Appendix B
NOA Concentrations in Road Surfacing Material, Slodusty Road, Garden Valley, California

Introduction

As part of a study to identify potential sources of naturally occurring asbestos (NOA) releases to ambient air, the Department of Toxic Substances Control (DTSC) collected soil and road surfacing samples in August and September of 2000 from a road cut, two serpentine quarries, and roads in Garden Valley that were surfaced with serpentine rock, . The analysis results showed that the average concentration of NOA was approximately 2%. The study concluded that the roads in Garden Valley were the main source of asbestos found in ambient air samples. One road, Slodusty, was selected for a followup study to evaluate NOA emissions from a typical road surfaced with serpentine aggregate. The emissions study collected air samples at various distances from the road under various traffic conditions both before and after resurfacing the road. The road was resurfaced to eliminate the emissions of asbestos fibers. To improve our understanding of the relationship between NOA concentrations in surfacing material and NOA concentrations in air, samples of surface soil and aggregate were collected from Slodusty Road during the initial part of the study.

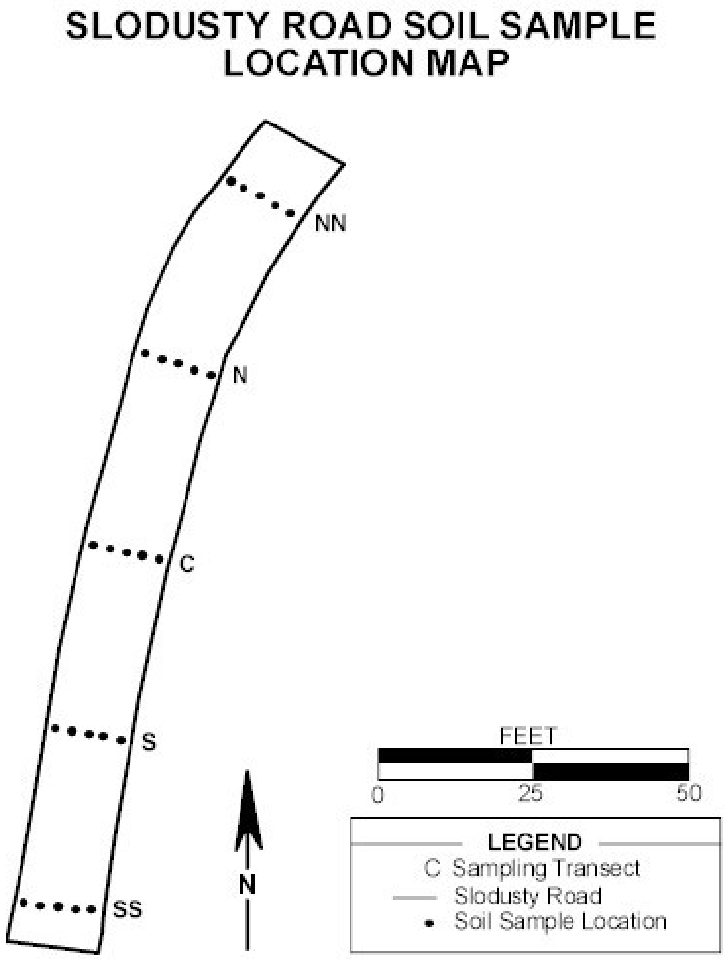
Two methods were chosen for analyzing the samples both using transmission electron microscopy (TEM) as the final analytical step: a conventional method (EPA/600/R-93/116) and a modified superfund method (EPA/540/R-97/028) referred to in this document as the Bulk Method and the Elutriator Method, respectively. Because the Elutriator Method requires a larger sample size to process, composites of five sampling points each were used for the Elutriator Method. For the Bulk Method the samples were discretely analyzed aftersubdividing by screening into less than 200 mesh particles and greater than 200 mesh particles. The finer particles were felt to be more representative of material that would enter the air during the study and the larger particles more representative of material released over time as the road was used.

The Elutriator Method was designed to measure asbestos that could be released into the air from soil. The method creates dust from the sample and collects it on a filter analogous to collecting air samples. The Bulk Method was designed to measure asbestos concentration in building materials and similar products. The soil is ground (milled) into smaller particles as necessary, dispersed in water, then filtered.

Sample Collection

Slodusty Road is a private road in the Garden Valley area maintained by individual homeowners. Prior to and during the initial emissions study, the road was surfaced with serpentine gravel. According to the residents, the gravel was obtained from local quarries about seven years prior to this study. At the time of the study the surface gravel had been well traveled, much of it reduced in size by the traffic. Travelers used the center of this narrow road resulting in parallel worn tire paths with a slight mounding of road material in the center and on the outer sides of the road. DTSC conducted an air study to measure the levels of asbestos in the air generated from the road during simulated traffic activity. This study and the results are described in a separate report. Bulk soil and aggregate samples from the road were tested to compare with the air monitoring results.

To get representative surface samples of the road, five transects, traversing the road, perpendicular to the traffic flow direction, were evenly spaced along the road segment being tested. Discrete samples were collected from each transect as follows: each of the tire paths (2 samples) and each of the mounded areas (3 samples). [Refer to diagram] Each discrete surface sample was collected in one quart plastic jars for a total of 25 samples. Each sample was composed of loose surface material and was dry. The depth of the material was usually no more than 1 to 2 inches and in places less than an inch. The samples were taken as scrapes at a right angle to the road direction using disposable plastic scoops that were disposed of after gathering an individual sample. The transects were spaced at 30 foot intervals covering a total linear road distance of 120 feet.



Sample Preparation

The samples were labeled, sealed in plastic bags, and initially stored in the evidence room at DTSC's Beatty Drive facility in Sacramento. All of the 25 samples were shipped under chain-of-custody to EMSL Analytical, Inc. in Westmont, New Jersey where each sample was dried for 24 hours at 65^{o} C then split into two portions using a riffle splitter. [Refer to diagram in Attachment 1] After each sample passed the splitter one half was saved as a discrete sample and the other half was allowed to accumulate in a second tray until five splits were collected then removed as a composite representing a road transect. The splitter was washed between each sample split.

The five composited samples, each representing a transect, were prepared for analysis according to the Elutriator Method [Superfund Method for Releasable Asbestos in Soils and Bulk Materials (EPA 540-R97-028) using the Modified Elutriator Method.[1]]. Each composite was sieved into less than 3/8" and greater

[1] Draft Modified Elutriator Method for the Determination of Asbestos in Soils and Bulk Material, Berman D. Wayne & Kolk, Anthony, May 23, 2000.

than 3/8" fractions and the dry weights for each fraction were recorded. The greater than 3/8" fraction was discarded. The superfund preparation was followed for the finer fraction and air samples were generated using an Elutriator unit. Several runs were performed for each sample to achieve an appropriate sample. A combination of experience and trial and error was used to obtain filters loaded near to but less than 10% or about 100 micrograms (ug) of dust. The run filters were directly prepared for Transmission Electron Microscope (TEM) analysis which included plasma ashing and carbon coating.

Each sample in the set of the 25 split samples was treated as an individual sample and not composited. Each sample was sieved into 2 fractions using a 200 mesh [75 micron (um)] sieve. The 200 mesh size is the smallest screen size that can sort particles by dry sieving. Particles passing through the 200 mesh sieve are most likely to become airborne. Each fraction was initially weighed and reported. The less than 200 mesh fraction was prepared using an indirect technique. Approximately 0.01 g of each sample was placed into 100 milliliter (ml) of deionized water in a plastic specimen cup where it was sonicated for 5 or more minutes. After sonication 1 to 5 ml was filtered with a 47 millimeter (mm) 0.2 um MCE filter then collapsed, plasma etched and carbon coated for TEM analysis. The greater than 200 mesh samples were shipped to ALS Chemex Laboratory in Sparks, Nevada for milling to grind particles to a size that will pass through a 200 mesh screen using a pulverizer equipped with a chrome steel ring set (lab method PUL-21[2]). These milled samples were returned to EMSL for indirect filter preparation and analysis.

Analytical Methodology

The 5 composite transect samples were analyzed by the Elutriator Method procedures. For each sample ISO 10312 counting rules were applied. To confirm visual identification of the fibers, a selected area electron diffraction micrograph (SAED) and an energy dispersive X-ray analysis (EDX) printout were obtained for each sample showing the typical diffraction pattern and mineral content of chrysotile asbestos. Results were reported, as per the method requirements, in Asbestos Structures/gram PM_{10} and Asbestos Structures/gram solid. PM_{10} refers to particle sizes up to 10 um in size that are detected by a standard air method (ref.: www.arb.ca.gov). Analytical sensitivities obtained were determined by filter loading, area analyzed, amount of respirable dust, and asbestos structures count. In some cases, the target analytical sensitivities could not be reached. The laboratory applied AHERA stopping rules that allowed stopping at a count of 50 asbestiform structures in a grid opening. Because of the many non protocol structures present, an insufficient number of protocol structures were counted to achieve the requested sensitivity and only 1 to 2 grids were counted. Protocol structures are asbestos structures specified in the method. [Protocol structures must be less than or equal to 0.5 um in diameter and greater than or equal to 5 um in length]

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[2] PUL-21: The entire sample is pulverized to better than 85% of the sample passing 75 microns.

The other 50 prepared samples were analyzed by the Bulk Method. For each sample, three areas were collected and analyzed from the filter (i.e., the center, the edge, and in between). The TEM analysis was performed by observing 6 to10 grid openings for each of the three TEM grids at 2,000x magnification, as well as three grid openings for each of the three TEM grids at 20,000x magnification. The mass of the observed fibers was then calculated[3]. Following extrapolation to the whole filter and to the whole mass of 0.01 grams, the asbestos percent value by weight was determined[4]. Fibers were individually sized or grouped. For filters with heavy loading, the lengths of small similarly sized fibers were added and calculated as a single mass. In addition, a SAED micrograph and EDX printout were obtained for each sample showing the presence of asbestos. Results were reported as percent asbestos by weight with a limit of quantification of 0.1%. All sample results were reported as above 0.1%.

Results

The analytical results are contained in attachment 2. The duplicate results are displayed below:

Duplicate Results				
Sample #	<200 Mesh	Duplicate Sample	Average	Relative % Difference*
S7	3.2%	3%	3.1%	6%
SS15	1.8%	1.3%	1.55%	32%
N20	0.6%	0.5%	0.55%	18%
			Ave. RPD =	**19%**
	>200 Mesh			
SS15	2.9%	1.4%	2.15%	70%
N18	0.6%	6.3%	3.45%	165%
NN24	2%	5.1%	3.55%	87%
			Ave. RPD =	**107%**

*RPD = $\frac{(sample - duplicate)}{average} X100\%$

Data Quality

Five of the six duplicates were considered as passing QC criteria by the laboratory. Sample N18 & its duplicate results were classed as fail. Lab blanks passed QC. Other internal laboratory checks, such as interanalyst control charts

[3] Mass of fibers/bundles = π/4 x length x diameter^2 x density x 10^{-6}; Mass of clusters/matrices = width x length x thickness x density x 10^{-6}. Measurements are in micrometer (µm). Densities: amphiboles = 3.0, chrysotile = 2.7.

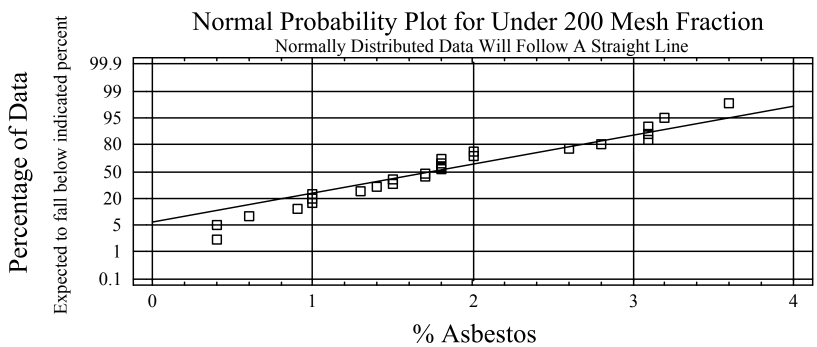
[4]

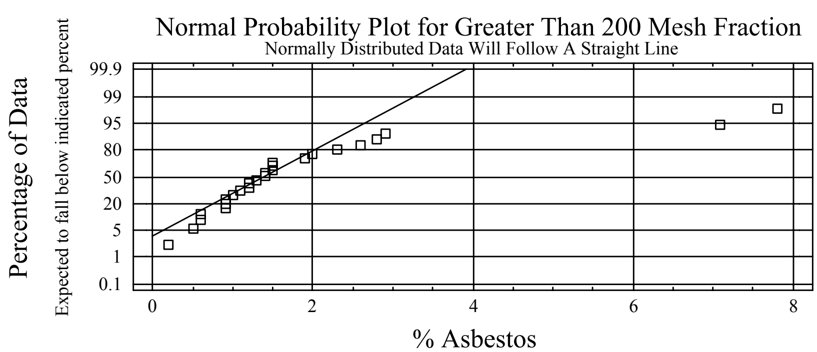
$$\% Asbestos = \left[total\ mass\ of\ asbestos\ x \frac{1295}{area\ analyzed}\ x \frac{100}{aliquot\ volume} \right] \Big/ \left(initial\ mass\ of\ sample\ x\ 0.01 \right)$$

and equipment performance checks were reported but not evaluated in this report.

Data Evaluation

The only asbestos type reported was chrysotile. No amphiboles were reported by either method involving two analysts. The average concentration of the 25 samples prepared by the bulk method was 1.9 % asbestos for both the less than 200 mesh and greater than 200 mesh fractions. The latter fraction displayed greater variability in the results. The less than 200 mesh fraction results appear to be normally distributed as shown by the cumulative normal probability plot (normally distributed data will form a straight line). The plot for the greater than 200 mesh shows two outliers that contained the highest concentrations reported.

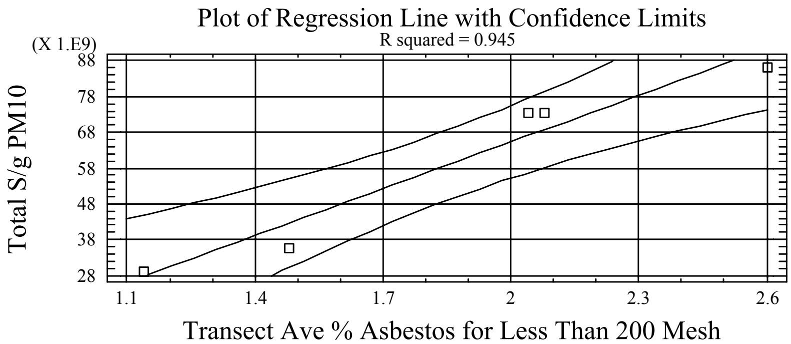




The superfund method produced the following averages:

Average Protocol structures per gram PM10 = 3.5×10^{9} (does not include one ND)
Average Asbestos structures per gram PM10 = 5.9×10^{10}
Average Protocol structures per gram solid = 1,148
Average Asbestos structures per gram solid = 22,498

There are an insufficient number of samples to perform adequate regression curves, but the less than 200 mesh fraction bulk results (averaged by transect) appear to track well with the average asbestos structures per gram PM10. The units are completely different, yet it is not unexpected that the <200 mesh fraction would be more likely to correlate with the PM10 fraction. The other paired regression combinations failed to show any significant correlation.



Method Differences

The Elutriator Method and the Bulk Method are very different methods. The sample through analysis scheme for the Slodusty Rd project is diagramed in attachment 1. The Superfund sample preparation method is considered a direct method because the dust is collected onto a filter and directly processed like an ambient air filter. The Bulk Method sample preparation places a subsample in water and sonicates it prior to filtering and is considered an indirect method. The indirect method results in more of the asbestos being broken into fibers. The direct method more or less results in the retention of bundles, clusters and other matrix forms as found in the original sample.

Once the sample is deposited on the filter the preparation for TEM analysis is essentially identical. The Elutriator Method filters are processed like air monitoring filters in accordance with ISO 10312. Specimens are taken from opposite wedges of the filter and analyzed. In the Bulk Method a portion is taken from the center, edge and in-between locations on the filter. In this case the Slodusty results were generated from a single wedge specimen in accordance with the laboratory's (EMSL) standard practice.

There are some differences in the counting rules which are primarily important for the Elutriator Method because of all the complex structures that appear on the filter and the sorting out of different types of fibers. The counting rules generally have the least effect on the outcome of the Bulk Method because the asbestos is more in fiber form following sonication. Fibers with an aspect ratio of 3:1 are counted in the Bulk Method as opposed to a 5:1 ratio by the ISO rules. This has little effect on the superfund protocol structures which must be less than 0.5 um wide and greater than 5 um long. The results reported for the Slodusty Road Study are for total structures, including all particles greater than 0.5 um long with a 3:1 aspect ratio or greater.

The raw asbestos count sheets using the ISO rules identify all of the particles observed in a detailed, systematic way. For instance, a dispersed cluster will be identified as a primary structure with the code CD followed by a two digit number. The first number indicates the total number of fibers and bundles within the cluster. The second number represents the number of fibers and bundles longer than 5 um. The overall dimensions of the cluster are measured and recorded. This is followed by a secondary count of the individual bundles and fibers within the cluster and the respective measurements of length and width. A fiber that is part of a cluster is designated CF while a free fiber, unassociated with a cluster, would be designated with the letter F. A hand drawn sketch is made of each of these structures.

The raw asbestos count sheets for the bulk method record the count of structures observed by width and length in accordance with the counting rules. The counting rules are referenced to the descriptions in “Analytical Method for Determination of Asbestos Fibers in Water” by E. J. Chatfield and M. Jane Dillon, 1983 (EPA600/4-83-043). The complex structures (aggregates, fibers attached to matrix, etc.) are not identified. Any fiber contained in the complex structures is counted as a fiber if the 3:1 aspect ratio is met. A bundle is counted as a fiber and the width is the estimated mean width of the bundle.

The two methods report asbestos content differently. The Superfund method reports total and long structures by type of asbestos according to a protocol. The fiber must be longer than 5 um and less than 0.5 um diameter. Long structures are those exceeding 10 um in length and less than 0.5 um diameter. All other structures are excluded. In this specific case all structures (greater than 0.5 um; 3:1 aspect ratio) were also reported by the lab. Thus the results are reported in units of the number of structures per gram of PM10 dust and structures per gram of total sample weight.

The bulk method reports percent by weight of asbestos. The volume is first calculated by adding the lengths of particles having the same width. The total length is then multiplied by the area of a circle having the width of the fiber class to determine the volume. The volume of each width class size is added and then multiplied by the density of the type of asbestos identified to determine the total weight of asbestos.

$$Weight\ of\ asbestos = (Total\ Lengths)\pi r^2 (Density)$$

<u>Conclusions</u>
The large number of variables involved in processing these samples precludes drawing many conclusions beyond presenting the results. For instance, the

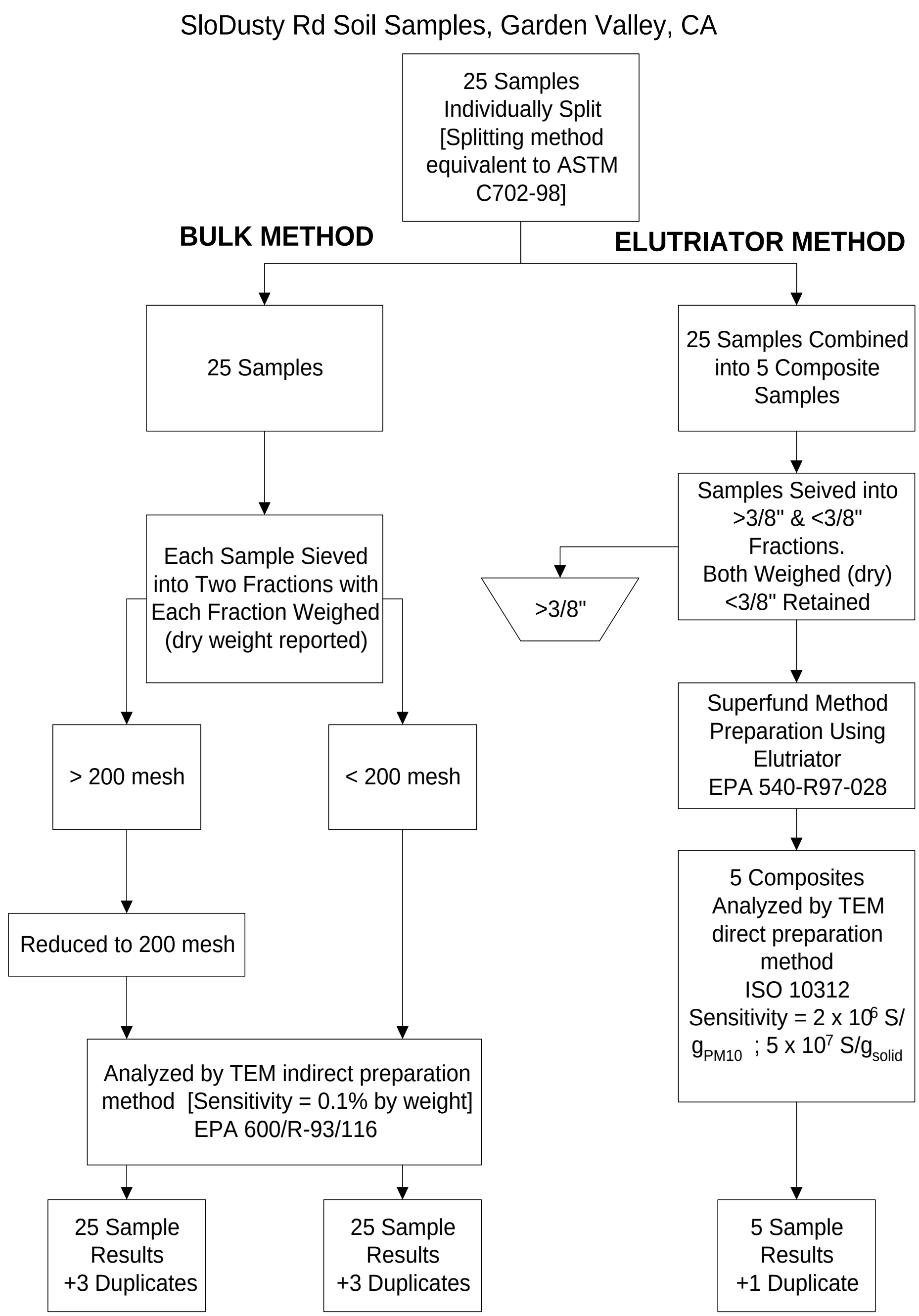
cause for the high variability noted for the greater than 200 mesh fraction is not clear. Possibilities for this variability may include:

- environmental variability,
- use of a second lab to mill the samples,
- the process of milling the larger particles

If future studies confirm that there is no significant difference in the overall results (1.9% in this case) between sieved and milled sample fractions, then it appears that simply sieving the samples will produce the more reproducible results, especially when smaller numbers of samples are collected.

The potential strong correlation between the bulk method and the superfund PM10 fraction suggested by the data is interesting. Further studies are needed on a larger array of samples to determine if there is a statistically significant correlation. It is important to note that this is a correlation with total structures per gram PM10 and not the protocol structures which may be most important for risk assessment.

Attachment 1: Analytical Flowchart



Attachment 2: Analytical Results

Sample ID	Bulk Method: <200 Mesh		>200 Mesh		Transect Ave. % Asbestos <200 Mesh		Transect Ave. % Asbestos >200 Mesh		Elutriator Method: Protocol Structures/ gram PM10	Total Structures/ gram PM10	Protocol Structures/ gram Solid	Total Structures/ gram Solid
C1	0.4	%	1.3	%								
C2	1.4	%	1.2	%								
C3	0.9	%	0.6	%								
C4	2	%	0.9	%								
C5	1	%	0.2	%	1.14	%	0.84	%	3.74E+09	2.89E+10	1.27E+03	9.79E+03
S6	1.3	%	0.5	%								
S7	3.2	%	1.2	%								
S8	3.1	%	1.1	%								
S9	2.8	%	1.4	%								
S10	2.6	%	2.3	%	2.6	%	1.3	%	<1.09E9	8.60E+10	3.33E+02	2.63E+04
SS11	1.7	%	1.5	%								
SS12	2	%	1.5	%								
SS13	1.8	%	0.9	%								
SS14	3.1	%	2.8	%								
SS15	1.8	%	2.9	%	2.08	%	1.92	%	4.05E+09	7.36E+10	2.13E+03	3.88E+04
N16	1.5	%	2.6	%								
N17	1.7	%	1	%								
N18	1.8	%	0.6	%								
N19	1.8	%	7.1	%								
N20	0.6	%	1.4	%	1.48	%	2.54	%	1.04E+09	3.57E+10	4.45E+02	1.54E+04
NN21	1	%	1.5	%								
NN22	3.1	%	0.9	%								
NN23	3.6	%	1.9	%								
NN24	1.5	%	2	%								
NN25	1	%	7.8	%	2.04	%	2.82	%	5.15E+09	7.34E+10	1.56E+03	2.22E+04

The Superfund method was performed on samples that were physical composites of the individual transect samples. The Bulk method transect results are the mathematical averaging of individual samples in a transect (ex.: sum of C1 through C5 divided by 5 equals 1.14% for <200 mesh).

Elutriator Method Detailed Results

Transect	Sample Mass Breakdown (g)		Total Asbestos Structures >0.5 um length 3:1 aspect		Reported Asbestos Structures		Normally Excluded Asbestos Structures
	>3/8”	<3/8”			Protocol >5 um L; <0.5 um W	Long >10 um L	
C	73.29	1619.83	54 Total	1 Long	7	0	47
S	226.98	1510.94	79 Total	0 Long	0	0	79
SS	266.12	1943.67	91 Total	1 Long	4	1	86
N	230.67	1809.74	69 Total	0 Long	2	0	67
NN	214.67	1810.61	57 Total	1 Long	3	1	53
NN(QC)	214.67	1810.61	51 Total	1 Long	1	0	50

Transect C: Structures/gram PM10	Mean	95% UCL
Total Chrysotile Protocol Structures	3.74E+09	7.34E+09
Long Chrysotile Protocol Structures	<5.35E+08	<1.05E+09
Total Amphibole Protocol Structures	<5.35E+08	<1.05E+09
Long Amphibole Protocol Structures	<5.35E+08	<1.05E+09
Long Asbestos Protocol Structures	<5.35E+08	<1.05E+09
Total Asbestos Protocol Structures	3.74E+09	7.34E+09
Total Asbestos Structures	2.89E+10	5.66E+10
Long Asbestos Structures	5.35E+08	1.05E+09
Estimated Sensitivity	5.35E+08	1.05E+09

Transect C: Structures/gram Solid	Mean	95% UCL
Total Chrysotile Protocol Structures	1.27E+03	2.49E+03
Long Chrysotile Protocol Structures	<1.81E+02	<3.55E+02
Total Amphibole Protocol Structures	<1.81E+02	<3.55E+02
Long Amphibole Protocol Structures	<1.81E+02	<3.55E+02
Long Asbestos Protocol Structures	<1.81E+02	<3.55E+02
Total Asbestos Protocol Structures	1.27E+03	2.49E+03
Total Asbestos Structures	9.79E+03	1.92E+04
Long Asbestos Structures	1.81E+02	3.55E+02
Estimated Sensitivity	1.81E+02	3.55E+02

Transect S: Structures/gram PM10	Mean	95% UCL
Total Chrysotile Protocol Structures	<1.09E+09	<2.13E+09
Long Chrysotile Protocol Structures	<1.09E+09	<2.13E+09
Total Amphibole Protocol Structures	<1.09E+09	<2.13E+09
Long Amphibole Protocol Structures	<1.09E+09	<2.13E+09
Long Asbestos Protocol Structures	<1.09E+09	<2.13E+09
Total Asbestos Protocol Structures	<1.09E+09	<2.13E+09
Total Asbestos Structures	8.60E+10	1.68E+11
Long Asbestos Structures	<1.09E+09	<2.13E+09
Estimated Sensitivity	1.09E+09	2.13E+09

Transect S: Structures/gram Solid	Mean	95% UCL
Total Chrysotile Protocol Structures	3.33E+02	<6.52E+02
Long Chrysotile Protocol Structures	3.33E+02	<6.52E+02
Total Amphibole Protocol Structures	3.33E+02	<6.52E+02
Long Amphibole Protocol Structures	3.33E+02	<6.52E+02
Long Asbestos Protocol Structures	3.33E+02	<6.52E+02
Total Asbestos Protocol Structures	3.33E+02	<6.52E+02
Total Asbestos Structures	2.63E+04	5.15E+04
Long Asbestos Structures	3.33E+02	<6.52E+02
Estimated Sensitivity	3.33E+02	6.52E+02

Transect SS: Structures/gram PM10	Mean	95% UCL
Total Chrysotile Protocol Structures	4.05E+09	7.93E+09
Long Chrysotile Protocol Structures	8.09E+08	1.59E+09
Total Amphibole Protocol Structures	<8.09E+08	<1.59E+09
Long Amphibole Protocol Structures	<8.09E+08	<1.59E+09
Long Asbestos Protocol Structures	8.09E+08	1.59E+09
Total Asbestos Protocol Structures	4.05E+09	7.93E+09
Total Asbestos Structures	7.36E+10	1.44E+11
Long Asbestos Structures	8.09E+08	1.59E+09
Estimated Sensitivity	8.09E+08	1.59E+09

Transect SS: Structures/gram Solid	Mean	95% UCL
Total Chrysotile Protocol Structures	2.13E+03	4.18E+03
Long Chrysotile Protocol Structures	4.26E+02	8.36E+02
Total Amphibole Protocol Structures	<4.26E+02	<8.36E+02
Long Amphibole Protocol Structures	<4.26E+02	<8.36E+02
Long Asbestos Protocol Structures	4.26E+02	8.36E+02
Total Asbestos Protocol Structures	2.13E+03	4.18E+03
Total Asbestos Structures	3.88E+04	7.60E+04
Long Asbestos Structures	4.26E+02	8.36E+02
Estimated Sensitivity	4.26E+02	8.36E+02

Transect N: Structures/gram PM10	Mean	95% UCL
Total Chrysotile Protocol Structures	1.04E+09	2.03E+09
Long Chrysotile Protocol Structures	<5.17E+08	<1.01E+09
Total Amphibole Protocol Structures	<5.17E+08	<1.01E+09
Long Amphibole Protocol Structures	<5.17E+08	<1.01E+09
Long Asbestos Protocol Structures	<5.17E+08	<1.01E+09
Total Asbestos Protocol Structures	1.04E+09	2.03E+09
Total Asbestos Structures	3.57E+10	7.00E+10
Long Asbestos Structures	<5.17E+08	<1.01E+09
Estimated Sensitivity	5.17E+08	1.01E+09

Transect N: Structures/gram Solid	Mean	95% UCL
Total Chrysotile Protocol Structures	4.45E+02	8.72E+02
Long Chrysotile Protocol Structures	<2.23E+02	<4.36E+02
Total Amphibole Protocol Structures	<2.23E+02	<4.36E+02
Long Amphibole Protocol Structures	<2.23E+02	<4.36E+02
Long Asbestos Protocol Structures	<2.23E+02	<4.36E+02
Total Asbestos Protocol Structures	4.45E+02	8.72E+02
Total Asbestos Structures	1.54E+04	3.01E+04
Long Asbestos Structures	<2.23E+02	<4.36E+02
Estimated Sensitivity	2.23E+02	4.36E+02

Transect NN: Structures/gram PM10	Mean	95% UCL
Total Chrysotile Protocol Structures	5.15E+09	1.01E+10
Long Chrysotile Protocol Structures	1.29E+09	2.53E+09
Total Amphibole Protocol Structures	<1.29E+09	<2.53E+09
Long Amphibole Protocol Structures	<1.29E+09	<2.53E+09
Long Asbestos Protocol Structures	1.29E+09	2.53E+09
Total Asbestos Protocol Structures	5.15E+09	1.01E+10
Total Asbestos Structures	7.34E+10	1.44E+11
Long Asbestos Structures	1.29E+09	2.53E+09
Estimated Sensitivity	1.29E+09	2.53E+09

Transect NN: Structures/gram Solid	Mean	95% UCL
Total Chrysotile Protocol Structures	1.56E+03	3.05E+03
Long Chrysotile Protocol Structures	3.89E+02	7.62E+02
Total Amphibole Protocol Structures	<3.89E+02	<7.62E+02
Long Amphibole Protocol Structures	<3.89E+02	<7.62E+02
Long Asbestos Protocol Structures	3.89E+02	7.62E+02
Total Asbestos Protocol Structures	1.56E+03	3.05E+03
Total Asbestos Structures	2.22E+04	4.34E+04
Long Asbestos Structures	3.89E+02	7.62E+02
Estimated Sensitivity	3.89E+02	7.62E+02