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# Reconstruction of a Century of Airborne Asbestos Concentrations

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Airborne asbestos concentrations have been reconstructed for the entire 20th century for the first time through a combination of paleolimnological methods, particle-separation techniques, and analytical transmission electron microscopy. Pb concentrations and respirable aerosol mass concentrations in air and sediments yielded collection efficiencies of ~3000 $m^3$ of air per gram of lake sediment. Airborne concentrations of chrysotile, the most common type of asbestos, reconstructed from control lake sediments echoed chrysotile's usage during the 20th century, with the highest concentrations mid-century (~0.1 fibers/$cm^3$) and then decreasing in the last quarter century. Reconstructed airborne concentrations of anthophyllite asbestos, a byproduct of local talc mining and milling, increased from <0.004 to 0.022 fibers/$cm^3$ from 1846 to 1967. These anthophyllite concentrations during the ~100-year period of talc mining correlated well ($r^2 = 0.80$, $p < 0.01$) with annual production of local talc and were much higher ($p = 0.004$) than concurrent concentrations in a control lake located upwind of the mines and mills. All of the chrysotile and more than 70% of the anthophyllite asbestos fibers were too narrow to be detected by phase-contrast light microscopy, the method used to measure airborne fiber concentrations before ~1980.

## Introduction

Asbestos fibers are naturally occurring hydrated silicate mineral fibers that have found myriad uses in the 20th century. However, airborne asbestos fibers became the well-recognized cause of asbestosis, bronchogenic carcinoma, and mesothelioma during the latter half of that century (*1–3*). Most asbestos diseases in the United States were caused by exposures to asbestos during the first 75 years of the 20th century, before legislation reduced environmental emissions and gave protection to workers. Airborne fiber concentrations were measured by phase-contrast light microscopy (PCM) starting in the 1950s. Development of analytical transmission electron microscope (TEM) methods for asbestos analysis during the 1980s revealed that PCM had been unable to detect the vast majority of airborne asbestos fibers. The fibers undetected by PCM were the thin fibers that are considered most biologically active (*4*). Hence, the dose–response models in current usage have not been based on accurate exposure measurements of the most significant fibers from those earlier high-exposure periods (*5*). This paper demonstrates the first reconstruction of airborne asbestos concentrations from the last century, including the periods of highest exposures.

**Analytical Approach.** TEM is the only tool able to detect and identify the thin asbestos fibers that are most likely to reach the deep lungs. TEM's high magnification easily resolves the narrowest (0.02 $\mu$m) asbestos fiber; its selected-area electron-diffraction (SAED) capability allows determination of crystalline structure, and its adjunct energy-dispersive X-ray spectrometer (EDXS) yields chemical composition (*6*).

Airborne asbestos, like any insoluble aerosol fallout, accumulates in lake bottoms. The most recent inputs are deposited on the surface of the existing sediments, while older inputs settle progressively deeper into the sediment profile. During the past two decades, paleolimnology has documented 20th-century trends in increased atmospheric deposition of anthropogenic pollution (*7,8*). $^{210}Pb$ ($t_{1/2} = 22.3$ years), a naturally occurring radionuclide in the $^{238}U$ decay series, can be used to date sediment accumulation over the past ~150 years (*9*). $^{137}Cs$ ($t_{1/2} = 30.2$ years) is a discrete chronostratigraphic marker that appeared with the onset of atmospheric testing of nuclear weapons in 1954 and peaked in 1963 (*10*). Both isotopes can be measured in a series of slices from a sediment core to estimate the corresponding aerosol-deposition date for each slice.

Calculation of aerosol concentrations from each time-slice is possible if the collection efficiency (CE) of the sediment as an accumulator of aerosols is known. We developed two independent empirical models that yielded essentially identical CEs.

## Methods

Collection and analytical methods as summarized below are detailed in a dissertation (*11*).

**Study Area.** Studies of talc workers near Gouverneur, New York, starting more than a half century ago reported high incidences of diseases similar to diseases of asbestos workers (*12–15*). Other investigators have contended that these abnormalities were not directly related to talc (*16,17*). An analysis of a high incidence of pulmonary fibrosis detected in residents of St. Lawrence and Jefferson Counties in the mid-1980s concluded that there was "...no evidence of widespread radiographic abnormalities resulting from ambient dust exposure" (*18*).

In fact, talc mined in the Gouverneur area is less than 30% talc on a mass basis (*19, 20*). Tremolite constitutes 50–60% of the talc ore, while anthophyllite constitutes another ~10%.

Mining of talc in the Gouverneur region began in the late 19th century (*21, 22*). Most of the half-dozen mines active at the turn of the century were in the immediate Talcville area (Figure 1). Annual talc production increased to more than 100 000 tons by the middle of the 20th century (*23*). Six active mines (two near Talcville and four near Balmat) and five mills were in operation at the time of World War II (*24*). By 1998, however, all talc mining and milling was restricted to an area just northeast of Sylvia Lake.

Talc mining and milling operations were capable of creating visible clouds of mineral dust. Operations at the mills were "terribly dusty", and surrounding trees were coated with the white dust (*25*). Dust collectors were installed in mills in the 1930s and 1940s. Ore dust concentrations were extremely high near talc operations (100–1000 mppcf (million

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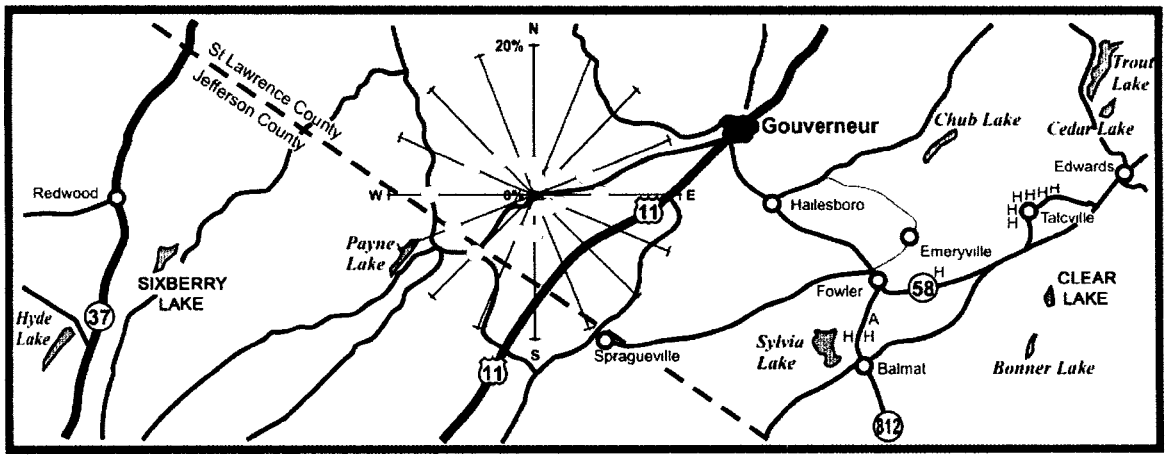


**FIGURE 1. Map of study area in St. Lawrence County in northern New York State. Talc mines active at some point during the 20th century are denoted by "H". Arnold quarry located at "A". Clear Lake was the study lake downwind of the talc mines, and Sixberry Lake served as the control lake. Superimposed wind rose denotes prevailing wind directions. Small circles represent percentage of time wind arrived from each of 16 sectors. For example, winds arrived from the west 14% of the time and from the north 4% of the time.**

particles per cubic foot)) before 1945 but were reduced to ~50 mppcf by 1972 (*15*). Even so, airborne fiber concentrations, which exceeded 50 fibers/cm$^3$ as recently as 1972, were extremely elevated compared to the current OSHA standard of 0.1 fibers/cm$^3$ (*26*).

**Sample Collection.** Because winds play a key role in the spread of airborne fibers, predominant wind directions were determined for this study by averaging approximately one-half a million hourly wind direction determinations measured by the National Weather Service (*27*) at sites near Gouverneur. As expected for temperate northern latitudes, 50% of the winds came from the western quadrant (225−315°) (Figure 1).

Sediment cores were collected from nine different lakes from a boat using a gravity-driven coring device (Wildco K−B Corer) fitted with removable plastic tubes (5.12-cm i.d.). Multiple cores were collected from the deepest parts of lakes (Figure 1) from 1995 to 1998. Cores were sectioned in the field with a laboratory-fabricated core-extrusion/slicing device that discarded the outer 2 mm of the core to minimize potential effects of sediment mixing along the tube's inner surface. Section thickness was adjusted to yield approximately 5 years' accumulation per slice, based on earlier experience with lakes from the same region. Clear Lake was selected as the study lake because it was near (~8 km) and downwind of the talc industry. This lake's watershed was heavily forested and contained several swampy areas. The lake surface was 0.16 km$^2$ and relatively flat-bottomed, with an 8-m maximum depth (*28*). Sixberry Lake was selected as the control lake because it was upwind and distant (~25 km). It occupied 0.52 km$^2$ and had a maximum depth of 27 m, which was limited to an area that was relatively smaller than in Clear Lake.

Samples of talc ore were collected from the study area in 1995 because talc was a potential source of anthophyllite asbestos (*29*). Several pieces of "fly rock" (fallout from blasting) were collected near Talcville, and several long, splintery, wood-like pieces of ore were collected inside the open Arnold quarry (A in Figure 1). A ~0.3-g piece from each site was crushed with a mortar and pestle, and the powder was elutriated (as described later for sediment preparation) for characterization. Additionally, crushed Arnold ore was dispersed onto membrane filters in an aerosol generator.

**Sediment Dating.** Sediment samples were oven dried at 60 °C or freeze-dried to constant weight for the determination of water content. Radionuclide analyses were done on sediments in their original field containers by gamma

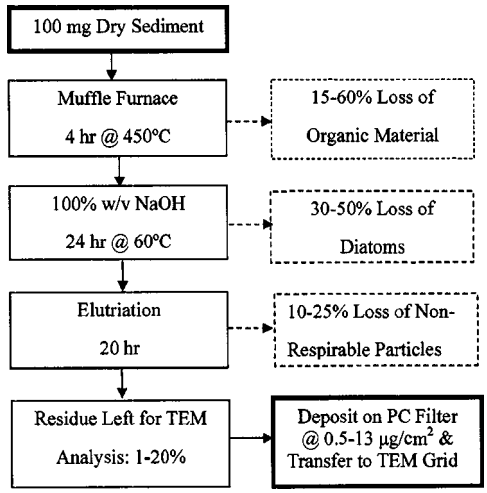


**FIGURE 2. Flow diagram of methods used to prepare lake sediments for TEM analysis.**

counting using a Princeton Gamma-Tech intrinsic Ge detector and multichannel analyzer. $^{137}$Cs and total $^{210}$Pb activities were determined from the peaks at 661.6 and 46.5 keV, respectively. The supported component of $^{210}$Pb, i.e., the $^{210}$Pb from the decay of $^{238}$U in the sediments, in each core was calculated from the average activities of $^{214}$Bi and $^{214}$Pb. For each sample, the supported $^{210}$Pb was subtracted from the total $^{210}$Pb to yield $^{210}$Pb$_{xs}$, the component derived from the atmosphere, which decays with a half-life of 22.3 years (*9, 30*). $^{214}$Bi and $^{214}$Pb activities were determined from the peaks at 609.3 and 351.9 keV, respectively. $^{137}$Cs and $^{210}$Pb$_{xs}$ activities were decay-corrected to the date of core collection. Quantification for all nuclides was based on analyses of NIST or NBS SRM traceable standards.

**Asbestos Extraction.** The paucity of airborne asbestos (mass concentrations less than ppm) in aerosols was expected to be exacerbated by the high proportion of nonaerosol inputs to lake sediments, such as diatoms and watershed debris. Because this presented an enormous hindrance to TEM's tedious visual analysis, several methods (Figure 2) were explored to reduce the number of particles.

Organic material was removed by ashing in a muffle oven. Approximately 0.1 g of dry sediment was transferred to a tared Vycor crucible and weighed before and after heating to 450 °C for 4 h. Inorganic residue from ashing was placed

in 100% w/v NaOH at 60 °C for 24 h to dissolve diatom shells. Following three dilute-and-centrifuge steps to dilute the NaOH, residue was place in an oven at 60 °C until dry.

Fibers (or any particles) that are small enough to negotiate the gauntlet of the upper respiratory tract and penetrate deeply into the lungs are termed *respirable*. For this study, an aerodynamic diameter smaller than 2.5 $\mu$m was considered respirable, i.e., capable of reaching the deep lungs (*31*). We processed sediment residues in an elutriator to separate larger, obscuring particles from the potentially respirable fibers of interest. The polypropylene elutriation funnel was 30 cm long, with an internal diameter tapering from 3.0 cm at the top to 0.3 cm at the bottom. A peristaltic pump delivered Graham's salt solution at an upward velocity of $3.4 \times 10^{-4}$ cm $s^{-1}$, the settling velocity of a respirable particle in water (*32*), at the outlet. The pump was run for 24 h to ensure collection of all potentially respirable fibers. An elutriation with ground "talc" revealed that respirable particle recovery in this elutriator was more than 95% by 24 h.

**Asbestos Analysis.** An aliquot of processed, suspended residue was filtered through a 0.1-$\mu$m polycarbonate (PC) filter to yield an analytical sensitivity of $1.1 \times 10^7$ fibers per gram of dried sediment. Particle concentrations on the filters varied between 0.5 and 13 $\mu g/cm^2$, a range which centered on the optimum value of 5 $\mu g/cm^2$ (*33*).

The surface of the sediment-covered 0.1-$\mu$m PC filter was coated with a ~20-nm carbon film in a high-vacuum carbon evaporator. Sections were excised and placed particle-side-up on gold 200-mesh relocator TEM grids, and the PC was dissolved in 2 mL of 99% ethylenediamine ($H_2NCH_2CH_2NH_2$) in 8 mL of 1-methyl-2-pyrrolidinone ($C_5H_9NO$).

A blank sample was prepared with a batch of samples from each of the two lakes studied. Each blank sample started as filtered, deionized water in an empty crucible during the ashing step and was run through the complete preparation and analysis procedure.

Samples were analyzed with a Hitachi H7110 scanning transmission electron microscope operated at 100 keV and a screen magnification of 15 300. Five grid openings from each grid were chosen using a random-opening list (*34*), for a total of 15 grid openings analyzed per sediment sample.

Fibers with parallel sides and an aspect ratio (length divided by width) of 5 or greater were measured to the nearest 0.5 mm (equivalent to approximately 0.03 $\mu$m) using calibrated markings on the phosphor screen. Fibers longer than 0.5 $\mu$m were selected for SAED analysis according to the Asbestos Hazard Emergency Response Act (AHERA) protocol (*35*). Fibers with electron-diffraction layer-line spacings between 0.51 and 0.55 nm were subjected to additional characterization (*36*). Chrysotile fibers were positively identified by SAED. Non-chrysotile fibers with 0.51−0.55 nm layer-line spacings were further characterized by EDXS (Princeton Gamma Tech IMIX/Omega). Final identifications of amphiboles were made by comparison of Mg, Si, Ca, and Fe ratios to ratios (mean ±95% confidence limit) collected from NIST SRM 1867 ("Uncommon Asbestos") or from Leake et al. (*37*). Talc fibers were identified by pseudohexagonal electron diffraction patterns that remained unchanged during tilting of the specimen goniometer through ±25°.

A Trout Lake composite sediment spiked at 35 $\mu g/g$ with milled amosite asbestos yielded concentrations of 31 $\mu g/g$ of amosite and 17 $\mu g/g$ of amosite during two independent preparations and analyses. This recovery was deemed satisfactory in light of the variability introduced by squaring fiber diameter for mass calculation, and hence the enormous impact of a single thick fiber. A second Trout Lake composite sediment was spiked with a New York State Department of Health Environmental Laboratory Approval Program proficiency-testing water sample (*38*) containing a known concentration (fibers/L) of amosite. Recovery from this sample was 47% of the calculated value, which was within the 95% confidence limits of the proficiency-test mean and was reasonable considering that some of the fibers in the spike may have been too large for elutriation recovery.

**FIGURE 3. Electron micrograph of respirable fraction from ground "talc" ore from Arnold quarry. Scale bar equals 5 $\mu$m.**

**Trace-Metal Analysis.** Subsamples (~0.5 g) from selected sediment sections were leached in nitric acid and hydrogen peroxide according to EPA Method 3050B (Revision 2) and were analyzed by inductively coupled plasma atomic emission spectroscopy (LEEMAN PS5) according to EPA Method 200.7 (Revision 4.4) for selected trace metals.

## Results and Discussion

**Source Characterization.** Crushed Talcville ore yielded 11% respirable particles by mass, including a substantial concentration of fibers. Common among these fibers were talc ribbons, notable for their characteristic twisting. Crushed Arnold ore yielded 15% respirable particles. The fiber assemblage included fewer talc ribbons but contained a larger proportion of asbestiform fibers, typified by aspect ratios exceeding 10 (often in the hundreds), curved fibers, and fibers terminating in frayed ends (Figure 3). Anthophyllite, tremolite, "intermediate" (combination of talc, anthophyllite, or other amphibole), and talc fibers constituted 40%, 6%, 48%, and 2%, respectively, of an aerosol generated from crushed Arnold ore.

**Geochronologies.** Only cores with field-observed intact water/sediment interfaces were prepared for further analysis. Isotopes were measured on six sections from five study-lake cores and on nine sections from two control-lake cores. The most geochronologically intact core from each lake was selected for further analysis, as presented in Table 1. The control-lake core yielded an exponential decrease of $^{210}Pb_{xs}$ activity with depth. Linear regression of log-transformed activities gave a mean sedimentation rate of 0.83 mm/year ($r^2 = 0.83$). Mass sedimentation rate was calculated as 0.016 g/cm²/year ($r^2 = 0.89$). Dating assignments for individual core sections based on these constant linear and constant mass sedimentation rate models agreed to within ~15 years. The $^{137}Cs$ profile did not show a single distinct peak that

**TABLE 1. Physical, Isotopic, Chemical, and Asbestos Data from Clear Lake (Study Lake) and Sixberry Lake (Control Lake)[a]**

| slice | depth (mm) | year | water content | $^{137}$Cs (pCi/g) | $^{210}$Pb (pCi/g) | Pb (mg/g) | chrysotile (f/cm$^3$) | anthophyllite (f/cm$^3$) |
|---|---|---|---|---|---|---|---|---|
| | | | | study lake | | | | |
| 1 | 0 | 1995 | 0.964 | na | na | 44 | 0.10 | 0.019 |
| 2 | 19 | 1989 | 0.953 | 8.16 | 43.64 | na | na | na |
| 3 | 38 | 1984 | 0.951 | 8.56 | 27.60 | na | 0.071 | 0.015 |
| 4 | 56 | 1978 | 0.952 | 10.65 | 29.80 | 190 | na | na |
| 5 | 75 | 1972 | 0.966 | 8.41 | 18.56 | 228 | na | na |
| 6 | 94 | 1966 | 0.950 | 6.25 | 20.95 | 197 | 0.13 | 0.022 |
| 7 | 113 | 1960 | 0.963 | 4.01 | 20.09 | 179 | na | na |
| 8 | 131 | 1955 | 0.950 | 2.98 | 14.59 | na | na | na |
| 10 | 169 | 1943 | 0.948 | 1.85 | 12.13 | na | na | na |
| 11 | 188 | 1937 | na | na | na | 26 | 0.093 | 0.011 |
| 12 | 206 | 1931 | 0.944 | 1.71 | 7.78 | na | na | na |
| 14 | 244 | 1920 | 0.941 | 1.25 | 5.42 | na | 0.082 | 0.015 |
| 16 | 281 | 1908 | 0.938 | 0.37 | 5.92 | na | na | na |
| 17 | 300 | 1903 | na | na | na | 19 | 0.071 | 0.011 |
| 18 | 319 | 1897 | 0.938 | 0.64 | 3.57 | na | na | na |
| 20 | 356 | 1885 | 0.941 | 0.07 | nd | nd | na | na |
| 22 | 394 | 1874 | 0.939 | 0.07 | nd | 6 | 0.018 | 0.004 |
| 24 | 431 | 1862 | 0.940 | na | na | na | na | na |
| 26 | 469 | 1850 | 0.941 | 0.07 | nd | nd | na | na |
| 27 | 488 | 1845 | na | na | na | 8 | 0.026 | nd |
| | | | | control lake | | | | |
| 1 | 0 | 1995 | 0.939 | 3.01 | 40.76 | 86 | 0.018 | nd |
| 2 | 6 | 1992 | 0.914 | 4.51 | 37.13 | na | na | na |
| 3 | 13 | 1989 | 0.920 | 4.03 | 42.60 | na | 0.012 | nd |
| 4 | 19 | 1985 | 0.901 | 9.48 | 22.86 | na | na | na |
| 5 | 26 | 1979 | 0.872 | 6.65 | 20.41 | 151 | 0.023 | nd |
| 6 | 32 | 1973 | 0.858 | 7.67 | 23.41 | 124 | na | na |
| 7 | 38 | 1966 | 0.829 | 5.90 | 21.18 | 133 | na | na |
| 8 | 45 | 1958 | 0.838 | 5.80 | 12.45 | 166 | 0.117 | 0.006 |
| 9 | 51 | 1950 | 0.824 | 7.23 | 14.68 | na | na | na |
| 10 | 58 | 1941 | 0.808 | 6.20 | 13.24 | na | na | na |
| 11 | 64 | 1931 | 0.777 | 2.59 | 10.36 | 118 | 0.129 | nd |
| 13 | 77 | 1908 | 0.749 | nd | 1.11 | na | 0.018 | nd |
| 15 | 90 | 1881 | 0.763 | nd | 1.44 | 33 | 0.018 | 0.006 |
| 17 | 102 | 1857 | 0.802 | nd | 0.06 | na | na | na |
| 18 | 109 | 1847 | 0.829 | na | na | 25 | nd | nd |

[a] na = not analyzed. nd = none detected.

could be unambiguously associated with the 1963 fallout maximum. Rather, $^{137}$Cs activity was elevated between about 20 and 60 mm depth. Because this observation was more consistent with the constant mass accumulation model (1963 $\approx$ 44 mm) than with the constant linear model (1963 $\approx$ 28 mm), dating assignments for the control lake were based on a constant mass accumulation of 0.016 g/cm$^2$/year.

Regression of the $^{210}Pb_{xs}$ data for the study lake gave average accumulation rates of 3.24 mm/year ($r^2 = 0.97$) and 0.019 g/cm$^2$/year ($r^2 = 0.96$). The constant linear model was used for dating assignments, because it placed the $^{137}$Cs peak closer to the mid-1960s.

Depth profiles of water content in both the control- and study-lake cores showed distinct minima at about 1906 (80 mm) and 1908 (300 mm), respectively, which likely resulted from extensive regional forest fires that occurred in 1908 (*7*). Forest fires typically reduce organic matter and increase erosional lithophilic input, both of which reduce water proportion in sediments.

**Sediment Compositions.** Study lake sediments were more than 50% organic (Table 2). Diatom composition varied from 25% to 35% of the dried sediment mass. Variation of large particles was even greater, 6−12%. The net result for TEM analysis was removal of 95% of particle mass in the most recent sediments to 99% of particle mass in the oldest sediments. Preparation of a second subsample (1966b in Table 2) of the 1966 section of the study lake core yielded excellent agreement with the original preparation.

**TABLE 2. Physical Characteristics of Lake Sediments[a]**

| year | % organic | % diatoms | % >2.5 μm | % analyzed by TEM |
|---|---|---|---|---|
| | | study lake | | |
| 1995 | 57 | 30 | 10 | 3.1 |
| 1984 | 57 | 30 | 12 | 2.0 |
| 1966 | 59 | 28 | 7.5 | 4.8 |
| 1966b | 58 | 28 | 10 | 3.7 |
| 1937 | 55 | 34 | 6.9 | 4.1 |
| 1920 | 55 | 32 | 12 | 1.7 |
| 1903 | 50 | 37 | 10 | 2.4 |
| 1874 | 57 | 35 | 7.1 | 0.6 |
| 1846 | 59 | 35 | 5.7 | 0.8 |
| | | control lake | | |
| 1995 | 23 | 50 | 13 | 14 |
| 1989 | 23 | 51 | 14 | 12 |
| 1979 | 20 | 47 | 16 | 17 |
| 1958 | 21 | 44 | 16 | 19 |
| 1931 | 20 | 46 | 13 | 21 |
| 1908 | 14 | 41 | 25 | 20 |
| 1881 | 15 | 37 | 27 | 20 |
| 1847 | 22 | 45 | 21 | 13 |
| 1847b | 21 | 47 | 21 | 11 |

[a] Percentages are mass-based

Sediments from the control lake were lower in organic content, deviating little from 20% organic composition during the period analyzed (Table 2). Lower organic content was probably due to reduced forest coverage in its watershed

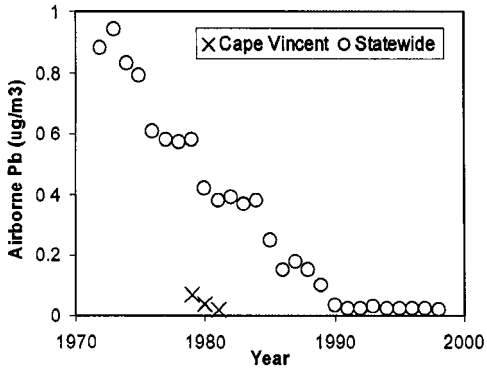


**FIGURE 4. Airborne Pb concentrations from 1973 to 1998 (statewide average) and from 1979 to 1981 (Cape Vincent).**

**TABLE 3. Pb Data Used for Calculating Collection Efficiencies (CE)[a]**

| | Pb | | | |
|---|---|---|---|---|
| | sediment ($\mu$g/g) | airborne ($\mu$g/m$^3$) | CE (m$^3$/g) | average CE (m$^3$/g) |
| | | study lake | | |
| 1978 | 184 | 0.054 | 3.4E+03 | |
| 1972 | 222 | 0.083 | 2.6E+03 | 3.0E + 03 |
| | | control lake | | |
| 1978 | 126 | 0.054 | 2.3E + 03 | |
| 1973 | 99 | 0.089 | 1.1E + 03 | 1.7E + 03 |

[a] Sediment Pb is raw data minus background (19th century) concentrations (6 and 25 $\mu$g/g for Clear Lake and Sixberry Lakes, respectively). Airborne Pb is NYSDEC statewide data divided by 11.

and clearer water, indicating reduced primary productivity versus the study lake. Diatoms were also consistent across the time series, constituting approximately 45%. The largest variation was observed in the large-particle fraction, which declined from almost 20% in 1852 to less than 10% a century later. More than 10% of the dried sediment remained for TEM analysis. Again, agreement for re-preparation was excellent (Sample 1847b).

**Collection Efficiencies.** For atmospherically derived components in sediment core sections, the atmospheric concentration to sediment concentration ratio is defined here as the collection efficiency (CE) of the core.

*Lead Model.* The nearest airborne Pb monitoring site was Cape Vincent, 50 km southwest of the control lake, where 0.07, 0.04, and 0.02 $\mu$g-Pb/m$^3$ were measured in 1979, 1980, and 1981, respectively. This trend of decrease followed concurrent statewide measurements but was 11-fold lower than the statewide average (*39*) (Figure 4). Hence, division by 11 of the annual statewide measurements approximated airborne concentrations of Pb for the study area.

Identical temporal trends in Pb concentrations were observed in the sediments of both lakes (Table 1). When turn-of-the-century concentrations (background) are subtracted from both lakes, sediment Pb concentrations in both lakes are similar and are chronologically synchronized with airborne Pb concentrations. Table 3 reveals CE of 3.0 $\times$ 10$^3$ m$^3$/g for the study lake and 1.7 $\times$ 10$^3$ m$^3$/g for the control lake.

*Aerosol Mass Model.* Aerosol masses have been measured across New York State in an effort to track air pollution (*39*). The air-pollution monitoring site closest to the study area was Nick's Lake, located 75 km southeast of the study lake. Samples of $PM_{10}$ (<10 $\mu$m in diameter) aerosols collected in the 1990s have averaged 12.9 $\mu$g/m$^3$. Because sulfate and nitrate particles (and their associated cations) dissolve in water before reaching the sediments, these anion and cation masses were subtracted from $PM_{10}$ aerosol masses to leave generally insoluble particles, 7.9 $\mu$g/ m$^3$.

The majority of aerosols that reach a lake will be in the respirable size range; larger particles quickly settle out of air masses. Thus, aerosol contribution to lake sediments was considered to be the TEM-analyzed residue left after removal of organic matter, diatoms, and nonrespirable particles. Potential respirable aerosol contribution in the 1995 slice for the control lake (14%) was much higher than for the study lake (3.1%) (Table 2). The proximity (43 km) of the two lakes indicates a nonaerosol source of respirable particles for the control lake. TEM analysis revealed an abundance of submicrometer quartz particles in sediments from the control lake, which lies within the Potsdam Sandstone and Theresa Formation. The study lake, which lies inside the Adirondack biotite gneiss area (as does Nicks Lake), lacked these quartz particles, reinforcing the assumption of a nonaerosol source for the abundant respirable particles in the control-lake sediments. When 19th-century (background) percentages of respirable particles were subtracted from each lake's most recent sediment section, the study lake yielded 2.4% (0.024 g/g) net respirable particles while the control lake yielded 2.0% (0.020 g/g) net respirable particles. When these percentages were divided by 7.9 $\mu$g/m$^3$, CEs of 3.0 $\times$ 10$^3$ and 2.5 $\times$ 10$^3$ m$^3$/g are derived for the study and control lakes, respectively.

Despite analytical uncertainties in the mass loss of some material (organic matter, bound water in silicates, carbonate decomposition) during ashing and in differences of particle behaviors in aerosol versus water (dissolution, attachment to other particles), these two sets of CEs, derived independently from Pb and aerosol masses, are in excellent agreement. While additional uncertainty is introduced by applying these CEs to asbestos fibers, a first-order estimate of airborne concentrations can be made. The average of the Pb and mass CEs for each lake, 3.0 $\times$ 10$^3$ m$^3$/g for the study lake and 1.9 $\times$ 10$^3$ m$^3$/g for the control lake, was chosen for the calculation of airborne asbestos concentrations. Coupled with the 1.1 $\times$ 10$^7$ fibers/g sensitivity, this computation yielded analytical sensitivities of 0.0037 and 0.0058 fibers/cm$^3$, respectively, for the study and control lakes.

**Asbestos.** Eight study-lake sections were selected for asbestos analysis: 1995, 1984, 1966, 1937, 1920, 1903, 1874, and 1845, where the year named represents the vertical midpoint of the section. Likewise, eight sections were selected from control-lake core: 1995, 1989, 1979, 1958, 1931, 1908, 1881, and 1847.

*Chrysotile Asbestos.* Analysis of blanks prepared alongside samples revealed nonuniform chrysotile contamination. On one grid, 13 grid openings yielded no fibers, while the two remaining openings contained a total of 10 chrysotile fibers. This type of contamination was not surprising, in light of PC filters' history of sporadic chrysotile contamination (*40*). Contaminant fibers were extremely thin (<0.05 $\mu$m) yet were unusually electron-opaque, with a high-contrast central canal. Some were partially embedded in the PC material itself, indicating a manufacturing source of contamination. To remove any effect of this contamination from further consideration, we subtracted chrysotile fibers that were morphologically similar to the contaminant fibers from all raw counts. This eliminated fibrils thinner than 0.05 $\mu$m and bundles thinner than 0.1 $\mu$m.

Chrysotile concentrations calculated from sediments of the control lake ranged from <0.006 to 0.129 fibers/cm$^3$ (Table 1). The dramatic rise in concentration during the middle of the 20th century coincides with increased use of asbestos during that period. The steep decline in the last quarter of the 20th century corresponds with the legislatively mandated reduction of asbestos use. The airborne chrysotile concen-

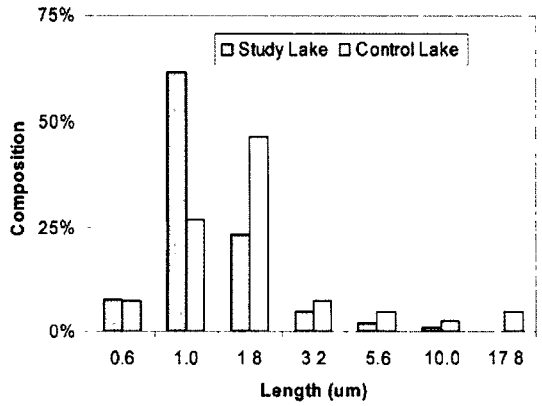


**FIGURE 5. Chrysotile fiber length distributions from study and control lake sediments.**

tration (0.023 fibers/cm$^3$) in the 1979 section is commensurate with the range measured in the early 1980s for nonurban southern Ontario (<0.002–0.033 fibers/cm$^3$) (*41*). Chrysotile concentrations derived from the study-lake sediments increased earlier in the 20th century and decreased less dramatically at the end of the century. Fibers from the study-lake sediments were much shorter than those from control-lake sediments (Figure 5). Some of this short chrysotile may have originated in the serpentine minerals that occur in the talc-tremolite schist. An earlier study in our laboratory revealed that entrained dust from crushed marble (the parent rock of the local talc) yielded substantial chrysotile concentrations (*42*). Because our aerosol/sediment-derived CE is validated by the agreement of airborne chrysotile concentrations with the earliest TEM-measured airborne concentrations and by chrysotile airborne concentrations' temporal correspondence to usage, we applied the model to airborne amphibole asbestos patterns during the same period.

*Amphibole Asbestos.* Amphibole asbestos was not detected in any of the blanks. Only one of the two "common" (term applied to "amosite" and crocidolite in NIST SRM 1866) amphibole asbestos types was detected in the 16 analyzed sections from the control- and study-lake cores: a single grunerite fiber. In contrast, all three "uncommon" (NIST SRM 1867 terminology) amphibole asbestos types were found in study-lake sediments, and two "uncommon" amphibole fiber types were detected in control-lake sediments. Many fibers were not identifiable as specific minerals because of their intermediate positions between two distinct minerals, e.g., between anthophyllite and talc (*43*).

Tremolite asbestos was detected only in the study-lake sediments. Airborne concentrations were low and did not exhibit a temporal trend; they reached a maximum of 0.007 fibers/cm$^3$ at the beginning of the 20th century. Some tremolite probably came from other local sources, such as marble mining and crushing operations (*42*). Actinolite asbestos was detected in six study-lake and three control-lake sediments, with a maximum concentration of 0.015 fibers/cm$^3$ in the 1966 and 1995 study-lake sections. Actinolite has not been reported from local "talc" mines nor did we detect it in either of the ore samples. Detected tremolite and actinolite fibers tended to be short, with mean lengths of 1.2 and 1.5 $\mu$m, respectively, and mean aspect ratios less than 10.

Anthophyllite asbestos was the most abundant amphibole asbestos in study-lake sediments, appearing in all but the earliest section (Table 1). Concentrations increased markedly during the 20th century, rising to 0.022 fibers/cm$^3$ by 1966. In contrast, control-lake sediments yielded significantly ($p = 0.004$ (*44*)) lower anthophyllite concentrations, with a single anthophyllite fiber (0.006 fibers/cm$^3$) each in two of eight sediment slices.

**TABLE 4. Relative Aerosol Loading (RAL) for Clear Lake and Sixberry Lake**

| sector (i) | wind % time ($w_i$) | km from talc ($k_i$) | relative aerosol loading ($RAL_i$) |
|---|---|---|---|
| | | **Clear Lake** | |
| WSW | 24 | 8 | 0.0045 |
| W | 13 | 9 | 0.0021 |
| WNW | 10 | 12 | 0.0012 |
| NNW | 7 | 3.5 | 0.0032 |
| N | 4 | 4 | 0.0015 |
| | | sum | 0.0126 |
| | | **Sixberry Lake** | |
| E | 7 | 28 | 0.0003 |
| ESE | 1 | 31 | 0.0001 |
| | | sum | 0.0004 |

Anthophyllite asbestos fibers were longer than the other two amphibole types, with a mean length of 2.5 $\mu$m and a mean aspect ratio of 14. Seventy percent of the fibers were thinner than 0.25 $\mu$m. Lengths and aspect ratios of study-lake anthophyllite asbestos did not demonstrate any temporal trends. Talc and fibers that contain both talc and anthophyllite ("intermediate") were equally abundant in the study-lake sediments. All three fiber types shared mean lengths, widths, and aspect ratios, indicating a common mineralogical source.

Interestingly, airborne chrysotile concentrations from the study lake correlated extremely well ($r^2 = 0.87$, $p < 0.001$) with airborne anthophyllite concentrations. This reinforces the postulation of a local mining source for the excess short-fibered chrysotile in the study lake sediments.

The large difference between airborne anthophyllite asbestos concentrations from the two lakes is consistent with the lakes' respective locations relative to the talc operations. Iterative calculations using the EPA's SCREEN3 air-quality model (*45*) to derive a source → receptor (Arnold quarry → study lake) relationship for the last half of the 20th century revealed that fiber concentrations decreased downwind at a rate of 0.19 km$^{-1.11}$. Table 4 presents relative aerosol loadings (RAL) from the talc industry for the two lakes

$$RAL_i = w_i 0.19 k_i^{-1.11}$$

where $w_i$ is the percent time wind travels from the talc sources along sector $i$ and $k_i$ is the distance (km) from the talc source to the lake along sector $i$.

When RAL for all winds from the talc area are summed, the study lake has a RAL of 0.0126, which is 32-fold greater than the RAL (0.0004) for the control lake. This is consistent with the 16-fold difference in mean 20th-century airborne anthophyllite concentrations measured in the study lake (0.016 fibers/cm$^3$) and control lake (0.001 fibers/cm$^3$).

These spatial, temporal, and compositional trends point strongly toward talc-related activities as the source of elevated airborne anthophyllite asbestos. This asbestos was essentially absent in the control lake sediments for the last 110 years, indicating that no widespread regional source was present in western New York or other upwind areas. The premining (19th century) study lake sediments contained concentrations less than 15% of the 20th century concentrations, evidence that natural runoff and bedrock within the watershed were not significant sources. Airborne anthophyllite asbestos concentrations were significantly correlated temporally ($r^2 = 0.80$, $p < 0.01$) with local talc production (Figure 6). Continued elevated concentrations at the end of the 20th century are consistent with the change from shaft mining to open-pit mining at the Arnold quarry ("A" in Figure 1) in the 1970s. Finally, the composition of the mineral fibers points

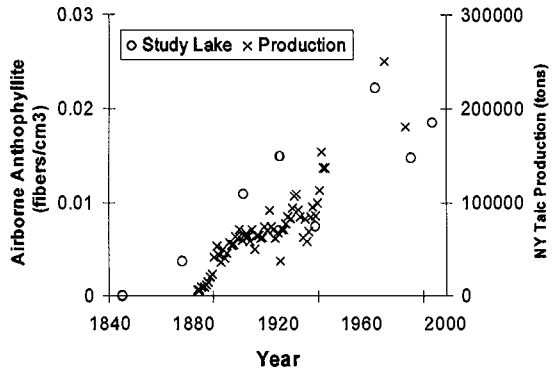


**FIGURE 6. Airborne anthophyllite asbestos concentrations calculated from study lake sediments and corresponding talc production in New York State.**

to talc-industry impact at the study lake. While talc and "intermediate" fibers were detected in all 20th-century sections from the study-lake sediments, no such fibers were detected in any of the control-lake sediment sections.

This study reinforces the assumption that PCM data do not accurately reflect concentrations during the mid-20th century when exposures were most severe. None of the chrysotile fibers detected in this study, including those that were longer than 5$\mu$m, was wide enough to be resolved by PCM. Even anthophyllite, typically much wider than the three commonly used types of asbestos, showed more than 70% of its population below PCM resolution.

Analytical attention has been focused on long asbestos fibers because of laboratory investigations indicating their increased contribution to carcinogenicity (*4*). The majority of anthophyllite fibers detected in this study were <5 $\mu$m long. This paucity of long fibers is consistent with absence of an environmental source related to asbestos diseases in the study area (*18*).

There is a clear need for application of this type of investigation to other geographic areas. Despite the decreased usage of asbestos in developed countries in the last quarter of the 20th century, mesothelioma rates are expected to continue to increase into the 21st century (*46*). In areas where mesothelioma is appearing in persons environmentally exposed (*3, 47*), airborne asbestos concentrations could be reconstructed using these techniques and then linked to the incidence of disease to create new exposure-based risk models.

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