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Environmental monitoring of airborne fluoro-edenite fibrous amphibole in Biancavilla (Sicily, Italy): a nine-years survey

Maria Rita Pinizzotto *, Carmelo Cantaro, Maria Caruso, Luciano Chiarenza, Carmelo Petralia, Sebastiano Turrisi, Antonio Brancato

Agenzia Regionale per la Protezione dell'Ambiente (ARPA) della Sicilia, Struttura Territoriale di Catania, Catania, Italy
* *Corresponding author: mrpinizzotto@arpa.sicilia.it*

ABSTRACT - Biancavilla was recognized as a National Priority Contaminated Site in 2002 due to environmental dispersion of amphibole fibres with fluoro-edenitic composition. The mining extraction in Monte Calvario quarries and the wide use of sand and rubble in local building industry were responsible for the inhalation of fluoro-edenite fibres by the resident population. Since 2001, environmental and health authorities have promoted a series of remediation and dust mitigation activities in order to reduce the airborne fibre concentration and population exposure.

Regional Environmental Agency of Sicily Territorial - Structure of Catania (Agenzia Regionale per la Protezione Ambientale della Sicilia, ARPA Sicilia) has started in 2009 an ongoing airborne fibre monitoring. The present report describes results of fluoro-edenite time trend concentrations obtained from 865 air samples collected in Biancavilla from July, 2009 to November, 2017 and analyzed by scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS). Results demonstrate a real improvement of Biancavilla environmental situation and a gradual reduction of exposure as a consequence of the dust mitigation measures. Nevertheless, a continuous environmental follow up should be carefully carried out particularly during high risk fibre releasing activities, such as excavations and demolitions, in order to prevent adverse health effects.

Keywords: Natural asbestos; fluoro-edenite; air fibre concentrations; population exposure; Biancavilla; asbestos-like.

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1. INTRODUCTION

Biancavilla is a municipality of the Metropolitan City of Catania, Sicily, Italy, with a resident population of about 20,000 inhabitants. Located between the towns of Adrano and S. Maria di Licodia, 32 kilometres northwest of Catania, Biancavilla covers an extensive area of about 70.7 km^2 situated in a rural setting at the slopes of the Etna volcano. This geological area is made up of domes and dikes associated with "autoclastic breccia", a fine-grained material in which amphibole fibres have been found that were initially classified as intermediate phases between tremolite and actinolite (Paoletti et al., 2000; Gianfagna et al., 2003; Mazziotti-Taglianti et al., 2009).

The first indication of an excess of pleural mesothelioma in Biancavilla was given in a 1996 report of the national programme of epidemiological surveillance of mesothelioma mortality in Italy for the period 1988–92 (Di Paola et al., 1996).

Those unexpected cases of malignant pleural mesothelioma, in the absence of detectable occupational exposure to asbestos, were found to be related to the widespread occurrence of amphibole fibres (Paoletti et al., 2000; Comba et al., 2003; Burragato et al., 2005) and environmental surveys suggested that the stone quarries (namely "La Cava" and "Di Paola") located southeast of the town in the "Monte Calvario" area (Fig. 1) might be the source of asbestos exposure (Manna and Comba, 2001). From a geological point of view, Mount Calvario is composed of brecciated domes of highly viscous, benmoreitic lavas (Romano, 1982). An abundance of altered , incoherent and very friable materials was found in the quarries originating from both benmoreitic lavas metasomatized by hot fluids rich in fluorine and pyroclastic deposits. Mineralogical analysis of these materials led to the identification of a new end-member of the calcic amphibole group of the edenite series, which has been identified and approved as fluoro-edenite [$Na_2Ca_2Mg_5(Si_7Al)O_{22}F_2$] by the Commission on New Minerals and Mineral Names of the International Mineralogical Association (IMA, code 2000-049) (Gianfagna and Oberti, 2001).

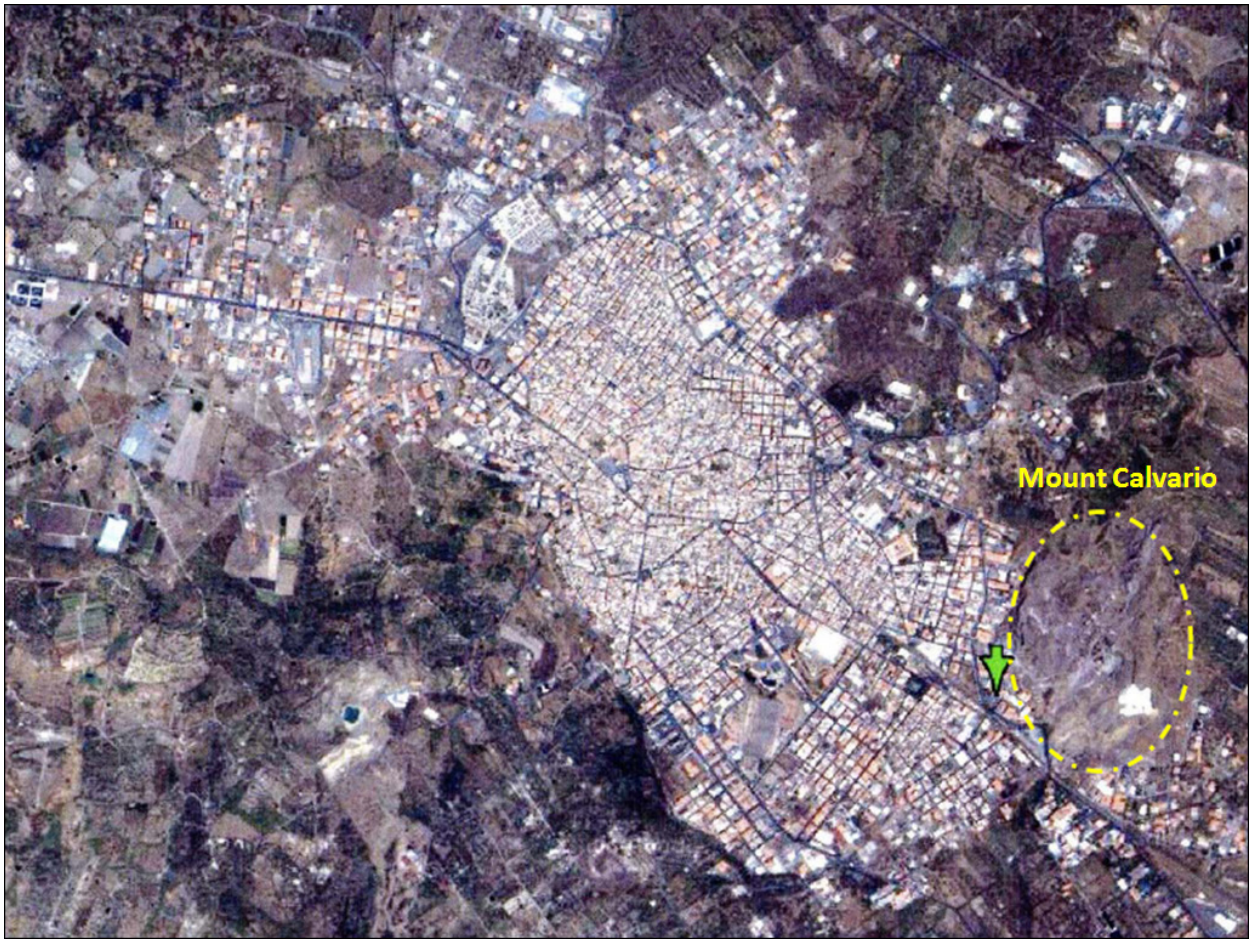

Fig. 1 - View of Biancavilla (Sicily, Italy) and Mount Calvario.

On the basis of such evidences, in 2001 Biancavilla was included, by law, in the National Priorities List of Contaminated Sites (NPL-CS) (Italia. Decreto Ministero dell'Ambiente e della Tutela del Territorio 18 settembre 2001, n. 468. Regolamento recante: "Programma nazionale di bonifica e ripristino ambientale").

Fluoro-edenite only occurs naturally. The fluoro-edenite crystals that have been identified in the geological formations of the Biancavilla area, may have prismatic or acicular or fibrous habit and often occur as parallel bundles. The fibres found in air samples in Biancavilla originate from the quarry materials that have been used in building materials for local structures since at least the 1950s (Bruni et al., 2006). Unpaved roads made from local quarry products have also been a primary source of airborne fluoro-edenite fibres, giving the town a nonpoint source condition (Manna and Comba, 2001).

Dust rising from the unpaved roads, as well as the one originating from building/demolition activities and from the mining extraction in Monte Calvario quarries, was in fact responsible for the inhalation of fluoro-edenite fibres by the resident population.

Starting from 2001, a series of dust mitigation measures were taken on the basis of the above mentioned evidences; particularly, the termination of quarrying activity and the asphalting of roads previously paved with local soil materials were among the public health recommendations adopted to decrease the exposure risk, and were implemented in 2003.

More recently (2008-2012), further mitigation measures were adopted as the remedy of plasters of some public buildings as schools, the town hall and the cemetery surrounding wall and the envelopment of the ridge rock, surrounding the quarry, with Spritz Beton, i.e. a material able to avoid the atmospheric dispersion of particulate. In the same period, remediation activity included also the removing of inert crushed materials, mined for decades and stocked in big piles in a large open area of "La Cava" quarry, were conducted. Withdrawn materials were safely deposited in a waste disposal site and quarry open areas covered with tested fibre-free crushed lava stones, in order to avoid any amphibole fibre release. The waste disposal site was appositely identified by Prefect's order inside the close "Di Paola" quarry; it was also used for stocking all potentially fluoro-edenite contaminated materials coming from Biancavilla urbanisation works.

A recent compendium study (Bruni et al., 2014) described three environmental airborne sampling surveys that were conducted in Biancavilla, in 2000, 2004-05 and 2009–13. All airborne membranes were analyzed

in SEM. Briefly, the analysis of data acquired in 2000, before mitigation measures were taken, found amphibole contamination levels ranging from 0.4 to 8.2 fibres per liter (ff/l), with an average of 1.76 ff/l. The highest concentrations were detected on unpaved roads covered with inert material, especially during heavy traffic, when up to 93-183 ff/l were measured. The 2004-2005 survey carried out by the University of Catania, demonstrated the efficacy of the clean-up interventions, measuring between 0.01 and 4.19 ff/l (mean, 0.35 ff/l) in outdoor air. Data provided by the Regional Environmental Agency of Sicily (ARPA Sicilia, Territorial Structure of Catania), referring monitoring activity in 2009-2013 period, were also included. ARPA monitoring showed a descending trend in the concentrations of airborne fibres, although few peaks have been observed in concomitance with specific kinds of public works (projects involving excavation) or under certain meteorological conditions.

In 2008, the Italian Ministry of the Environment and Protection of Land and Sea (Ministero dell'Ambiente e della Tutela del Territorio e del Mare, MATTM) gave ARPA Sicilia the task of controlling air quality of Biancavilla, particularly as regards activities undertaken for the environmental remediation, in order to monitor both inhabitants' exposure levels and the respect of working methods issued.

The environmental Biancavilla monitoring by ARPA started in 2009. Since then, airborne fibre sampling is performed on a routine basis, not only during everyday situation but also with the aim of monitoring all the situations which can cause a serious risk of fibre release in the Biancavilla environment.

In the present study, the data of environmental monitoring carried out at Biancavilla from 2009 to 2017 are reported in order to highlight the temporal trend of the fibrous fluoro-edenite concentrations in air.

The carcinogenic hazard to humans of fluoro-edenite fibrous amphibole appeared in The Lancet Oncology (Grosse et al., 2014) and definitively established in the one-hundred-and-eleventh volume (111) of the International Agency for Research on Cancer Monographs, "Some nanomaterials and some Fibres" (IARC, 2017) by means of well documented chemical, epidemiological, in vitro and in vivo studies.

2. MATERIALS AND METHODS

Currently, there is no asbestos fibres limit value for the outdoor environment. In order to have a reference value, it was decided to comply with the indications of the Italian Ministry of the Environment and Protection of Land and Sea (MATTM) on the basis of the indications of the working groups of the World Health Organization (WHO) using the value of 1 ff/l. In fact, since a threshold value is not known to exist and no safe levels can be proposed for the carcinogen asbestos, in 2000 the WHO produced epidemiological estimates considering a lifetime exposure to 1000 F/m^3 with a view to providing adequate health protection ranges for the general population (WHO, 2000).

Eight-hundreds and sixty-five air samples have been collected by technicians of the Catania Structure of ARPA Sicilia from July, 2009 to November, 2017 in about 3.3 km^2 area of Biancavilla, mainly inside the perimeter of the "Contaminated Site" (Fig. 2), as delimited by the Italian Environment Ministry decree of July 18, 2002 for the environmental remediation procedures to be taken (Italia. Decreto Ministero dell'Ambiente e della Tutela del Territorio, 18 luglio 2002. "Perimetrazione del sito di interesse nazionale di Biancavilla" GU n. 231 del 02/10/2002).

The sampling and analysis procedures used were those for conventional asbestos. It should be noted that all monitoring activities in Biancavilla have been established in a series of ministerial meetings. Particularly, ARPA Sicilia was asked to collect outdoor samples in accordance with the technical indications of the Italian Ministry of Health decree (September 06, 1994) as further stated also in the INAIL (National Institute for Insurance against Accidents at Work, ex ISPESL) 2010 procedures for the correct management of asbestos remediation activities inside the NPL-CS (INAIL, 2010 - Linee guida generali da adottare durante le attività di bonifica da amianto nei siti da bonificare di interesse nazionale).

Briefly, air volumes of at least 3000 liters were sampled on 315 mm^2 surface polycarbonate 0.8 micron pore sized membrane filters, 25 mm diameter, preloaded in black conductive polypropylene cassettes. All samples have been collected using portable Delta MK2 (TECORA) battery and power operator sampler, with electronic control flow system in order to maintain a constant air flow rate of 6-9 liters/min ±10%. Then, filters have been mounted on 25 mm aluminum pin stubs and sputter coated with a gold layer. The analyses have been carried out using SEM Zeiss EVO MA 10 with Energy Dispersive X-ray (EDX) Analysis (Oxford INCA Energy 250 Drycool).

The SEM operating conditions have been adjusted to produce a visible image, when scanning at 2500X or greater magnification, with the lens current's accelerating voltage of 20 kilovolts (kV), spot size, working distance, apertures etc, set in the format for routine fibre counting and analysis, as defined in the above mentioned decree. Before any systematic search, a low magnification scan of the filter surface was conducted, to ensure that the dust deposit was uniform (not too dense for fibre counting) and that the surface has not been damaged.

Airborne fibre concentrations have been measured by counting the number of respirable fibres inside the effective filter area (at least 1 mm from the edges); a total number of fields covering the minimum surface of 1 mm^2 was scanned, carefully avoiding any overlapping in the examined fields of view.

Any counted respirable fibre has been analysed by EDX. The morphology of the fibres, the EDX spectrum together with the relative integrated intensities of peaks seen were used as a 'fingerprint' for fibre identification.

Fig. 2 - Perimeter of the "Contaminated Site" of Biancavilla (Decreto Ministero dell'Ambiente e della Tutela del Territorio del 18/07/2002).

Fibres of fluoro-edenite were identified on the basis of the comparison of their EDX spectra with those obtained from minerals containing fluoro-edenite collected in the Monte Calvario quarry (kindly provided by Università di Catania, Dipartimento di Chimica), used as reference standards.

3. RESULTS AND DISCUSSION

The present paper describes results obtained from the whole airborne fluoro-edenite monitoring activity performed by ARPA from July, 2009 (i.e. when SEM-EDX instruments were acquired) to November, 2017. Therefore, data obtained in everyday situation but also during specific kinds of public works, such as excavation and remediation activities, in various meteorological conditions, are reported.

Table 1 summarises the number of air samples per year, the mean fibre concentrations with range of minimum and maximum values associated and the number of air samples with concentration $\geq$1 ff/l.

Figure 3 shows the linear regression of airborne fluoro-edenite amphiboles calculated from the mean values of fibre concentrations per each year of monitoring activity. Despite the great variability of data, the trend of airborne fluoro-edenite fibres concentrations in Biancavilla decreases with time clearly, confirming the downward trend already reported in previous study (Bruni et al., 2014).

In 2009 and 2010 averages of 0.24 (range values 0-1.97) and 0.14 (range values 0-1.75) ff/l have been respectively obtained, with higher concentrations registered mainly during a series of dust mitigation and clean up interventions, such as roads paving, commenced

Year	Number of air samples	Fibre mean concentration value (ff/l)	Fibre range concentration (min - max, ff/l)	Number of air samples > 1ff/l
2009	42	0.24	0 - 1.97	2
2010	91	0.14	0 - 1.75	7
2011	111	0.30	0 - 4.34	10
2012	113	0.20	0 - 2.65	7
2013	105	0.09	0 - 0.62	0
2014	181	0.21	0 - 2.24	6
2015	98	0.15	0 - 2.15	1
2016	74	0.06	0 - 0.49	0
2017	50	0.04	0 - 0.37	0
	865°			33°°

°Total number of air samples collected and analysed from July 1, 2009 to November 20, 2017
°°Total number of airborne samples with fluoro-edenite concentration ≥ 1fibre per litre

Tab. 1 - Results for each year of airborne fluoro-edenite monitoring activity in Biancavilla (Sicily, Italy).

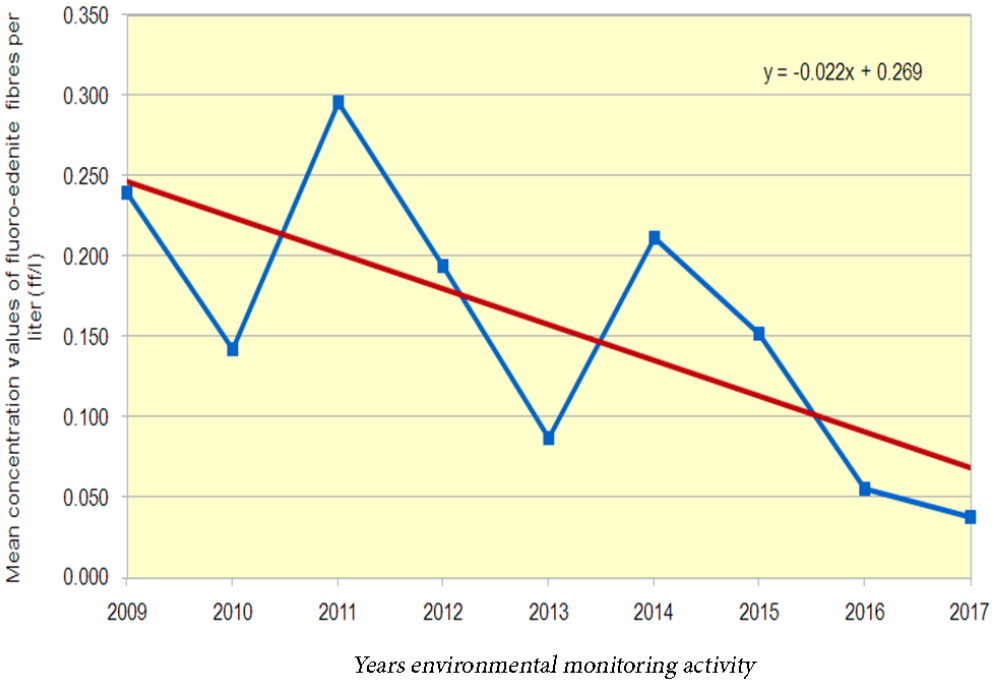

Fig. 3 - Linear regression of mean values fluoro-edenite fibre concentrations of the 2009-2017 survey.

in previous years to reduce the main risk factor for population exposure.

The highest average concentration of 0.30 (values ranging from 0 to 4.34) ff/l was detected in 2011, when the airborne monitoring activity was conducted in concomitance of remedy works for the envelopment with Spritz Beton of the ridge rock surrounding the quarries of Monte Calvario and the removing of inert crushed materials piles in the "La Cava" quarry. These works continued in 2012 and can be also considered cause of the concentration mean value of 0.20 (ranging from 0 to 2.65) ff/l, registered during that year.

Despite the low 2013 average of 0.09 ff/l, a peak of 0.21 (values ranging from 0 to 2.24) ff/l was observed in 2014. It can be mainly attributed to other activities characterized by high risk of fibre release, such as excavation works for gas station fuel tanks removal.

Mean values of 0.15, 0.06 and 0.04 ff/l in 2015, 2016 and 2017 respectively, confirm the decreasing airborne dispersion of fluoro-edenite fibres.

The highest number of samples with fluoro-edenite concentration ≥ 1fibre per litre, assumed for Biancavilla outdoor air quality by the Italian Ministry of Environment, has been similarly observed during the above described remediation and/or excavation works executed in 2011 (10 samples), while no exceeding sample has been recorded in 2013, 2016 and 2017 environmental monitoring activity (Tab. 1). The six samples observed in 2014 can be related

to gas station fuel tanks removal but, interestingly, some exceeding samples have been registered also in absence of any excavation and/or remediation works. The single 2015 sample exceeding the fluoro-edenite concentration ≥ 1 ff/l was collected during road excavation works realized by Biancavilla Municipality and, at present, is the last non-compliant sample found.

A total number of 33/865 (3.8%) exceeding samples has been observed during all nine-years monitoring activity described in the present paper.

SEM image of the fluorine amphibole in atmospheric particulate of Biancavilla, with EDX spectrum associated, is shown in figure 4. An example of fluoro-edenite bundle, found in a 2010 sample collected in urban area, before road paving works to be commenced (ante operam monitoring), is depicted in figure 5.

4. CONCLUSION

Biancavilla is one of the well known world localities in which population experienced an environmental contamination from naturally occurring asbestos.The

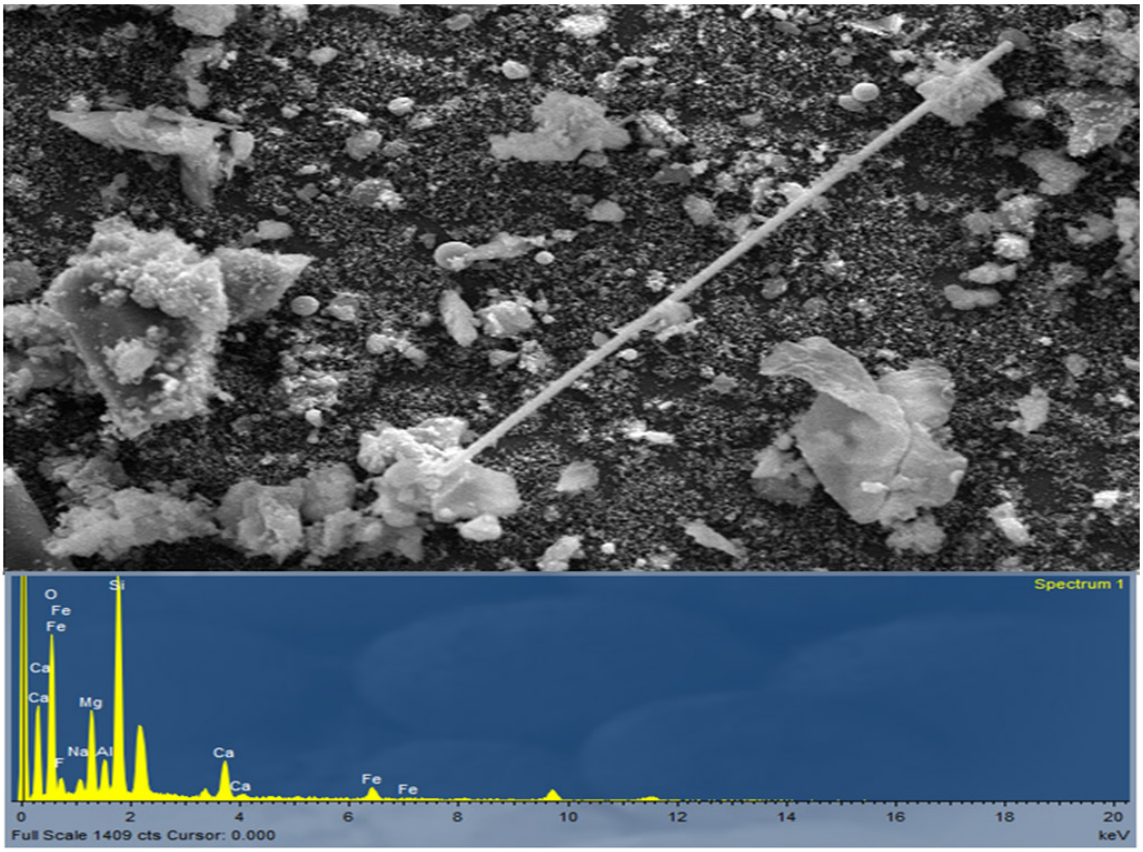

Fig. 4 - SEM photograph of airborne fluorine fibrous amphibole with EDX spectrum.

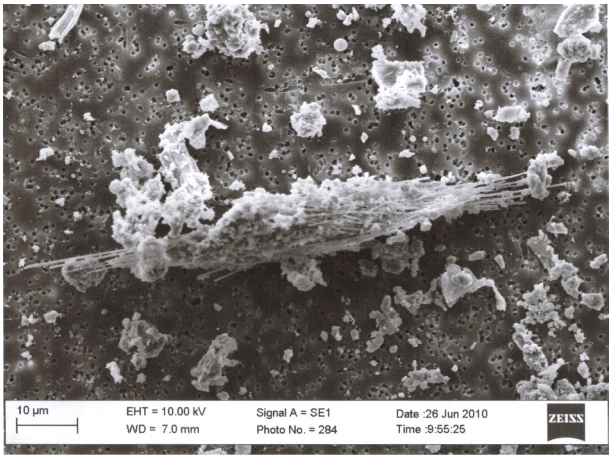

Fig. 5 - Fluoro-edenite bundle found in a Biancavilla 2010 airborne sample.

clean-up interventions adopted since the town has been included in the National Priorities List of Contaminated Sites (NPL-CS) gradually reduced population exposure levels, as already shown in the spatial and temporal picture of fibre concentrations in Biancavilla described by Bruni et al. (2014).

Data reported in the present paper confirm the descending trend. Nevertheless, the peak of 0.21 (values ranging from 0 to 2.24) ff/l in 2014, supported by six samples exceeding the fluoro-edenite concentration ≥ 1 ff/l registered in the same year, should be examined with particular attention. In fact, the samples with higher fibre levels were obtained not only during excavation works but also in some samples collected in urban settings, mainly nearby Monte Calvario and other unbuilt areas, in particular meteorological situations (i.e. windy weather

conditions).

In conclusion, data reported in the present paper demonstrate that Biancavilla, despite the really improved environmental situation, should be carefully and continuously monitored, with particular attention on high risk of fibre releasing activities, such as excavations and demolitions.

Further mitigation works should also be considered for areas of town limits which were still not paved in order to avoid sporadic fibre release, especially in particular meteorological conditions.

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