Reports

Asbestiform Amphibole Minerals: Detection and Measurement of High Concentrations in Municipal Water Supplies

Abstract. *Asbestiform amphibole minerals, which have been demonstrated to be associated with human health problems, have been detected in substantial quantities in municipal water supplies taken from western Lake Superior water. The total concentration of amphibole minerals in the Duluth, Minnesota, water supply, as measured by x-ray diffraction for daily samples of suspended solids, averages 0.19 milligram per liter with large fluctuations due to seasonal and climatological effects on lake circulation. Electron microscopic examination of these water samples confirms the presence of asbestiform amphibole fibers. A conservative estimate of the fiber count for 1973 Duluth water supply samples is (1 to 30) $\times$ 10^6 amphibole fibers identifiable by electron diffraction per liter of water with a mass concentration of 1 to 30 micrograms per liter.*

The inhalation of asbestos fibers has long been recognized as a serious occupational and environmental health problem. Moreover, excessive rates of gastrointestinal and peritoneal cancer are associated with occupational exposure to asbestos (*1*). Recently it has been suggested that the ingestion of asbestiform minerals causes an increased incidence of gastrointestinal cancers (*2*). The presence of asbestiform particles in parenteral drugs (*3*), beverages (*4, 5*), food (*6*), and drinking water (*5, 7*) has been reported, and the migration of these fibers through the rat bowel wall has been demonstrated by several workers (*8*). The rapid transport of large intact starch granules and other particles throughout the human body after ingestion has also been reported (*9*).

Although natural sources of asbestiform minerals are known to contribute to fiber concentrations in drinking water, particularly in areas of serpentine rock, industrial discharge and mining operations can also produce high concentrations of asbestiform minerals in drinking water supplies (*7*). The contribution to water supplies from asbestos-cement pipe is now being studied by the Environmental Protection Agency. Such contamination is invariably due to chrysotile asbestos, since approximately 95 percent of the asbestos fiber used in North America is chrysotile (*10*). Other asbestos minerals, all of which are in the amphibole group of hydrated silicates, include amosite, crocidolite, anthophyllite, tremolite, and actinolite.

We report here the discovery of asbestiform amphibole fibers in public water supplies taken from western Lake Superior water. We have studied the variations in the concentration of asbestiform minerals in this water over the past year by x-ray diffraction and electron microscopic techniques. The predominant amphibole present is cummingtonite-grunerite, which is represented by the formula $(Mg,Fe)_7Si_8O_{22}(OH)_2$. The asbestiform cummingtonite-grunerite of commercial importance is amosite. In addition, smaller amounts of tremolite-actinolite and hornblende are found in the amphibole fraction of suspended solids filtered from western Lake Superior water. The concentration of amphibole (*11*), particularly cummingtonite-grunerite, was found to be below detection limits (< 0.02 mg/liter) at Thunder Bay, Ontario, and Grand Marais, Minnesota; detectable at Silver Bay, Minnesota; high (> 0.1 mg/liter) at Beaver Bay, Two Harbors, and Duluth, Minnesota; and detectable in Cloquet, Minnesota, water, which is also used by Superior, Wisconsin.

Examination of samples of suspended solids from the Duluth water supply by transmission electron microscope reveals the presence of diatom fragments, organic debris, quartz particles, some clay minerals, and amphibole particles ranging from blocky cleavage fragments to asbestiform fibers (Fig. 1). High-magnification electron micrographs (Fig. 1b) show that many fibers consist of smaller fibers, or fibrils, held together in bundles. The bundle nature, the lineation observed owing to the presence of fibrils within the fiber, and the ragged ends of the fibers have all been listed as criteria for the morphological identification of asbestos fibers by transmission electron microscopy (*12*).

Although amphibole fibers as long as 20 μm have been observed in Duluth

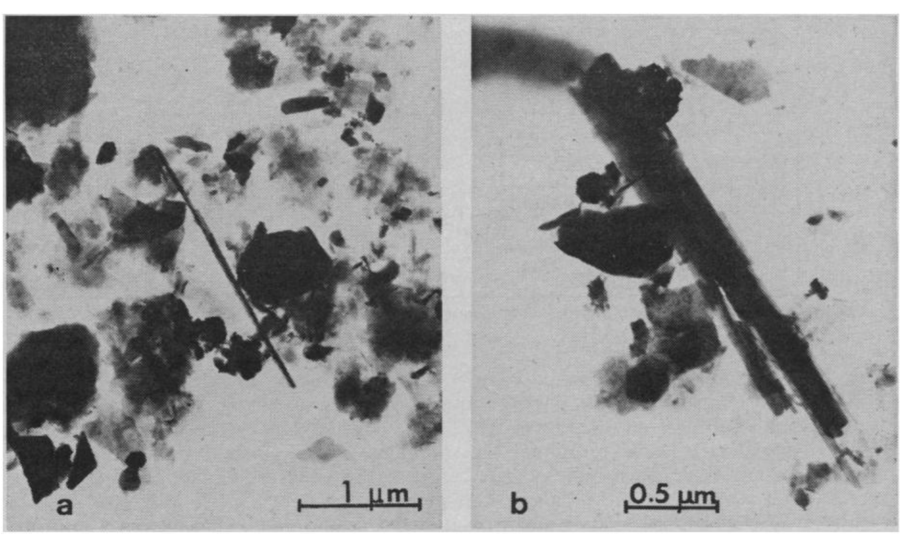

Fig. 1. Electron micrographs of amphibole fibers filtered from Duluth drinking water: (a) fiber approximately 2.2 μm long and 0.04 μm wide; (b) fiber approximately 2.9 μm long which is a bundle of many individual fibrils. Amphibole fibers are present with other minerals, diatoms, and organic detritus; thus it is difficult to identify all the amphibole fibers present.

water samples, most are less than 5 μm long with many less than 1 μm long. There has been considerable debate (*13*) over the carcinogenicity of inhaled asbestos fibers smaller than 5 μm, although occupational and environmental exposure to asbestos which results in cancer invariably involves more fibers smaller than 5 μm than fibers larger than 5 μm. Less is known of the significance of fiber length when the fibers are ingested.

Amphibole fiber counts by electron microscopy (*14*) showed millions of amphibole fibers per liter in samples of Duluth water. The amphibole-like fibers may be positively identified by their selected-area electron diffraction patterns (SAED). For reasons of size, orientation, or particulate interference many amphibole fibers do not provide diagnostic diffraction patterns, and thus not all the fibers present were counted. The presence of some chrysotile fibers was also noted.

A comparison of the analysis of the water samples by x-ray diffraction and electron microscopy permits the estimation of fiber counts for other Duluth water samples. The comparison rests on the assumption that the mass of total amphibole present is related to the number of amphibole fibers. This requires a constant particle size distribution for the samples compared, as was observed for the Duluth water samples. We estimate a range of (1 to 30) $\times 10^6$ SAED identified amphibole fibers per liter of water with a mass concentration of 1 to 30 μg/liter. The concentration of fibers in the drinking water varies with lake conditions and tends to decrease with the increasing residence time of the water in the distribution system. Occasional peak concentrations (up to 10^9 fibers per liter) can result from the resuspension of settled sediment in the water lines. These amphibole asbestiform fiber counts and particularly mass concentrations are much higher than the values reported for chrysotile fiber contamination in 22 municipal water supplies in the Province of Ontario (*7*). At Thunder Bay, which, like Duluth, uses unfiltered Lake Superior water, 0.8×10^6 chrysotile fibers per liter with a mass concentration of 0.0002 μg/liter were found.

The daily variations in the amphibole concentrations of Duluth water supply samples, as calculated from the amphibole x-ray diffraction peaks (*11*), are depicted in Fig. 2. During 1973, the amphibole concentrations varied from 0.03 to 0.80 mg/liter with a mean concentration of 0.19 mg/liter. The mean percent (by weight) of the suspended solids identified as amphibole was 23 percent.

The effect of climatological conditions on the amount and mineralogical nature of the suspended solids in the Duluth water supply is most evident when heavy rainfalls are followed by an increase in the amount of suspended solids resulting from river runoff and shore erosion. On 24 May, for example, 4.1 cm of rainfall was recorded; this was followed by a brief period, beginning on 26 May, characterized by high concentrations of suspended solids in the Duluth water supply. The lag time represents the time needed for the river runoff to move downshore to the water intake. These storm-caused high concentrations of suspended solids have low percentages of amphibole; this finding was expected, since our study shows that suspended river sediments entering Lake Superior contain only 0 to 3 percent amphibole, mainly hornblende. The prevailing water circulation in western Lake Superior is known to be counterclockwise (*15*), consistent with the pattern of progressively increasing amphibole concentration which we find in lake water to the northeast of Duluth. The Duluth water intake, located at a depth of 20 m, may receive water with increased amphibole concentration when the surface water circulation from the northeast is promoted by extended periods of easterly and northeasterly winds, as during the periods of 29 March to 9 April, 29 April to 1 May, and 1 to 7 May. These same winds may also cause the resuspension of recently settled amphibole-rich sediment by wave action in the shallow water area around the water intake. A period characterized by very high concentrations of suspended solids (approximately 20 percent amphibole) occurred in December 1973 when strong easterly winds resuspended surface sediments and the river sediment input was low. Ice cover, which normally begins in January, prevents such wind-generated resuspension of lake sediment.

Amphibole concentrations in Duluth water diminish during the period of increasing summer stratification of western Lake Superior water until fall overturn (the time period in Fig. 2 when water temperatures were greater than 4°C), probably because of the decreased circulation of deeper lake water from the northeast. During times of isothermal conditions without ice cover this circulation is more pronounced, and thus the peak amphibole concentrations

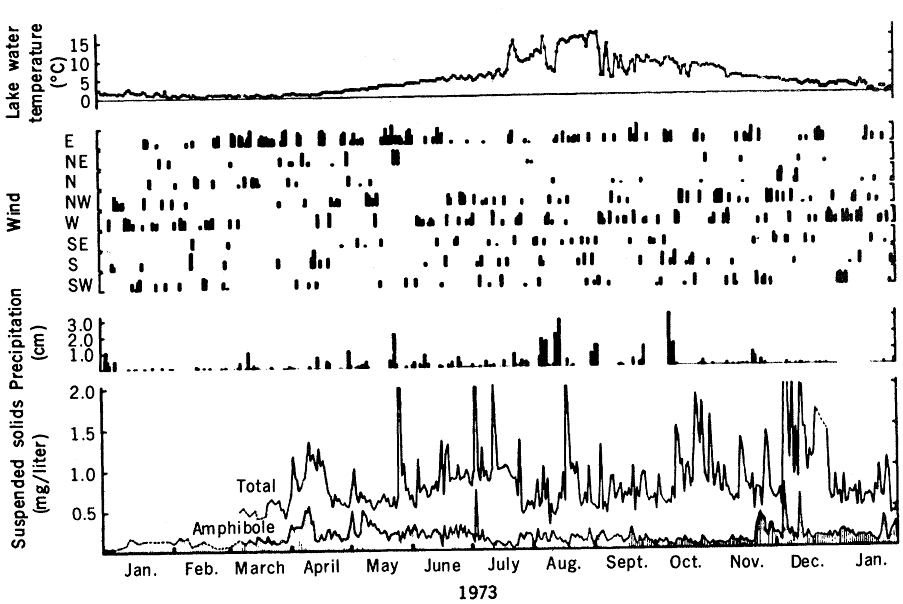

Fig. 2. Results of analyses (January 1973 through January 1974) of 10-liter Duluth, Minnesota, drinking water samples for amphibole and suspended solid concentrations. Daily sampling began on 19 March 1973. The dashed plot for prior dates indicates the period of less frequent sampling. Measurements of the concentrations of suspended solids were not made on samples taken before 6 March. Resultant wind direction and speed (wind scale, 0 to 30 km/hour) and precipitation data are the values as reported by the U.S. Department of Commerce, National Oceanic and Atmospheric Administration, National Weather Service, for Duluth International Airport. Daily mean water temperatures are calculated from hourly Duluth water intake temperature data provided by the Duluth Water and Gas Department Lakewood pumping station. Climatological events which affect the amount and mineralogical nature of the suspended solids normally precede the observed change in water quality by 1 to 2 days.

occur in spring and late fall. Changes of water temperature at the intake during the months of summer stratification are often wind-related. Offstore winds (westerly or northwesterly) can cause upwelling which brings colder water to the intake such as on 6 and 11 September. Easterly or northeasterly winds during the months of stratification push warm surface water into the Duluth water intake area, causing higher water temperatures such as on 24 July.

A historical record of the types of amphibole minerals previously suspended in Lake Superior water may be derived from a study of the bottom sediments. Dell (*16*) reported hornblende as the predominant amphibole in the sand fraction of Lake Superior postglacial sediments with a trace of tremolite-actinolite also present in some cases. Our study (*17*) of the surficial sediments of western Lake Superior shows a clear pattern of a recently deposited sediment layer rich in cummingtonite-grunerite on top of older sediment which does not contain detectable amounts (< 1 percent) of cummingtonite-grunerite. This layer rich in cummingtonite-grunerite is thickest (90 m or more) and coarsest in the vicinity of a large taconite tailings discharge at Silver Bay, Minnesota (*18*). It spreads throughout much of western Lake Superior, becoming thin and diluted with other sediment at Duluth, which is at the western tip of the lake. Indication of recent changes in the mineralogy of suspended solids in western Lake Superior water is provided by our x-ray diffraction analysis of suspended sediment samples collected for several periods in the past by the City of Duluth water utility. Samples from 1939–1940 and 1949–1950 contain only trace amounts of amphibole with no detectable cummingtonite-grunerite, but all samples studied for the period 1964–1965 contained large amounts of amphibole (average, 31 percent of the total inorganic solids), most of which was cummingtonite-grunerite. The geological and limnological data indicate that the source of this large increase in amphibole material is the taconite tailings (*18*) that, since 1956, have been discharged into western Lake Superior at Silver Bay.

PHILIP M. COOK
GARY E. GLASS
JAMES H. TUCKER
U.S. Environmental Protection Agency, National Water Quality Laboratory, 6201 Congdon Boulevard, Duluth, Minnesota 55804

References and Notes

1. E. E. Keal, *Lancet* **1960-II**, 1214 (1960); I. J. Selikoff, J. Churg, E. C. Hammond, *J. Am. Med. Assoc.* **188**, 142 (1964); P. E. Enterline and M. A. Kendrick, *Arch. Environ. Health* **15**, 181 (1967); I. J. Selikoff, E. C. Hammond, J. Churg, *J. Am. Med. Assoc.* **204**, 106 (1968); M. L. Newhouse and J. C. Wagner, *Br. J. Ind. Med.* **26**, 302 (1969).
2. Joint National Institute of Environmental Health Sciences–Environmental Protection Agency Conference on Biological Effects of Ingested Asbestos, Durham, North Carolina, 18–20 November 1973.
3. W. J. Nicholson, C. J. Maggiore, I. J. Selikoff, *Science* **177**, 171 (1972).
4. C. L. Berry, *Nature (Lond.)* **219**, 93 (1968).
5. H. M. Cunningham and R. D. Pontefract, *ibid.* **232**, 332 (1971).
6. R. R. Merliss, *Science* **173**, 1141 (1971); H. E. Blejer and R. J. Arlon, *J. Occup. Med.* **15**, 92 (1973).
7. G. Kay, *Water Pollut. Control* **111**, 33 (1973).
8. G. E. Westlake, H. J. Spjut, M. N. Smith, *Lab. Invest.* **14**, 2029 (1965); R. D. Pontefract and H. M. Cunningham, *Nature (Lond.)* **243**, 352 (1973); H. M. Cunningham and R. D. Pontefract, *J. Assoc. Off. Anal. Chem.* **56**, 976 (1973).
9. G. Volkheimer and F. H. Schulz, *Qual. Plant. Mater. Veg.* **18**, 17 (1968); G. Schreiber, *Arch. Environ. Health* **29**, 39 (1974).
10. S. Speil and J. P. Leineweber, *Environ. Res.* **2**, 166 (1969).
11. By x-ray diffraction analysis of suspended solids filtered from 10-liter water samples, we made semiquantitative estimates of the amphibole concentration with the use of an external standard. This technique has been used to estimate trace amounts of chrysotile asbestos and amphibole asbestos in dust samples on membrane filters [A. L. Rickards, *Anal. Chem.* **44**, 1872 (1972); J. V. Crable, *Am. Ind. Hyg. Assoc. J.* **27**, 293 (1966)] and fulfills the need for rapid, standardized estimates of amphibole concentration in samples that are not amenable to the use of an internal standard.
12. P. Gross, R. T. P. deTreville, M. N. Haller, *Arch. Environ. Health* **20**, 571 (1970).
13. Doubts about the carcinogenicity of small fibers stem primarily from the absence of tumors in animals subjected to short fibers. A recent study [F. Pott, F. Huth, K. H. Friedricks, *Zentralbl. Bakteriol. Parasitenkd. Infektionskr. Hyg. Abt. I Orig.* **155** (5/6), 463 (1972)], however, reported that rats intraperitoneally injected with chrysotile fibers incurred about a 40 percent incidence of tumors for two different tests with small fibers (95 percent less than 5 μm and 99 percent less than 3 μm).
14. The fiber counts were carried out by the Ontario Research Foundation (ORF), Sheridan Park, Ontario. A comparison with literature values is normally not possible since different preparation and counting methods are often used. Because ORF results have been reported for other water samples (*7*), these values can be compared with those results. The ORF fiber-counting technique consists of filtering the water sample with a 0.1-μm membrane filter, ashing the filter by maintaining it at 450°C for 3 hours, dispersing the ashed sample in 4 ml of distilled water, and centrifuging a 1-ml aliquot onto a carbon-coated electron microscope grid which is examined at × 25,000 magnification on a transmission electron microscope (Jeolco model JEM 100U) at 80 kv. The Environmental Protection Agency is currently developing a standard method for the counting of asbestos fibers in environmental samples.
15. C. E. Adams, *Proc. 13th Conf. Great Lakes Res.* (1970), p. 862.
16. C. I. Dell, "Late Quaternary Sedimentation in Lake Superior," thesis, University of Michigan (1971).
17. P. M. Cook, G. E. Glass, R. W. Andrew, in preparation; R. W. Andrew and G. E. Glass, in *Proceedings of a Conference on the Matter of Pollution of Lake Superior* (U.S. Department of Interior–Federal Water Quality Administration hearings, 2nd session, April 1970) (O-401-869, Government Printing Office, Washington, D.C., 1970), vol. 1, pp. 226–250.
18. Cummingtonite-grunerite is found almost exclusively in metamorphic rocks, usually in metamorphosed iron formations. The eastern Biwabik iron formation in northeastern Minnesota has been contact-metamorphosed by the Duluth gabbro. B. M. French [*Minn. Geol. Surv. Bull.* **45**, 1 (1968)] has described in detail the formation of cummingtonite-grunerite in the metamorphosed iron formation near the Duluth gabbro. This cummingtonite-grunerite in many cases is acicular to asbestiform in habit and varies from iron-rich grunerite to magnesium-rich cummingtonite. (The infrared spectrum of a sample of cummingtonite-grunerite from the taconite iron ore body is identical to that of amosite asbestos. The infrared interpretation technique described by R. G. Burns and R. G. J. Strens [*Science* **153**, 890 (1966)] for cummingtonite-grunerite indicates that both samples have an Fe/(Fe + Mg) atom ratio of 0.76.) The taconite iron ore body has been mined, and, after the extraction of magnetite, the amphibole-rich tailings have been discharged since 1956 into western Lake Superior at Silver Bay, Minnesota.

25 January 1974; revised 31 May 1974

Electrical Resistivity Variations Associated with Earthquakes on the San Andreas Fault

Abstract. *A 24 percent precursory change in apparent electrical resistivity was observed before a magnitude 3.9 earthquake of strike-slip nature on the San Andreas fault in central California. The experimental configuration and numerical calculations suggest that the change is associated with a volume at depth rather than some near-surface phenomenon. The character and duration of the precursor period agree well with those of other earthquake studies and support a dilatant earthquake mechanism model.*

Laboratory studies (*1*) have shown significant variations in electrical resistivity of rock samples subjeced to compressive stress. Fieldwork by Barsukov (*2*) showed that variations of up to 20 percent in apparent resistivity are associated with thrust-type earthquakes in the Garm region of the Soviet Union. Two years ago we initiated a study to monitor the deep resistivity across a strike-slip section of the San Andreas fault south of Hollister, California (Fig. 1). Frequent microearthquakes occur in this areas with hypocenters from 2 to 12 km deep.

To monitor resistivity changes to such depths requires surface electrode arrays of comparable dimensions. The field problems of current cable installation over such distances dictated the