

Waterborne Naturally Occurring Asbestos: a case study from Piedmont (NW Italy).



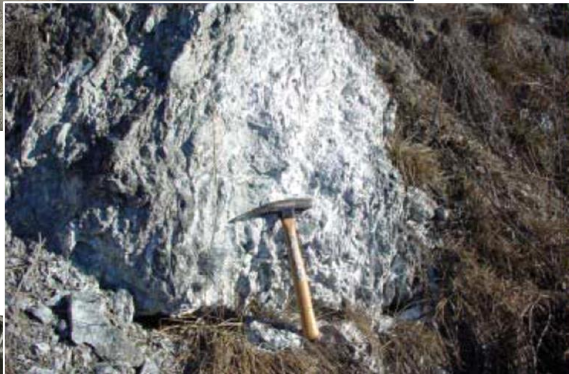
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INTRODUCTION – NOA and human exposure

NOA sources of exposure



Health risk: environmental / occupational exposure (resident population, workers)

Pan et al., Am J Respir Crit Care Med. 2005
Baumann et al., Environ Health Persp. 2010
Bloise et al., Environ Earth Sci. 2017



Airborne NOA fibres

e.g. Indoor fibres release due to polluted drinking water for shower
Roccaro, Vagliasindi, Chemosphere 2018

e.g. Air dispersion of asbestos fibres during roads or tunnels construction

air release from polluted water
 fibres deposition

fibres deposition
 air release from soil/rocks

e.g. Agricultural use of asbestos-polluted waters
Koumantakis et al., J Haz Mat. 2009
Turci et al., J Haz Mat. 2016

Waterborne NOA fibres

NOA fibres in soil/rocks

watering or flood in soil
 atmospheric phenomena/weathering

According to currently available data, ingestion is not considered a risk for humans
Millette et al., Environ Health Persp. 1980

Is it necessary to fix a maximum contaminant level (MCL) for waterborne fibres?

Following the lack of evidence between the occurrence of asbestos fibres in drinking water and the development of cancer, WHO recently stated that it isn't possible to define a limit level [*World Health Organization. Guidelines for drinking-water quality. 4th Edition. Geneva: WHO; 2011*] even taking into account the danger linked to the release of airborne fibres from vaporization of polluted water. As a consequence, at the present moment UE and Italy don't indicate a limit value for fibres in drinking water.

On the contrary, following some *in vivo* studies, USEPA (U.S. Environmental Protection Agency) defines a MCL of asbestos in drinking water of **7x10⁶ ff/L**, considering only fibres longer than 10 µm [*EPA-Environmental Protection Agency (1998) Technical factsheet on asbestos*].

In addition, the methods and techniques used for analysis on waterborne fibres are not the same everywhere.

3 principal analytical methods to be used on water samples (details in the next slide):

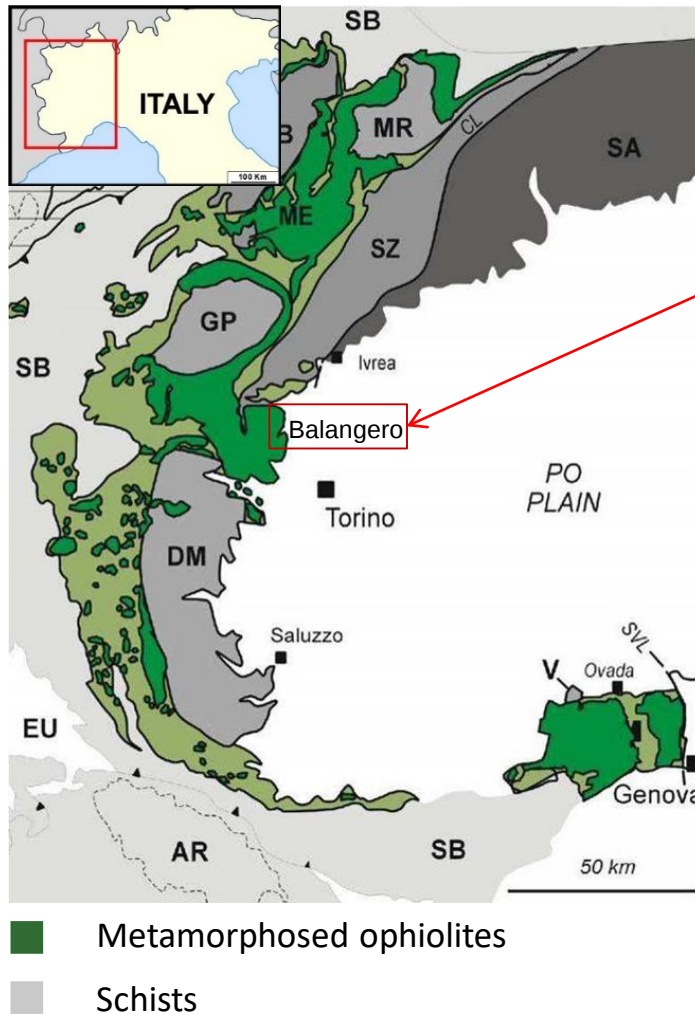
- **EPA-Environmental Protection Agency, Analytical method for determination of asbestos fibers in water: method 100.1 (1983) / method 100.2 (1994), for drinking water**;
- **ARPA Piemonte, Protocollo U.RP.M842, Amianto in acqua in Microscopia Elettronica a Scansione, revisione 03 (2016), for water samples in general**;
- **ISS.EAA.000 ISPRA-Italian Health Ministry (2015), for drinking water**
[http://www.salute.gov.it/portale/temi/documenti/acquepotabili/parametri/Val_Amianto_documento_completo.pdf].

INTRODUCTION – Analytical methods for waterborne fibres

EPA Method 100.1 (1983)/100.2 (1994)	U.RP.M842 ARPA Piemonte (2016)	ISS.EAA.000 ISPRA (2015)
TEM-SAED-EDS	SEM-EDS	SEM-EDS
0.1-0.22 µm pores mixed cellulose esters (MCE) or polycarbonate (PC) filters	0.8 µm pores PC filters	MCE filters / 0.8 µm pores PC filters
Filtration of ≥10 mL for a 25 mm diameter filter / ≥50 mL for a 47 mm diameter filter	0.2 L filtrated for the analysis in general (not less than 100 mL)	2 mL/mm ² of filter
Carbon coating	Gold coating	Gold or carbon coating
A 3 mm ² portion of the filter is placed on a TEM grid and MCE or PC base is removed by dissolution	---	---
10000-20000x magnification, at least 4 grid openings must be analysed	1 mm ² of filter observed, 4000x magnification	4000x magnification
Fibre length > 10 µm (method 100.2), AR (length to width) > 3, any width	No dimention limits for fibres count (no airborne fibres dimensional limits)	Length > 5 µm, AR > 3, any width
MCL → 7*10⁶ ff/L	No MCL	No MCL
Morphology + structural information by selected area diffraction + chemistry	Morphology + chemistry	Morphology + chemistry
MCL internationally recognised, analytical method mostly used in USA and Canada	Mostly used in Italy	Mostly used in Italy

THE CASE STUDY – Introduction

The former asbestos mine of Balangero (North-West Italy)



Former asbestos mine of San Vittore, Balangero, Italy – the largest in Western Europe

The mine was highly exploited for asbestos extraction during the XX century, till the beginning of the '90s. From 1995, **RSA S.r.l.** is the society in charge of the remediation and the monitoring of the site (air, soil and water) and also the promotion of environmental education and dissemination activities.
<http://www.rsa-srl.it/>

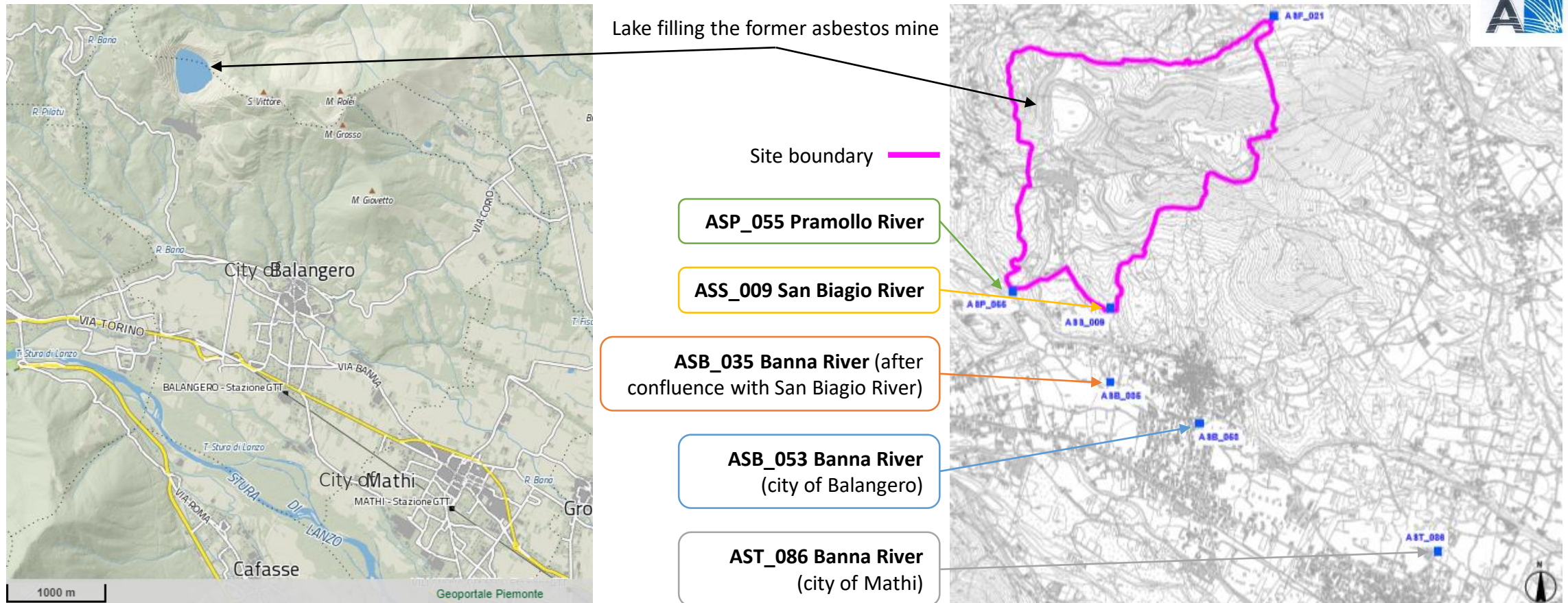
Considering the great significance of the site, a collaboration between RSA S.r.l. and the University has been established to monitor the superficial hydrographic network of the area. In particular, the objectives of the study were:

- to evaluate asbestos concentration verifying the possible correlation with the precipitation pattern over the four seasons;
- to evaluate asbestos concentration verifying the possible correlation with the distance from the site, which is the main source of superficial water pollution;
- to study fibres characteristics (dimension, morphology, chemical composition) to reveal their nature;
- to verify if there is a correlation between asbestos concentration in term of number per liter (ff/L) and as mass per liter (ng/L).

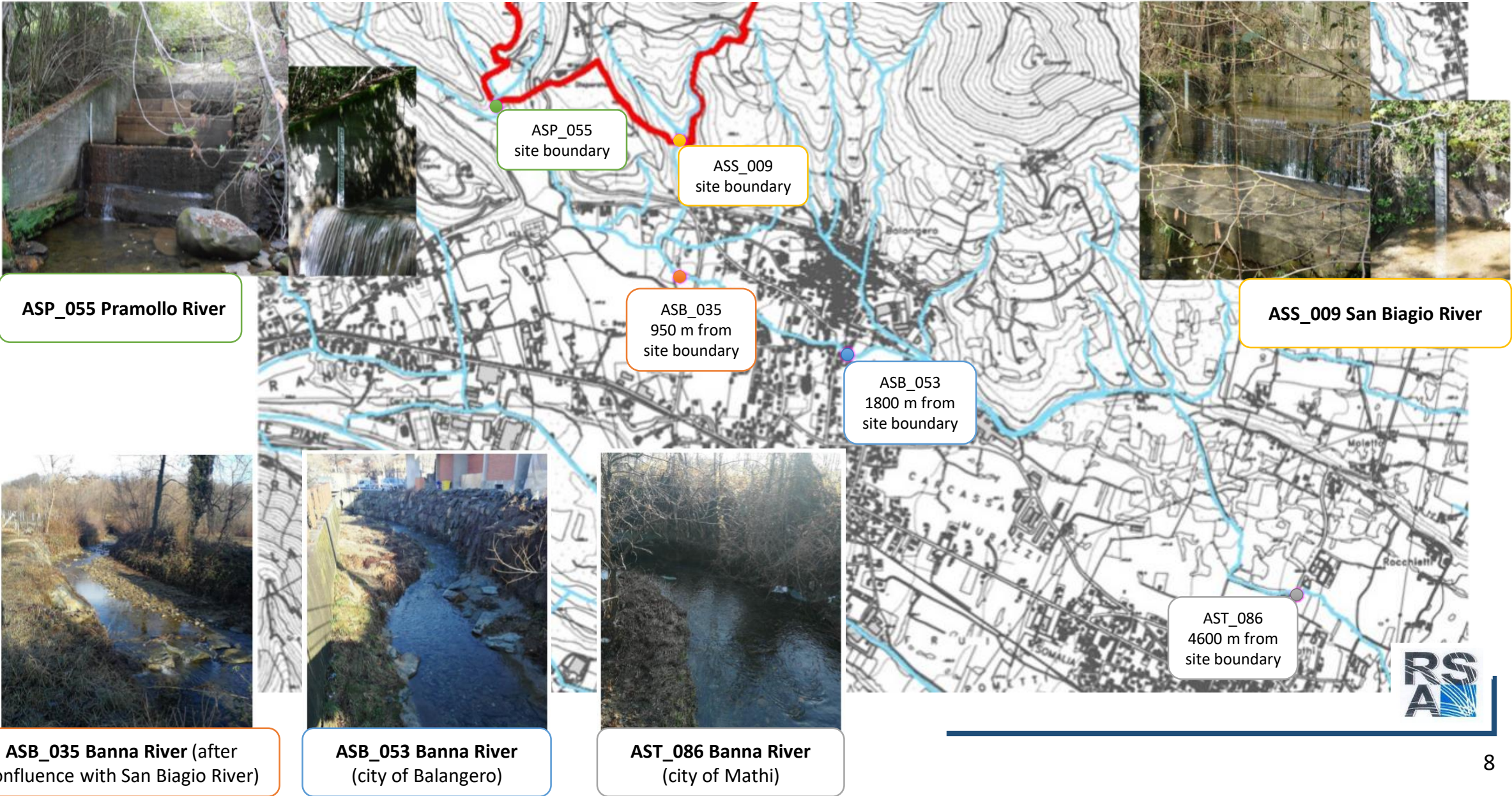
THE CASE STUDY – Sampling campaign

As part of the monitoring activities, a sampling and analysis campaign regarding the superficial hydrographic network was settled: 5 different sampling points were selected, 2 of them on the boundary of the principal site and 3 in the villages situated downstream of the site. They have been monitored from January 2018 to May 2019, to evaluate the seasonal variability.

[maps and images from http://www.rsa-srl.it/RapportoMonitoraggioAmbientaleAnno2018_19.pdf]



THE CASE STUDY – Sampling campaign



THE CASE STUDY – Method and analysis

As the analysed samples were not drinking water, the **U.RP.M842 method** from ARPA Piemonte was followed, using Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopy (SEM-EDS).

The fibres concentration in water is calculated in fibres per liter [ff/L] as follows:

$$C = \frac{ff \cdot A_T}{A_L \cdot V}$$

where

ff = n. fibres counted

A_L = observed area of the filter [mm²]

A_T = total filter area [mm²]

V = filtered volume of water [L]

Furthermore, another analytical step was added: for each fibre or fibre bundle found, length and width are measured, then volume is calculated (considering each fibre as a cylinder). Multiplying volume by density (2,6 g/cm³ for chrysotile and 3 g/cm³ for amphiboles), total asbestos mass is found. Following a procedure similar to that described by the Italian law for massive samples (D.M. 06/09/1994, All. 1B), the concentration is calculated in ppt (ng/L):

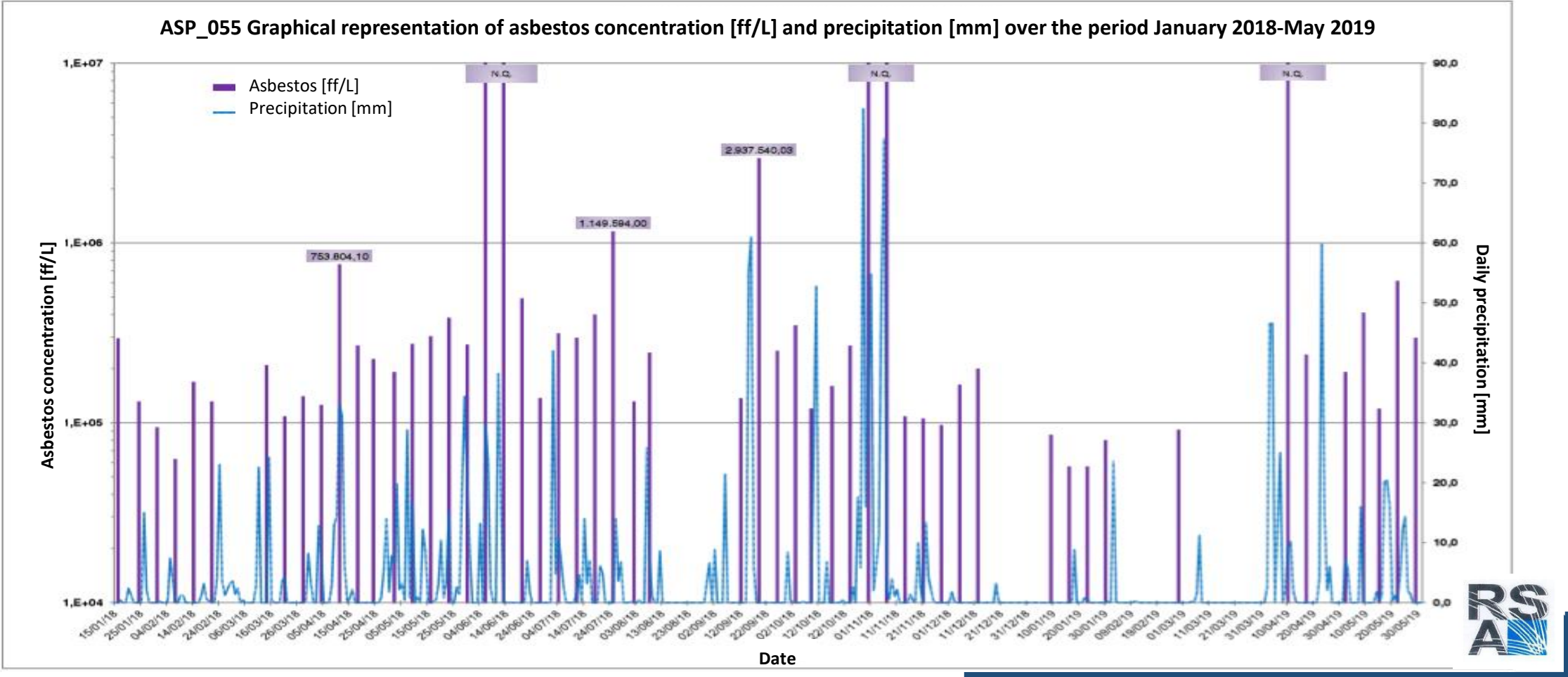
$$C = \frac{m_a \cdot A_T}{A_L \cdot V}$$

where

m_a = total asbestos mass in the observed area of the filter [ng].

THE CASE STUDY – Data analysis

Every point was monitored weekly: asbestos concentration [ff/L], suspended solids quantity [mg/L], river flow [m³/s] and precipitation [mm] were recorded [for complete data review see http://www.rsa-srl.it/RapportoMonitoraggioAmbientaleAnno2018_19.pdf].
Analysing data, it is clear that the quantity of fibres found in water samples is strongly dependent from the precipitation, as shown in the following graph.



N.Q. = not quantifiable, ff/L > $n \cdot 10^6$

THE CASE STUDY – Data analysis

In the period of the sampling campaign (January 2018-May 2019) 275 samples were analysed (55 for each sampling point). Here there is a table reporting the mean value of ff/L calculated over the whole period per sampling point.

SAMPLING POINT	DISTANCE FROM THE SITE	ASBESTOS CONCENTRATION MEAN VALUES [ff/L] (January 2018 – May 2019)
ASP_055 Pramollo River	Boundary	0,296 *10 ⁶
ASS_009 San Biagio River	Boundary	2,657 *10 ⁶
ASB_035 Banna River (after confluence)	950 m	0,213 *10 ⁶
ASB_053 Banna River (city of Balangero)	1800 m	0,083 *10 ⁶
AST_086 Banna River (city of Mathi)	4600 m	0,018 *10 ⁶



Data analysis reveals:

- high concentration values for the sampling point ASS_009 which had undergone hydraulic arrangements of the river-bed during the campaign period;
- comparing data from ASP_055 and ASS_009, situated on the site boundary, with the others situated further (ASB_035 is 950 m far from the site, ASB_053 is 1800 m and AST_086 is 4600 m) it is evident how the average concentration decreases drastically with the distance from the site;
- such a great decrease in concentration should depend on the progressive suspended solids (and asbestos fibres) sedimentation leaving the mountainous part of the site.

THE CASE STUDY – Data analysis

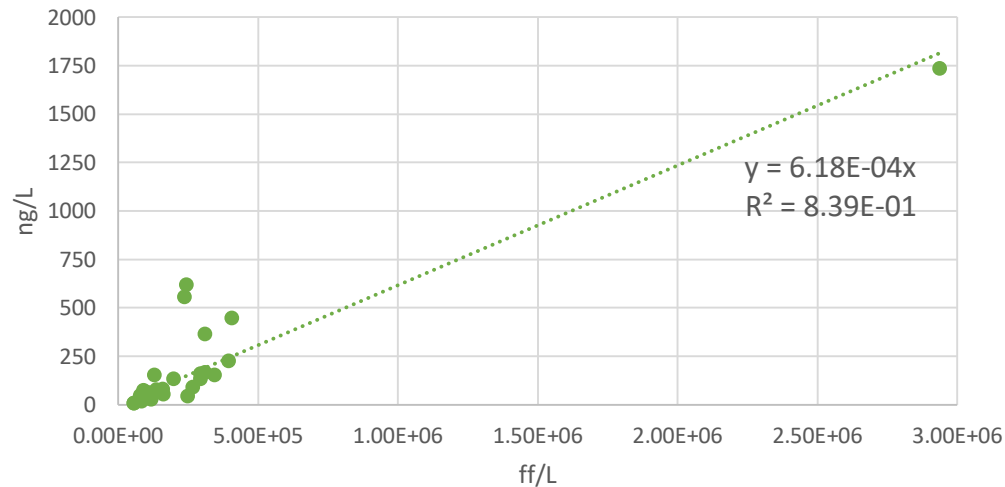
From July 2018 to May 2019, fibre dimensions were measured and asbestos concentration in ppt [ng/L] calculated consequently. In the following plots, we tried to identify a correlation between number of fibres per liter [ff/L] and mass per liter [ng/L], for each sample, grouped for different sampling points.

Trendline function correlating ng/L to ff/L is reported for each sampling point.

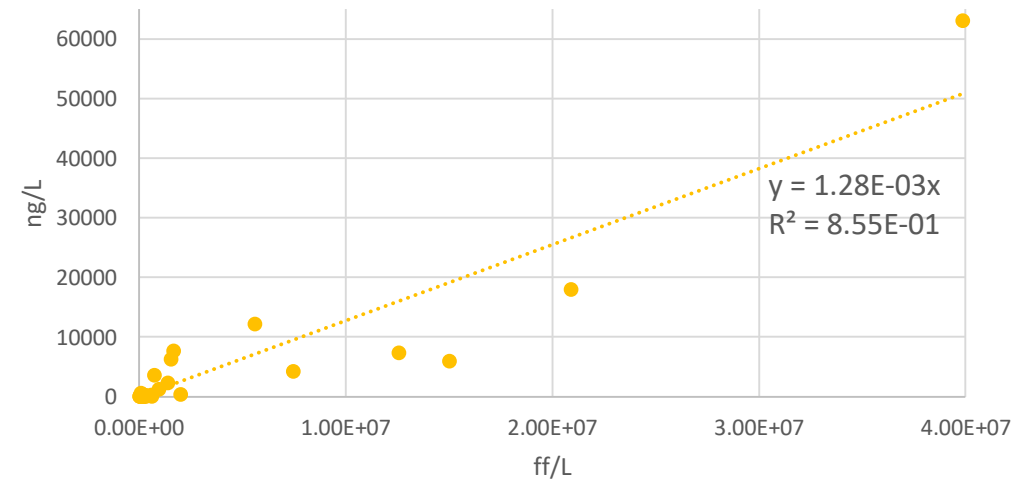
The **slope** of the line in every plot is the proportionality coefficient between the number of fibres and the mass; the R^2 value is the **determination index** which describes the dispersion of values: as $0 \leq R^2 \leq 1$, the closer R^2 is to 1, the better the trendline fits data points.

Very **thick fibre bundles** (see slide 14) were found in few samples: these were considered as **outliers** because they don't follow the indicated trendline functions. For this reason outliers were omitted from the the function calculation, in order to obtain R^2 value of 0,8 or more.

ASP_055 - Pramollo River - site boundary



ASB_009 - San Biagio River - site boundary



N.B.: Overloaded samples or ones that showed number of fibers under the limit of detection have been omitted from the statistic.

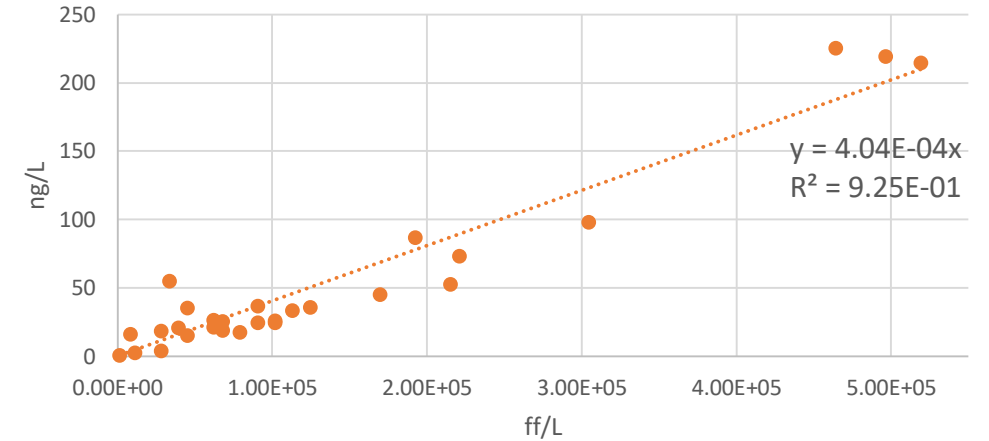
THE CASE STUDY – Data analysis

The slope is slightly higher in ASP_055 and ASS_009, the two sampling points on the site boundary, indicating that average size of fibres is bigger than the average size found further from the site perimeter.

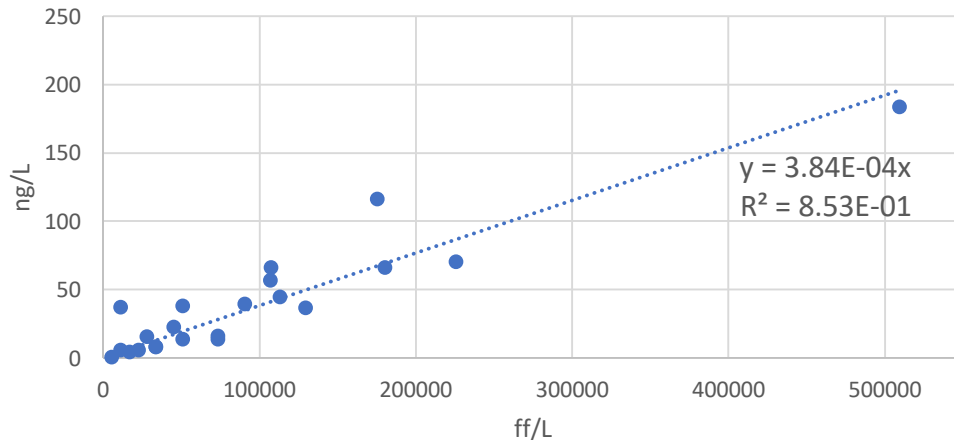
In particular, for the San Biagio River point, the one which undergone hydraulic arrangements, the slope is one order of magnitude higher than the others, suggesting that arrangement activities mobilized a lot of fibres and of a bigger order of magnitude in term of dimensions.

The slope remains almost stable for the three sampling points situated further from the site boundary, indicating that a smaller fibre dimension range is selected by water transport: the value decreases from 4 to $2.77 \cdot 10^{-4}$ in nearly 4000 m showing a gentle but constant diminution in the average fibre size.

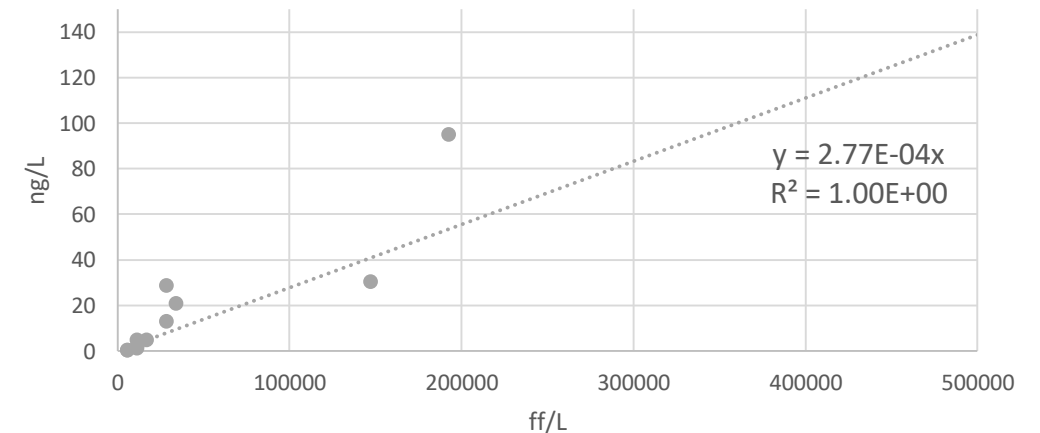
ASB_035 - Banna River (after confluence) -
950 m from site boundary



ASB_053 - Banna River (city of Balangero) -
1800 m from site boundary



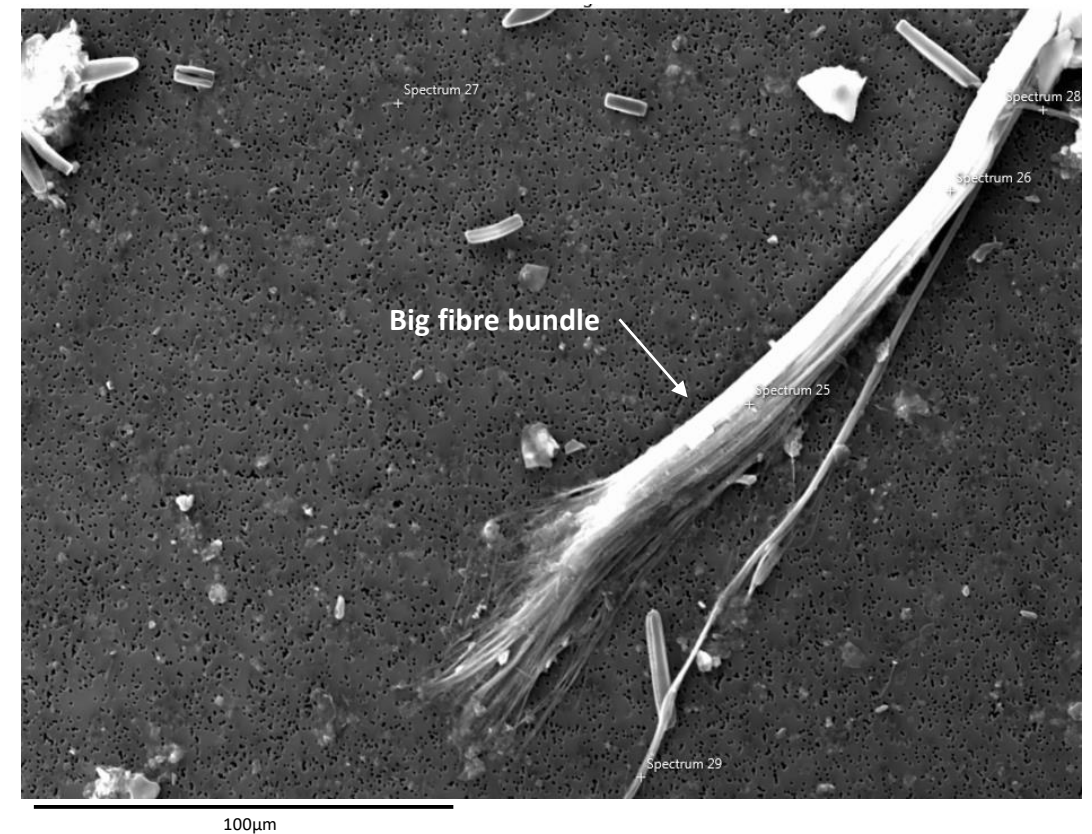
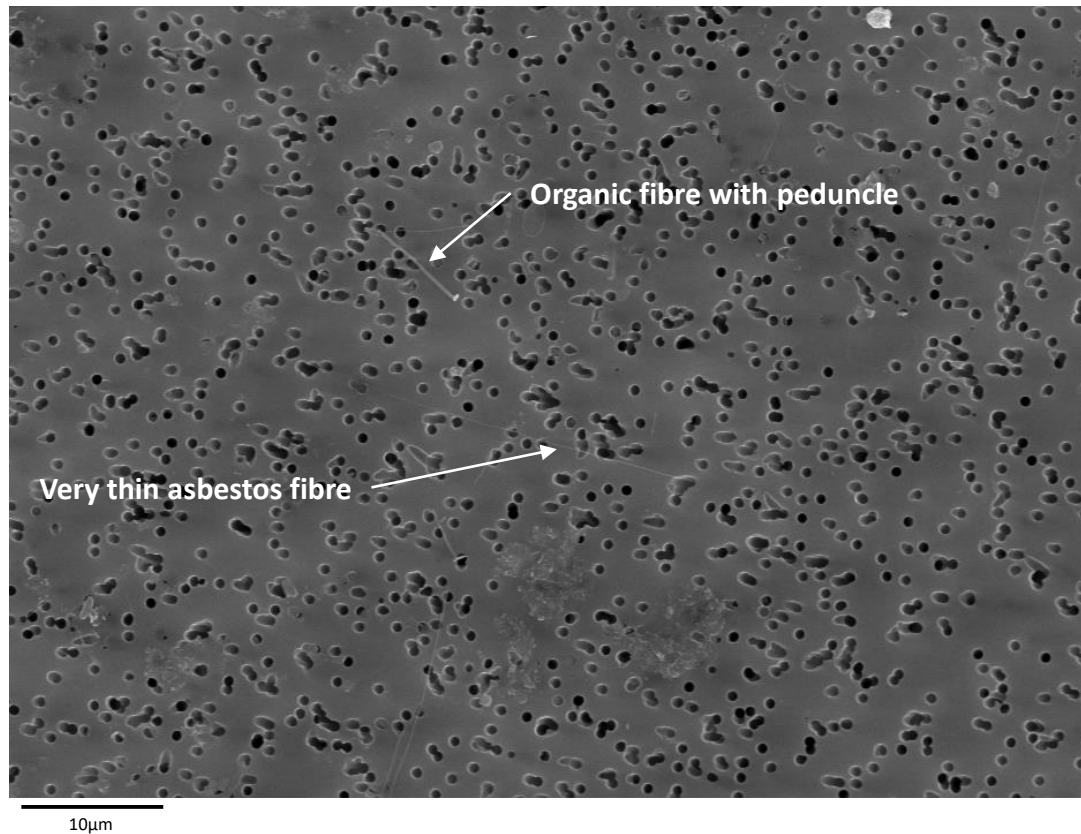
AST_086 - Banna River (city of Mathi) -
4600 m from site boundary



THE CASE STUDY – Data analysis

As the calculation of the concentration in ppt is time consuming, due to the necessity of fibres measurement, we tried to find an average mass value for asbestos fibres, in order to simplify the procedure. In this way, it would be sufficient to multiply the number of fibres found by the average mass value to find the total concentration in ppt.

Unfortunately, this approach is not possible for the great variability in asbestos fibres dimension and morphology: in fact, very thin fibres (width<0.1µm) and fibre bundles were detected in the samples, as it's shown in the following secondary electron images acquired by means of SEM.



CONCLUSION

The first step of a complex study on waterborne fibres has been settled and a great data quantity has been collected.

Main **results obtained** are:

- suspended solids quantity and, consequently, asbestos concentration appear to be dependent on precipitation;
- asbestos concentration increases for sampling points where hydraulic arrangements of the river-bed are done;
- asbestos concentration and mean fibres dimension decrease with the distance from the former mine site boundary, showing a crucial role of solids deposition;
- a correlation between asbestos concentration in ng/L and ff/L was found, but an average mass value for fibres can not be calculated, due to the presence of both thick bundles and very thin fibres.

In the **future** some **critical points** will be deepened:

- a method will be defined to deal with the presence of fibres bundles or aggregates which can constitute a problem in the evaluation of the asbestos concentration, in particular for the correlation between ff/L and ng/L;
- the statistics on the 5 sampling points will be enlarged;
- new sampling and monitoring points will be selected inside and outside the site perimeter;
- the study will be enriched by groundwater data;
- an attempt will be done to relate the number of waterborne fibres to those that can eventually be released in air.

MANY THANKS TO ALL THE PEOPLE WHO CONTRIBUTED TO THIS STUDY!

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