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Airborne concentrations of chrysotile asbestos in serpentine quarries and stone processing facilities in Valmalenco, Italy

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ABSTRACT

Asbestos may be naturally present in rocks and soils. In some cases, there is the possibility of releasing asbestos fibres into the atmosphere from the rock or soil, subsequently exposing workers and the general population, which can lead to an increased risk of developing asbestos-related diseases.

In the present study, air contaminated with asbestos fibres released from serpentinites was investigated in occupational settings (quarries and processing factories) and in the environment close to working facilities and at urban sites.

The only naturally occurrence of asbestos found in Valmalenco area was chrysotile; amphibole fibres were never detected. An experimental cut-off diameter of 0.25 µm was established for distinguishing between Valmalenco chrysotile and antigorite single fibres, using selected area electron diffraction analyses.

Air contamination from chrysotile fibres in the examined occupational settings was site-dependent as the degree of asbestos contamination of Valmalenco serpentinites is highly variable from place to place. Block cutting of massive serpentinites with multiple blades or discs and drilling at the quarry sites that had the highest levels of asbestos contamination generated the highest exposures to (i.e., over the occupational exposure limits) asbestos. Conversely, working activities on foliated serpentinites produced airborne chrysotile concentrations comparable with ambient levels. Environmental chrysotile concentrations were always below the Italian limit for life environments (0.002 f/ml), except for one sample collected at a quarry property boundary.

The present exposure assessment study should encourage the development of an effective and concordant policy for proper use of asbestos-bearing rocks and soils, as well as for the protection of public health.

KEYWORDS: Asbestos, chrysotile, occupational exposure, atmospheric contamination, public policy, quarrying and stone processing

INTRODUCTION

Valmalenco is located in the Raethian Alps, in the northern part of Italy. The largest outcrop of serpentinites within the Pennine area occurs there (Trommsdorff and Evans, 1977). The Malenco serpentinite occurs in schistose or massive textures, which determine its use as raw material in the building industry. Massive serpentinites are generally subjected to machine cutting and finishing, while foliated serpentines are manually split into tiles. The final products are wall coverings, roof and floor tiles, stove components and cooking plates. Tectonically, the Malenco serpentinite represents a huge ultramaphic nappe covering an area of about 180 km^2, with a thickness of about 2 km. The typical mineralogical association is antigorite, forsterite and diopside, but also chlorite and Ti-rich magnetite are frequently present as accessory minerals (Burkhard and O'Neil, 1988). Among serpentine minerals, antigorite is highly prevalent in Malenco serpentinites, but chrysotile asbestos veins may also occur locally. Not only is asbestos a well-known carcinogen, but it is also easily split and adheres poorly to the host rock. Thus, occupational activities such as extraction, transportation and processing of asbestos-bearing rocks should be controlled even when asbestos is present in very low levels.

Airborne concentrations of asbestos fibres arising from the extraction and use of serpentine rocks in occupational and living environments were measured in the U.S. (Rohl et al., 1977), Japan (Sakai et al., 2001) and Italy (Falcone et al., 2001). Environmental contamination by asbestos arising from working activities on rocks other than serpentinites was assessed in some European countries (Junttila et al., 1997; Selden et al., 2001) and in the U.S. (Anderson et al., 2005; Perkins et al., 2008). The consensus conclusion of these studies was that asbestos concentrations are higher in areas near ophiolitic rock quarries and roads paved with crushed asbestos-containing serpentinites, while fibre concentrations in urban centres near active quarries remain generally very low. In Italy, a study on asbestos fibre dispersion in the workplace during serpentinite extraction and processing showed that slab cutting and dry finishing activities produced the highest occupational exposures to amphibole fibres (Falcone et al., 2001).

The analytical characterization of bulk and airborne asbestos in rocks and soils is a very complex issue due to the presence of asbestos mineral phases and their polymorphs (and/or non-asbestiform varieties) together, which is uncommon in asbestos containing materials. In Malenco serpentinites, chrysotile is commonly found associated with other fibrous polymorphs of serpentine, mainly antigorite. For risk assessment purposes it is crucial to distinguish between chrysotile and the other fibrous polymorphs of serpentine. This distinction cannot be correctly performed by elemental analyses using electron microscopes (Harper et al., 2008; Lee et al., 2008; Van Orden et al., 2008; Wylie et al., 1985), as chrysotile and antigorite have the same chemical composition but different crystal structures (Wicks and O'Hanley, 1988).

Conversely, clear identification of chrysotile asbestos in the presence of other serpentine polymorphs (antigorite and lizardite) can be accomplished by examining structural characteristics by selected area electron diffraction (SAED) using transmission electron microscopy (TEM). Different structural arrangements give rise to specific electron diffraction patterns. The electron diffraction patterns of chrysotile asbestos exhibit a peculiar streaking due to the bending of lattice planes, and antigorite may easily be distinguished from lizardite on the basis of superstructure spots (Uehara, 1998; Wunder et al., 1997; Yada, 1979; Zussman et al., 1957). The high magnification and resolution of TEM analyses can also facilitate the identification of serpentine minerals (Keenan and Lynch, 1970), whose morphology derives directly from their crystal structure.

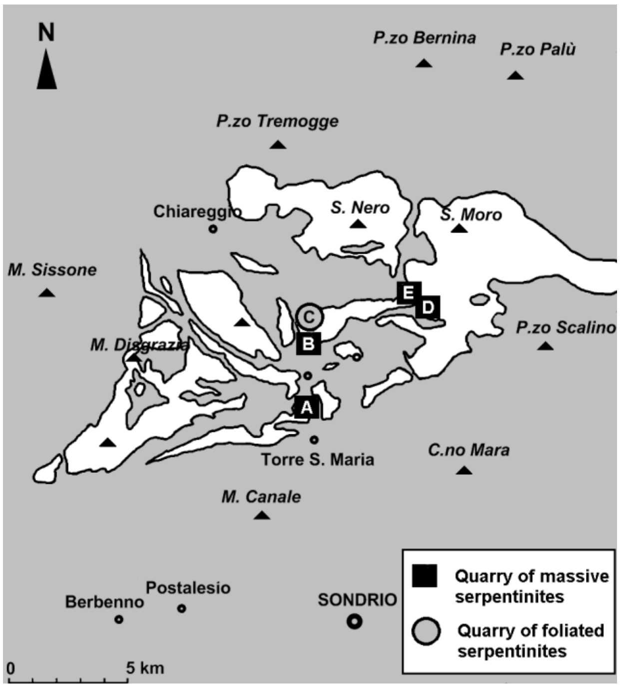
It should be noted that chrysotile and antigorite can both exhibit a fibrous morphology (Cardile et al., 2007) and dimensions consistent with the World Health Organization (WHO) and ISO Method 14966 fibre definition (length > 5 µm, diameter < 3 µm and aspect ratio > 3) (WHO, 1997; ISO 2002). Therefore, the presence of antigorite fibres could lead to an overestimation of chrysotile concentrations if analyses of airborne samples are conducted only by conventional energy dispersive spectroscopy (EDS).

The toxicity and carcinogenicity of chrysotile have been studied extensively (Kanarek et al 2011) whereas some mechanisms of toxicity and carcinogenicity of fibrous antigorite have only been examined recently (Cardile et al., 2007; Pugnaloni et al., 2010). This is another reason to differentiate chrysotile and antigorite fibres for risk assessment purposes. The distinction between chrysotile and antigorite fibres is also important for determining whether asbestos exposures are within regulated limits that have been developed in most countries as antigorite is not classified as a typical asbestos mineral.

The aim of this study was to quantify the airborne concentration of asbestos in the field resulting from extraction and processing of serpentinites at Valmalenco, and to examine the environmental asbestos concentrations in towns and areas nearby quarries and processing facilities.

METHODS

Fig. 1. Geographical representation of serpentinite outcrops (white areas) in Valmalenco and location of selected quarrying sites (A-E).



Study design

Air contamination from asbestos fibres was investigated in occupational settings, in environments close to working facilities and at urban sites. The production cycle is organized around three main activities: quarrying, transport and processing. In the present study, occupational exposures to asbestos and the possible ambient contamination arising from extraction and processing of Malenco serpentinites were investigated. Five different quarrying sites were selected for the study (Fig. 1).

Occupational exposures were studied by both personal and static sampling for each selected working activity. Moreover, two ambient samples, one close to the working facility boundary and one in the centre of the nearest town or village, were collected during each monitoring session. Each monitored extraction activity produced serpentinite blocks that were marked with spray paint to ensure traceability of raw material origin in the subsequent processing activities.

The production cycle and working activities were very similar in all the selected occupational environments, with the exception of manual splitting (MS) that was performed only on foliated serpentinites (extraction site C). Selected quarrying activities were wet drilling (WD), dry drilling (DD) and string cutting (SC); activities examined at processing sites included multi-blade cutting (MBC), multi-disc cutting (MDC), monodisc cutting (MC), dry finishing (DF) and MS. MBC was investigated only by static sampling (in front of and behind the multi-blade cutters) as workers did not monitor such activity.

Sampling

As previously described, air samples were collected in the breathing zone of workers and at fixed sites within proximity (3 m) of emission sources. Static sampling was carried out at 1.5 m from ground level.

Personal samplers (Ego and Chronos; Zambelli Srl, Bareggio, Italy) were used in occupational settings to draw air over 25 mm diameter polycarbonate filters with 0.8 µm porosity (Osmonics, Livermore, CA, USA) placed in filter-holders fitted with an electrically conductive cylindrical cowl at a flow rate of 1 l min^{-1}. Total volume sampled was limited to 30-100 l due to the high dust content of the occupational environments and was dependent on estimated airborne particle concentrations.

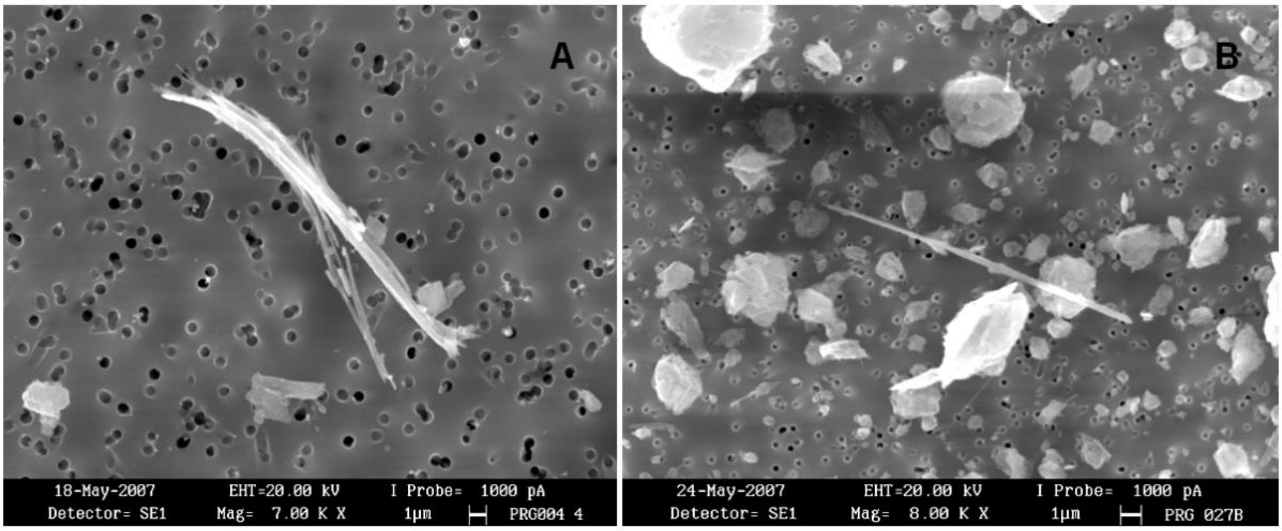
Environmental sampling was carried out through portable samplers (PQ 100, BGI Inc., Waltham, MA, USA) operating at a flow rate of 6-9 l min^{-1} using 25 mm diameter polycarbonate filters with 0.8 µm porosity (Osmonics, Livermore, CA, USA) placed in filter-holders fitted with an electrically conductive cylindrical cowl. The volume sampled was higher than 3000 l. All pumps were calibrated prior to and after each field sampling using a NIST-traceable soap bubble meter (mini-Buck Calibrator Model M30, AP Buck Inc., Orlando, FL, USA). Collected samples were sealed in clean filter-keepers and transported to the two analytical laboratories that performed electron microscopic analyses. Scanning electron microscopy (SEM) analyses were carried out in the laboratory of the Environmental Protection Agency of Lombardy Region, while TEM observations were performed at the Department of Earth Sciences of the University of Milan.

SEM-EDS Analysis

Airborne asbestos fibre concentrations were measured using a Scanning Electron Microscope (Stereoscan 420; Leica Microsystems, Heidelberg, Germany) equipped with X-ray microanalysis (eXLII; Oxford Instruments, High Wycombe, UK). The analysis was performed using the method described in the Italian legislation (Italian Ministry of Health, 1994), which is very similar to the International Standard Organization (ISO) Method 14966 (ISO, 2002). The fibre-definition criteria are those cited above and are compliant with the ISO 14966 and WHO standard (ISO, 2002; WHO, 1997). The sampling filter was divided into 4 parts. One part was fixed with bi-adhesive carbon tape onto the electron microscope stub and subjected to surface metallization by a thin carbon film.

Fibre identification was determined using both fibre morphology (Fig. 2) and fluorescence X-ray spectra. The analyses were conducted at a magnification of 4,000X. Some heavily loaded filters were analyzed at 12,000X. The limit of detection (LOD) was calculated on the basis of the ISO method 14966 (section 8.3) and was affected by the sampling volume, the effective filter area and the area of the filter analyzed. The sampling volume also depended on the airborne dust concentration and was chosen so that the filter was not excessively loaded. In general, the filter area to be examined was calculated for each filter in order to obtain a LOD which is at least 1/5 of the recommended value. Accordingly, the LOD in the present investigations varied from 0.0001 f/ml to 0.0076 f/ml.

Fig. 2. Aggregates of chrysotile fibres (A) and an antigorite fibre (B) observed by SEM.

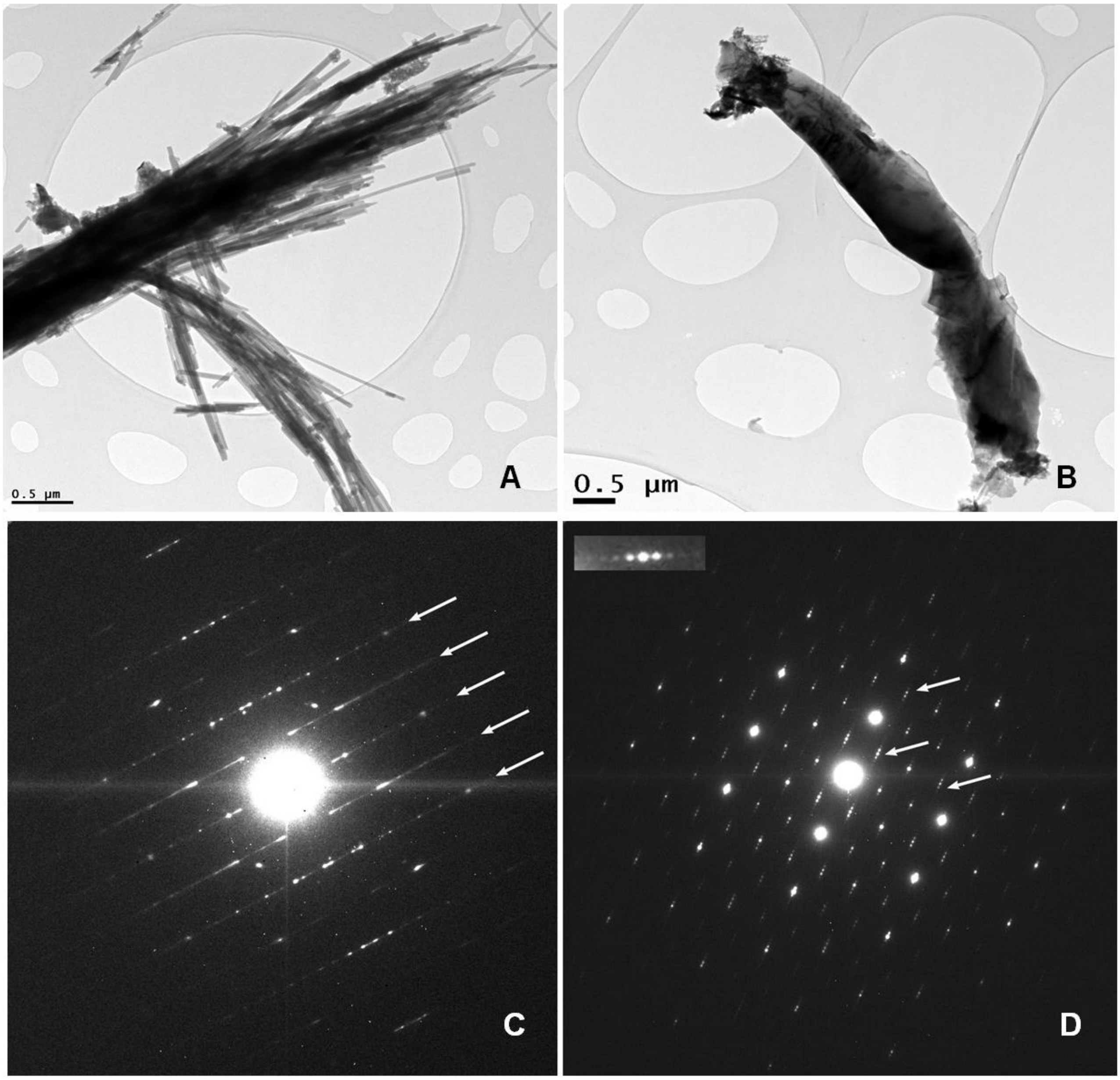


TEM-EDS-SAED analysis

Only the filters showing a high amount of fibres by SEM were subjected to TEM analysis. A quarter of the filter was excised, inserted into a porcelain crucible and ashed at low temperature by a K 1050X oxigen plasma asher (Emitech Ltd, Ashford, UK) for 20 minutes. The residual powder was suspended in 0.5 milliliters of isopropyl alcohol. The resulting suspension was not subjected to further treatment. A carbon film copper grid was placed on a sheet of blotting paper. Two drops of the suspension were deposited on the grid, which acts as a filter and retains the suspended particles while the alcohol is absorbed by the paper. TEM observations were used for qualitative identication of serpentine polymorphs to establish criteria for dimensional and morphological fibre characterization and did not provide quantitative results. These criteria were subsequently used to obtain accurate airborne chrysotile concentrations free from interferences due to fibrous antigorite. For this reason, incidental fragmentation of asbestos fibres in TEM preparation is not critical as quantitative results were only obtained by a direct preparation method for SEM. TEM observations were carried out on a Tecnai F20ST electron microscope (FEI Co., Hillsboro, OR) operating at 200 kV and equipped with an EDS spectrometer and a 794 Slowscan CCD camera (Gatan, Pleasanton, CA, USA).

The samples were observed at 13.500X. Each crystal that exhibited a fibrous morphology compliant with WHO and ISO/FDIS 14966 fibre definition (WHO, 1997; ISO, 2002) (Fig. 3 A,B) was further analyzed using EDS. If the crystal had a serpentine composition, a SAED pattern (Fig. 3 C,D) was collected after positioning the selected area diaphragm onto the investigated crystal, in order to avoid diffraction from nearby grains. If characteristic streaking was observed, the fibre was considered to be chrysotile. If not, the crystal was oriented in the nearest zone axis and the pattern was indexed with the antigorite unit cell. Note that if lizardite was also contained in the sample, indexing was attempted with both structures to distinguish between them.

Fig 3. Aggregates of chrysotile fibres (A) and an antigorite fibre (B) as they appear under TEM analysis. In the bottom part of the Fig. SAED patterns of a single chrysotile fibre (C), and an antigorite WHO-fibre (D) are shown. The chrysotile pattern is longitudinal to the fibre and shows the characteristic lines of streaking that are marked by arrows. The antigorite pattern is oriented in the [001] zone axis and shows reflections surrounded by superstructure spots (marked by arrows and enlarged at the top left).



Statistical analysis

Data below the LOD (16 out of 105) were considered as LOD/2 and included in the analysis. Data were tested for normal distribution using the Kolmogorov–Smirnov test. All groups were not normally distributed, so they were transformed into logarithms. The normality test was performed again, demonstrating that log-transformed data were always normally distributed. Therefore, parametric statistics were used on the log-transformed data.

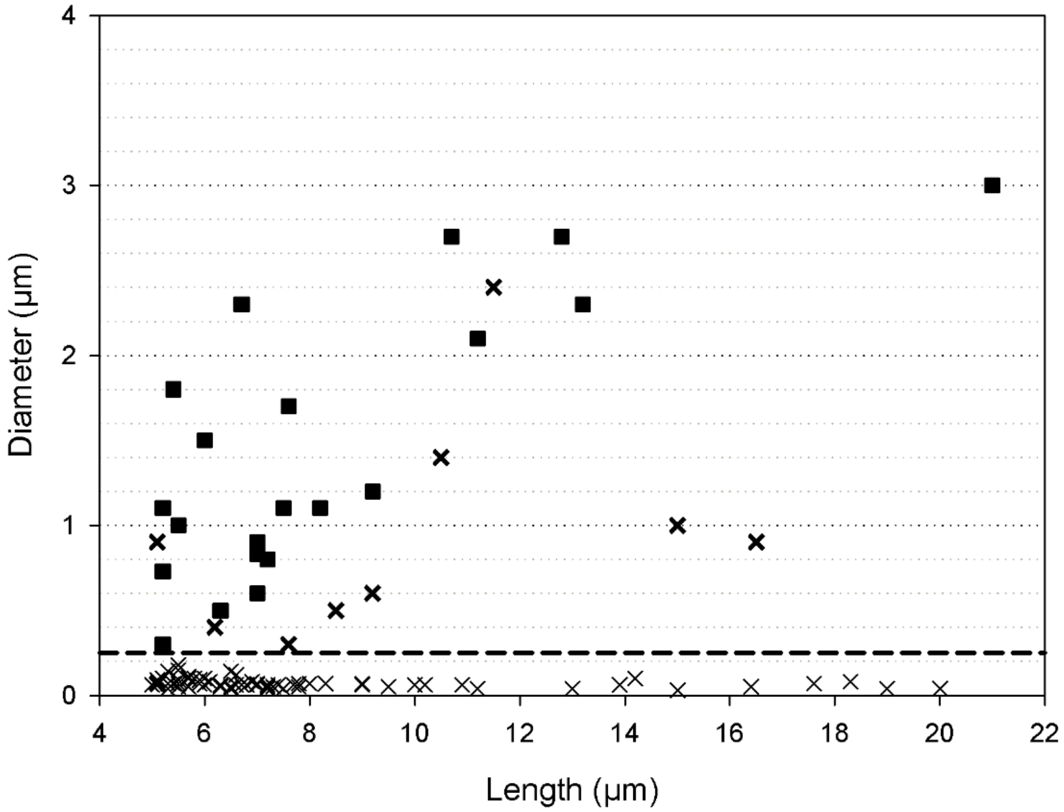
Descriptive statistics were used to tabulate mean, standard deviation, median, 95th percentile, minimum and maximum. A t-test was performed to determine differences in the means of two groups of paired data and the Mann-Whitney U-test was used to assess the difference between two groups. One-way ANOVA, followed by Bonferroni post-hoc test, was used to determine differences among means of more than two groups.

RESULTS

TEM SAED analyses

TEM revealed only two serpentine polymorphs among the observed WHO fibres: chrysotile and antigorite. Between the two, chrysotile was the more prevalent, as 74 out 96 serpentine fibres exhibited SAED patterns consistent with the structural disorder of this mineral (Fig. 3C). Chrysotile was reported either in single fibrils or, with less prevalence, in bundles. The mean diameter of chrysotile fibrils, chrysotile bundles and antigorite fibres was 0.07 µm (0.03-0.18), 0.85 µm (0.07-2.4) and 1.42 µm (0.3-3.0) respectively. In Fig. 4 the width of each fibre or aggregate of fibres as a function of their length is depicted. It is clearly shown that antigorite and chrysotile single fibres occupy two distinct dimensional regions. Thus, a diameter cut-off of 0.25 µm was proposed as a threshold marker for the differentiation of chrysotile and antigorite fibres from Valmalenco. In this way, the selected threshold was used as a diagnostic element for the subsequent SEM analyses, as EDS spectra cannot be useful for this purpose. Moreover, chrysotile bundles can be easily distinguished by antigorite fibres by means of typical morphological characteristics. On the contrary, the length of WHO fibres was comparable for the serpentine polymorphs, as chrysotile, chrysotile bundles and antigorite fibres showed mean lengths of 8.1 µm (5.0-20.0), 9.5 µm (5.1-16.5) and 8.2 µm (5.2-21.0) respectively.

Fig 4. TEM dimensional analysis of airborne serpentine WHO fibres. Thin crosses = chrysotile fibrils, Thick crosses = chrysotile bundles, Black squares = antigorite fibres. The dashed line shows the width threshold that separates the chrysotile single fibre region from the antigorite single fibre region.



Airborne chrysotile concentrations

In the collected atmospheric samples only chrysotile and antigorite fibres were detected; amphibole fibres were not present.

Five samples out of 111 were discarded due to excessive filter loading and one as it was collected in a location not in accordance with the study design. In work environments 83 valid samples were obtained: 40 during extraction and 43 during processing activities. Ambient concentrations gave valid results in 22 cases.

Sixteen valid samples showed concentrations falling below the LOD (0.0001 – 0.0008 f/ml for ambient measures; 0.0004 – 0.0076 f/ml for occupational measures, depending on sampled volumes) and were analysed assigning a value of half the LOD.

On average, chrysotile fibre concentrations measured at processing sites were higher than those measured in quarry areas ($p_{MANN\text{-}WHITNEY}$ = 0.086), while ambient concentrations were below 0.0053 f/ml (Table 1). Median levels were always below 0.005 f/ml, indicating that most airborne chrysotile levels were quite low and high exposure peaks were sporadic.

Table 1. Chrysotile fibre concentrations (f/ml) obtained by personal and fixed sampling in working and living environments.

ENVIRONMENT	n	AM (SD)	Median	95^{TH} perc	Range	p_{ANOVA}	$p_{K\text{-}S}$ [a]
All samples	105	0.0500 (0.2275)	0.0021	0.1333	0.00005-1.8517	-	-
Extraction	40	0.0265 (0.1184)	0.0023	0.0439	0.0004-0.7530		
Processing	43	0.0971 (0.3333)	0.0047	0.3520	0.0004-1.8517	<0.001	<0.001 0.273
Ambient	22	0.0005 (0.0011)	0.0003	0.0012	0.00005-0.0053		

[a] = Significance of Kolmogorov-Smirnov test before and after log-transformation

Airborne chrysotile contamination by extraction site

On average, airborne chrysotile concentrations due to release of asbestos from raw materials at work site E were an order of magnitude higher than those at both sites A and

C (Table 2) ($p_{BONFERRONI}$ < 0.04). Also, concentrations of serpentinites at site B were greatly higher than those at site C ($p_{BONFERRONI}$ = 0.03). The significance of the comparison between concentrations at sites E and D was $p_{BONFERRONI}$ = 0.06.

Table 2. Chrysotile fibre concentrations (f/ml) obtained by personal and fixed sampling in working environments where serpentinites were extracted and processed, sorted by extraction site.

	EXTRACTION SITE	n	AM (SD)	Median	95^{TH} perc	Range	p_{ANOVA}	p_{K-S} [a]
OVERALL OCCUPATIONAL SETTINGS	A	20	0.0118 (0.029.5)	0.0030	0.0831	0.0004-0.1333		
	B	15	0.0455 (0.090.6)	0.0112	0.3520	0.0004-0.3520		
	C	10	0.0012 (0.000.9)	0.0008	0.0030	0.0004-0.0030	0.001	0.000 0.058
	D	29	0.0092 (0.012.1)	0.0038	0.0348	0.0004-0.0502		
	E	9	0.4488 (0.676.6)	0.0375	1.8517	0.0006-1.8517		
QUARRIES	A	7	0.0019 (0.0011)	0.0023	0.0033	0.0004-0.0033		
	B	7	0.0101 (0.0114)	0.0019	0.0280	0.0008-0.0280		
	C	6	0.0014 (0.0011)	0.0010	0.0030	0.0004-0.0030	0.061	<0.001 0.365
	D	16	0.0109 (0.0147)	0.0043	0.0502	0.0004-0.0502		
	E	4	0.1983 (0.3702)	0.0194	0.7530	0.0012-0.7530		
PROCESSING FACILITIES	A	13	0.0171 (0.0359)	0.0057	0.1333	0.0008-0.1333		
	B	8	0.0764 (0.1182)	0.0401	0.3520	0.0004-0.3520		
	C	4	0.0011 (0.0007)	0.0008	0.0021	0.0005-0.0021	0.026	<0.001 0.357
	D	13	0.0071 (0.0080)	0.0032	0.0305	0.0015-0.0305		
	E	5	0.6493 (0.8365)	0.1923	1.8517	0.0006-1.8517		

One-way ANOVA test conducted on airborne chrysotile concentrations determined at the different quarrying areas shown in Fig. 1 indicated a statistical significance (p_{ANOVA} = 0.06) close to the conventional threshold of significance (p = 0.05) (Table 2) and Bonferroni post-hoc tests did not reveal any significant differences between the observed concentrations measured at the Valmalenco sites ($p_{BONFERRONI}$ > 0.1). However, raw material extraction activities at sites A, B, C and D were associated with mean asbestos concentrations that were 1-2 orders of magnitude lower than those observed during the extraction of serpentinites from area E (Table 2).

The analysis of chrysotile concentrations during processing activities revealed some differences between rocks coming from different extraction sites (Table 2). Airborne chrysotile concentrations from processing of rocks extracted at site E was again the highest.

Airborne chrysotile contamination by working activity

MBC generated higher mean concentrations of chrysotile fibres than other occupational activities (Table 3). The comparison of MBC concentrations with WD, SC and MDC data showed Bonferroni-corrected p-values < 0.001, those with DF and MS were < 0.041 and those versus MDC and DD data were 1.000.

Table 3. Airborne chrysotile concentrations (f/ml) sorted by working activity during serpentinite extraction and processing.

	ACTIVITY	n	AM (SD)	Median	95^{TH} perc	Range	p_{ANOVA}	$p_{K\text{-}S}$ [a]
	WD	19	0.0443 (0.1718)	0.0026	0.7530	0.0004-0.7530		
	DD	8	0.0171 (0.0136)	0.0182	0.0348	0.0019-0.0348		
	SC	13	0.0062 (0.0138)	0.0016	0.0502	0.0004-0.0502		
OCCUPATIONAL SAMPLES	MBC	12	0.3110 (0.5920)	0.0509	1.8517	0.0004-1.8517	<0.001	<0.001
	MDC	4	0.0833 (0.0950)	0.0697	0.1923	0.0015-0.1923		0.065
	MC	13	0.0037 (0.0037)	0.0022	0.0121	0.0006-0.0121		
	DF	12	0.0051 (0.0040)	0.0038	0.0136	0.0005-0.0136		
	MS	2	0.0007 (0.0003)	0.0007	0.0010	0.0005-0.0010		

[a] = Significance of Kolmogorov-Smirnov test before and after log-transformation

A comparison between personal exposure and fixed sampling concentrations was performed using a t-test on paired samples, using valid data pairs collected while performing WD, DD, SC, MDC, MC and DF. Possible differences between personal and fixed-site concentrations in these analyses ($p_{t\text{-test}}$ = 0.164) were far from the conventional threshold of significance (0.05).

Occupational exposure to chrysotile and comparison with occupational exposure limit (OEL) values

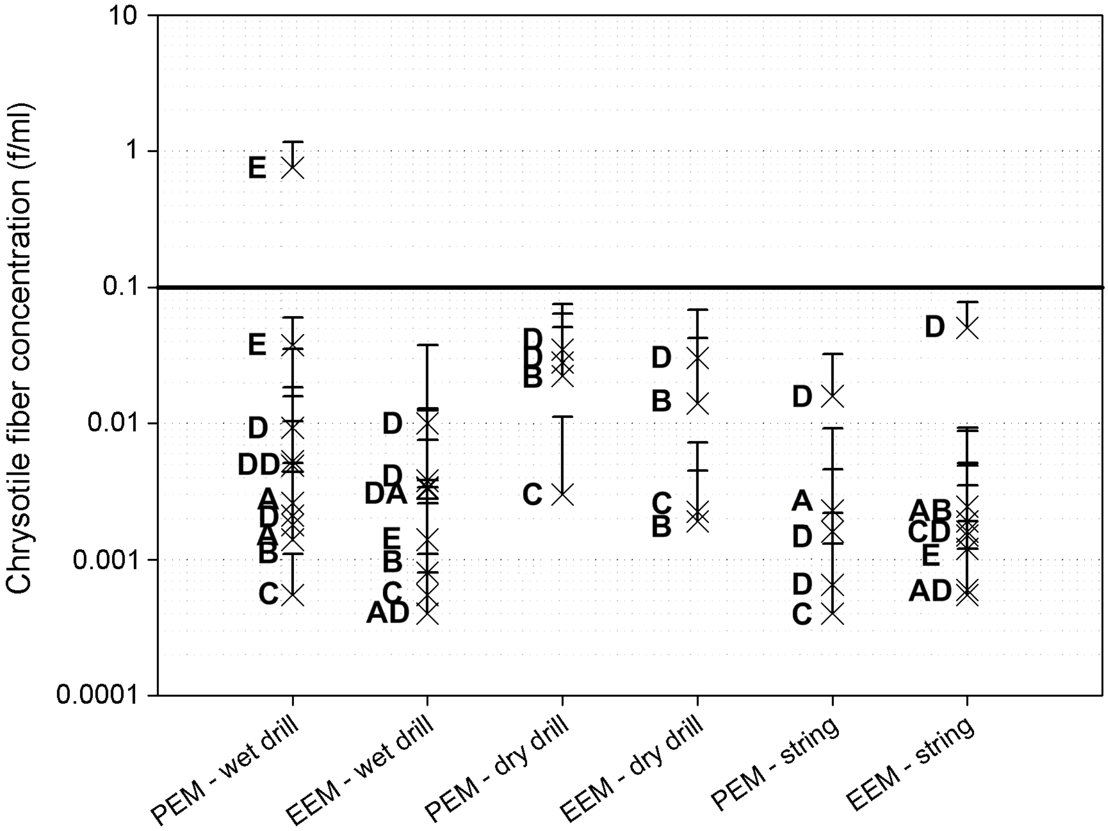
Approximately 8% (7 out 83) of the samples collected in occupational environments showed airborne asbestos levels over the OEL value of 0.1 f/ml for a time-weighted average over an 8-hr period (ACGIH, 2010).

Airborne chrysotile levels (Fig. 5) collected during quarrying activities were lower than the international and Italian OEL (0.1 f/ml) with one exception that was sampled in the breathing zone of a worker who was performing wet drilling on a quarry front in work site E. Atmospheric concentrations of chrysotile fibres higher than 0.030 f/ml were also observed during the extraction of serpentinites from area D. In such cases the 95% upper confidence level was between 0.080 and 0.090 f/ml. Extraction activities from rocks in area B produced asbestos concentrations greater than 0.01 f/ml only during dry drilling. The extraction of serpentinites from areas A and C always showed personal and ambient concentrations below 0.004 f/ml (Fig. 5).

Fig. 5. Airborne chrysotile fibre concentrations (logarithmic scale) for the different working activities carried out in Valmalenco quarrying sites (A-E).

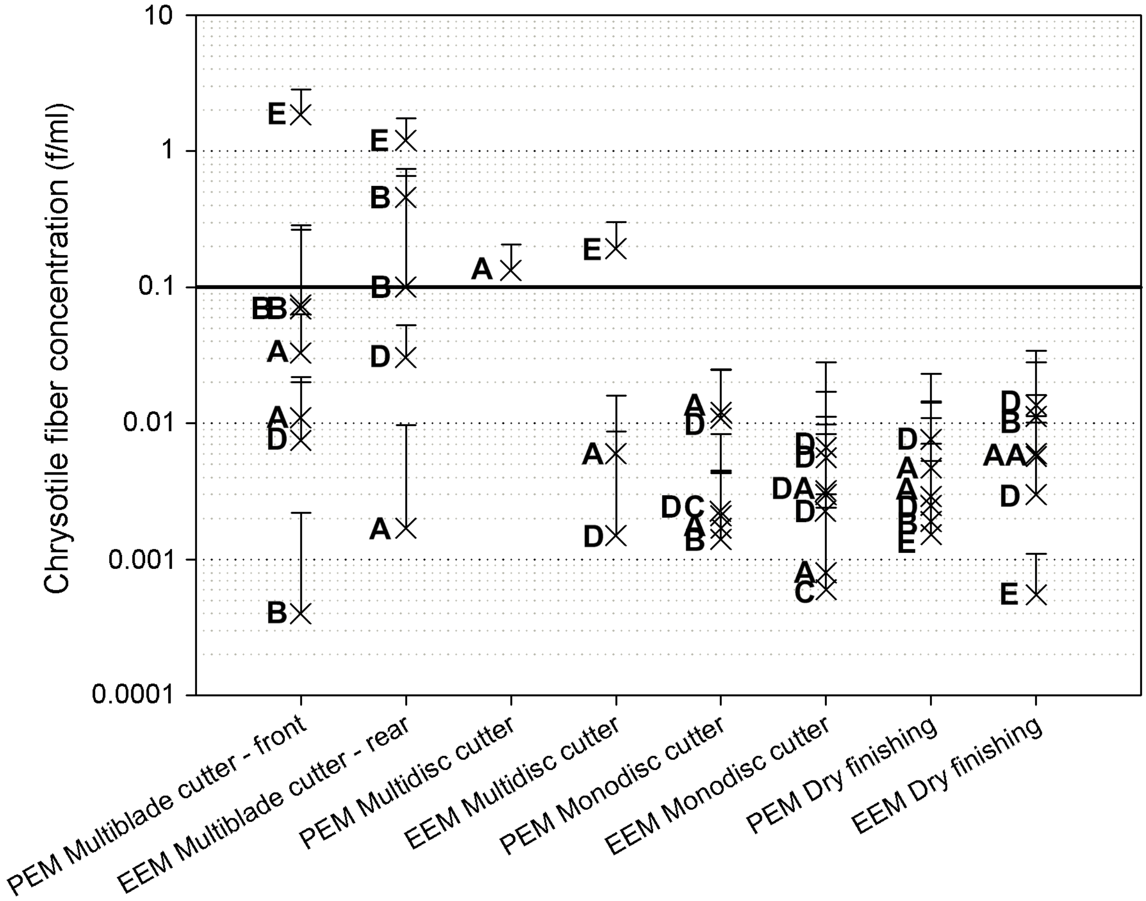
Error bars represent the upper 95% confidence interval of single measurements, the reference line reports the ACGIH TLV-TWA, OSHA PEL and NIOSH REL (0.1 f/ml) occupational exposure limits.

PEM = Personal Exposure Monitoring; EEM = Environmental Exposure Monitoring



Regarding processing, most of the measurements (5 out of 6) exceeding the occupational exposure limit (OEL) were observed during block cutting activities performed indoors (Fig. 6) using multi-blade or multi-disc cutters.

Fig. 6. Airborne chrysotile fibre concentrations (logarithmic scale) for the different occupational activities carried out during the processing of rocks extracted from the Valmalenco quarrying A, B, C, D and E sites. Error bars represent the upper 95% confidence interval of single measurements. Reference line = OEL, PEM = Personal Exposure Monitoring, EEM = Environmental Exposure Monitoring



Ambient atmospheric contamination

Ambient chrysotile contamination near extraction sites was somewhat higher than in outdoor environments contiguous to processing facilities and to the centre of villages or towns, although this did not reach statistical significance (Table 4).

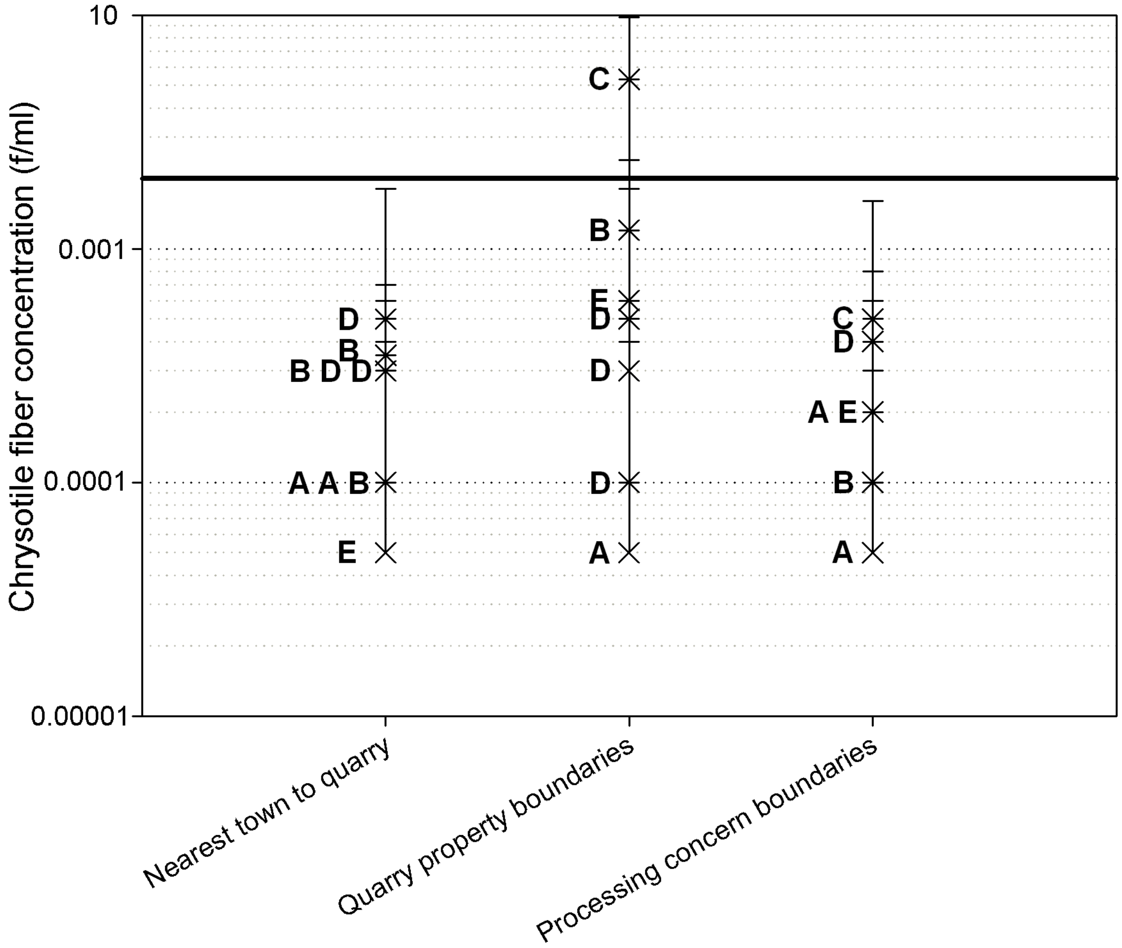
Table 4. Chrysotile fibre concentrations (f/ml) measured at the inhabited place nearest to the location of extraction and processing activities, at quarry boundaries and at processing factory boundaries.

	LOCATION	n	AM (SD)	Median	95^{TH} perc	Range	p_{ANOVA}	p_{K-S}[a]
AMBIENT SAMPLES	NEAREST TOWN	9	0.00023 (0.00015)	0.00030	0.00050	0.00005-0.00050	0.521	0.004 0.414
	QUARRY PROXIMITIES	7	0.00109 (0.00190)	0.00030	0.00530	0.00005-0.00530		
	PROCESSING PROXIMITIES	6	0.00024 (0.00017)	0.00020	0.00020	0.00005-0.00050		

[a] = Significance of Kolmogorov-Smirnov test before and after log-transformation

The Italian environmental exposure limit (0.002 f/ml) (DM 6/9/1994) was exceeded in one location adjacent to a quarry property boundary (Fig. 7). Mean airborne chrysotile concentrations collected at quarry property boundaries were approximately 5-fold higher than other collected ambient levels, while median concentrations were comparable (Table 4).

Fig 7. Ambient chrysotile fibre levels (logarithmic scale) determined at places located at different distances from the A-E Valmalenco extraction sites and processing activities of rocks extracted from the same sites. Error bars represent the upper 95% confidence interval of single measurements. Reference line = Environmental limit of Italian regulation (0.002 f/ml)



DISCUSSION

Discrimination between chrysotile and antigorite

TEM observations allowed establishment of a dimensional criterion to distinguish between chrysotile and antigorite fibres or their cleavage fragments. In the study area, single fibres with serpentine composition having a width of less than 0.25 microns should be reasonably categorized as chrysotile. Conversely, fibres having width of greater than 0.25 microns should be categorized as antigorite or chrysotile fibre bundles, which were easily distinguishable on a morphological basis.

Occupational exposure to chrysotile and comparison with OEL

Six out of 83 (7%) airborne samples exceeded the ACGIH Threshold Limit Value (TLV) and Italian OEL (0.1 f/ml), but 5 of them were obtained by fixed sampling in confined environments that do not require workers to be present during stone cutting activities. Such concentrations should not significantly affect the time-weighted concentrations during the entire work-shift; it should be remembered that OELs are expressed as 8-hour time-weighted averages. The other example of concentrations exceeding OELs was in cases of wet drilling on the quarry front of area E. This is consistent with previous results from another recent study showing that most occupational chrysotile exposures in Valmalenco were below the OEL, except for sporadic and localized cases (Massera et al., 2010).

High standard deviations can be caused by the localized occurrence of chrysotile in the host rock. Thus, the release of asbestos fibres into atmosphere might act as an intermittent process, occurring when veins of chrysotile are intercepted by drilling, cutting or finishing activities.

Airborne chrysotile contamination by extraction site

Extraction and processing activities conducted on serpentinites in area E produced the highest airborne concentrations of chrysotile fibres when compared with other extraction sites. This finding could be explained by the presence a higher density of veins mineralized with asbestiform crystals in the quarry front of area E, which are well-documented in the geological literature (Gorga and Mottana, 1997). In fact, in the past chrysotile was extracted from area E and there are still tunnel entrances to inactive mines nearby the quarry fronts of area E. However, the airborne asbestos concentrations (n=10) determined during extraction and processing activities on foliated serpentinites (typical of area C) were always below 0.004 f/ml. These findings are consistent with field observations that such rocks have fewer and thinner chrysotile veins than massive serpentinites.

Airborne chrysotile contamination by working activity

On average, MBC, WD, DD, MDC were all associated with the highest occupational exposures to chrysotile fibres (Table 3). Median chrysotile concentrations measured during MBC, DD and MDC were the highest (>0.018 f/ml) while TLV was exceeded only during MBC, MDC and WD activities (Fig. 5 and 6). MBC and MDC generated the greatest atmospheric contamination by chrysotile fibres. This may be explained by multiple cuttings of serpentinite blocks, which may increase the probability of crossing a chrysotile vein. Moreover, these activities are performed in confined indoor environments that are not equipped with local or general exhaust ventilation systems.

Conversely, WD and DD were performed outdoors in open-pit quarries. Chrysotile concentrations measured during WD were lower than 0.01 f/ml (median = 0.0026 f/ml) with two exceptions that were measured in the breathing zone of subjects working at quarry site E (Fig. 5). As stated before, area E is highly contaminated with asbestos veins. DD, an extraordinary activity which is not technically required, was evaluated only in quarries in areas B, C and D. Although the OEL was not exceeded during DD, the central tendency values were both quite high (Table 3). No significant differences were found in the comparison of exposures measured during WD and DD ($p_{BONFERRONI}$ = 1.000). This could be explained by the fact that DD was not monitored at quarry site E (the most contaminated by chrysotile) and by the small number of data collected during DD, as it is an unusual and unnecessary activity.

Ambient atmospheric contamination

As expected, ambient chrysotile levels (Table 4) at these locations were significantly lower than those found near active asbestos mines or asbestos processing sites (Hansen et al., 1997, Marconi et al., 1989). Atmospheric asbestos concentrations measured in non-occupational environments were lower than the Italian environmental limit with the exception of a sample collected at the quarry property boundary in quarrying area C. This observation is not in line with occupational levels measured at the same site, but was consistent with the observation that there were large amounts of suspended dust near the sampling location caused by busy truck traffic on a dirt road accessing the quarry in area C.

Risk management implications

The results of site-specific analysis (Table 2) made clear that atmospheric contamination is dependent on extraction site; thus site-specific risk management strategies should be adopted on the basis of hazard identification through periodic geomechanical surveys of quarry fronts and occupational hygiene surveys (exposure assessments).

Dry working activities should be avoided at quarry sites as these seem to produce higher dust concentrations when compared with wet activities performed in the same quarry site (Fig. 5); this is important because dry drilling is not technically essential. It is well known that working in dry conditions can lead to increased dispersion of fibres into the atmosphere (Cheng and McDermott, 1991).

Regarding processing, workers should not be present during the multi-blade or multi-disc cutting of serpentinites. The presence of workers during such activities is not required for productive or technical purposes because multi-cutting activities (especially MBC) can be almost completely automated. In addition, to avoid environmental contamination, indoor environments in which multi-cutting activities are performed should be decontaminated before entry using local and/or general exhaust ventilation systems. In addition, cutting equipments should be periodically cleaned by wet methods to remove possible accumulation of asbestos fibres. Dry finishing, which was supposed to be a high-exposure activity, was performed using downdraft tables and produced exposures and fixed-site concentrations below 0.014 f/ml (Table 3). All other work areas should be furnished with efficient particle aspiration systems.

The prevention and control of occupational exposures to low chrysotile levels should be pursued using all the other well-established procedures for management of occupational health and safety (including periodical washing of processing machinery and workers' overalls, correct use of proper personal protective equipment, education and training, etc.).

CONCLUSION

Air contamination by asbestos fibres in the quarrying and processing of Valmalenco serpentinites was site-dependent, as the degree of asbestos contamination was shown to be highly variable from place to place. Working activities on foliated serpentinites produced airborne chrysotile concentrations that were comparable with ambient levels. Occupational activities that generated the highest exposures of airborne contaminations (over the OEL) were block cutting with multiple blades or discs and drilling at quarry sites with the highest asbestos contamination. Ambient chrysotile levels were always under the Italian limit for living environments (0.002 f/ml), except for one sample collected at a quarry property boundary.

The present study offers an exposure assessment which could be useful not only for occupational risk management but also for the development of an effective and concordant policy for proper use of asbestos-bearing rocks and soils, as well as for public health purposes (Lee et al., 2008). Currently, scientifically-based legislation concerning risk assessment and management of asbestos occurring at low levels in rocks and soils is a high priority. On the one hand this will help to protect workers and preserve public health; and, on the other hand, will help to avoid incorrect alarms by populations and adverse impacts on local economies.

The only asbestos found in Valmalenco area was chrysotile; amphibole fibres were never detected. Thus, future studies could also be aimed at quantifying the health effects in occupational populations exposed to pure chrysotile from Valmalenco to gain more information about the carcinogenic effects of chrysotile (Pierce et al., 2008).

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