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PRELIMINARY STUDIES OF ASBESTIFORM FIBERS IN DOMESTIC WATER SUPPLIES

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Major technical areas discussed included ecosystem modeling, water pollution, water reuse, toxic hazards evaluation of fire extinguishants, environmental carcinogenesis, and cellular toxicology.

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PAPER NO. 5

PRELIMINARY STUDIES OF ASBESTIFORM FIBERS IN DOMESTIC WATER SUPPLIES

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INTRODUCTION

It has been evident for some years that there exists a strong positive association between inhaled asbestos fibers and carcinoma of the lung (NIOSH, 1972; Selikoff, 1965 and 1967). This association has been particularly notable in occupational groups such as insulation workers employed in industrial environments having high concentrations of asbestos fibers. An even more dramatic phenomenon is the increased number of rare pleural mesotheliomas among these workers. Selikoff (1973) has presented data which indicate that the incidence of some abdominal cancers, including peritoneal mesothelioma, is also greatly increased (more than three-fold) among asbestos workers.

If asbestos fibers are carcinogenic, they may well be expected to act as carcinogens by various routes of entry into the body, including the oral route. Recently, Pontefract and Cunningham (1973) presented data which gave some evidence that asbestos fibers pass through the gut and into the organs of experimental animals.

A potential source of exposure to asbestos fibers which could be ingested is through municipal drinking water supplies. Such supplies may be contaminated with asbestos from industrial operations or naturally in supplies which are collected from and maintained in reservoirs and aquifers which are exposed to serpentine or other geologic formations which contain asbestos.

The presence of asbestos fibers in drinking water supplies, located in Ottawa and Montreal, Canada, has been reported by Cunningham and Pontefract in 1971. In this instance filtered water was reported to contain from 2.9 x 10^6 to 5.9 x 10^6 asbestos fibers per liter and unfiltered (raw) water was proportionately higher. More recently, Cook et al. (1974) have reported the presence of 1 to 30 million amphibole asbestos fibers per liter in the city of Duluth water supply. In this latter instance the source of the asbestos was from a nearby milling operation.

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In this paper we wish to report upon the results obtained in the analysis of numerous drinking water sources for asbestiform fibers in the United States, with emphasis on Northern California. In this effort we have developed a technique for asbestos analysis which seems to compare favorably with the results of others who are using a similar methodology. The development of an acceptable standard method of analysis is essential to the conduct of a rational epidemiological assessment of the impact of asbestiform fibers in drinking water supplies upon human health.

METHODS

Samples were collected from the various water sources by the authors, representatives of the Environmental Protection Agency, or by employees of the various water districts involved. All of these were grab samples ranging from 1 to 4 liters in volume.

The method of analysis for the presence of asbestos fibers required concentration of the sample by filtration and the examination of the concentrate using the Siemens Elmiskop I or IA Electron Microscope. A measured amount of sample was filtered through a sequence of 0.47 mm diameter, 0.8μ and 0.2μ pore size, polycarbonate Nuclepore filters (Nuclepore Corporation, Pleasanton, California). Both filter sizes were necessary in order to facilitate filter rates and to capture small fibers. The ultimate amount of water filtered was proportional to the original turbidity of the collected samples; normally from 300 to 1000 ml of sample were filtered.

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A pseudo-replica was made of the particulates concentrated on the filters by coating them with silicon monoxide in a high-vacuum optical coater. A 1/8 inch diameter disc was cut from the coated filter with a sharp boring tool and mounted, coated side down, on a 200-mesh nickel electron microscope grid previously placed on top of a block of polyurethane soaked in chloroform. A small petri dish is used to hold the polyurethane and chloroform. The Nuclepore filter is dissolved by the chloroform by wick action through the pores of the SiO replica on the filter surface. The replica is left on the grid with the particles and fibers on top of the SiO substrate. The latter process takes from 4 to 6 hours. At the end of this time, the prepared grids are ready for electron microscopy.

The Siemens Elmiskop Electron Microscope was operated at 100 KV. The fibers were counted and sized directly on the microscope viewing screen on which was ruled a 1 cm^2 grid with 2 mm intervals. The magnification used for sizing and counting was 2000 and/or 20,000X. For identification of fibers by morphology and electron diffraction, the magnification used was 20,000X. At this magnification selected area diffraction can be used to obtain the electron diffraction pattern of a crystal or group of crystals. This pattern is usually a spot pattern which is characteristic of various types of material.

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Fibers were counted and recorded for each of 5 to 20 fields in a 200-mesh specimen grid. A field is defined as a single opening in the specimen grid. The ratio of the total number of fields in a grid to the number of fields counted is used in the calculation of the number of fibers on the whole grid. The total number of openings in a grid was determined using a photographic enlargement of an electron microscope grid. A fiber was defined as a particle whose length was at least 3 times its diameter.

RESULTS

Using the described method 19 samples of water from California, 5 from Houston, Texas, 1 from Wisconsin, and 9 from Duluth, Minnesota, were examined for their asbestiform fiber content. The results of these examinations are shown in Tables 1 and 2.

TABLE 1. ASBESTOS FIBER ANALYSIS OF VARIOUS WATER SOURCES IN CALIFORNIA

Geographic Area	Sample Date	Sample Source	Treatment	Fiber Count Millions of fibers/liter Chrysotile
Marin Co.	2/73	Lake A (Rainy Season)	Raw	200
Marin Co.	2/73	Stream into Lake B (Rainy Season)	Raw	Present(1)
Marin Co.	2/73	Lake C (Rainy Season)	Raw	Present
Marin Co.	2/73	Lake A (Rainy Season)	Coag., filtered	Not analyzed due to presence of colloid
Marin Co.	7/73	Lake A (Dry Season)	Raw	0.3
Marin Co.	7/73	Lakes A & B (Dry Season)	Raw	0.5
San Francisco Co.	7/73	Office Bldg. Tap (from Crystal Springs Res.; Hetch Hetchy Syst)	Not Coag., not filtered	1.0
San Francisco Co.	7/74	Office Bldg. Tap (from Crystal Springs Res.; Hetch Hetchy Syst)	Not Coag., not filtered	0.2

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TABLE 1 (Continued)

Geographic Area	Sample Date	Sample Source	Treatment	Fiber Count Millions of fibers/liter Chrysotile
Alameda Co.	7/74	Filter Plant Effluent	Coag., filtered	---
Alameda Co.	7/74	Treatment Plant Effluent	Not Coag., not filtered	---
Contra Costa Co.	7/74	Filter Plant Effluent	Coag., filtered	---
Burlingame City	7/74	Tap-Lateral Hetch Hetchy, Crystal Springs	Not Coag., not filtered	---(2)
Redwood City	7/74	Tap-Calavaras Lake (Surface and/or Hetch Hetchy), infiltration gallery	Not Coag., not filtered	---
Millbrae City	7/74	Tap-San Andreas Res, local surface water	Not Coag., not filtered	---
Lawrence Livermore Laboratory	5/74	Tap in Lab., Hetch Hetchy before Crystal Springs	Not Coag., not filtered	---
San Jose City	7/74	Tap-groundwater	Not Coag., not filtered	---
Southern Calif.	7/74	Effluent-Filter Plant A, SWP(3)	Coag., filtered	---
Southern Calif.	7/74	Effluent-Filter Plant B, CRA(4)	Coag., filtered	---
Southern Calif.	7/74	Effluent-Filter Plant C, CRA	Coag., filtered	---

(1) Fibers could not be counted because of gross amounts of turbidity present in sample.
(2) Fibers not detected.
(3) Water originates from the California State Water Project.
(4) Water originates from the Colorado River.

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TABLE 2. ASBESTOS FIBER ANALYSIS OF VARIOUS WATER SOURCES OUTSIDE OF CALIFORNIA

Geographic Area	Sample Date	Sample Source	Treatment	Fiber Count Millions of fibers/liter Amphibole
Houston, Texas	7/73	Water Syst. A groundwater		---(1)
Houston, Texas	7/73	Water Syst. B groundwater		---
Houston, Texas	7/73	Water Syst. C groundwater		---
Houston, Texas	7/73	Water Syst. D groundwater		---
Houston, Texas	7/73	Water Syst. E groundwater		---
Silver Bay, Minnesota	7/73	Lake Superior	Not Coag., not filtered	2
Beaver Bay, Minnesota	7/73	Lake Superior	Not Coag., not filtered	3
Two Harbors, Minnesota	7/73	Lake Superior	Not. Coag., not filtered	2.5
Duluth, Minnesota	7/73	Lake Superior, Dist. Syst. 1	Not Coag., not filtered	5
Duluth, Minnesota	7/73	Lake Superior Dist. Syst. 2	Not Coag., not filtered	2
Duluth, Minnesota	7/73	Lake Superior Dist. Syst. 3	Not Coag., not filtered	1
Duluth, Minnesota	7/73	Lake Superior Dist. Syst. 4	Not Coag., not filtered	1
Duluth, Minnesota	4/74	Lake Superior spring turnover	Not Coag., not filtered	10

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TABLE 2 (Continued)

Geographic Area	Sample Date	Sample Source	Treatment	Fiber Count Millions of fibers/liter Amphibole
Duluth, Minnesota	4/74	Lake Superior spring turnover	Not Coag., not filtered	8
Ashland, Wisconsin	7/73	Groundwater	Not Coag., not filtered	---

(1) No fibers detected.

Samples of water taken from the San Francisco Bay Area (Marin Co., San Francisco Co., Alameda Co., Burlingame City, Redwood City, Millbrae City, San Jose City, and the Lawrence Livermore Laboratory; see Figure 1) originate from sources both indigenous to the area and from sources outside the area. The Marin County water source is from local runoff collected in lakes located in areas which include a good deal of sheared (friable) serpentine rock. These waters contained from 300,000 to 200 million chrysotile fibers per liter, the latter in the dry season and the former during the wet time of the year. The majority of San Francisco County water originates in the granitic Sierra Nevada Mountains near Yosemite (Hetch Hetchy Reservoir) and is stored, along with local water, in the Crystal Springs Reservoir. This latter lake is situated in a serpentine area.

Only 2 samples were taken from the San Francisco system, and these were taken a year apart (both during the dry season). The first sample contained 1 million fibers per liter while the subsequent sample was an order of magnitude less. A good deal of highway construction was underway along the edge of this lake from 1965 until early 1974, and the occurrence of these chrysotile fibers may well have resulted from the disturbance caused by the construction effort. It is interesting to note that the Lawrence Livermore Laboratory water, the source of which is Hetch Hetchy water before it reaches Crystal Springs, had no detectable fibers present ($< 1 \times 10^4$ fibers/liter). It is also of interest that Millbrae City water, which originates in the San Andreas Reservoir located just north of Crystal Springs (See Figure 1), contained no detectable asbestiform fibers ($< 2 \times 10^4$ fibers/liter). In this instance the local geological formation is more Franciscan than ultrabasic (just the reverse of Crystal Springs), as one might suspect a less pronounced source of chrysotile asbestos fibers. No fibers were detected ($< 2 \times 10^4$ fibers/liter) in either Redwood City or the City of Burlingame's water supply. Both these districts receive Hetch Hetchy water, and the latter may or may not receive Crystal Springs water depending upon the operational mode of the system.

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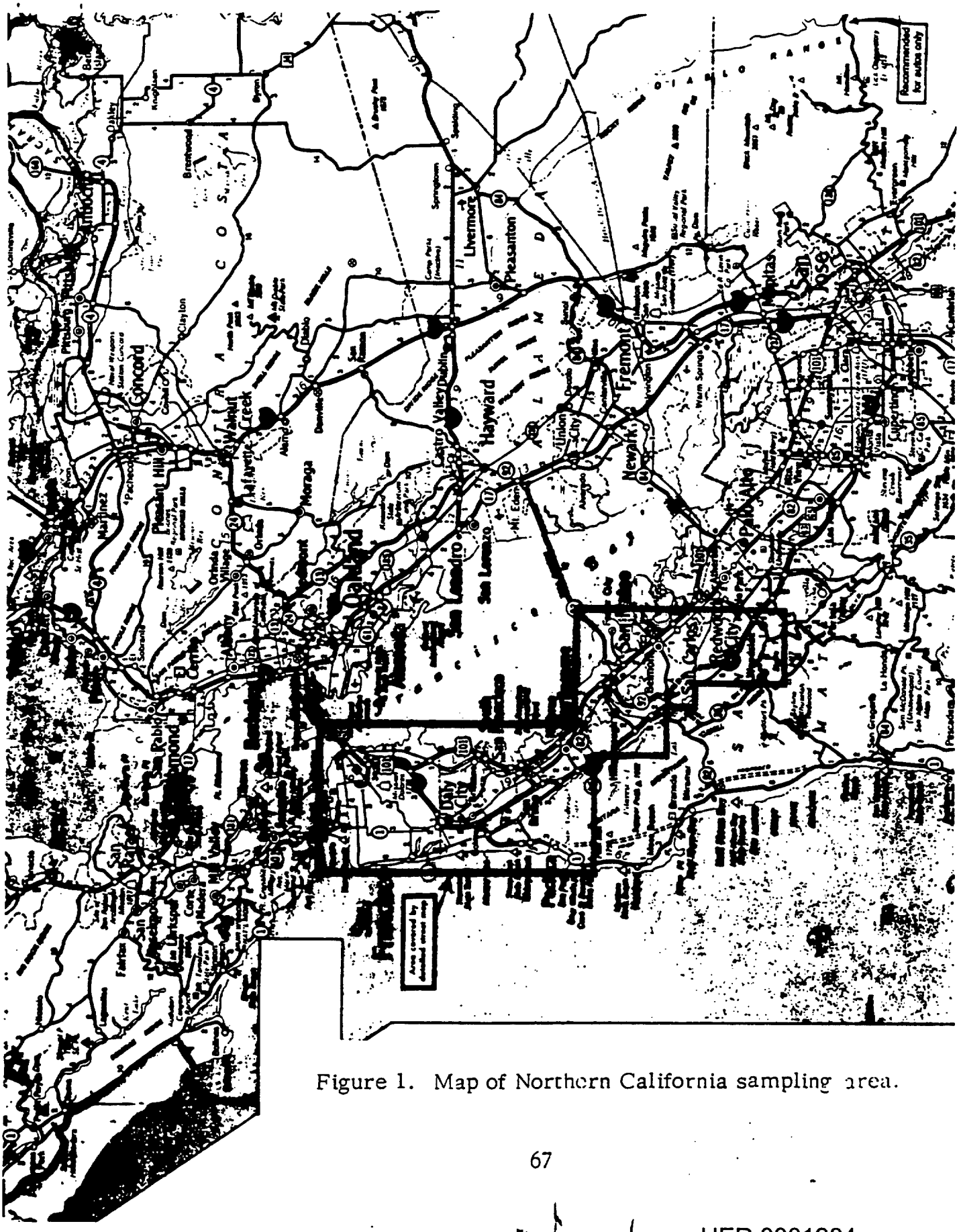

Figure 1. Map of Northern California sampling area.

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San Jose City water supply is from a local groundwater source and no fibers were detected (<1 x 10^4 fibers/liter). Water samples from Alameda and Contra Costa Counties (San Francisco East Bay Area) contained no detectable fibers (<1 x 10^4 to 4 x 10^4 fibers/liter). None of the sources are associated with obvious serpentine formations. The samples from Southern California were from either the State Water Project or from the Colorado River and had all received complete water treatment including coagulation and filtration; these were all negative (<1 to 2 x 10^4 fibers/liter).

Results from samples taken from areas outside of California are shown in Table 2. Groundwater from Houston, Texas and from Ashland, Wisconsin were found to be negative (<1 to 4 x 10^4 fibers/liter). All the samples originating in Lake Superior (Silver Bay, Beaver Bay, and Two Harbors) and those used in the Duluth water system were found to be positive ranging from 1 x 10^6 to 10 x 10^6 fibers per liter. All of these fibers were identified as amphibole asbestos (Grunerite-Cummingtonite). Eighty-five percent of these fibers ranged from 0.1 to 0.5μ in diameter by 0.5 to 3.0μ in length. The remainder were 0.5 to 1.0μ in diameter by 4.0 to 7.0μ in length. These originated from Taconite milling operations about 40 miles northeast of Duluth.

The asbestos found in California waters was identified as chrysotile with fibers 2 to 10μ long and about 0.03μ in diameter for single fibers and bundles of fibers 0.5 to 1.0μ in diameter (see Figures 2 and 3 for examples of these fibers seen in water).

The results obtained using the electron microscope method herein described appear compatible with the results reported from Lake Superior by Cook et al. (1974) who used a different method of sample preparation. We also had the opportunity to analyze samples collected by the Environmental Protection Agency which were simultaneously analyzed by Mr. Ian Stewart of McCrone Associates, Inc. (Chicago, Illinois). The latter used a method similar to ours except that a millipore filter was used (Millipore Filter Corporation, Massachusetts) to concentrate the sample and a collodion-covered, carbon-coated grid was used for the pseudo-replicate and the membrane filter dissolved with acetone in a soxhlet apparatus. The comparative results are shown in Table 3.

TABLE 3. COMPARISON OF ANALYTICAL RESULTS OBTAINED BY TWO LABORATORIES USING VARIATIONS OF THE ELECTRON MICROSCOPIC METHOD

Water Source	Univ. of Calif. Method*	McCrone Method*
Silver Bay, Minnesota	2.0	4.4
Beaver Bay, Minnesota	3.0	5.3
Two Harbors, Minnesota	2.0	2.5
Duluth, Minnesota	5.0	2.8
Houston, Texas	None detected	None detected

*Measured in million fibers per liter.

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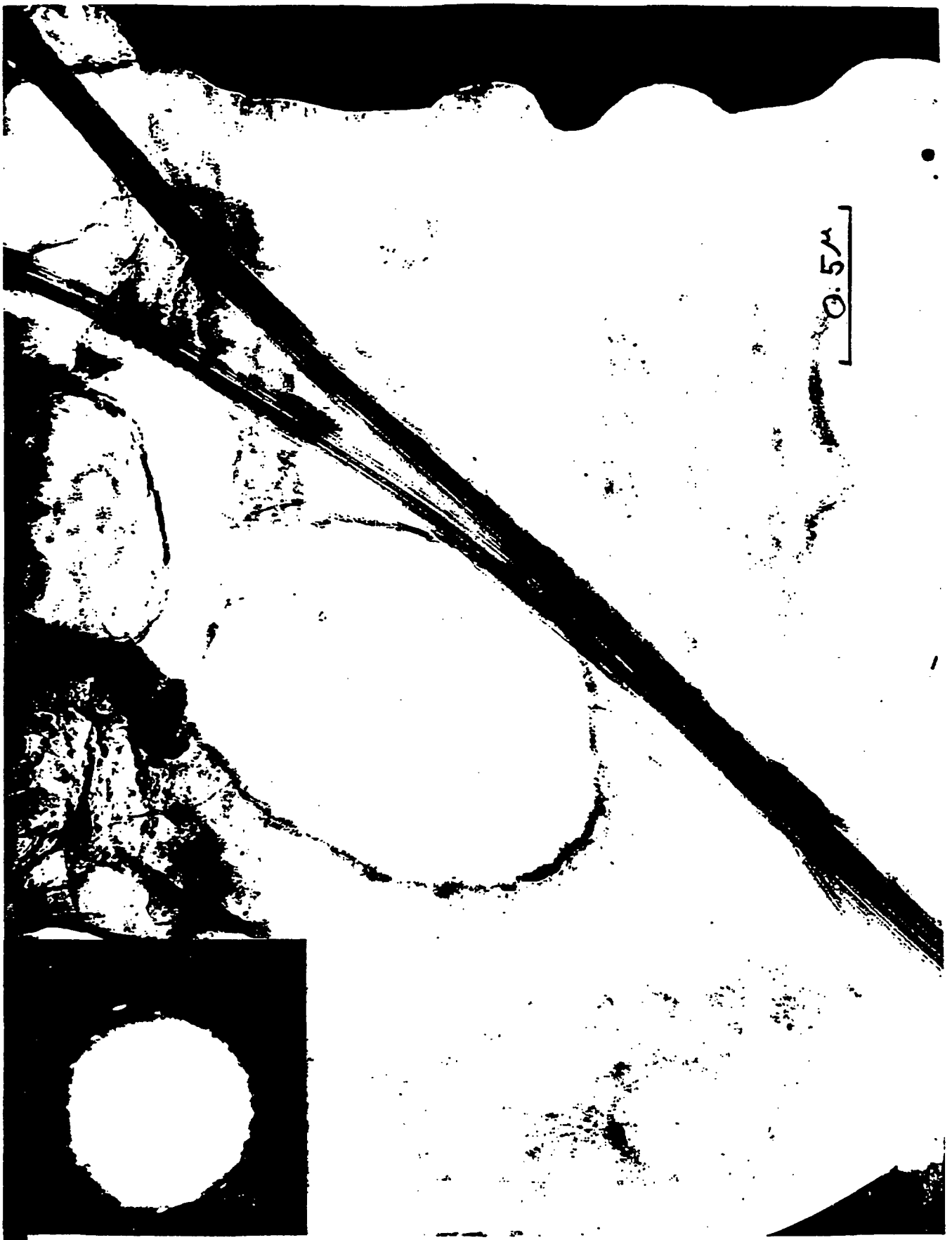

Figure 2. Electron photomicrograph of chrysotile asbestos fiber found in a Northern California raw water supply



Figure 3. Electron photomicrograph of amphibole asbestos fibers found in Lake Superior water.

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As can be seen in Table 3, there is good agreement between the two laboratories.

DISCUSSION

The method developed in our laboratory for the electron microscopic analysis for asbestiform fibers in natural waters appears to be a satisfactory analytical tool. The results obtained using this method agree reasonably with the results of analyses reported by others using variations of the electron microscopic approach. We feel it is preferable to the other methods thus far developed because it is the simplest to perform and disturbs the sample less than methods which require ashing, sonication, and/or centrifugation prior to enumeration. Light microscopic techniques, such as are often used in the analysis of air for fibrous material, are unsatisfacory in the analysis of water for these substances because of the relatively large amounts of extraneous material present. With the electron microscope, even used at light microscope magnification levels, the resolution is much greater, which is important in defining the morphology of fibers particularly when they are mixed with a variety of debris and microplankton. Also, the capability to obtain selected area electron diffraction patterns for crystal identification is not available with the light microscope.

The major limitation of all the methods presently employed is the restricted volume of water which can be filtered through fine-pore filters within a reasonable time. Because of the frequent presence of much extraneous matter, particularly in raw water, the technician is usually limited to processing a liter or less. This, of course, in turn limits the sensitivity of detection of fibers to no less than 100,000 fibers per liter of the original sample.

The results of our analysis of waters from various areas of the country are certainly preliminary. The numbers of samples taken from each supply have been limited and these have been isolated (grab) samples only. It would be of far more value if these samples were composited over time and we hope that funds will become available to allow such sampling of selected supplies. However, even with these imposed limitations, the results obtained have been most instructive of the distribution and types of asbestiform fibers found in water supplies. The samples taken from Lake Superior in the Duluth, Minnesota region contained fibers identified as amphibole asbestos, whose origin was from an industrial operation. The numbers we found were similar to those reported by Cook et al. (1974). We became interested in the potential introduction of asbestos fibers from natural sources, prior to the national concern about the Duluth situation, when we became aware that certain water impoundments were located in areas which contained large outcroppings of serpentine rock. Our analyses results from the various Northern California water supplies certainly indicate that water thus exposed can contain considerable amounts of chrysotile asbestos

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fibers, equivalent or even greater in number than amounts of amphibole fibers found in the Duluth area. Thus, if asbestiform fibers are a problem in water supplies, it is not a problem brought about solely by pollution of water sources but can arise from contact with natural geologic formations as well.

It appears from our data that, as stated above, one can predict the occurrence of these materials by understanding the geology of the watershed. It also was seen that such geologic diagnosis should be made locally and on-site since even the water of two adjacent but separate reservoirs (Crystal Springs and San Andreas Lake in San Francisco County) were exposed to different geologic formations and such exposure was reflected in the fiber content found in each of these waters. The geologic difference may not be recognized from small maps of the general area.

No fibers were detected in any of the groundwater samples collected. We were able to analyze some fully treated waters (coagulated and filtered) and could detect no fibers. However, in the case of the Southern California samples, we have not yet been able to perform the analysis of the raw water prior to treatment and in the case of the Marin County treated water there were technical difficulties with colloidal material in the finished water which made particle analysis impossible. Thus, no statement as to the ability of water treatment processes to remove asbestiform fibers can be made.

It would be premature to draw conclusions concerning the impact upon the public health of exposure of large populations to asbestiform fibers through water supplies. The serious impact of industrial exposure is clear and by inference gives us cause for concern regarding the presence of asbestos in water supplies. Information concerning the efficacy of water treatment processes in the removal of these fibers is urgently needed as well as epidemiological studies of populations exposed to water supplies containing asbestiform fibers in the amounts thus far detected.

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