) with relative EDS spectra.

It was possible to calculate the concentration of fibres in water, as described in the Materials and Methods session. In addition, the concentration in mass per litre (µg/L) has been quantified calculating the volume of each fibre (approximation to a cylinder or a parallelepiped as a function of the shape observed) and therefore the mass, multiplying the volume for the density (2.55 g/cm³ for chrysotile, 3.05 g/cm³ for tremolite/actinolite asbestos).

Table 3 reports the calculated concentration value in ff/L and µg/L, considering all fibres or just asbestos ones alternatively.

The calculated concentration in ff/L regarding just asbestos constitute one fourth of the total, as pointed out before describing the relative amount of minerals.

	Concentration ff/L	Concentration µg/L
All asbestiform particles detected	27'195'185	2.2
Asbestos	6'731'482	2.0

Tab. 3 - *Calculated concentration in number of fibres per litre (ff/L) and mass per litre (µg/L) counting all asbestiform particles and asbestos fibres (chrysotile/asbestiform antigorite + tremolite/ actinolite asbestos)*
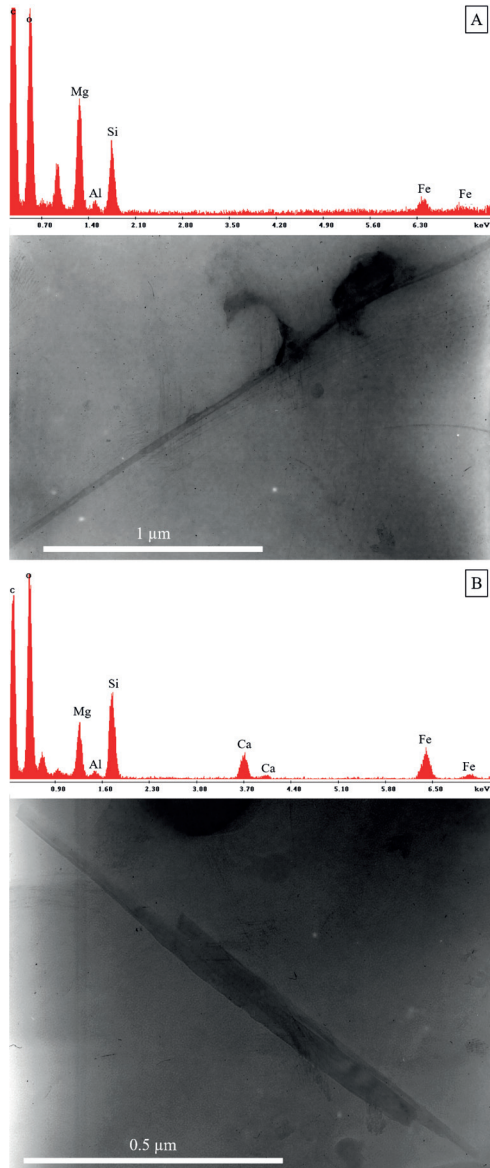
Fig. 10 - *TEM images of a chrysotile fibre (A) and tremolite/actinolite asbestos fibres bundle (B) with relative EDS spectra. Concerning A, it is possible to recognise a chrysotile fibre univocally because of the central hollow core (5-8 nm)*

A different situation emerges from concentration data in µg/L, where the value calculated considering just asbestos is slightly lower than the total concentration value: this indicates that asbestos volume constitutes the 90% of the total, considering that densities of found mineral all fall in the small range 2.15-3.2 g/cm^3. These results pose the question of which concentration expression is better to accurately represent the quantity of asbestos detected, which has been object of discussion also in the paper by AVATANEO *et alii* (Chrysotile asbestos dispersion in air from contaminated water: an experimental simulation, in preparation).

The number of ff/L detected is greater in comparison to RSA data for the same sampling point, obtained by SEM-EDS analysis. A variability should be linked to seasonal fluctuations in groundwater particulate content and to the sampling mode, but an underestimation of particles concentration could occur if the analytical technique doesn't permit the detection of thin fibres, which are common in raw water.

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. All these aspects strengthen the fact that differences in detection methodology can greatly affect the final asbestos concentration expression (MILLETTE *et alii*, 1980).

It is evident that a standardised and shared method for sampling, preparation and analysis of raw water samples finalised to asbestos detection is needed to get reliable results, comparable among different laboratories (TURCI *et alii,* 2016).

CONCLUSIONS

The results of this study show the occurrence of different types of mineral fibres (either asbestos and non-asbestos classified) in groundwater and a not negligible presence of asbestos. Chemical parameters in both surface waters and groundwater reflect the local occurring lithologies, with higher Ca in the valleys and Mg in the Balangero Plain. Weakly alkaline pH seems to be linked to groundwater circulation in serpentinites and metabasites host rocks. Among trace metals, only Ni shows a behaviour in line with NOA occurrence with concentrations increasing towards the Balangero Plain, depending on water interaction with the lithological matrix. It was not possible to outline a clear relation between other trace metals and asbestos occurrence in water samples, thus further studies are needed to deepen this aspect.

In addition, it is important to underline the main problems we faced during this study project. A crucial point to discuss is the relation between asbestos concentration and the sampling mode: in fact, in case of wells and piezometers a static or a dynamic sampling could affect the fibres content. Once defined a reliable sampling mode, 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, which is not a clear aspect and needs to be deepened in future works.

Other important aspect is the lack of a really suitable analytical method for groundwater samples shared by the whole scientific community. It is clearly important to underline that, 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 such a technique. This could lead to difficulties in inter-laboratories validations.

Indeed, the definition of a common and shared method is urgent because sampling, preparation and analysis procedure greatly affects the results.

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