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SEMI-QUANTITATIVE DETERMINATION OF ASBESTIFORM AMPHIBOLE MINERAL CONCENTRATIONS IN WESTERN LAKE SUPERIOR WATER SAMPLES

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ABSTRACT

The amphibole mineral, cummingtonite-grunerite, has been used as a tracer for taconite tailings discharged into Western Lake Superior. The discovery of many asbestiform amphibole fibers in the tailings and Western Lake Superior water lead to concern over fiber concentrations in municipal water supplies using this water. This concern was based on the association between human asbestos exposure and increased rates of cancer of the gastrointestinal tract and peritoneum. An x-ray diffraction external standard technique has been developed for rapid, inexpensive, semi-quantitative determinations of amphibole mass concentration in water. The average amphibole mass concentrations for different Western Lake Superior water intakes compare very well with the average electron microscope fiber counts for the same samples. Daily amphibole analysis of the Duluth water supply indicates an average amphibole concentration of 0.19 milligrams per liter.

INTRODUCTION

For several years x-ray diffractometry has been the key analytical technique for National Water Quality Laboratory studies of the distribution and fate of taconite tailings which have been discharged into Western Lake Superior at Silver Bay, Minnesota since 1956. A major component of this 67,000 ton per day discharge, the amphibole mineral cummingtonite-grunerite, provides an ideal tracer for the tailings. The cummingtonite-grunerite (310) peak at 29.1° 2θ for copper K_α radiation (d = 3.07 Å) is not found in x-ray diffraction patterns for natural lake sediments or suspended solids. X-ray diffraction patterns (Figure 1) of lake water suspended solids which contain taconite tailings and sediment from successive 25 mm sections of the lake bottom in an area of tailings deposition show a clear gradation from large amounts of cummingtonite-grunerite (shaded peaks) in very recent surficial sediments to no cummingtonite-grunerite and little amphibole in the older, underlying sediments (75-100 mm). X-ray diffraction study of hundreds of river suspended sediment samples also indicates no detectable cummingtonite-grunerite (<1%) and only 1-2% amphibole in the natural sediments entering Western Lake Superior. Much or all of the trace amphibole is the common, non-asbestiform mineral hornblende.

Further indication of the recent addition of cummingtonite-grunerite to Western Lake Superior water is provided by x-ray diffraction patterns of many suspended sediment samples saved from the years 1940, 1950, and 1964 (Figure 2). All samples from 1940 and 1950 did not contain detectable amounts of cummingtonite-grunerite and little if any other amphibole minerals as indicated by a (110) peak at 10.6° 2θ (d = 8.34 Å). All of the 1964 samples, however, contained large concentrations of cummingtonite-grunerite as shown by the appearance of large (110) and (310) peaks. The (110)/(310) peak ratios for these samples are typical of those found for taconite tailings samples.

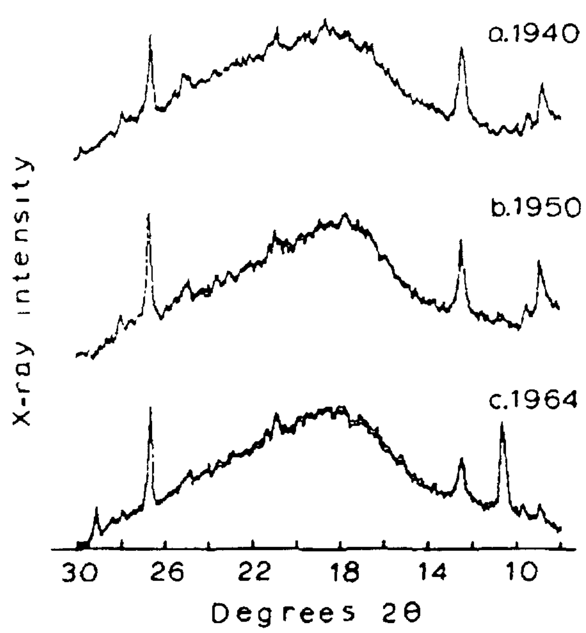

FIGURE 2---X-RAY DIFFRACTION PATTERNS FOR SUSPENDED SOLID SAMPLES OBTAINED FROM THE DULUTH MUNICIPAL WATER SUPPLY INTAKE: A HISTORICAL RECORD OF AMPHIBOLE CONCENTRATIONS IN DULUTH'S DRINKING WATER

FIGURE 3---ELECTRON MICROGRAPH OF <2μ TACONITE TAILINGS. a) LOW MAGNIFICATION (2,500X). b) HIGHER MAGNIFICATION (12,500X) VIEW OF AN AMPHIBOLE FIBER BUNDLE

causes the (110) reflection and, to a lesser extent, the (310) reflection intensities to be enhanced, permitting the detection of trace amounts of amphibole. As little as 0.05 mg of <2μ cummingtonite-grunerite produces measurable (110) and (310) peaks.

A semi-quantitative measurement of the amphibole concentration is made by an external standard technique. This technique has been intensity of filter background in the x-ray diffraction pattern with increasing sample weight to 10 mg; and the linearity of a plot of quartz peak (d = 3.33 Å) intensity versus weight of quartz, regardless of total sample weight in the range 0-12 mg.

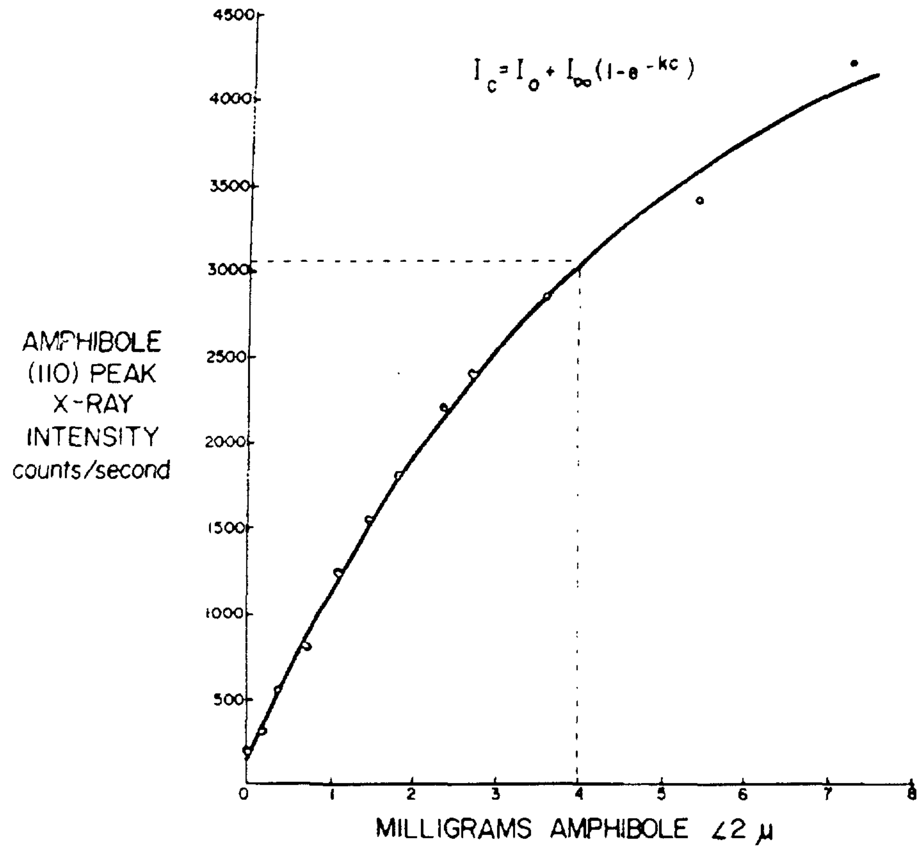

FIGURE 4—EXTERNAL STANDARD CURVE FOR AMPHIBOLE SEMI-QUANTITATIVE ANALYSIS

The non-linearity of the external standard curve (Figure 4) is due to a decreasing degree of preferred orientation as the amount of amphibole increases. This is indicated by decreasing amphibole (110)/(310) and amphibole (110)/quartz peak ratios with increasing weight of the standard amphibole-quartz mixture on the filter. The utility of the external standard curve depends on how well the curve models amphibole preferred orientation in environmental samples. Similar curves based on samples prepared with increased amounts of natural sediment agreed well with the standard curve used. With large amounts of natural sediment, the amphibole peak intensity is weakened which would cause an underestimation of amphibole concentrations. Other standard curves were employed to estimate the amphibole concentration in the few samples with a very high concentration of non-amphibole minerals.

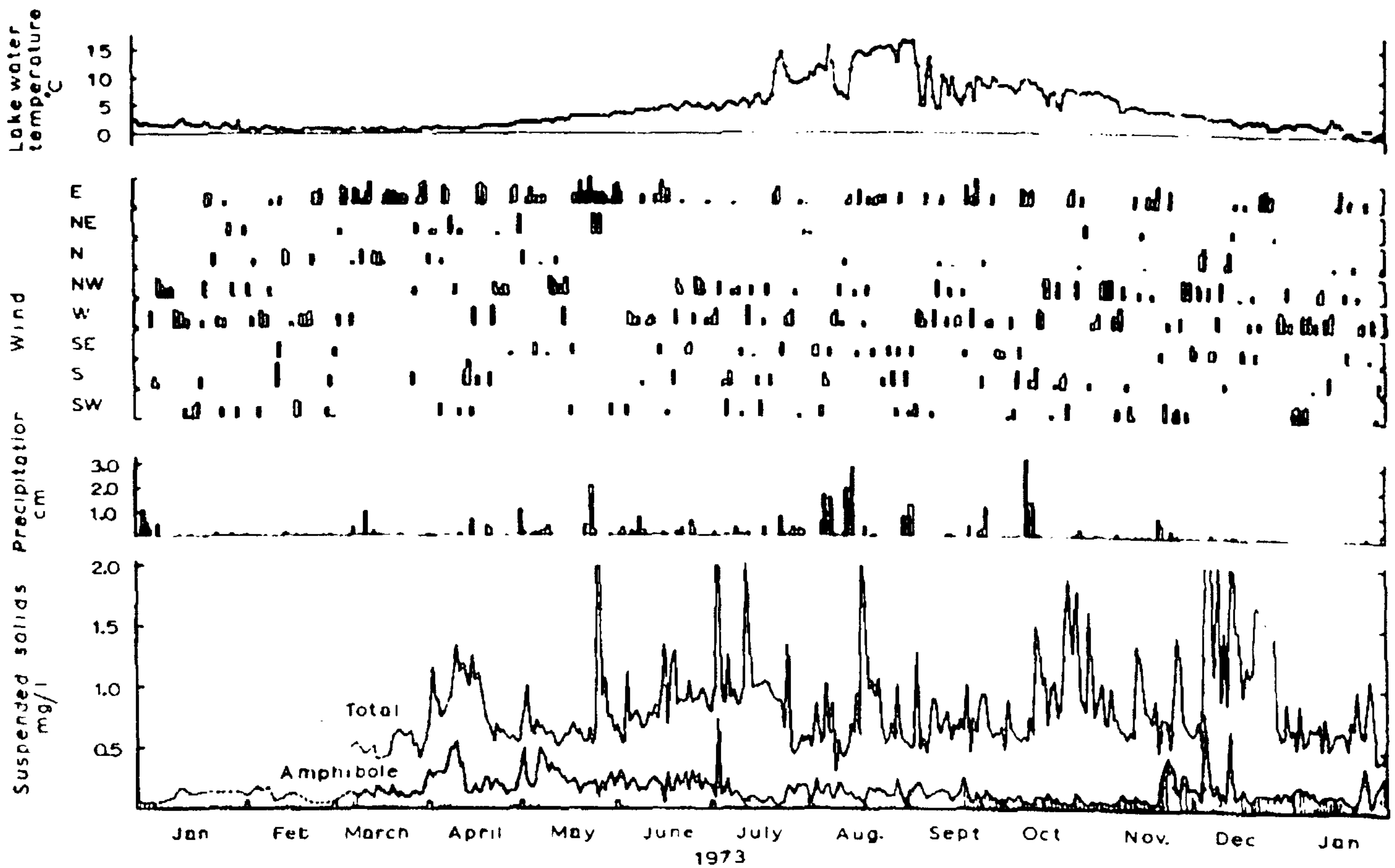

FIGURE 5---DAILY AMPHIBOLE AND SUSPENDED SOLIDS CONCENTRATIONS FOR DULUTH WATER WITH CLIMATOLOGICAL DATA AND WATER INTAKE TEMPERATURES

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REFERENCES

1. I. J. Selikoff, E. C. Hammond and J. Churg, "Carcinogenicity of Amosite Asbestos," Arch. Environ. Health 25, 183-186 (1972).

2. J. G. Eaton and G. E. Likens, "Use of Membrane Filters in Gravimetric Analyses of Particulate Matter in Natural Waters," Water Resources Res. 5, 1151-1156 (1969).

3. A. L. Rickards, "Estimation of Trace Amounts of Chrysotile Asbestos by X-Ray Diffraction," Anal. Chem. 44, 1872-1873 (1972).

4. J. V. Crable, "Quantitative Determination of Chrysotile, Amosite, and Crocidolite by X-Ray Diffraction," Am. Ind. Hyg. Assoc. J. 27, 293-298 (1966).

5. C. E. Adams, "Summer Circulation in Western Lake Superior," Proc. 13th Conf. on Great Lakes Res., 862-879 (1970).