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Short communication

Trees as reservoirs for amphibole fibers in Libby, Montana

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Abstract

Tree bark and core samples were collected from areas surrounding the asbestos-contaminated vermiculite mine in Libby, MT. These samples were collected to provide preliminary data in support of a proposed study to determine if trees can serve as reservoirs for amphibole fibers and to determine if there is a potential for exposure to those that harvest contaminated wood in the Libby mine area, specifically during firewood harvesting and commercial logging. Initially, three sets of samples were taken both within and directly outside of the EPA restricted area surrounding the mine site. Based on the results of the initial samples, a follow-up sampling program was conducted both in the town of Libby and directly outside the city limits.

Gravimetric reduction of a tree core sample did not indicate the presence of amphibole fibers. However, transmission electron microscopy analysis of bark samples collected near the vermiculite mine yielded substantial amphibole fiber concentrations ranging from 41 million to 530 million fibers/g of bark. In addition, a bark sample collected approximately 7 miles west of the town next to a railroad line had concentrations of 19 million fibers/g. A conversion of these mass-based concentrations to areal concentrations (to reflect surface area contamination) revealed concentrations in excess of 100 million amphibole fibers/cm^2. These preliminary results suggest that trees in the Libby valley and along vermiculite shipping corridors can serve as reservoirs for amphibole fibers, and that a potential for exposure exists for those who harvest contaminated wood.

Keywords: Libby; Montana; Asbestos; Amphibole; Fibers; Tree bark; Electron microscopy

1. Introduction

Vermiculite was originally discovered 6 miles northeast of Libby, MT, in 1881. In 1919, Dr. Edward Alley found that vermiculite expanded (or "popped") when heated, creating pockets of air that made the material suitable for use in building insulation and as a soil conditioner. In the early 1920s, Alley founded the Zonolite Company in Libby and developed the mine and processing facility at Vermiculite Mountain (also known as Zonolite Mountain). W.R. Grace purchased the site in 1963 and continued the mine and associated operations until 1990. The mine operated nearly 70 years, and at one time, Vermiculite Mountain was the source of over 80% of the world's vermiculite (ATSDR, 2006; USEPA, 2006).

Despite the beneficial uses of vermiculite, the Libby ore was contaminated with naturally occurring fibrous

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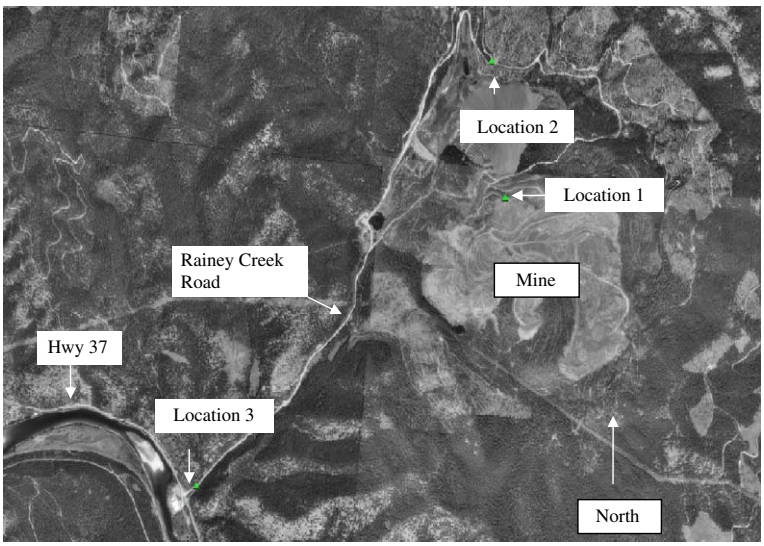
and asbestiform amphiboles that occurred in veins throughout the deposit (Pardee and Larsen, 1929). These amphibole fibers have caused a very high incidence of pleural plagues, asbestosis, lung cancer, and mesothelioma in not only the former mine and mill workers, but in the general population of Libby itself (McDonald et al., 1986; Amandus and Wheeler, 1987; Amandus et al., 1987; Dearwent et al., 2000; Peipins, 2003). The relationship between mesothelioma and asbestos exposure has now been well documented, (Hammond et al., 1965; McDonald and McDonald, 1977, 1980; McDonald et al., 1986), with at least 70% of people with mesothelioma reporting being exposed to asbestos (National Cancer Institute, 2005).

Asbestos fibers are strong and heat resistant and have historically been used in thousands of products such as building materials and heat-resistant fabrics. Their extremely thin diameters allow them to remain airborne following liberation for hours or even days before settling into soil, sediment, or other indoor materials such as carpet. Since asbestos fibers are durable silicates and do not decompose in the environment, the airborne asbestos fibers released and dispersed from the Libby mine and processing areas throughout 70 years of operation have likely deposited throughout the surrounding areas.

Historically, much of the economy in Libby has been supported by the harvesting and processing of natural resources such as vermiculite and timber. Western Montana logging companies own approximately 315,000 acres of land surrounding the Libby mine that could potentially be harvested. To date, no definitive efforts have been made to identify potential exposure of loggers and logging support personnel to amphibole fibers from the Libby mine and processing facilities. In addition, there are also currently an estimated 1300 wood stoves in use in Libby, with at least some of the firewood harvested within the Libby valley and surrounding forests. Because firewood is the cheapest source of fuel in the Libby area, it is the most common source of residential heating during the cold Libby winters. This manuscript presents the results of preliminary tree bark and core samples that were collected to evaluate the potential for current exposures during commercial logging and firewood harvesting processes.

2. Methods

Tree (bark and core) samples were collected around the former W.R. Grace vermiculite mine and former processing structures on November 2, 2004 in support of a proposed firewood harvesting/commercial logging exposure study. Samples were collected from three separate, heavily forested locations to simulate a probable amphibole fiber concentration gradient emanating from the mine (see Fig. 1). The first sampling site (Location 1) was approximately 100 yards from the former pump house site at the mine, serving as the anticipated high-concentration “hot” site. The second



Note: For scale, the distance between Locations 2 and 3 is approximately 4 miles.

Fig. 1. November 2004 sampling sites at the vermiculite mine site in Libby, MT. Note: for scale, the distance between Locations 2 and 3 is approximately 4 miles.

site (Location 2) was immediately outside of the mine property, approximately 4 miles from the bottom of Rainy Creek Road. This was our "mid" amphibole fiber concentration site. The final site (Location 3) was approximately 20 yards from the decontamination trailer and access gate for Rainy Creek Road, outside of the EPA restricted area (expected low-concentration site). A bark sample was also collected in Albany, NY, to serve as a control (no anticipated Libby amphibole fibers) sample.

On the basis of unexpectedly high fiber concentrations in the initial bark samples, a follow-up bark collection program was conducted in June 2005. This included expanding the program to collecting tree bark from areas west of Libby along the railroad line and from within the town of Libby. To date, only a subset of these additional samples have been analyzed, with the results presented in this manuscript.

At all sampling locations, bark was collected from representative coniferous tree types [lodgepole pine (*Pinus contorta*), ponderosa pine (*Pinus ponderosa*), larch (*Larix occidentalis*), and Douglas fir (*Pseudotsuga menziesii*)]. During the bark sampling, a pry-bar or spatula was used to collect a "chunk" (~200 g) of bark approximately 4 ft from the base of the tree, with samples then placed into labeled plastic bags. The spatula and pry-bar were wiped down after each sample collection with isopropyl alcohol and laboratory tissues. Tree core samples were only collected from the locations surrounding the mine in the initial sampling program. Tree core samples were collected at approximately 4 ft from the base of the tree using a hand-driven incremental borer. Each 12–15-in. core sample was immediately placed in a sterile plastic cylinder and then sealed in a large labeled plastic bag. The borer was wiped down after each sample collection with isopropyl alcohol and laboratory tissues. Global Positioning System (GPS) coordinates were collected at all of the sampling locations, with these coordinates used to plot sampling locations on an area map (Fig. 1). Each sample was provided a unique identifier and sent to the Wadsworth Center, New York State Department of Health in Albany, NY, for analysis.

At the Wadsworth Center, samples (or subsamples) of approximately 1 g were weighed, dried to stable mass at 60–100 °C, ashed at 450 °C and re-weighed to determine percentage loss of organic material. Residue

Table 1
Sample location and results

Sample point	Location, description	Type of tree	Amphibole fiber/gram bark	Analytical sensitivity [a] (fibers/gram)	Amphibole fiber/cm^2
Location 1, [b] sample 1A	Approximately 100 yards from the former pump house site at the W.R. Grace vermiculite mine	Lodgepole pine	530 million	28 million	100 million
Location 1, [b] sample 1B	Approximately 100 yards from the former pump house site at the W.R. Grace vermiculite mine	Lodgepole pine	330 million	21 million	260 million
Location 1, [b] sample 1D	Approximately 100 yards from the former pump house site at the W.R. Grace vermiculite mine	Larch	140 million	10 million	40 million
Location 2 [b]	4-mile mark (from bottom of Raney Creek Rd). Immediately outside of the mine property	Lodgepole pine	160 million	23 million	110 million
Location 3, sample 3B	Approximately 20 yards from the decontamination trailer and access gate for Raney Creek Rd. (outside of the restricted area)	Ponderosa pine	41 million	4.1 million	14 million
Location 3, sample 3C	Approximately 20 yards from the decontamination trailer and access gate for Raney Creek Rd. (outside of the restricted area)	Lodgepole pine	95 million fibers	10 million	54 million
Location 4	Albany, NY (control)	Pine	None detected	19 million	None detected
Location 5, sample 11	On the railroad line, approximately 7 miles west of Libby, MT	Ponderosa pine	19 million	1.2 million	5.8 million
Location 7, sample 18	Libby Middle School track	Douglas fir	0.13 million	0.13 million	0.25 million
Location 8, sample 23	Asa Wood Elementary School	Larch	None detected	0.42 million	None detected

[a] Based on one fiber detected.
[b] Locations 1 and 2 samples were collected within the EPA restricted area surrounding the mine site.

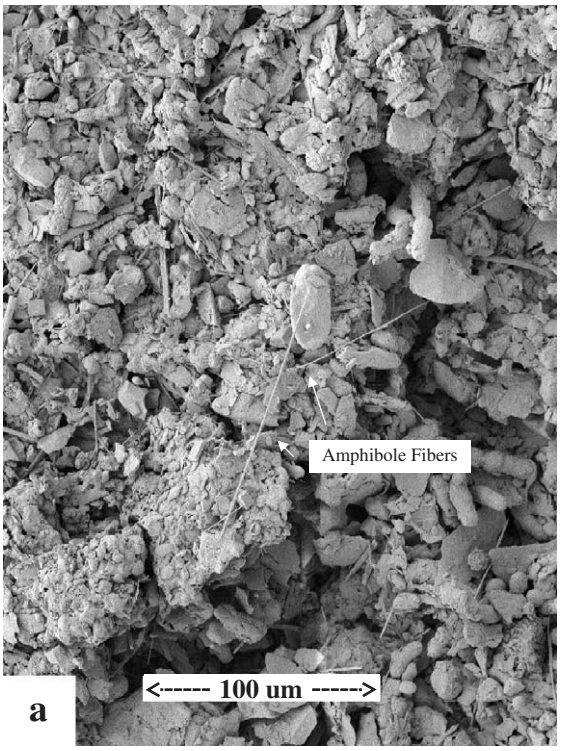


Fig. 2. Scanning electron micrographs of amphibole fibers on bark in Sample 1. Surface at 500× nominal magnification.

from one tree core sample was less than 0.5% of the original mass so additional preparation and analytical steps were not taken. Bark samples, typically with 5% post-ash residue, had ~1 g subsamples placed into a muffle furnace for 12–16 h. Residue was suspended in filtered deionized water and filtered through 0.1-μm polycarbonate filters before being prepared for transmission electron microscopy (TEM) analysis using carbon coating and ethylene-diamine dissolution onto TEM grids. TEM analysis was performed at a screen magnification of at least 15,000× on a Hitachi 7100 STEM interfaced to a PGT IMIX Image-Analyser/X-Ray Detector. Identification and measurement of fibers was conducted according to AHERA protocol (USEPA, 1987), with fibers identified by Energy-dispersive X-ray analysis (EDX) and Selected Area Electron Diffraction (SAED). Greater proportions of subsamples were analyzed for the June samples (city limit and railroad samples) to improve the analytical sensitivity needed for the generally lower fiber concentrations.

Intact bark samples were also examined by scanning electron microscopy (SEM) using a Leo 1550vp FEGSEM interfaced to a PGT Omega X-Ray Detector. Surfaces were coated with gold to promote conductivity and minimize charging.

3. Results

For the initial set of samples (November 2004) from the mine site, both core and bark samples were collected to investigate the potential mechanisms of amphibole fiber incorporation into trees. The lack of amphibole fibers in the tree core sample indicated that amphibole fibers were not taken up by the root system of the tree to be incorporated into the wood itself. Fibers found in the bark samples would support our hypothesis that fibers can become embedded on the outside of the trees by diffusion and/or impaction-type processes.

For the three different tree species located about 100 yards from the former pump house site at the vermiculite mine, all bark samples yielded substantial amphibole fiber concentrations (see Table 1). TEM analysis of bark from two lodgepole pines detected 19 amphibole fibers and 16 amphibole fibers in single grid openings, yielding concentrations of 530 million and 330 million amphibole fibers/g of bark. Bark from a larch tree at the same location yielded 140 million amphibole fibers/g, while bark from a lodgepole pine located 4 miles from the bottom of Rainy Creek Road yielded 160 million amphibole fibers/g. Bark samples collected near the

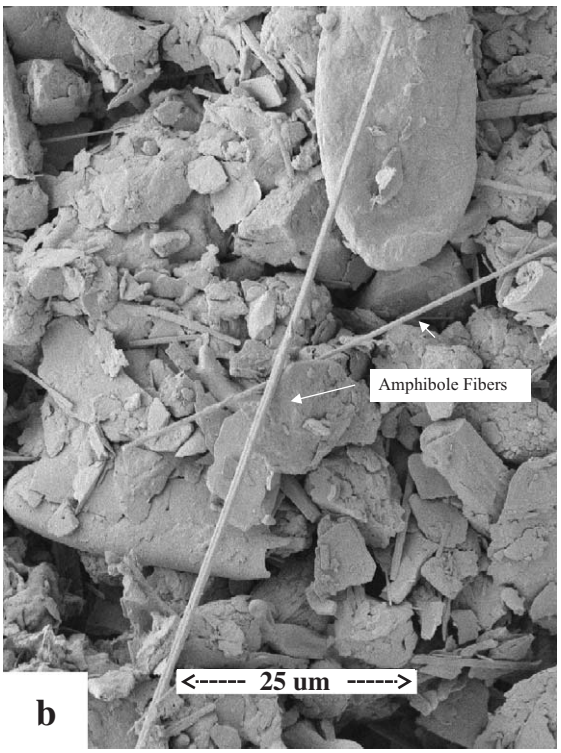


Fig. 3. Scanning electron micrographs of amphibole fibers on bark in Sample 1. Same field as Fig. 2, but at higher (2000× nominal) magnification.

decontamination trailer and access gate for Rainy Creek Road (directly outside of the EPA restricted area) yielded 41 and 95 million amphibole fibers/g, respectively. Simultaneous preparation and analysis of bark from a pine tree in Albany, NY, (control sample) produced no fibers at an analytical sensitivity of 19 million fibers/g.

Results from the second round of sampling (June 2005) collected approximately 7 miles west of Libby next to the railroad line revealed 19 million amphibole fibers/g of bark. Two additional samples collected within the Libby city limits yielded 0.13 million amphibole fibers/g (analytical sensitivity of 0.13 million fibers/g), and no fibers detected at an analytical sensitivity of 0.42 million fibers/g.

SEM observation revealed that the amphibole fibers were deposited on the surface of the bark and not through its depth. Most of the fibers were located in the crevices and wrinkles of the bark rather than on its smooth surfaces. In Figs. 2 and 3, note that the higher magnification image reveals thinner fibers. Continuation at even higher magnifications revealed correspondingly thinner fibers.

4. Discussion

One shortcoming of the laboratory protocol surfaced when a second preparation and analysis of the railroad-line sample (Location 5) yielded only 3 million amphibole fibers/g (vs. the earlier 19 million amphibole fibers/g). Reconstruction of the preparation revealed that the second subsample was much thicker and, therefore, included less exposed surface area per gram than the first subsample. This inclusion of unexposed bark effectively diluted the concentration of asbestos fibers on a mass basis. To standardize measurement units on a deposition-related basis, future preparation and analysis of bark samples should be based on the bark's exposed surface area (the gray, wrinkled outer part). To estimate this areal concentration, we determined that the exposed surface areas of bark subsamples we prepared were approximately 2 cm^2. We then divided the total number of fibers for each bark subsample by 2 cm^2 to produce the areal concentrations that are presented in the last column of Table 1.

Comparison of these areal concentrations to asbestos measured in settled dust in the United States portends the significance of the Libby bark contamination. Ewing (2000) discusses concentrations of surface dust found in a variety of settings and suggests that a concentration of 1000 structures (fibers)/cm^2 may be considered clean whereas concentrations exceeding 100,000 fibers indicate contamination. Concentrations on Libby bark near the mine were in the hundred million fibers per square centimeter range, concentrations that were measured infrequently in settled dust elsewhere, and only on surfaces under exposed asbestos-containing fireproofing. Any comparisons should be made with caution, however. The surfaces in previous investigations were generally smooth, and these smooth surfaces undoubtedly allow easier re-entrainment of asbestos than do the crevices of the bark in which most of the asbestos fibers were detected. Furthermore, the wrinkled/convoluted surface of the bark presented a much larger surface area than the nominal 2 cm^2.

Meeker et al. (2003) conducted the first comprehensive study on the Libby asbestos to determine the mineralogy and morphology of both fibrous and non-fibrous amphiboles, supporting the earlier results of Wylie and Verkouteren (2000) and Gunter et al. (2003). The composition of the Libby amphiboles indicated the presence of winchite, richterite, tremolite, and magnesioriebeckite, with the majority of structures displaying a gradient of morphologies between prismatic crystals and asbestiform fibers. Meeker et al. (2003) also showed that (for the most part) all of the vermiculite samples produced amphibole fibers in a similar size range, and that the fibril diameter of the Vermiculite Mountain asbestiform amphibole ranges from approximately 0.1 to 1 μm, with approximately 40% of the fibers longer than 5 μm. Results from the bark samples collected in this program showed that all identified fibers were typical of the Libby vermiculite amphibole contaminants, with standard elemental composition of Si>Mg>Ca>Fe>Na>K, mean length of 4.9 μm, and mean aspect ratio of 17.

5. Conclusion

From the samples collected and analyzed in and around the Libby area, we conclude that trees can serve as reservoirs for amphibole fibers. Amphibole fibers likely come in contact with trees through direct impaction-type processes such as wind-blown dust. These findings point to a potential fiber exposure to those who harvest timber or firewood from the contaminated areas in the Libby valley. The result of the railroad sample raises the possibility that the transportation corridors through which Libby vermiculite was hauled to other locations throughout the United States may also be contaminated. This suggests that similar studies of bark from trees near vermiculite processing sites across the country could be used to determine the extent of amphibole fiber contamination in those locales.

Our future studies will investigate the potential for exposure from disturbing contaminated bark and determining the spatial extent of airborne contamination from vermiculite-related point source operations in Libby. Future studies will also address the variability of fiber retention by the various tree species in the Libby area.

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