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HYDROGEOLOGICAL STUDY ON THE PRESENCE OF ASBESTOS FIBRES IN WATER OF NORTHERN ITALY

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Abstract—A large mine has been in operation in Italy for over 70 years producing chrysotile, whose residual rock was disposed of at two different sites near the mine. This report refers to a hydrogeological survey on the surface water and the ground water located downstream of the mine. The study has been supported by the Turin Municipal Waterworks Company, to reveal the presence of asbestos fibres in its distribution network or in the raw water of different supplies, wells and rivers. The analytic method consists in vacuum filtering of water samples, observation with Scanning Electron Microscope of the particles and analysis with microprobe. After 12 months of monitoring, asbestos pollution has been revealed both in ground water and in surface water, likely due to both anthropic pollution of the mine and natural presence of asbestos fibres in the rocks of the acquifers and in the river-bed. In any case, the absence of asbestos fibres in water provided to consumers shows that the potabilisation method is able to retain this mineral from raw water. © 2000 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Asbestos is a fibrous mineral having distinctive physical and chemical characteristics that are in high demand. From a mineralogical point of view there are two groups of asbestos: amphibole-asbestos and serpentine-asbestos. The most important serpentine mine in Western Europe has been in production in Piedmont (Italy) near Balangero (Fig. 1) for over 70 years, where chrysotile serpentine was quarried until 1990. Chrysotile is a good refractory material, fire proof, traction and bending resistant (Fig. 2). Thanks to the flexibility and strength of asbestos fibres, this mineral was normally used in producing asbestos cement for pipes, slabs, corrugates and is consequently widespread in sewerages, water pipelines and water reservoirs. Several cases of pollution have been recognised in the factory producing asbestos cement.

Since it was discovered that asbestos fibres are responsible for causing many kinds of lung cancer when inhaled, the USA and Canada have led many studies concerning the presence of asbestos in drinking water. Asbestos fibres have been discovered, even in small amounts, in water pipelines, beer, sherry and medicines. This fact is due to the ageing and damaging of pipelines, which may release fibres into the water and, therefore, also into all products where water is used in the production process (Biles and Emerson, 1968; Nicholson *et al.*, 1972; Olson,

The epidemiological research previously carried out, with the aim of comparing, for example, the presence of certain categories of tumors in some kind of workers employed in mining and working with asbestos, often gave uncertain and sometimes contradictory results. As a matter of fact, one researcher noticed an increase in tumour cases of the gastrointestinal organs, when others deny pathologies due to asbestos exposition.

Although health authorities are concerned, there is no evidence to support the hypothesis that asbestos is harmful when ingested with beverages or food and, moreover, opinions differ (Kuschner *et al.*, 1974). The US EPA fixed a safety limit value for asbestos concentrations in water at 7.1 MFL (MFL=1 million fibres per litre of water, approximately equal to $0.2 \, \mu g/l$).

In 1992 the Turin Municipal Waterworks Company (AAM) supported a survey to verify the

^{1974;} Kay, 1974; Kuschner *et al.*, 1974). Inhaled asbestos fibres are unequivocally known as the main cause of many serious illnesses (asbestosis, pleura cancer, bronchus cancer, mesothelioma) (McDonald, 1972; Amavais and Hunter, 1977; Mossman, 1988; Mossman *et al.*, 1990). Nevertheless, the effects of ingested asbestos fibres contained in food or water on the digestive tract are still unknown (Mossman *et al.*, 1990). Currently, there are no final results, and indeed, studies about pathologies due to this material are only at an initial stage.

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distribution and to quantify asbestos fibres present in its distribution network, analysing both the water provided to consumers and the sources of different supplies. The latter are groundwaters from different fractured aquifers and porous media, and treated waters from the Po river and other Alpine creeks, one of which crosses the Balangero district (Fig. 1).

MATERIALS AND METHODS

The process of identification and quantification of asbestos in water is strongly influenced by the small size and low concentration of fibres. The method consists in vacuum filtering of samples in order to obtain a deposit of the solid particles on suitable cellulose membranes. These membranes are then transferred onto metallic bearings and metallized by gold sputtering, in order to be analysed through the Scanning Electron

Microscope (SEM). SEM has been chosen because the water sample preparation is always easier and faster than by TEM and because of the greater representativity of the sample.

After the described preparation of the membrane, it is observed at high resolution and analysed by electron microprobe.

As mentioned above, observation of these membranes is made difficult by the many microscopic particles in the suspension, which may hide or mingle with asbestos fibres. To solve this problem and to shorten the observation and analysing time of each particle on the membranes, a new analytic routine has been elaborated, the specifics of which are as follows:

- 1. it is exhaustive, it does, in fact, allow the analysis of all the visible objects;
- it combines the morphological observation with chemical analysis;

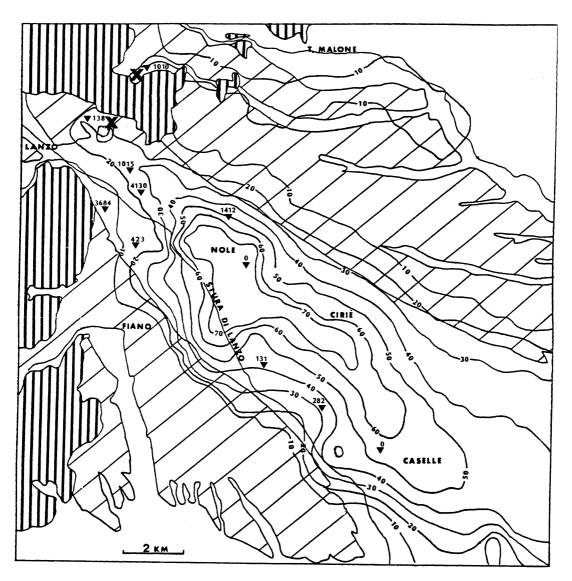


Fig. 1. Diffusion of nickel and asbestos in the phreatic acquifer. Nickel diffusion is shown with isocone lines (in PPB), asbestos concentration (in PPT) is signed near black triangles. Black cross: waste disposal of Balangero mine; vertical lines: cristalline basement; oblique lines: "Mindel" fluvial deposit; white: "Riss" and Olocene fluvial deposit.

3. the sequence of analytical routine is organised in order to accelerate the identification of asbestos fibres.

After establishing, as first step, that asbestos from Balangero is particularly rich in magnesium (Compagnoni *et al.*, 1980), the analytical elaborated routine is:

- back scattered electron observation: it is possible during observation, because of different coloration, to locate objects containing mainly low atomic number elements (as colloids and other organic particles) from objects that contain high atomic number elements, this step permits the immediate exclusion of many organic particles;
- map of magnesium: within the 'heavy' particles, this step points out the magnesium-rich ones, which could indicate the presence of asbestos due to their closer chemical composition;
- semi-quantitative chemical analysis through electron microprobe due to the difficulty in properly preparing the specimen on the membrane;
- morphological study of the particles, with the aim of finding the typical patterns of the local asbestos fibres, when the longitudinal/trasversal dimensions ratio is at least 1:20 (Fig. 2).

It is evident that the procedure is organised in order to go from one step to another, only if the previous step was successful.

The quantification of asbestos content in water is the last phase and is based on the count of the identified fibres and the measurement of their size. For this purpose the percentage of observed membrane is measured, considering that it statistically corresponds to the same percentage of the liquid previously filtered (i.e. 2% of analysed membrane corresponds to 2% of the water volume taken for filtration). At the final step the number of identified fibres (or their weight, obtained by measuring the volume of fibres and multiplying it by their specific weight of 2.55) is

compared to the original volume of water to express the asbestos content as mg/l. The amount of fibres found were calculated on the grounds of the volume of the fibre found multiplied by the density of the mineral (2.55). The value obtained accords with the asbestos amount in grams per litre of water.

Blank samples from distilled water prepared in the same row and also those of analysed samples have been used as internal standard.

The anlytical sensitivity of the methods depends on the percentage of the filtered water volume in the 2% of filter used.

RESEARCH ON PRESENCE OF ASBESTOS FIBRES

The control of asbestos in sources of water supplies is a basic question, because these minerals are natural constituents of rocks and form the mineralogical matrix of alluvial deposits and soils. Thus it is possible that asbestos fibres are naturally present in surface waters and ground waters.

As a matter of fact, previous studies of surface water courses and the ground water near Balangero's asbestos mine, have shown the presence of dissolved sulphate, heavy metals pollution due to oxidation of sulphide and asbestos fibres (Caramuscio *et al.*, 1992).

Dissolved sulphates and heavy metals are the consequence of water–rocks interaction on discarded rocks stocked in the mine discharge. The main mineralogical components of serpentine (the discarded rock) are iron and nickel sulphides.

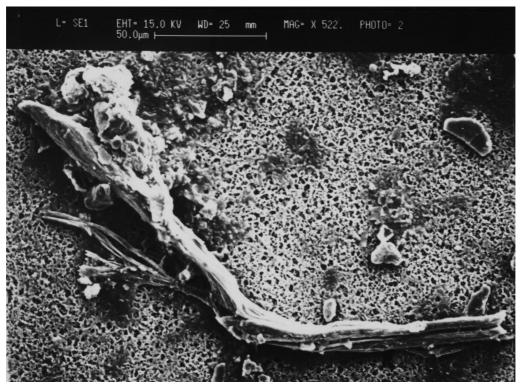


Fig. 2. Asbestos fibres as seen with the SEM (Scanning Electron Microscope). Magnification: ×522 (photo: G. Pesando).

To easily separate asbestos fibres, rocks are chopped in small grain-size pieces. Thus, the water-rock interaction is fast due also to the high hydraulic conductivity of dumped rocks. The mobility of dissolved components is controlled by retardation factors different for each tracers as a result of physico-chemical behaviour in the aquifer.

This data being unavailable, the sulphate retardation factor was assumed to be of the order of 10, which can be considered an acceptable value on the basis of the natural sulphate concentration in the solid matrix of the area (Caramuscio *et al.*, 1992).

For Ni and asbestos fibres no valid data exist in literature. Therefore, from experimental experiences (Caramuscio *et al.*, 1992), the retardation factors are 0.1 and 1×10^{-3} , respectively.

The choice of the sites for sampling has been influenced by the double source of asbestos pollution, both natural and anthropic; the first due to the fibres present in the different environments of the surface water and in the mineralogical matrix of aquifers (rivers, aquifers), the other due to human activity (industrial production, asbestos cement pipelines, discharge of polluted material). According to this hypothesis, sampling sites were chosen that had been exposed to at least one of those potential pollution sources. So it has been analysed that:

- water flowing in asbestos cement pipelines and to make a comparison—in cast-iron pipelines, show the difference in fibres content in water;
- superficial water flowing in creek beds containing asbestos bearing rocks;
- water from the Po river, whose basin is partially in serpentine rocks has a great deal of polluted water and waste material.

In addition, the present study points out the efficiency of the potabilisation techniques applied by the AAM, making a comparison between Po river water and the waterworks' pipeline water, after the treatment of sedimentation, while the fibres precipitate together with colloidal organic material in suspension.

The individuation of asbestos in water samples is difficult owing to the small size of fibres (few microns) and their low concentration (Fig. 2). Moreover, in Po river samples, the individuation of fibres is made more complex by a great deal of microscopic particles in suspension, which may hide or mingle with asbestos fibres. In the analysed samples, the composition of mineral particles is quite constant, being composed mainly of fragments of quartz, micas, amphiboles, serpentine, carbonates, olivine, silica and iron oxides.

RESULTS AND DISCUSSION

Drinking water

The results of the research on the samples drawn during the 12 months survey are shown in Table 1, from which is evident that the amount of asbestos found in one year is very low or even absent, particularly in respect of the piping system water.

As a matter of fact asbestos fibres are present only in three samples:

- 1. raw Po water, which in the autumn survey contained 1.12 mg/l of asbestos;
- water of Stura sampled in Viù Valley—section no. 4; 1.01 mg/l of asbestos was found during the autumn survey;
- water entering the pilot plant placed on the Stura in Viù Valley; 0.12 mg/l was found during the winter survey.

Table 1 also shows the number of particles per

Table 1. Results of the analysis carried out in the water samples drawn during the four surveys

SAMPLE	1° Survey		2° Survey		3° Survey		4° Survey		
	Asbestos (mgl ⁻¹)	Part./screen (n°)	Asbestos (mgl ⁻¹)	Part./screen (n°)	Asbestos (mgl ⁻¹)	Part./screen (n°)	Asbestos (mgl ⁻¹)	Part./screen	
Water tap 69380	0	1.7	0	3	0	1.6	-	0.8	
Water tap 38366	0	5	0	3.9	0	1.5	_	1.8	
Water tap 36576	0	8	0	4	0	4.5	-	23.2	
Water tap 34664	0	5.2	0	2.9	0	4.7	-	0.4	
Water tap 69444	0	20.6	0	1.7	0	1.3		3.2	
Raw Po water	1.12	31.2	0	38.5	0	> 40	0	> 100	
Pian della Mussa Plant	0	1.8	0	0.3	0	1.8	0	1.7	
Venaria Plant	0	1.4	0	13.5	0	3.9	0	2.1	
Stura Bridge Plant (out)	0	0.9	0	1.1	0	1.4	0	0.4	
Stura Bridge Plant (in)	0	3.7	_	_	_	-	_	_	
Viù Valley—Sect. 1	0	0.8	0	16.7	0	2.3	0	25.6	
Viù Valley—Sect. 2	0	2.2	0	17.2	0	22.7	0	27.2	
Viù Valley—Sect. 3	0	2.2	0	19.8	0	16.8	0	31.4	
Viù Valley—Sect. 4	1.01	0.7	0	13.8	0	14.2	0	2.5	
Viù Valley—Sect. 5	0	3.4	_	_	_	-	_	_	
Viù Valley—Pilot plant (out)	0	1.7	0.12	16.8	0	22.7	_	_	
Viù Valley—Pilot plant (in)	0	13.8	0	15.4	0	20.8	_	_	
Viù Valley—Sect. 6	0	0.6	0	17.2	0	23.4	0	28.2	
Viù Valley—Balangero downstream		100–1000							

screen found during the analysis with the SEM. In each analysis the number of particles present was counted. This value shows chiefly the turbidity of the analysed water and it is not at all an evaluation parameter for the filtered material quality.

Ground water

It is interesting to make a comparison with the results of the previous study carried out near Balangero's asbestos mine (Caramuscio *et al.*, 1992) dealing with asbestos pollution both in ground water and in surface water. The research revealed the presence of asbestos fibres in progressively higher concentrations near the mine and the mine's dump area. Creek waters sampled near the mine's dump indicate 1.00–3.60 mg/l of asbestos content, while ground waters are 1.00–4.10 mg/l. At a distance of 5 km from the mine discharge, the presence of fibres is reduced of a factor 10. These values are similar to those found in the present research.

CONCLUSIONS

In order to interpretate the results obtained, it is necessary to keep in mind the 'quantified' nature of the fibres' release, the finding of which is strictly related to the seasonal period in which the sampling took place. Under natural conditions the fibres' release from the rocks occurs as a consequence in a totally unforeseeable way and in an inconstant manner, because only some quantities are released each time owing to the erosive action caused by water on the asbestos containing rocks.

The fibres found in the analysed samples show the existence of different situations: for instance, the raw Po water, the presence of fibres is surely due to the pollution either of anthropic origin (deriving from the discharge of fibres containing materials) or of natural origin due to the release from rocks present in the mountain tract of the riverbed. A large part of this kind of pollution seems to be due to the continuous process of rielaboration and crashing of river sediments owing to the transport action caused by the flow, particularly when the sediments are made from a percentage of 'Pietre Verdi' ranging from 10 to 60% as happens for the rivers of Piedmont.

The asbestos is eliminated in the potabilisation treatment, during the course of which the deposit and the retention of this mineral from raw water occurs. This phenomenon is confirmed by the absence of the mineral in the piping system water.

Concerning the precise origin of the fibres found in raw Po water, owing to the high flow and long distance of the river, it is not possible to determine with certainty the real provenance of the fibres found

The contamination observed in the Stura of Viù Valley, which is very low and not constant, shows that the asbestos fibres can be mobilised by stream-

ing water from asbestiferous rocks outcropping and percolating through permeable sediments of similar nature. The range of the experimental data allows for another indication regarding the quantified, in block nature of the fibres' release and the consequent difficulty in their individuation. The asbestos fibres, which are a solid non-mixable pollutant, have a hydrodispersive behaviour completely different from that of a soluble pollutant. They can indeed move in the liquid without mixing with it as a consequence of diffusion and dispersivity coefficients (Freeze and Cherry, 1979). In disagreement with the Fick law the fibres found during the sampling follows only the chemical statistic laws.

Finally, the analysis of piping system water dealt out with either asbestos cement material or cast iron pipes does not show a release from the former ones, because in none of the samples analysed was the presence of fibres found. This situation could be attributed to either the limited length of the pipes made of asbestos cement, or to the chemical characteristics of water which is non-aggressive to the pipe-forming material.

The concentration of fibres found at the end of the four quarterly surveys is not at all relevant and worrying for the public health.

Even if it has limitations due to the peculiar way of release of the solid analysed particles, the applied method is thought to be a useful means to finding the fibres and also confirms:

- the presence of a constant pollution likely due to the double-acting natural and anthropic phenomenons in the shallow water drawn by the waterworks of Turin;
- the efficiency of the potabilisation system employed to remove the asbestos;
- the absence of the hypothesised fibres released from the asbestos cement pipes still employed in some tracts of the piping system of the town.

FURTHER DEVELOPMENTS OF THE ANALYTICAL METHOD

Improving the analytical method hereby described can be obtained during water sampling and it must aim at the individuation of the *Minimal Representative Volume* of the contamination degree in the considered river. This can be obtained by either sampling a great mass of water and thereafter filtering it on a unique membrane or by sampling different reduced samples of water in the same place and filtering them on distinct membranes. Obviously the two methods can be applied respectively to minor or abundant solid contents in water owing to the problems of the cellulose membrane obstruction.

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