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Effects of Holocene climate change on mercury deposition in Elk Lake, Minnesota: The importance of eolian transport in the mercury cycle

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ABSTRACT

Sediments in Elk Lake, Minnesota, consist of 10,400 varve layers that provide a precise chronology for Holocene fluctuations in climate and biota recorded in the strata. Progressively greater concentrations and accumulation rates of mercury since ca. A.D. 1875 reflect deposition of anthropogenic mercury additions to the atmosphere. Within the Holocene record are numerous short intervals in which mercury concentrations and accumulation rates exceed the modern values. The highest mercury concentrations formed ca. 8 ka, coincident with a rapid change from cool, moist conditions to warm, dry conditions. A related change in flora from pine forest to prairie caused destruction of organic forest soils and the release of mercury that had been sequestered in them, resulting in a short-lived pulse of mercury to the lake. Accumulation rates of mercury were highest during the 4 k.y. mid-Holocene dry interval and show a correlation with periods of rapid deposition of eolian dust. The mercury was probably bound to wind-borne mineral particles, which were derived from an unidentified mercury-rich source region west of Elk Lake.

Keywords: mercury, lake sediments, eolian, paleoclimate, Minnesota.

INTRODUCTION

Mercury in lake sediments has received much attention in recent years because the widely observed increase in mercury concentrations and accumulation rates in sediments deposited during the past century is commonly accepted as a record of increasing anthropogenic input of mercury to the atmosphere and subsequent atmospheric deposition to lakes (e.g., Swain et al., 1992; Engstrom and Swain, 1997, for lakes in Minnesota). Fewer studies have examined longer-term mercury trends, documented preindustrial mercury variations, or discussed causes of those variations. We present here data on mercury accumulation in sediments of Elk Lake for the past 11 k.y. These data not only show a recent anthropogenic component of mercury deposition, but also record many intervals during the past 8 k.y. when natural processes produced mercury accumulations greater than the modern anthropogenic accumulations. We document a correspondence between these intervals and paleoclimatic events, and interpret causative factors for variations in prehistoric mercury deposition.

Elk Lake (Fig. 1) is a small seepage lake, the bottom sediments of which preserve a detailed record of climate and related biotic changes for the past 11 k.y. Cores containing a continuous sequence of 10,400 varves were the basis for extensive and varied studies, mostly reported in Bradbury and Dean (1993). Those studies documented climatic oscillations during the past 11 k.y. and the resulting physical and chemical changes in the lake, its biota, and the vegetation in the surrounding region. Elk Lake thus provides an extraordinary opportunity to relate variations in mercury accumulation during the Holocene to a host of potential causative factors.

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PROCEDURES

Sediment cores were taken from the deepest part of Elk Lake (29.5 m) with a modified Livingston piston corer. Details of coring and construction of the varve time scale were given in Anderson et al. (1993a). Each sample for geochemical analysis was a composite of 50 varves (Dean, 1993). Samples for the interval 3000–5000 varve years were also collected from overlapping oriented piston cores collected for paleomagnetic studies (Sprowl and Banerjee, 1985, 1993). Samples of unlaminated sediment below the oldest varved interval (~10,400 varve yr ago) were assumed to have the same sedimentation rate as the oldest varve interval. This extends the time series to 11 ka. The samples were dried, ground, and stored in plastic vials. We analyzed 114 samples for total mercury. Sufficient sample for mercury analyses did not exist for a few samples, hence the sample density is not constant. The densest sampling was for the interval 3000–5000 varve years, where we had overlapping cores. Additional samples were collected at 1 cm intervals (representing an average of 2.4 yr per sample) from a frozen box core for the period ca. A.D. 1870–1977 (Dean et al., 1994). Most of this uppermost interval of Elk Lake sediments is not varved and is disturbed because of logging activities that began in 1903.

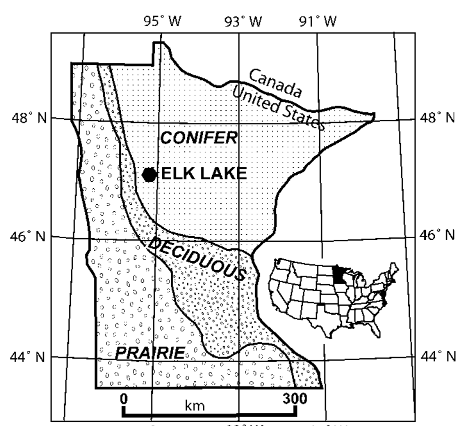

Figure 1. Map of Minnesota showing location of Elk Lake and present zones of natural vegetation.

Constant-volume samples (1.0 cm^3) centered on every 50th varve were weighed wet, dried, and weighed dry. This provided water content and dry bulk density (DBD) (Dean, 1993). Values of DBD combined with linear sedimentation rate provided bulk-sediment accumulation rates.

Mercury concentrations (total Hg) were determined using a cold vapor–atomic absorption (CV-AA) technique. After digestion with nitric acid, sulfuric acid, and vanadium pentoxide, the samples were mixed with air and a solution of sodium chloride, hydroxylamine hydrochloride, and sulfuric acid. Hg^{2+} was reduced to Hg^0 with stannous chloride solution in a continuous flow manifold. Elemental mercury vapor was separated and measured using CV-AA spectrometry. The method has a lower detection limit of 0.02 ppm and relative standard deviation of 10%. Four reference materials, which included a stream sediment (GSD-6), soil (NIST 2709), hot springs deposit (GXR-3), and porphyry copper mill heads (GXR-4), were analyzed along with the unknown samples. Results for all reference materials were within 10% of their certified values. A digestion duplicate was also performed

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on an unknown sample. The difference between these samples was <8%. A more detailed explanation of the uses of reference materials and digestion duplicates can be found in Bullock et al. (2002).

ELK LAKE CLIMATE AND VEGETATION RECORD

Elk Lake is ideally situated for studies of Holocene climate change because it is near the intersection of three air masses that control the climate of this continental interior region (Bryson and Hare, 1974). A small change in the behavior of any of these masses can produce a substantial change in the local climate. The lake is within a steep gradient of climatically controlled ecological zones (Fig. 1), so Holocene climate changes have produced major variations in flora.

The Holocene climate history of the Elk Lake area has been divided into three phases (Anderson et al., 1993b). From glacial retreat until about 8 ka, the climate was cold and moist and the region was covered with conifer forests. At ~8000 varve years, a rapid change to warmer and drier conditions resulted in eastward migration of the prairie, and Elk Lake was transformed from a lake that was wind-protected in a boreal pine forest to a prairie lake (Whitlock et al., 1993) receiving dust blown from a northwesterly source (Anderson, 1992; Dean et al., 2002). Prairie conditions prevailed for the ensuing 4 k.y. Conditions were sufficiently dry that fields of sand dunes east and southeast of Elk Lake became active ca. 8 ka (Grigal et al., 1976). At ~4000 varve years the climate reverted to cooler and moister conditions and a mixed hardwood-conifer forest returned to the Elk Lake area.

MERCURY IN ELK LAKE SEDIMENTS

Modern Record

Sediments deposited from ca. 1870 to 1977 (frozen box core samples) show a trend toward higher mercury concentrations and faster mercury accumulation rates (MARs) in younger sediments. MARs were calculated assuming constant bulk sedimentation rates for this interval, and are considered approximate inasmuch as actual sediment accumulation rates may vary. Concentrations vary from 75 ppb at the base to ~200 ppb at the top and MARs are ~10 $\mu g \cdot m^{-2} \cdot yr^{-1}$ at the base and ~20 $\mu g \cdot m^{-2} \cdot yr^{-1}$ at the top. These values are consistent with those reported by Swain et al. (1992) and Engstrom and Swain (1997) for other midcontinent North American lakes. The increase in mercury deposition through this time interval is probably the result of progressive increases in anthropogenic releases of mercury to the atmosphere and consequent increases in atmospheric mercury deposition to the lake.

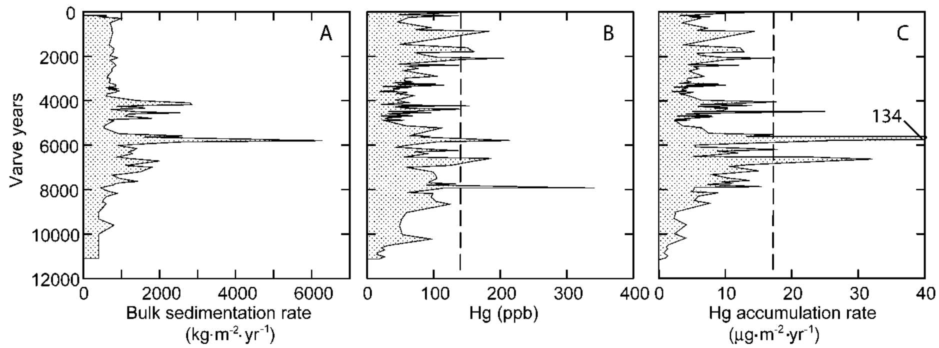

Figure 2. Profiles of bulk sedimentation rate (A), Hg concentration (B), and Hg accumulation rate (C) for past ~11 k.y. in Elk Lake. Values are for total Hg. Each data point is composite of 50 varve couplets. Dashed vertical lines in B and C are average mercury values for period 1924–1977.

Holocene Record

Figure 2 shows bulk sedimentation rate, mercury concentration, and MARs for the past 11 k.y. Although modern MARs, controlled by anthropogenic activity, are higher than the long-term average for the lake, they have been exceeded several times during the Holocene as a result of natural processes. Bulk sedimentation rates (Fig. 2A) are highest in the interval 4000–8000 varve years, caused by eolian deposition during dry, windy periods (Bradbury et al., 1993; Dean et al., 1996, 2002; Dean, 1997). Many of these peaks in sedimentation rate correspond to peaks in Hg concentration in the sediments (Fig. 2B). Peaks in MAR (Fig. 2C) reflect both increased sedimentation rate and, in part, peaks in mercury concentrations. Thus it appears that two aspects of eolian deposition are important in determining the MAR for Elk Lake. First, increases in bulk sedimentation rate produce expectable increases in MAR. However, because most peaks in bulk sedimentation rate also correspond to peaks in mercury concentration, the material deposited by winds during periods of high sedimentation rates appears to have had mercury concentrations greater than those of sediments produced within the lake. Some other Hg peaks do not correlate with bulk sedimentation rates, particularly the concentration maximum at 8000 varve years, indicating that additional factors have been significant.

CAUSATIVE FACTORS IN MERCURY VARIATIONS IN THE ELK LAKE RECORD

The Elk Lake sediment record provides a rich history of both century-scale and millennial-scale variability in mercury concentration and accumulation rates. In the following sections we discuss six of the most prominent peaks in mercury accumulation and document that they correlate either with variations in rates of eolian sedimentation or with rapid climate and vegetation change. Several additional peaks, particularly in the interval from ~1500–3000 varve years, do not show such correlations, indicating that additional, as yet undefined processes, also have played a role in producing variations in mercury deposition on a time scale of roughly a century.

Climate and Vegetation Change

Figure 3 shows that the highest concentration of mercury in the Elk Lake sediments (340 ppb average for 50 yr) formed at ~8000 varve years and is coeval with a rapid shift from a wind-protected lake in a conifer forest to an unprotected prairie lake, indicating a change from a cool, moist climate to warmer and drier conditions (Dean et al., 2002). The 8000 yr spike is not related to increased bulk sedimentation rates. We suggest that this spike records release of mercury that had been sequestered in forest floor organic material, similar to the present-day mercury-bearing O horizons. The rapid, climatically induced change from conifer forest to prairie lead to a breakdown of the forest floor organic layer and the release of its mercury content. The concentration maximum is defined by a single sample, and adjacent younger (94 ppb) and older (116 ppb) samples are only slightly above background levels, attesting to the short-lived nature of this mercury depositional event. Although the climate change may have spanned several hundred years, the response of the ecosystem may have been more abrupt. The conifer forest may have persisted through initial climate modification and eventually died rapidly as some threshold tolerance was exceeded or as forest fire frequency increased because of drier and windier conditions.

Modern forest soils near Elk Lake average 130 ppb mercury in the organic layer (Nater and Grigal, 1992). Mercury in soils is largely bound to sulfur in carbonaceous organic matter (Skyllberg et al., 2000) and thus is susceptible to mobilization during decomposition of the organic matter. We suggest that deforestation of the Elk Lake watershed ca. 8 ka and breakdown of the organic forest soils released mercury in a largely soluble form that was

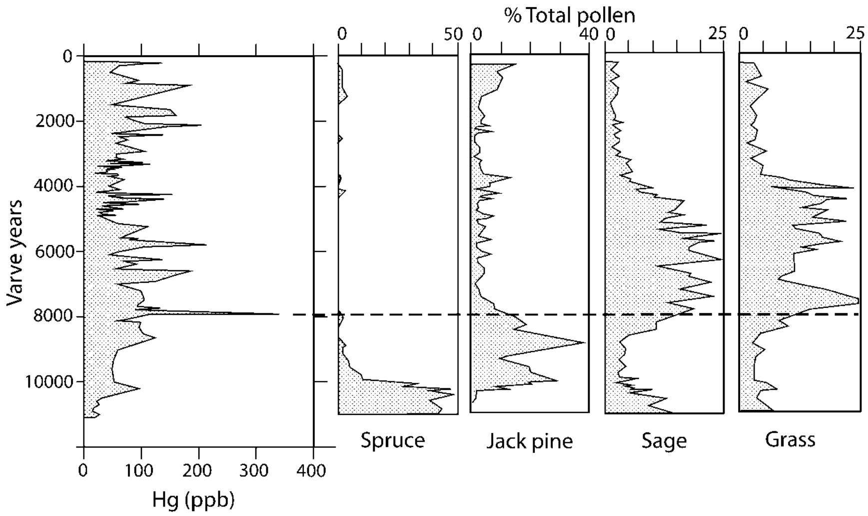

Figure 3. Profile of mercury concentration compared to some major pollen types (pollen data from Whitlock et al., 1993).

transported to Elk Lake by groundwater or surface runoff. This mechanism provides a mercury source indigenous to the Elk Lake watershed and is not dependent on increased sediment input to the lake.

Mid-Holocene Aridity and Eolian Deposition

The mid-Holocene (4000–8000 varve years) in Elk Lake was a time of relatively rapid deposition of eolian dust, and mercury depositional patterns vary in accord with the eolian patterns. The mean mid-Holocene MAR (12.2 $\mu g \cdot m^{-2} \cdot yr^{-1}$) is twice as high as the mean late Holocene rate (6.1 $\mu g \cdot m^{-2} \cdot yr^{-1}$) and about four times higher than the early Holocene rate (3.0 $\mu g \cdot m^{-2} \cdot yr^{-1}$). The probability that the means represent different populations is 0.98. In more detail, four peaks of mercury concentration and five peaks of MAR correspond to times of high bulk sediment accumulation rates. Figure 4 shows three of numerous variables that have been measured previously and interpreted to record varying rates of eolian input. The relative abundance of quartz and aluminum reflects additions of wind-borne mineral dust (Dean, 1993), and the abundance of *Aulacoseira*, a diatom that thrives during periods of high water turbulence, is a measure of windiness (Bradbury and Dieterich-Rurup, 1993). Peaks in mercury concentration at ~900 (183 ppb), ~4200 (154 ppb), ~5800 (214 ppb), and ~6600 (186 ppb) varve years correspond to peaks of input of eolian dust. The most direct interpretation of this correspondence is that wind-borne dust particles were derived from a source that had higher mercury concentrations than did sediments produced within watershed. Data on the mercury content of fine-grained materials in the region are sparse. One obvious potential source for dust is the extensive beds of glacial Lake Agassiz, which cover a very large area west and north (upwind) of Elk Lake. We have determined the Hg content for 13 samples from a region within 100 km west of Elk Lake. The samples were from drill holes and were selected to represent a spectrum from nearshore to deeper water deposits of Lake Agassiz. Although our samples are from the shallow subsurface, similar facies likely occur at the surface in various parts of the Aggasiz basin. The mean Hg concentration was <30 ppb and the highest concentration was 49 ppb. If these are representative of Lake Agassiz sediments as a whole, the Agassiz lake plain does not appear to be a likely source for Hg-enriched dust. One might speculate that more organic surficial material on the Aggasiz plain could have contributed to the dust source and may have been richer in mercury. However, source areas for eolian dust are likely to be dry and have at best poorly developed organic soils. Furthermore, there are no corresponding carbon peaks accompanying the mercury peaks as might be expected if the mercury were transported on organic particles. Soils in part of Manitoba and Saskatchewan, several hundred kilometers or more northwest of Elk Lake, have an average background concentration of ~180 ppb mercury for the clay-sized fraction (McMartin et al., 1999). Therefore, it seems possible that fine-grained fractions of some glacial materials could contain adequate mercury to account for the concentrations observed in Elk Lake, assuming that winds had winnowed sediment sources and extracted the relatively mercury-rich fine mineral fraction. The lack of an obvious source of Hg in nearby surficial materials suggests a more distant source of dust, possibly the northern Great Plains of the west-central United States and Canada, where extensive dune fields have been active repeatedly during the Holocene

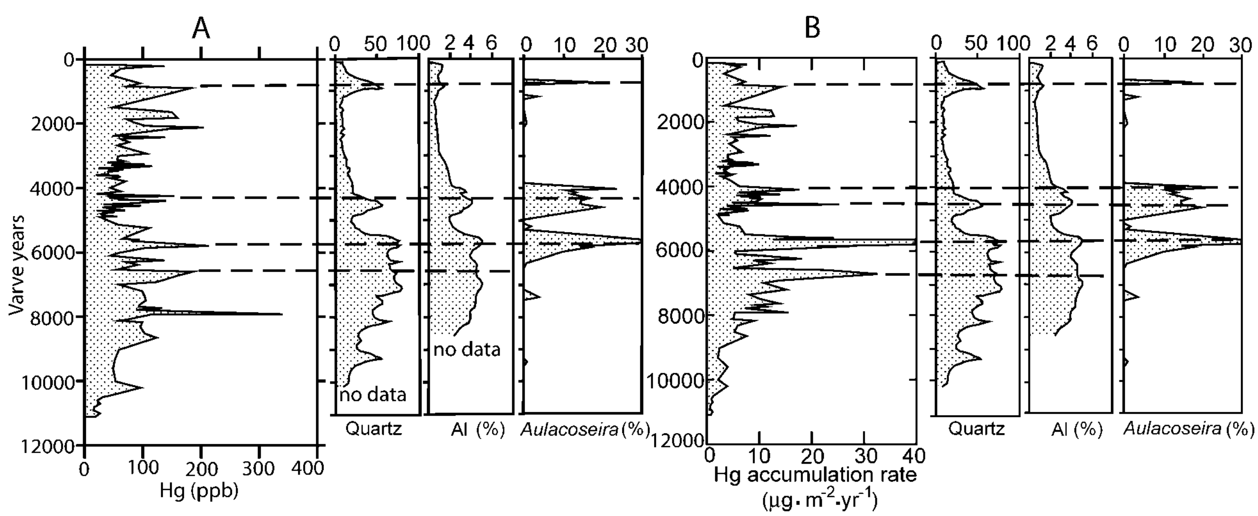

Figure 4. Correspondence between some mercury concentration peaks (A) and accumulation rate peaks (B) and indicators of eolian deposition. Quartz is expressed as relative peak height on X-ray diffractograms and Al as weight percent Al (Dean, 1993), *Aulacoseira* as percent of total diatoms (Bradbury and Dieterich-Rurup, 1993).

(Muhs and Wolfe, 1999). The most recent peak in Hg accumulation rates, at ~900 varve years, is coeval with the most recent reactivation of dunes in the Nebraska sand hills and an inferred regional drought (Swinehart and Loope, 2001), further indicating that Elk Lake records the history of wind erosion in regions remote from its watershed (Dean et al., 1996). The correlation between windiness and mercury concentration may also indicate that the source of mercury-rich dust was geographically remote. Extremely windy conditions may have been necessary to achieve long-distance transport of this material in sufficient quantity to significantly affect the sediment composition. During less windy conditions, more local dust may have dominated.

CONCLUSIONS

Elk Lake sediments record the widely recognized trend of increasing concentration and accumulation rate of mercury in its most recent sediments—a trend almost universally accepted as a reflection of increased anthropogenic release of mercury to the atmosphere. In addition, Holocene sediments record several intervals during the past 8 k.y. when natural processes produced concentrations and/or accumulation rates equal to or greater than modern values. The highest concentration of mercury, about twice the modern average, accumulated ca. 8 ka, when a sudden warming and drying of the climate resulted in destruction of a long-lived conifer forest surrounding Elk Lake and its replacement by prairie flora. We speculate that mercury had been sequestered in organic matter in the forest soil and was released as that soil was modified or destroyed by the climatic and related floral changes. Additional peaks in concentration and accumulation rate of mercury were coeval with periods of dry, windy conditions and accelerated rates of sedimentation of wind-borne mineral particles, mostly during the mid-Holocene. This is most simply interpreted as derivation of eolian dust from a source with relatively high mercury concentrations in the fine-grained fraction. The mercury-enriched dust does not appear to have a local source, and may have been derived from areas in the northern Great Plains of North America where Holocene dune fields are widespread.

The mercury depositional record of Elk Lake sediments demonstrates the effectiveness of eolian transport of mercury bound to mineral particles and shows that during periods of dry and windy conditions, eolian transport and deposition of mercury is the dominant process in controlling lake sediment mercury loads. This suggests that future climate change toward warmer, drier conditions in midcontinent North America, if adequate to induce increased eolian erosion and long-distant transport of mineral dust, could greatly increase the mercury flux to downwind lakes, many of which are already undergoing unhealthy mercury loading.

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Manuscript received 2 August 2002
Revised manuscript received 22 October 2002
Manuscript accepted 24 October 2002

Printed in USA