

Sediment chronologies of atmospheric deposition in a precipitation-dominated seepage lake

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Abstract

Chronologies of Pb, polycyclic aromatic hydrocarbons (PAHs), Al, carbon, and *n*-alkanes in pelagic sediments of Crystal Lake, a precipitation-dominated seepage lake in north-central Wisconsin, were determined to investigate the geochemistry of sediments derived from atmospheric deposition and to evaluate the impact of environmental changes in the region on the geochemistry of this oligotrophic lake. Concentrations of Pb and combustion-derived PAHs in Crystal Lake sediments have increased by factors of 8 and 3, respectively, over the past 150 years. In contrast, levels of perylene increased with depth in the sediment, indicating that postdepositional formation of this PAH might be occurring. Atmospheric fluxes of anthropogenic Pb and combustion-derived PAHs were estimated to be 10,000 $\mu\text{g m}^{-2} \text{a}^{-1}$ and 34 $\mu\text{g m}^{-2} \text{a}^{-1}$, respectively. The settling sediment fluxes of planktonic *n*-alkanes ($\Sigma C_{15}, C_{17}, C_{19}$) and terrestrial *n*-alkanes ($\Sigma C_{25}, C_{27}, C_{29}, C_{31}$) in Crystal Lake were 4,400 $\mu\text{g m}^{-2} \text{a}^{-1}$ and 10,500 $\mu\text{g m}^{-2} \text{a}^{-1}$, respectively, whereas their accumulation rates in pelagic sediments were 270 $\mu\text{g m}^{-2} \text{a}^{-1}$ and 7,100 $\mu\text{g m}^{-2} \text{a}^{-1}$, respectively. The large difference between the settling sediment flux and the accumulation rate of the planktonic *n*-alkanes in the sediments is ascribed to microbial degradation during or soon after deposition. In contrast, the terrestrial *n*-alkanes are incorporated in a wax matrix and are protected from degradation. The contribution of terrestrial *n*-alkanes to the organic carbon of the sediments has remained relatively constant over the past 150 years. About 20% of the organic carbon that is incorporated in the present-day sediments of Crystal Lake can be attributed to the deposition of pine pollen in the lake. Deforestation of the region in the late 1800s apparently caused terrigenous inputs and primary productivity of nonsiliceous plankton to increase, because planktonic and terrestrial *n*-alkane concentrations in the sediment increased at about the same time. However, since about 1900 concentrations of organic carbon and of terrestrial and planktonic *n*-alkanes in Crystal Lake sediments have decreased, and concentrations of Al and combustion-derived PAH have increased. These occurrences might reflect a decrease in pollen dispersal in the region and an increase in the atmospheric deposition of fly ash from coal-burning power plants.

The pelagic sediments of precipitation-dominated seepage lakes provide a unique opportunity to study the chronology and preservation of atmospherically and internally derived chemical species. Seepage lakes have no surface water inlets or outlets and receive water exclusively from precipitation and groundwater, so that allochthonous (external) sources of organic matter are restricted to the atmosphere, surface runoff, and groundwater. Autochthonous (internal) sources of organic matter in seepage lakes include plankton, bacteria,

and other aquatic organisms and plants. However, organic substances of allochthonous and autochthonous origin are not equally preserved in sediments (*see, e.g., Meyers and Ishiwatari 1993*). Some organic substances, primarily those derived from in situ production, are decomposed by bacteria during transport to surface sediments and during incorporation into deeper sediment layers. If the organic matter in seepage lakes is apportioned into allochthonous and autochthonous source contributions by using, for example, the biomarker approach (Gagosian and Peltzer 1985), a comparison of the air–water exchange rates of biomarker compounds with their downward fluxes in the lake and their rates of accumulation in bottom sediments can be used to investigate processes controlling the cycling of atmospherically derived organic matter.

Doskey (2000) estimated the air–water exchange rates of semivolatile *n*-alkanes (C_{15} – C_{31}) in Crystal Lake, a precipitation-dominated seepage lake in north-central Wisconsin, by using an air–water exchange model and a mass balance approach. The air–water exchange rates were compared with fluxes for settling sediments within the water column to determine the contribution of atmospheric deposition to the accumulation of organic matter in the lake. Atmospheric deposition and in situ production by plankton were estimated

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to contribute approximately 50% and 30%, respectively of the *n*-alkanes to the water column. The source of the remaining 20% of the external *n*-alkane flux could not be determined, but the material might originate from surface runoff or atmospheric deposition of coarse particles (10–100 μm in diameter). Approximately 30% of the atmospherically derived *n*-alkanes enter the lake during a two-week episode of pine pollen dispersal in the spring. The remaining atmospheric input was also dominated by *n*-alkanes of biogenic origin and resulted from wet and dry atmospheric deposition of particles derived from plant detritus and soil. An insignificant fraction of the *n*-alkanes produced internally within the lake by plankton or entering the lake by atmospheric deposition are volatilized from its surface.

The purpose of this study was to examine the chronology and preservation of atmospherically and internally derived chemical species in the pelagic sediments of a lacustrine system. The investigation was facilitated by focusing it on Crystal Lake, a precipitation-dominated seepage lake located in a semiremote region. In this paper, settling sediment fluxes of terrestrial and planktonic *n*-alkanes are compared with their respective accumulation rates in underlying sediments to evaluate the preservation of *n*-alkanes derived from atmospheric inputs and in situ production (Doskey 1982). Chronologies of Pb (Talbot 1981) and combustion-derived PAHs (Harvey 1986) in pelagic sediments are used to investigate the chronology of anthropogenic material inputs. Sediment profiles of Al, carbon, and the *n*-alkanes are also examined to understand the impact of environmental changes in the Crystal Lake region on the geochemistry of this oligotrophic lake.

Study site

Crystal Lake (46°09'22"N, 89°10'49"W) is located in a semiremote region of the upper Midwestern United States in the Northern Highlands State Forest of Vilas County, Wisconsin, about 80 km southeast of Lake Superior and 190 km west of the northern basin of Lake Michigan. Crystal Lake is a small (36 ha, $3.8 \times 10^6 \text{ m}^3$), oligotrophic, seepage lake (Fig. 1) that receives 90% of its water input from direct precipitation (Armstrong et al. 1987). Sandy sediments are abundant in the littoral zone, extending into the lake for 100–125 m from shore to a water depth of 8–10 m (Twenhofel and Broughton 1939). The sands consist primarily of quartz with little carbonate content. Sediments of the pelagic zone are organic-rich biogenic material exhibiting a mass loss on ignition of 50% (Twenhofel and Broughton 1939). Sources of this organic matter include terrestrial plant and plankton detritus, as well as pollen (Doskey 1982). Conger (1939) estimated that pine and other pollen species compose about 50% of the mass of the pelagic sediments. Diatoms are the major phytoplankton species in the lake (Conger 1939; Hurley et al. 1985).

Methods

Cleaning of labware and sampling apparatus—Extensive precautions were taken to avoid trace metal and organic

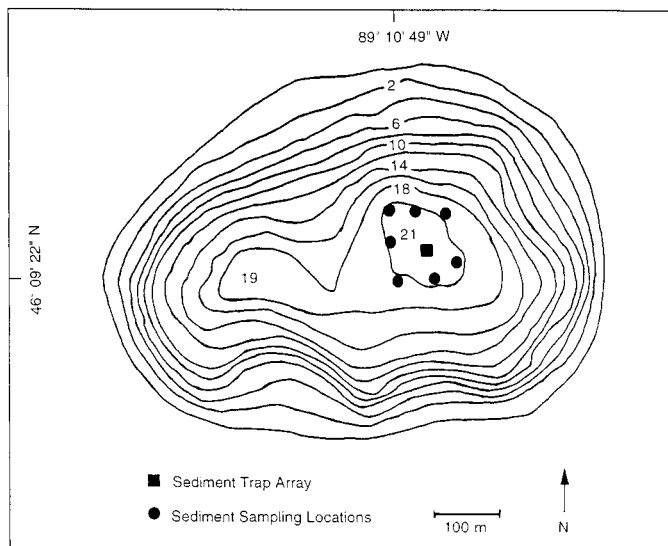


Fig. 1. Morphometry of Crystal Lake and locations of sampling sites. Contours represent water depth in meters.

chemical contamination of the sampling apparatus and analytical labware. New Teflon®, polyethylene, and quartz ware that was used in the trace metal analysis was initially washed with acetone. Teflon® and quartz were soaked for at least five days in 50% HNO₃ while polyethylene was soaked in 50% HCl. Final acid soaking was performed in dilute HNO₃ (0.05%) and then dilute HCl (0.05%) for at least three days in each acid. After acid cleaning, Teflon® and quartz ware were rinsed with subboiling point quartz distilled water and stored in polyethylene bags. Polyethylene sample bottles were filled with subboiling point distilled water and soaked until use. Polyethylene bags were cleaned by shaking with a small amount of concentrated HNO₃. The bags were rinsed and soaked in 0.1% HCl for two days and then rinsed with subboiling point distilled water. Polyethylene core tubes for sediment sampling were cleaned using 1% HCl and rinsed with subboiling point distilled water. Sampling gear was transported to the field in sealed polyethylene bags and handled with nontalced polyethylene gloves during deployment.

Glassware and polyethylene core tubes that were used for trace organic analysis were scrubbed with laboratory detergent, rinsed with distilled water, and rinsed with organic free water. The organic free water was prepared by refluxing distilled water with potassium persulfate and phosphoric acid with subsequent distillation. Laboratory glassware and aluminum foil were rinsed immediately before use with redistilled ACS grade acetone. Sampling gear was transported to the field in foil packets.

Sample collection—Sediment cores were collected in 1979 from the deepest sections of Crystal Lake (Fig. 1), at water depths of at least 17 m. Abundant growths of the moss *Depranocladus aduncus* var. *aquaticus* (Juday and Birge 1932) inhibited coring at shallower depths. Undisturbed cores, approximately 30 cm long, were collected in polyethylene tubes. Visual examination of the cores immediately after collection indicated that the sediment was very ho-

mogeneous and not layered. Intact, chironomid burrow tubes projecting above the sediment surface indicated that the surface flocculent layer was preserved.

Cores were sectioned immediately after collection, stored at 4°C, and transported to the laboratory within 24 h for sample preparation and analysis. Four cores were collected for ^{210}Pb , Pb, Al, and carbon analyses. The upper 3 cm of each core was sectioned at 0.5-cm intervals, and the remainder was sectioned at 1- or 2-cm intervals. Extruded sections were stored in polyethylene bags at 4°C. Three cores were collected for *n*-alkane and PAH analyses; and these cores were sectioned at 3-cm intervals. The sections were placed in glass jars and stored at 4°C until they were returned to the laboratory, where they were stored at -10°C.

Sample analysis—Details of the analytical methods for trace metals and organic compounds have been described elsewhere (Talbot and Andren 1983, 1984; Doskey and Andren 1986; Helfrich and Armstrong 1986). Briefly, for ^{210}Pb analysis a portion of freeze-dried sediment was placed in a quartz beaker, spiked with several dpm of ^{208}Po (a yield tracer), and digested with a 3:2 mixture of HNO_3 and 70% HClO_4 . Polonium was plated onto silver discs by spontaneous deposition as described by Flynn (1968). Simultaneous activity measurements of ^{208}Po and ^{210}Po were performed by alpha-spectrometry with silicon surface-barrier diode detectors. After the initial separation of ^{210}Po , samples were stored for 6 months to 1 year to allow regeneration of ^{210}Po from decay of ^{210}Pb . The newly produced ^{210}Po was determined as a measure of the ^{210}Pb present in the sample. The activity of ^{210}Pb at the time of sample collection was calculated from the two activities of ^{210}Po . Analytical precision for the ^{210}Pb measurements was $\pm 10\%$.

Stable Pb and Al were determined in samples digested as described above. Analysis of Pb and Al were performed on a Perkin-Elmer 603 atomic absorption spectrophotometer with air-acetylene and nitrous oxide-acetylene flames, respectively. Analytical precisions for Pb and Al were $\pm 3\%$ and $\pm 2.5\%$, respectively. Total and organic carbon were measured with a Leco carbon analyzer. Total carbon was determined after dilution of the dry sediment with silica. Tin metal was added to the mixture to facilitate oxidation. Organic carbon was determined similarly after the sediment was pretreated with 3% phosphoric acid to remove inorganic carbon. Analytical precision was $\pm 3.5\%$ for the carbon measurements.

Sediments were freeze dried in preparation for extraction of *n*-alkanes and PAHs with a Virtis (model 10-100) freeze drier modified to eliminate contamination from vacuum pump oil (Doskey 2000). Dried samples were Soxhlet extracted with methylene chloride. Concentrated extracts were eluted through silica gel to isolate an aliphatic hydrocarbon fraction and a fraction containing unsaturated and aromatic hydrocarbons (Doskey and Andren 1986; Helfrich and Armstrong 1986). The PAHs were separated from the unsaturated compounds using Sephadex LH-20 (Harvey 1986; Helfrich and Armstrong 1986). Analysis was performed on a Hewlett-Packard 5840 gas chromatograph equipped with a flame ionization detector and SE-30 and SE-54 wall-coated open-tubular, vitreous-silica capillary columns to resolve the

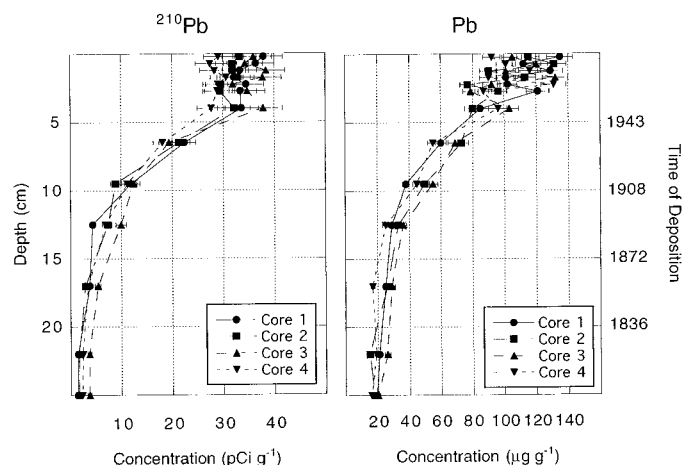


Fig. 2. The concentrations of ^{210}Pb and Pb in four sediment cores from Crystal Lake.

n-alkanes (Doskey and Andren 1986) and PAHs (Helfrich and Armstrong 1986; Harvey 1986). Precision for the *n*-alkane and PAH analyses was $\pm 8\%$.

Results and discussion

Mass sedimentation rate—The vertical profile of unsupported ^{210}Pb in pelagic sediments of Crystal Lake was developed as the arithmetic mean of measurements obtained from four cores (Fig. 2). Evidence that the pelagic zone provided a relatively unbiased depositional environment, from which fluxes of ^{210}Pb could be estimated, included (1) results from the analyses of several cores from the pelagic zone, which indicated that spatial variations of Pb were insignificant (Talbot 1981), and (2) data from Twenhofel and Broughton (1939), which show that sand, silt, and clay fractions vary little within the upper meter of pelagic sediments. The invariant vertical distribution of ^{210}Pb in the upper 4 cm of the profile is ascribed to biological mixing. Evidence for biological mixing is circumstantial, but chironomid worms and their burrow tubes were observed near the sediment-water interface of each core. The benthic activities of tubificid oligochaetes are known to alter sediment particle distributions to depths as great as 10 cm below the sediment-water interface (Davis 1974; Robbins et al. 1977; Krezoski and Robbins 1985; Robbins 1986). The age at the base of the mixed zone in Crystal Lake was estimated to be 29 a, according to the method of Guinasso and Schink (1975). A linear sedimentation rate of 0.14 cm a^{-1} was determined from the undisturbed portion of the ^{210}Pb profile according to the procedure of Robbins et al. (1977). This value corresponds to a mass accumulation rate of $80 \text{ g m}^{-2} \text{ a}^{-1}$. The steady-state flux of unsupported ^{210}Pb to the sediments was estimated to be $0.79 \text{ pCi cm}^{-2} \text{ a}^{-1}$.

The estimate of the ^{210}Pb flux from analysis of pelagic sediments ($0.79 \text{ pCi cm}^{-2} \text{ a}^{-1}$) is in good agreement with the atmospheric deposition rate for ^{210}Pb of about $0.70 \text{ pCi cm}^{-2} \text{ a}^{-1}$ at this site (Talbot and Andren 1983) and a removal rate of $0.81 \text{ pCi cm}^{-2} \text{ a}^{-1}$ based on vertical water column profiles in Crystal Lake (Talbot and Andren 1984). Consequently,

the mass flux of $80 \text{ g m}^{-2} \text{ a}^{-1}$ derived from the ^{210}Pb profile of the pelagic sediments appears to be a good estimate of the mass flux to Crystal Lake. Annual mass sedimentation rates of $200 \text{ g m}^{-2} \text{ a}^{-1}$ and $120 \text{ g m}^{-2} \text{ a}^{-1}$ were measured by Doskey (1982) and Hurley (1984), respectively, with sediment traps that were poisoned to inhibit microbial activity. Both of these values are greater than the time-averaged value determined from ^{210}Pb dating of sediments; however, the values indicate that the year-to-year variability in the mass sedimentation rate is at least 45%. The large disparity between mass sedimentation rates derived from sediment traps versus ^{210}Pb dating of sediments may be due to copepods collected in poisoned traps during grazing, which contribute mass at rates greater than their natural downward flux. Hurley (1984) determined a mass sedimentation rate of $76 \text{ g m}^{-2} \text{ a}^{-1}$ with unpoisoned sediment traps, in excellent agreement with the value determined by ^{210}Pb dating of pelagic sediments.

Chronologies of Pb—A vertical profile of the sediment Pb concentrations of four cores is presented in Fig. 2. Surficial sediment mixing has resulted in a blurred record of the most recent Pb accumulations. The profile exhibits an active mixing zone extending down to a depth of about 4 cm, similar to the one observed for ^{210}Pb . Extrapolating the apparently undisturbed Pb profile to the sediment–water interface indicates that the surface Pb concentration without mixing may be $145 \mu\text{g g}^{-1}$. The present-day (1979) concentration of Pb in the sediment has, therefore, increased approximately eight fold over the past 150 years, with the greatest accumulation occurring in the past 100 years. A present-day steady-state Pb flux of $12,000 \mu\text{g m}^{-2} \text{ a}^{-1}$ can be calculated by assuming that the extrapolated surface Pb concentration is representative of the present-day sediment Pb concentration. Similarly, the pre-1800 Pb flux estimated from a deep sediment Pb concentration of $19 \mu\text{g g}^{-1}$ is $2,000 \mu\text{g m}^{-2} \text{ a}^{-1}$. The present-day anthropogenic flux of Pb is therefore around $10,000 \mu\text{g m}^{-2} \text{ a}^{-1}$.

The increasing concentration of Pb in more recent sediments of Crystal Lake most likely reflects atmospheric inputs of Pb from vehicles that were fueled with leaded gasoline before its use was discontinued in the United States. However, without an evaluation of the isotopic composition of the sediment Pb (*see, e.g.,* Monna et al. 1997) we can only speculate about its origin. For example, Chillrud et al. (1999) suggest that solid waste incineration has been underestimated as a source of atmospheric Pb in aquatic systems in the United States and Europe.

The eight fold increase in Pb concentrations over the past 150 years in Crystal Lake sediments is similar to the approximately 10-fold increase that Furlong et al. (1987) observed in sediments of Big Moose Lake in the Adirondacks region. These increases are greater than the four fold increase over the last 130 years that Shirahata et al. (1980) observed in remote, subalpine pond sediments. Martin (1985) observed an increase in Pb from 4 to $60 \mu\text{g g}^{-1}$ over the past 150 years in sediments of a crater lake in a remote area of France. He estimated that the atmospheric deposition of Pb was $5,000 \mu\text{g m}^{-2} \text{ a}^{-1}$. Hermanson (1991) estimated from sediment core data that the atmospheric flux of Pb to a remote region of Canada was $2,000 \mu\text{g m}^{-2} \text{ a}^{-1}$. We esti-

mate the atmospheric flux of anthropogenic Pb to Crystal Lake to be $10,000 \mu\text{g m}^{-2} \text{ a}^{-1}$, which is 2–5 times greater than the estimates for remote regions of France and Canada. Our estimates are reasonable for the region of our study, which is in an area frequented by vacationers during summer. Elevated levels of atmospheric Pb were observed during summer before its use was discontinued (Talbot and Andren 1983). Consequently, atmospheric fluxes of Pb are expected to be higher for Crystal Lake than for lakes in remote locations. The anthropogenic Pb flux for Crystal Lake is lower than the estimated anthropogenic Pb flux of $15,000 \mu\text{g m}^{-2} \text{ a}^{-1}$ at a midlake site in Lake Michigan, also in the Midwestern United States (Edgington and Robbins 1976). Inputs to Lake Michigan are expected to be higher because of urban runoff and tributary contributions of anthropogenic Pb.

Chronologies of PAHs and Al—Similar vertical profiles were observed in Crystal Lake sediments for several PAHs (phenanthrene, fluoranthene, pyrene, benz(a)anthracene, triphenylene/chrysene, benzo(e)pyrene, and benzo(a)pyrene) that are typically associated with the combustion of organic matter. The profiles exhibited decreasing concentrations to the present and three subsurface maxima. Combining the individual PAH profiles into a single profile for combustion-derived PAHs indicated that their concentration has increased by nearly three fold over the past 150 years (Fig. 3). The present-day flux of combustion-derived PAHs to Crystal Lake is $34 \mu\text{g m}^{-2} \text{ a}^{-1}$, while the pre-1800 flux was $12 \mu\text{g m}^{-2} \text{ a}^{-1}$.

The nearly three fold increase in combustion-derived PAH concentrations over the past 150 years in Crystal Lake sediments is comparable to the five fold increase in PAH concentrations in western Lake Superior sediments over the past 100 years (Gschwend and Hites 1981). Tan and Heit (1981) found concentrations of PAHs in the sediments of two remote Adirondack lakes that were higher by a factor of 5–10 than the levels we observed in Crystal Lake. Concentrations in Sagamore Lake had increased by a factor of 26 from 1913 to 1978, while levels in Woods Lake sediment had increased by a factor of 47 from 1895 to 1978. Furlong et al. (1987) observed nearly a three fold increase in the PAH concentrations in the sediments of Big Moose Lake in the Adirondacks from 1900 to 1980. The PAH flux they measured in about 1980 was $1,500 \mu\text{g m}^{-2} \text{ a}^{-1}$, much greater than the PAH fluxes reported for lakes in the Midwestern United States (Gschwend and Hites 1981; Simcik et al. 1996). The fluxes of PAHs in the Adirondack region are probably greater than fluxes in the Midwest because of long-range transport of emissions from the coal-burning power plants of the Midwestern United States. Combustion-derived PAH fluxes of $350 \mu\text{g m}^{-2} \text{ a}^{-1}$ and $46 \mu\text{g m}^{-2} \text{ a}^{-1}$ were determined for the southern and northern basins of Lake Michigan (Simcik et al. 1996), respectively. Gschwend and Hites (1981) measured a value of $45 \mu\text{g m}^{-2} \text{ a}^{-1}$ for the PAH flux to sediments of western Lake Superior. These values are greater than the PAH flux we calculated for Crystal Lake ($34 \mu\text{g m}^{-2} \text{ a}^{-1}$); however, the fluxes are expected to be higher for Lake Superior and Lake Michigan because they receive PAH inputs from urban runoff and petroleum transportation losses in addition to atmospheric deposition. Furlong et al. (1987) re-

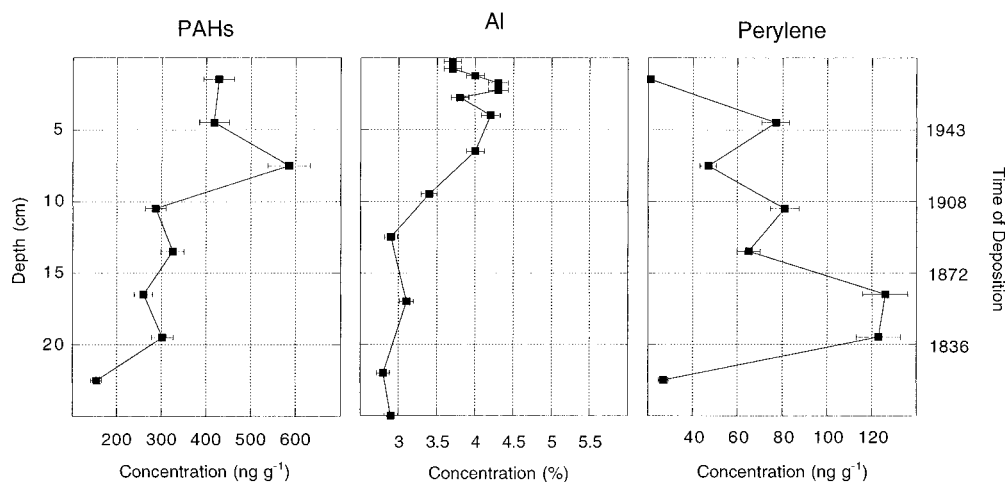


Fig. 3. Concentrations of combustion-derived PAHs (phenanthrene, fluoranthene, pyrene, benz(a)anthracene, triphenylene/chrysene, benzo(e)pyrene, and benzo(a)pyrene), Al, and perylene in Crystal Lake sediment cores. (The concentrations of Al and the combustion-derived PAHs and perylene represent averages from analyses of four and three sediment cores, respectively.)

ported PAH fluxes of $100 \mu\text{g m}^{-2} \text{a}^{-1}$ and $50 \mu\text{g m}^{-2} \text{a}^{-1}$ for McNearney Lake and Hustler Lake, respectively, two small lakes in northern Minnesota. Gschwend and Hites (1981) and McVeety and Hites (1988) estimated PAH fluxes of $36 \mu\text{g m}^{-2} \text{a}^{-1}$ and $57 \mu\text{g m}^{-2} \text{a}^{-1}$, respectively, for Siskiwit Lake on Isle Royale in Lake Superior. The value determined by Gschwend and Hites (1981) for Siskiwit Lake is in good agreement with our estimate for Crystal Lake. The similarity of the two values is expected, because PAHs in Siskiwit Lake sediments, like those in Crystal Lake sediments, are derived solely from the atmosphere (McVeety and Hites 1988). Fernández et al. (1999) investigated high altitude mountain lakes located in remote regions of west and central Europe in which the sole source of allochthonous material was atmospheric deposition. They reported PAH fluxes of $25\text{--}60 \mu\text{g m}^{-2} \text{a}^{-1}$, which are similar to the value we estimate for Crystal Lake and which appear to be typical of atmospheric deposition in remote regions.

The PAHs of anthropogenic origin are derived from the combustion of organic matter and also from petroleum residues. The latter are not expected to be a major source of PAHs in Crystal Lake, because the accumulation rate of an unresolved complex mixture of branched and cyclic aliphatic hydrocarbons in bottom sediment, which is also associated with petroleum residues (Wakeham and Farrington 1980), was less than $0.1 \mu\text{g m}^{-2} \text{a}^{-1}$. The PAHs are also found in vehicle tailpipe emissions; however, they are formed when any organic material (e.g., coal, oil, wood) is combusted (Daisey et al. 1986). If the PAHs were derived from vehicle emissions the concentration profile in Crystal Lake sediments should be similar to the profile of Pb. However, the PAHs exhibited a three fold increase in concentration in Crystal Lake sediments, while Pb exhibited an eight fold increase. These differences may indicate that the most recent accumulations of the PAHs in Crystal Lake sediments are derived from the combustion of coal in power plants and oil and wood for residential heating. More definitive proof of

the PAH sources may be derived from an analysis of their alkyl homolog distributions (see, e.g., Wang et al. 1999).

The Al chronology of the sediments lends support to the hypothesis that a fraction of the most recent accumulations of combustion-derived PAHs in Crystal Lake sediments came from atmospheric deposition of fly ash from coal-burning power plants. Goldberg et al. (1981) report a value of 76 mg g^{-1} for the Al content of fly ash; however, Al in sediments may also be derived from erosional and riverine inputs of aluminosilicate clays. Through an analysis of charcoals in Lake Michigan sediments, Griffin and Goldberg (1983) and Goldberg et al. (1981) showed that material inputs from fossil fuel combustion have increased in the Lake Michigan basin since 1900. Comparing sediments deposited in the 1800s with those of recent origin, they also found that Al concentrations increased from 5% to 5.6%. If the concentration profile of Al in Crystal Lake sediments (Fig. 3) is extended from below the mixed layer to the sediment-water interface, the present-day concentration of Al there is 5.5% while the average concentration in deep sediment ($>15 \text{ cm}$) is 2.2%. Over a 150-year period, the average Al concentration has increased by a factor of 2.5, which is greater than the increase in Lake Michigan sediments, but similar to the increase in the combustion-derived PAH concentration. The increase in Al concentrations in Crystal Lake sediments is expected to be greater than the increase observed in Lake Michigan sediments because of the low clay content of Crystal Lake sediments (Twenhofel and Broughton 1939) and the absence of riverine and erosional inputs to the lake basin.

Natural events such as forest fires might also contribute combustion-derived PAHs to Crystal Lake sediments. An analysis of charcoal and pollen grains in lakes of the region and the observation of fire-scarred trees indicated that forest fires occurred in 1856, 1894, and 1910 in this area (Swain 1978). The width of the core sections (3 cm) obtained for organic chemical analysis precludes assigning an accurate

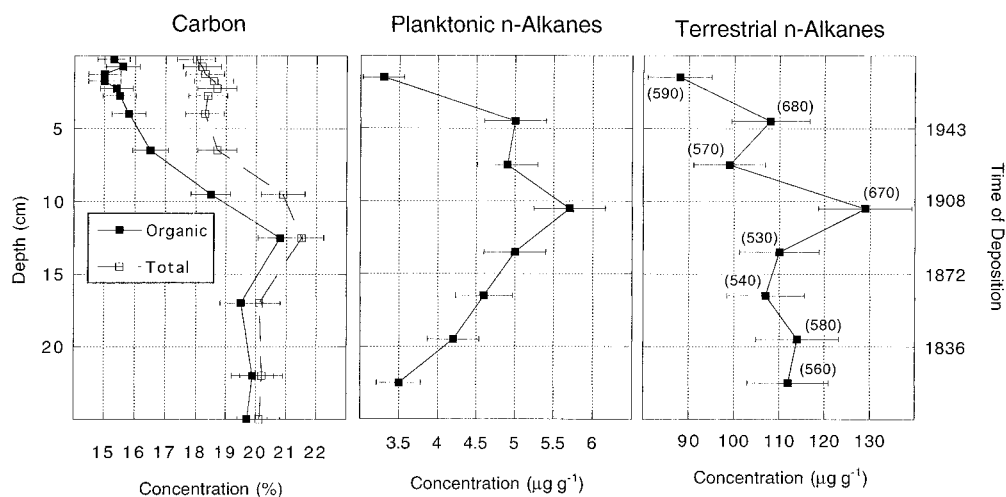


Fig. 4. Concentrations of carbon, planktonic *n*-alkanes ($\Sigma C_{15}, C_{17}, C_{19}$), and terrestrial *n*-alkanes ($\Sigma C_{25}, C_{27}, C_{29}, C_{31}$) in Crystal Lake sediment cores. (The concentrations of carbon and of the planktonic and terrestrial *n*-alkanes represent averages from analyses of four and three sediment cores, respectively. Numbers in parentheses are concentrations of terrestrial *n*-alkanes in organic carbon [$\mu\text{g g}^{-1}$].)

date to characteristics of the vertical sediment profiles; however, the times at which the PAH maxima occurred in Crystal Lake sediments roughly correspond to the occurrences of these events. In sediments of Hustler Lake in northern Minnesota, Furlong et al. (1987) observed a concentration maximum of PAHs that was deposited in approximately 1930 and attributed the increase in PAH flux to logging operations that used rail transport powered by coal- or wood-fired locomotive engines. Interestingly, a PAH concentration maximum in Crystal Lake sediments occurs at approximately the same time; however, the northern Wisconsin region was extensively deforested in the late 1800s (Swain 1978).

The profile of perylene, a PAH believed to be formed in sediments from the diagenesis of biogenic precursors (Orr and Grady 1967; Aizenshtat 1973; Wakeham et al. 1979, 1980b; Hites et al. 1980), was unlike the profiles of the combustion-derived PAHs (Fig. 3). The vertical profile exhibits concentration maxima of similar magnitudes at the base of the mixing zone and at 11.5 cm, with the largest maximum below 15 cm in a sediment layer deposited before the layer containing the largest planktonic and terrestrial *n*-alkane concentrations. Similar sediment chronologies for perylene have been observed in lakes in Switzerland and the United States (Wakeham et al. 1980b). Perylene might be formed in reducing sediments from perihydroxyperylenequinone precursors originating from terrestrial and aquatic sources (Orr and Grady 1967; Aizenshtat 1973). Kinetic models for its formation have been developed (Gschwend et al. 1983). Wakeham et al. (1979) and Hites et al. (1980) also found perylene in sediments characterized as diatomaceous ooze. Because the main species of plankton in Crystal Lake are diatoms (Conger 1939; Hurley et al. 1985) and terrestrial contributions of organic matter to pelagic sediment are substantial (Doskey 2000), precursors from both terrestrial and aquatic sources might be present in Crystal Lake.

Chronologies of carbon and n-alkanes—The *n*-alkanes in pelagic sediments exhibit a distribution indicative of terrestrial sources with a minor contribution from plankton. The major *n*-alkane homologs in many species of nonsiliceous plankton, such as blue-green, green, red, and brown algae, are most often C_{15} , C_{17} , and C_{19} , with the predominant compound being species dependent (see, e.g., Weete 1976). Longer-chain *n*-alkanes such as C_{29} are prevalent in some species of diatoms (Clark and Blumer 1967), the dominant phytoplankton species in Crystal Lake (Conger 1939; Hurley et al. 1985). Blumer et al. (1971) found that *cis*-3,6,9,12,15,18-heneicosahexaene ($C_{21}H_{32}$) was the major hydrocarbon produced by centric diatoms. Although mass spectrometric analyses of the samples were not performed, a gas chromatographic peak eluting before *n*- C_{21} , which could have been this olefinic hydrocarbon, was observed in all extracts of settling and pelagic sediments. Terrestrial plants typically contain *n*-alkanes in the range C_{21} – C_{35} (Eglinton and Hamilton 1963) with carbon preference indices (CPIs; Bray and Evans 1961) of 4–10 (Brassell et al. 1978). The range of the CPI_{20-32} values for the *n*-alkanes in the upper 24 cm of the pelagic sediments of Crystal Lake was 3.9–5.0, indicative of a terrestrial source. For the sake of further discussion, we define the terrestrial *n*-alkanes as $\Sigma C_{25}, C_{27}, C_{29}, C_{31}$ and the planktonic *n*-alkanes as $\Sigma C_{15}, C_{17}, C_{19}$.

Concentrations of terrestrial *n*-alkanes were greater by at least a factor of 20 than the concentrations of planktonic *n*-alkanes throughout the vertical profile of the sediment (Fig. 4). The profile of the planktonic *n*-alkane concentrations exhibits a steady increase from 1800 to 1900, with levels then decreasing to the present. The terrestrial *n*-alkane and organic carbon (OC) profiles (Fig. 4) are similar and also show decreasing concentrations from about 1900 to the present. The highest sediment carbon, planktonic *n*-alkane, and terrestrial *n*-alkane concentrations occurred in about 1900. Ter-

restrial *n*-alkane contributions to the OC have not changed appreciably throughout the length of the core, except for a layer at the base of the mixing zone and the maximum occurring in about 1900 (Fig. 4). However, OC levels have decreased relative to total carbon concentrations in the upper layers of the sediment since that time.

Maxima in the profiles of OC and in the planktonic and terrestrial *n*-alkane profiles were observed in sediments deposited in about year 1900. Swain (1978) found an increase in ragweed pollen (*Ambrosia*) in sediments of northern Wisconsin lakes deposited just before the turn of the 20th century and attributed the change to extensive deforestation of this area in the late 1800s. The terrestrial *n*-alkane profile indicates that the period of deforestation coincided with a period of elevated terrigenous inputs of material to Crystal Lake. Terrestrial *n*-alkane concentrations normalized to the levels of organic carbon in the sediment increased by a factor of 1.3 during this time (Fig. 4), possibly indicating a change in the external source of organic matter. The new sources might have been diffuse surface runoff or atmospheric inputs of pollen from herbaceous plants. Conger (1939) estimated that pine and other pollens contributed about 50% of the mass of Crystal Lake sediments; however, no chronology of pollen types and numbers in the sediments is available for use in evaluating changes in the composition of pollen and pollen loadings. Another source of terrestrial *n*-alkanes during this period could have been diatoms. Clark and Blumer (1967) reported concentrations for ΣC_{15} , C_{17} , C_{19} and ΣC_{25} , C_{27} , C_{29} , C_{31} of $11 \mu\text{g g}^{-1}$ and $43 \mu\text{g g}^{-1}$, respectively, in *Skeletonema costatum*. However, Hurley et al. (1985) reported that the net accumulation in Crystal Lake sediments of particulate biogenic silica (PBS), which is largely composed of diatom frustules, has not changed significantly over the past 175 years. Thus, the diatom population of Crystal Lake has apparently been stable since about 1800 and was not responsible for the elevated levels of terrestrial *n*-alkanes around the turn of the century.

The nutrient dynamics of the lake were apparently altered approximately when the region was deforested, because the planktonic *n*-alkane content of the sediments reached a maximum at this time and then declined. Because the diatom population of Crystal Lake has been stable since about 1800, changes in the sediment accumulation of planktonic *n*-alkanes might coincide with variations in the population of nonsiliceous phytoplankton. Phosphorus is a limiting nutrient for the growth of phytoplankton in many aquatic systems. Phosphorus enrichment of a lake can result in biogenic reductions in silica levels so severe that diatoms cannot effectively compete with the nonsiliceous phytoplankton (Kilham 1971; Schelske and Stoermer 1971). This condition apparently has not occurred in Crystal Lake over the last 175 years, even though the productivity of phytoplankton species other than the diatoms reached a peak during the period of deforestation.

The external sources of phosphorus during the period of deforestation are unknown but may have included (1) pollen dispersal from herbaceous plants, (2) diffuse surface runoff of nutrient-rich soils, and (3) elevated groundwater inputs of nutrients. Doskey and Ugoagwu (1989) estimated that pine pollen is currently responsible for approximately 45% of the

external input of total phosphorus to Crystal Lake. About 60% of this phosphorus is in a dissolved, reactive form that is readily available for uptake by phytoplankton. Therefore, the planktonic *n*-alkane maximum might represent a peak in the nonsiliceous phytoplankton population of the lake just before deforestation, with pollen dispersal from a mature forest being the primary external source of nutrients. It is also possible that in the years immediately following deforestation, pollen dispersal from herbaceous plants might have been responsible for higher nutrient loadings and greater nonsiliceous phytoplankton production in Crystal Lake. The concentration of total phosphorus in pollen of *Ambrosia trifida* is greater by nearly a factor of 2 than the concentration in *Pinus resinosa* pollen (Doskey and Ugoagwu 1992). The abrupt change in the concentration of terrestrial *n*-alkanes in the sediment OC is indicative of a new source of terrestrial material and coincides with the peak in the planktonic *n*-alkane concentration. If the new source of terrestrial material was also the source of the nutrients, then a change in the pollen source or diffuse surface runoff might have been the external source of nutrients during this period. Diffuse surface runoff in the area immediately surrounding the lake could have increased when the forest canopy was eliminated. However, if the sources of organic matter and nutrients were different during this period, then groundwater inputs of phosphorus might have increased when the region was deforested. Elimination of the forest canopy could have increased the flow of precipitation to a groundwater recharge area. Doskey and Ugoagwu (1989) estimated that groundwater currently contributes about 2% of the annual input of total phosphorus to Crystal Lake; pine pollen dispersal and atmospheric deposition contribute nearly equal amounts of the remaining annual phosphorus loading.

The present-day source of terrestrial *n*-alkanes in Crystal Lake sediments is terrestrial plant waxes associated with plant detritus, soil, and pine pollen that enter the lake primarily by atmospheric deposition (Doskey and Andren 1986; Doskey 2000). The contribution of terrestrial *n*-alkanes to the OC of the sediments in Crystal Lake has not changed appreciably over the last 150 years, except for sediments deposited around 1900 and 1950 (Fig. 4). Armstrong et al. (1987) estimated that the present-day flux of OC to Crystal Lake sediments is $33 \text{ g C m}^{-2} \text{ a}^{-1}$, with $17 \text{ g C m}^{-2} \text{ a}^{-1}$ being incorporated into the sediments. Doskey and Ugoagwu (1989) estimated the OC flux from pine pollen to be $3.3 \text{ g C m}^{-2} \text{ a}^{-1}$ or 10% of the flux of OC to Crystal Lake sediments. Because the pollen exine is resistant to biodegradation, it might represent nearly 20% of the OC that is incorporated into Crystal Lake sediments. This value is consistent with analyses of the atmospheric and settling sediment fluxes of *n*-alkanes in Crystal Lake, which showed that pine pollen dispersal is responsible for approximately 15% of the terrestrial *n*-alkanes in the settling sediments (Doskey 2000).

Two hypotheses may explain the decrease in OC concentrations relative to the total carbon concentrations in Crystal Lake sediments since about 1900. If the concentration profile of carbon (Fig. 4) is extended from below the mixed layer to the sediment-water interface, the present-day concentrations of OC and total carbon are 14.7% and 17.1%, respectively, while the average deep-sediment concentrations (>15

Table 1. Annual sediment trap fluxes and surface sediment accumulations of *n*-alkanes in Crystal Lake.

<i>n</i> -Alkane*	Flux or accumulation rate at depth indicated ($\mu\text{g m}^{-2} \text{a}^{-1}$)	
	18 m†	0–3 cm‡
15	400	ND§
17	3,700	100
19	280	170
25	2,800	1,700
27	3,700	2,600
29	2,500	1,600
31	1,500	1,200

* Number of carbon atoms in *n*-alkane.

† Depth of sediment trap below surface of water.

‡ Depth of sediment core section. Mass sedimentation rate = $80 \text{ g m}^{-2} \text{a}^{-1}$.

§ Not detectable.

cm) are 19.6% and 20.2%, respectively. Over a 150-year period, the average Al concentration (Fig. 3) has increased approximately as much (3.3%) as the total carbon has decreased (3.1%), while the OC has decreased by 4.9%. The reasons for the increase in Al and the decrease in OC relative to total carbon in sediments deposited after 1900 are not readily apparent. One hypothesis, that pollen inputs are decreasing as a result of land clearing in the region, is supported by a decrease in terrestrial *n*-alkane concentrations in pelagic sediments since about 1900. Another hypothesis is that the increases in Al and inorganic carbon concentrations in recent Crystal Lake sediments reflect an increase in atmospheric inputs of fly ash from coal combustion, a theory supported by the chronology of the combustion-derived PAHs. The increase of inorganic carbon in the sediments of Crystal Lake might also be attributed to atmospheric inputs of inorganic carbon from fly ash. We suspect that a decrease in pollen inputs and an increase in atmospheric deposition of fly ash have both contributed to recent changes in the carbon accumulation rates in Crystal Lake sediments.

Early diagenesis of n-alkanes—To examine the early diagenesis of *n*-alkanes in Crystal Lake, annual sedimentation rates derived from sediment trap deployments (Doskey 2000) are compared with accumulation rates in sediment in Table 1. Accumulation rates were calculated as the product of the sediment *n*-alkane concentrations in the surface 3 cm of sediment and the mass sedimentation rate calculated from ^{210}Pb activity. The flux of planktonic *n*-alkanes in settling sediments is 16 times greater than their accumulation rate in the sediment. Some of the disagreement could be due to overtrapping of zooplankton. However, the effect of this process on planktonic *n*-alkane fluxes is unknown. Previous studies have indicated that planktonic lipids are more susceptible to microbial decomposition than are the terrestrial plant lipids sequestered within a protective wax matrix (Prahl et al. 1980; Wakeham et al. 1980a; Bates et al. 1984; Meyers et al. 1984). Our data support these investigations, which show a rapid decomposition of planktonic *n*-alkanes in aquatic systems.

The flux of terrestrial *n*-alkanes in settling sediments is 1.5 times greater than their accumulation rate in pelagic sed-

iments. We defined the terrestrial *n*-alkanes as $\Sigma C_{25}, C_{27}, C_{29}, C_{31}$. Clark and Blumer (1967) reported a predominance of C_{29} in a fairly uniform *n*-alkane homolog distribution over the range C_{25} – C_{31} for the diatom species *S. costatum*. The concentrations of $C_{25}, C_{27}, C_{29}, C_{31}$ in this species of diatom were 10, 11, 13, and $9 \mu\text{g g}^{-1}$, respectively. Thus, a fraction of the *n*-alkanes in settling and pelagic sediments of Crystal Lake that we define as being derived from terrestrial plant waxes might in fact originate from diatoms. In addition, because the *n*-alkanes of planktonic origin are degraded more rapidly during sedimentation and burial in the sediments than are *n*-alkanes of terrestrial origin, the flux of $\Sigma C_{25}, C_{27}, C_{29}, C_{31}$ by settling sediments would be greater than their accumulation rate in surface sediments of Crystal Lake. The contribution of diatom *n*-alkanes to $\Sigma C_{25}, C_{27}, C_{29}, C_{31}$ can be calculated by using the PBS flux of $4.5 \text{ g m}^{-2} \text{a}^{-1}$ to Crystal Lake sediments (Hurley et al. 1985). Assuming that the PBS is entirely diatoms, we calculate the flux of $\Sigma C_{25}, C_{27}, C_{29}, C_{31}$ by diatoms to be about $200 \mu\text{g m}^{-2} \text{a}^{-1}$, which indicates that the flux of terrestrial hydrocarbons by settling sediments remains greater than their accumulation rate in Crystal Lake sediments by about $3,200 \mu\text{g m}^{-2} \text{a}^{-1}$. A detailed hydrocarbon analysis of the different plankton species in Crystal Lake, specifically for biomarkers such as *cis*-3,6,9,12,15,18-heneicosahexaene, would be useful in apportioning the autochthonous and allochthonous source contributions of the settling and pelagic sediments.

Conclusions

A mass sedimentation rate of $80 \text{ g m}^{-2} \text{a}^{-1}$ was calculated for Crystal Lake by using ^{210}Pb dating of pelagic sediments. Sediment trap deployments indicated that the year-to-year variability of the mass sedimentation rate could be as high as 45%. Concentrations of Pb and combustion-derived PAHs in Crystal Lake sediments have increased by factors of 8 and 3, respectively, over the past 150 years. Atmospheric fluxes of anthropogenic Pb and combustion-derived PAHs were estimated to be $10,000 \mu\text{g m}^{-2} \text{a}^{-1}$ and $34 \mu\text{g m}^{-2} \text{a}^{-1}$, respectively, values consistent with fluxes derived for other lacustrine systems in the Midwestern United States. Sources of the most recent Pb accumulation are most likely emissions from vehicles fueled by gasoline that contained Pb before its use was discontinued in the United States. Origins of the combustion-derived PAHs are probably fly ash from coal-burning power plants; emissions from coal, wood, and oil combustion in home heating plants; and forest fires. Concentrations of perylene increased with depth in pelagic sediment, indicating that this compound was being formed in Crystal Lake sediments.

The annual flux of terrestrial *n*-alkanes by settling sediments in Crystal Lake is 2.4 times greater than the flux of planktonic *n*-alkanes. Comparisons of the fluxes of planktonic and terrestrial *n*-alkanes in settling sediments with their accumulation in underlying sediments indicated that (1) the planktonic *n*-alkanes are degraded during or soon after deposition, and (2) the terrestrial *n*-alkanes accumulate in the sediments, most likely because they are protected from microbial decomposition by a plant wax matrix. Maxima in the

OC, planktonic *n*-alkane, and terrestrial *n*-alkane sediment chronologies coincided with a period of deforestation during which terrigenous inputs and primary productivity of non-siliceous plankton apparently increased; however, concentrations of these same chemical species have decreased since that time, indicating that primary productivity of nonsiliceous algae and terrigenous inputs have been decreasing. The diatom population of Crystal Lake has apparently been stable over the same time period. Decreasing levels of OC in the sediments might reflect reductions in pollen loadings as a result of land clearing in the region. However, the increases in concentrations of inorganic carbon, Al, and combustion-derived PAHs in pelagic sediments over the same period suggest that an increase in the atmospheric deposition of fly ash from coal-burning power plants also contributed to the decrease in OC concentrations relative to total carbon levels. The contribution of the terrestrial *n*-alkanes to the OC levels in sediment has remained relatively constant over the past 150 years, with 20% of the OC that becomes incorporated in present-day sediments of Crystal Lake being attributed to the deposition of pine pollen in the lake. Pollen dispersal might have been, and might presently be, uniquely involved with the productivity of Crystal Lake, because this episodic input of organic matter is also responsible for a substantial fraction of the present-day nutrient loading to the lake.

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