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Historical deposition of mercury and selected trace elements to high-elevation National Parks in the Western U.S. inferred from lake-sediment cores

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ABSTRACT

Atmospheric deposition of Hg and selected trace elements was reconstructed over the past 150 years using sediment cores collected from nine remote, high-elevation lakes in Rocky Mountain National Park in Colorado and Glacier National Park in Montana. Cores were age dated by ^{210}Pb, and sedimentation rates were determined using the constant rate of supply model. Hg concentrations in most of the cores began to increase around 1900, reaching a peak sometime after 1980. Other trace elements, particularly Pb and Cd, showed similar post-industrial increases in lake sediments, confirming that anthropogenic contaminants are reaching remote areas of the Rocky Mountains via atmospheric transport and deposition. Preindustrial (pre-1875) Hg fluxes in the sediment ranged from 5.7 to 42 $\mu g\,m^{-2}\,yr^{-1}$ and modern (post-1985) fluxes ranged from 17.7 to 141 $\mu g\,m^{-2}\,yr^{-1}$. The average ratio of modern to preindustrial fluxes was 3.2, which is similar to remote lakes elsewhere in North America. Estimates of net atmospheric deposition based on the cores were 3.1 $\mu g\,m^{-2}\,yr^{-1}$ for preindustrial and 11.7 $\mu g\,m^{-2}\,yr^{-1}$ for modern times. Current-day measurements of wet deposition range from 5.0 to 8.6 $\mu g\,m^{-2}\,yr^{-1}$, which are lower than the modern sediment-based estimate of 11.7 $\mu g\,m^{-2}\,yr^{-1}$, perhaps owing to inputs of dry-deposited Hg to the lakes.

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1. Introduction

Mercury (Hg) is released to the environment from both natural and anthropogenic sources and enters remote aquatic ecosystems via atmospheric deposition (Swain et al., 1992). Mercury tends to accumulate in stream and lake sediment where it can be taken up by benthic organisms and passed up through the food web to fish (Driscoll et al., 2007). High levels of Hg in fish pose health risks to humans and wildlife that consume large amounts of contaminated fish. Although Hg contamination of remote lakes has been documented in the Midwest and eastern U.S. (Wiener et al., 2006; Lorey and Driscoll, 1999), less is known about Hg deposition to and accumulation in aquatic ecosystems of the Rocky Mountains, particularly at higher elevations. Mercury deposition may be enhanced in mountainous areas due to high rates of precipitation and the process of cold condensation, which causes volatile compounds to preferentially accumulate in cold environments, as has been shown for volatile organic compounds (Blais et al., 1998; Grimalt et al., 2001). Van Metre and Fuller (2009) suggest that increased Hg deposition in high-elevation areas might occur because of high concentrations of reactive gaseous mercury in the troposphere that could be scavenged by convective storms (Selin and Jacob, 2008).

Age-dated lake sediments are a commonly used tool for reconstructing historical trends in atmospheric Hg deposition. Lake sediments are thought to provide a reliable record because the majority of incoming Hg is retained in sediments (Engstrom et al., 1994) and post-depositional remobilization does not appear to substantially alter the Hg record (Lockhart et al., 2000; Rydberg et al., 2008). Reconstructions based on sediment cores from over 30 lakes in the northeastern U.S. indicate that Hg deposition has increased substantially over the past 150 years (coincident with industrialization) and that present-day rates are 2–4 times higher than during preindustrial times (Kamman and Engstrom, 2002; Lorey and Driscoll, 1999; Perry et al., 2005). Similar patterns in the timing and magnitude of deposition have been reported for remote lakes in the upper Midwest (Swain et al., 1992; Wiener et al., 2006) and in subarctic regions of Canada (Lucotte et al., 1995). Several recent studies have reported historical trends for Hg deposition in mountainous areas of the western U.S. (Schuster et al., 2002; Sanders et al., 2007; Landers et al., 2008; Van Metre and Fuller, 2009), which show that mercury deposition in some areas of the west may be as high as 10–20 times higher than preindustrial levels.

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The objective of this study was to investigate historical changes in atmospheric Hg deposition in high-elevation areas of the Rocky Mountains. This was accomplished by using age-dated sediment cores collected at remote lakes in National Parks in Colorado and Montana. Historical trends in other trace elements released by anthropogenic activities also were examined. A technique relating sediment Hg flux to basin ratio (watershed area: lake area) was used to estimate net atmospheric deposition rates during preindustrial and modern times.

2. Materials and methods

2.1. Study area description

The study lakes are located in Rocky Mountain National Park (ROMO) in north-central Colorado and Glacier National Park (GLAC) in northwestern Montana (Fig. 1). Both parks are dominated by high-elevation, mountainous terrain, and climate is characterized by cold, long winters and a short growing season. More than half of precipitation occurs as snow that accumulates in a seasonal snowpack between November and April (Finklin, 1986; Baron, 1992). Bedrock in ROMO is granite and gneiss (Baron, 1992) and in GLAC is argillite, quartzite, and carbonate rocks (Ross, 1959). Land in both parks is designated wilderness, and human activities are limited to tourism and recreation. ROMO is situated less than 40 km to the west of the Front Range urban corridor, which contains the most concentrated population density in the Rocky Mountain region. Land-use activities in areas adjacent to GLAC include timber harvesting and ranching.

The 9 lakes cored for this study are high-elevation, oligotrophic lakes that typically are ice-covered more than 6 months each year. Characteristics of the study lakes are provided in Table 1. The lakes are similar in size although the ROMO lakes were generally 1500 m higher in elevation than those in GLAC. Subalpine forests cover 6–52% of the lake watersheds and the remainder is predominantly alpine tundra, talus, and bedrock. ROMO lakes are chemically more dilute than the GLAC lakes reflecting differences in bedrock geology.

2.2. Sediment coring and age dating

Sediment cores were collected from each lake during summer months of 2002 and 2003. Cores were collected from a small inflatable raft anchored near the deepest point by using a miniature gravity corer (Glew, 1991) with a core tube diameter of 3 cm. The cores, which ranged in length from 14 to 32 cm, were sectioned into 0.5–2 cm increments in the field by using a portable core extruder. Core sections were freeze-dried and mechanically homogenized in their original collection containers. The cores were age dated by ^{210}Pb using alpha spectroscopy at MyCore Scientific Inc. in Ontario, Canada (http://www.mycore.ca/). Dates and sedimentation rates were determined by the constant rate of supply (CRS) model, which assumes a constant rate of unsupported ^{210}Pb from atmospheric fallout but allows sediment accumulation to vary (Appleby and Oldfield, 1992). Dates and sedimentation rates for sections below the zone of unsupported ^{210}Pb were extrapolated using a polynomial fit of date versus depth in the dated section of the core. To help constrain the CRS modeled sediment ages for Ypsilon Lake, selected sections from this core also were analyzed for ^{226}Ra and ^{137}Cs (C.C. Fuller, USGS, written communication).

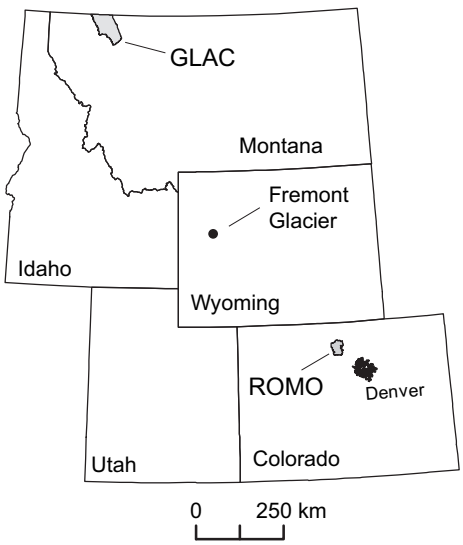

Fig. 1. Location of Glacier National Park (GLAC) in Montana, Rocky Mountain National Park (ROMO) in Colorado, and Fremont Glacier in Wyoming.

2.3. Analytical methods

Sediment sections from all nine cores were analyzed for total Hg, and sections from four cores were analyzed for selected trace elements. The freeze-dried sediments were microwave digested in Teflon vessels using a mixture of HNO_3, HF, and HCl according to the method described by Roth (1994). One standard reference sample (Buffalo River Sediment NIST-RM 8704) and one blank were digested with each batch of four samples for quality control. Approximately 2 g of digest was diluted with 100 g of a saturated boric acid solution and 4 mL of dichromate/HNO_3 preservative, and analyzed for total Hg by cold vapor atomic fluorescence spectrophotometry. The remainder of the digest was heated to dryness, redissolved in 100 mL of 10% HNO_3, and then analyzed for trace elements by inductively coupled plasma-mass spectrometry. Freeze-dried sediment also was analyzed for total carbon and nitrogen using an automated CHN analyzer. Percent organic matter was determined from loss on ignition (LOI) by heating freeze-dried samples for 4 h at 550 °C and 1 h at 1000 °C. All digestions and chemical analyses were conducted at a USGS research laboratory in Boulder, Colorado.

3. Results

3.1. ^{210}Pb dating and sedimentation rates

Profiles of unsupported ^{210}Pb activity and CRS modeled sedimentation rates for the nine sediment cores are shown in Fig. 2. The unsupported ^{210}Pb profiles in the ROMO lakes show more or less exponential declines with depth, whereas the profiles in GLAC decreased more linearly, indicating increases in sediment input rates over the period of record. In several of the cores, there was a flattening or reversal in the ^{210}Pb activities near the top of the core, which might indicate mixing caused by bioturbation or water movement (Van Metre et al., 2004). The reliability of the dating for most of the cores was good based on consistent decreases in ^{210}Pb with increasing depth. The exception was the core from Akokala in GLAC, which likely was not deep enough to reach background (supported) ^{210}Pb activities. For this core, the background ^{210}Pb activity was estimated from the average of the supported ^{210}Pb activities in the other cores collected in GLAC. The Ypsilon core had very high background ^{210}Pb activities (0.428 Bq g^{-1}) that were about twice those of the ^{226}Ra activities (0.245 Bq g^{-1}). For this core, CRS modeled ages were calculated using the ^{226}Ra activity instead of the background ^{210}Pb activity. The CRS modeled ages were checked against some limited ^{137}Cs data for this core, which indicates the first occurrence of ^{137}Cs at sediment depths between

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Table 1
Characteristics of the study lakes.

Lake	Park	Latitude	Longitude	Elev. (m)	Max. depth (m)	Lake area (ha)	Basin ratio	Forest cover (%)	Glacier cover (%)	Spec. cond. ($\mu S\,cm^{-1}$)	DOC ($mg\,L^{-1}$)
Black	ROMO	40° 15′ 55″	105° 38′ 28″	3200	30	3.2	163	6	1.2	14	1.3
Fern	ROMO	40° 20′ 12″	105° 40′ 36″	2903	10.4	2.9	191	42	1.1	12	1.1
Lone Pine	ROMO	40° 13′ 24″	105° 43′ 54″	3078	10.1	4.8	380	31	0.0	16	2.0
Nanita	ROMO	40° 15′ 21″	105° 42′ 59″	3290	25	13.4	21	17	0.0	16	1.4
Ypsilon	ROMO	40° 26′ 38″	105° 39′ 50″	3210	15.8	3.1	111	16	0.0	12	1.5
Akokala	GLAC	48° 52′ 44″	114° 11′ 54″	1463	6.4	9.5	167	52	0.3	79	2.9
Lower Snyder	GLAC	48° 37′ 36″	113° 48′ 09″	1615	3.5	2.4	147	46	0.0	17	1.1
Noname	GLAC	48° 28′ 44″	113° 26′ 50″	1817	5.5	4.2	78	49	0.7	84	0.7
Redrock	GLAC	48° 47′ 45″	113° 42′ 22″	1550	6.1	10.7	177	25	3.3	111	1.2

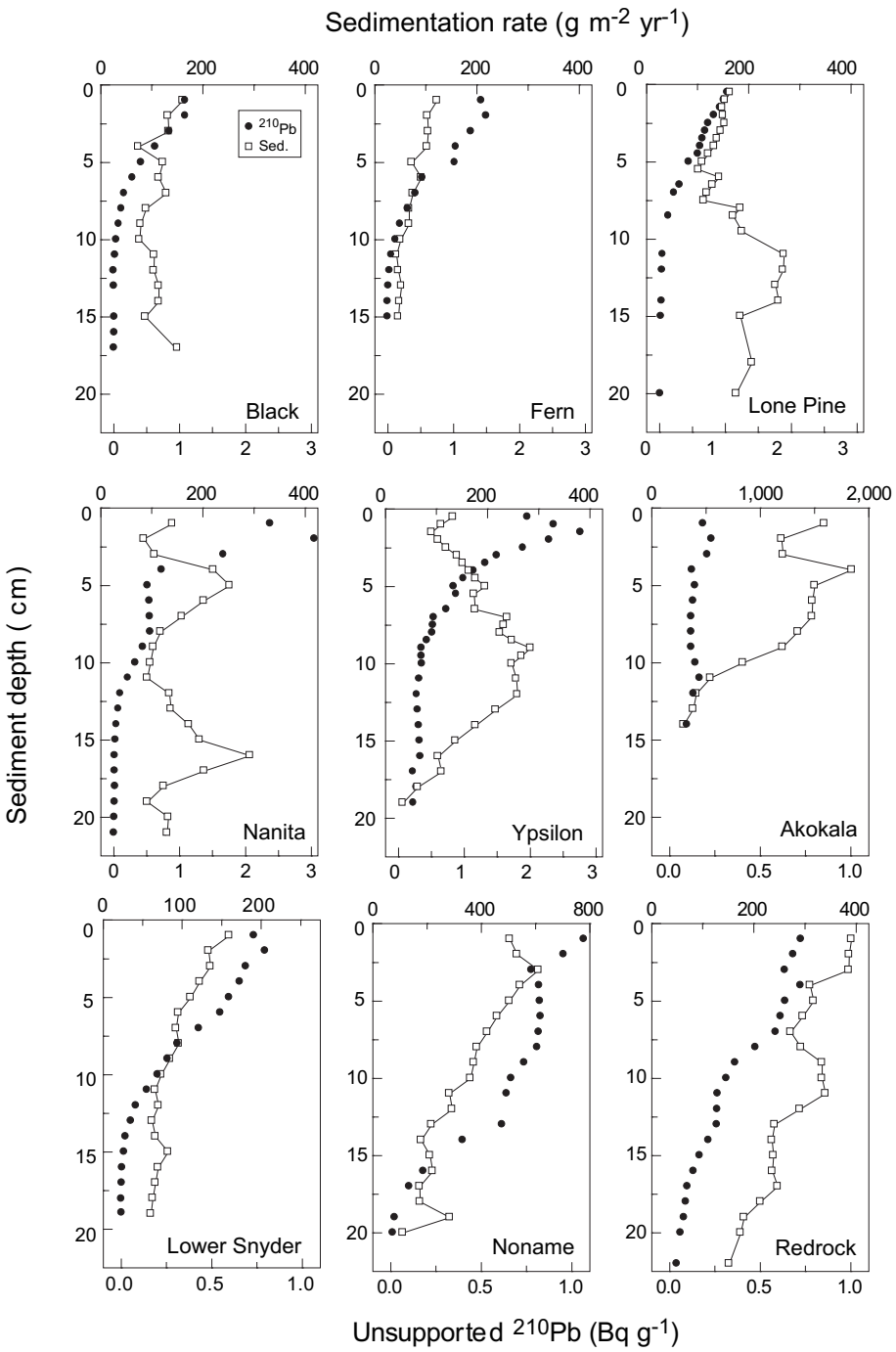

Fig. 2. Sediment-core profiles of unsupported ^{210}Pb activity and sedimentation rates.

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12 and 15 cm. The ^{137}Cs data are in agreement with the CRS age of 1952 at a sediment depth of 13 cm indicating the modeled dates, at least in the upper part of the core, are reasonable. Dating precision (1 standard deviation) in most of the cores was better than ±3 years over the past 50 years and ± 17 years over the past 50–100 years. There was considerably greater uncertainty in dates prior to 1900 (±17–69 years) particularly in the GLAC lakes, which had low unsupported ^{210}Pb activities.

Focus factors were determined for each lake by dividing the unsupported ^{210}Pb inventory in the core by 0.45 Bq cm^{-2}, which is a regional average based on unsupported ^{210}Pb inventories measured in soil cores (Graustein and Turekian, 1986). This value is very close to the unsupported ^{210}Pb burden of 0.50 Bq cm^{-2} determined from soil cores collected near a high-elevation lake in Wyoming (Van Metre and Fuller, 2009). The focus-factor correction accounts for the preferential deposition of the finest grained sediment to the deepest part of the lake. Focus factors ranged from 1.09 to 1.84 for the ROMO lakes and from 0.87 to 3.96 for the GLAC lakes.

CRS model sedimentation rates ranged from 40 to 600 g m^{-2} yr^{-1} with the exception of Akokala, which had rates exceeding those in the other cores by as much as an order of magnitude (Fig. 2). The elevated sedimentation rates at Akokala result from the very low unsupported ^{210}Pb activities in this core. All four cores from GLAC showed an increase in sediment accumulation over the period of record that more than doubled between the bottom and top of the cores. A possible explanation is the rapid retreat of glaciers and perennial snowfields that has occurred in the park over the past century as a result of climate warming (Fagre, 2007), which has resulted in increased sediment transport to streams and lakes (Bogen, 2008). The lakes in ROMO showed a mixed response. Relatively constant sedimentation profiles were observed at Black and Fern, whereas periods of elevated sedimentation were observed in the Lone Pine (1912–1927), Nanita (1877 and 1984), and Ypsilon (1962–1980) cores. The different timing of the sedimentation peaks among lakes indicates they may reflect local watershed disturbance (i.e. post-fire erosion, landslides). Alternatively, the peaks in sedimentation could be due to errors in the CRS model, which is particularly sensitive to incomplete ^{210}Pb profiles and to counting errors, especially in older sediments (Heyvaert et al., 2000).

Mean mass and linear sedimentation rates were calculated for each lake over the past 150 years and are presented in Table 2. Excluding Akokala, mass sedimentation rates varied by less than a factor of 4 (range 68–258 g m^{-2} yr^{-1}) and linear rates varied by a factor of two (0.07–0.16 cm yr^{-1}). The reason for high sedimentation at Akokala (710 g m^{-2} yr^{-1}) is unknown; however, the modest degree of sediment focusing (focus factor = 2.18) and the low total C content (3.9%) indicates most of the accumulating sediment is from influx of inorganic sediment from the watershed.

3.2. Hg concentrations and fluxes

Total Hg concentrations measured in the individual core sections ranged from 69 to 338 ng g^{-1} of sediment (dry weight). Hg concentrations in all the lakes except Akokala began to increase around 1900, reaching a peak sometime after 1980 (Fig. 3). At some lakes, for example Black and Nanita, Hg concentrations showed declines from peak values over the last decade. Preindustrial Hg concentrations for each core were calculated as the average value of sections deposited prior to 1875 and modern concentrations were calculated as the average of sections deposited after 1985 (Table 2). Preindustrial Hg concentrations ranged from 69 to 182 ng g^{-1} and were not notably different between the two parks. Modern concentrations ranged from 92 to 288 ng g^{-1} and were 2–3 times higher in ROMO than in GLAC. The lower values in GLAC partly reflect the upward trends in sedimentation rates in these lakes, which would progressively dilute sediment Hg concentrations towards the surface, assuming sediment sources are depleted in Hg relative to atmospheric inputs (Engstrom et al., 2007). Our results for GLAC are comparable to a previous study that reported Hg concentrations ranging from 90 to 100 ng g^{-1} in surface sediments collected from 2 lakes in GLAC (Watras et al., 1995).

To normalize the concentration profiles for changes in sediment accumulation over time, flux rates of Hg to the sediment were calculated by multiplying the sediment concentration by the CRS sedimentation rate for each analyzed section. Flux profiles show much stronger increases in Hg than concentrations particularly for lakes in GLAC (Fig. 3). Nanita and Ypsilon showed substantial declines in Hg flux near the surface due to decreases in both concentration and sedimentation rates. Because the ^{210}Pb profiles showed a reversal near the surface (Fig. 2), it is possible that sediment mixing may have disturbed the flux profile in this interval. Average preindustrial (pre-1875) and modern (post-1985) Hg fluxes were calculated over the same intervals as described for the concentration data (Table 2). Modern fluxes were clearly elevated over preindustrial fluxes for all the lakes. Hg fluxes in Akokala were nearly 3 times higher than the other lakes due to elevated sedimentation rates in this lake.

3.3. Other trace elements

In addition to Hg, sediment cores from Nanita, Ypsilon, Lower Snyder, and Redrock also were analyzed for As, Cd, Co, Cr, Cu, Ni, Pb, and Zn, which are trace elements often used as indicators of anthropogenic activities (Mahler et al., 2006). Sediment concentrations were similar among the lakes, and relative concentrations generally decreased in the order Zn > Pb ≈ Cr ≈ Cu > Ni > As ≈ Co > Cd. Trace-element concentrations were normalized to Ti, an aluminosilicate reference element that is used to correct for

Table 2
^{210}Pb inventories and focus factors, mean mass and linear sediment accumulation rates, preindustrial (pre-1875) and modern (post-1985) mercury concentrations, and mercury fluxes for the 9 sediment cores.

Lake	Unsupported ^{210}Pb inventory (Bq cm^{-2})	Focus factor	Mass rate (g m^{-2} yr^{-1})	Linear rate (cm yr^{-1})	Preindustrial Hg conc. (ng g^{-1})	Modern Hg conc. (ng g^{-1})	Preindustrial Hg flux (μg m^{-2} yr^{-1})	Modern Hg flux (μg m^{-2} yr^{-1})	Hg flux ratio
Black	0.61	1.36	103	0.07	94	224	9.0	31.6	3.5
Fern	0.59	1.31	68	0.07	182	243	7.8	26.6	3.4
Lone Pine	0.49	1.09	138	0.15	93	288	16.3	43.8	2.7
Nanita	0.79	1.76	140	0.11	96	223	11.4	33.5	2.9
Ypsilon	0.83	1.84	144	0.16	155	288	15.2	43.5	2.9
Akokala[a]	0.98	2.18	710	0.17	123	97	42.0	141	3.5
Lower Snyder	0.39	0.87	83	0.09	91	141	5.7	17.7	3.1
Noname	1.78	3.96	258	0.13	84	92	12.5	45.4	3.6
Redrock	0.95	2.11	240	0.16	69	96	11.4	37.0	3.2

[a] Hg fluxes for this lake may be unreliable due to uncertainties in the age dating discussed in the text.

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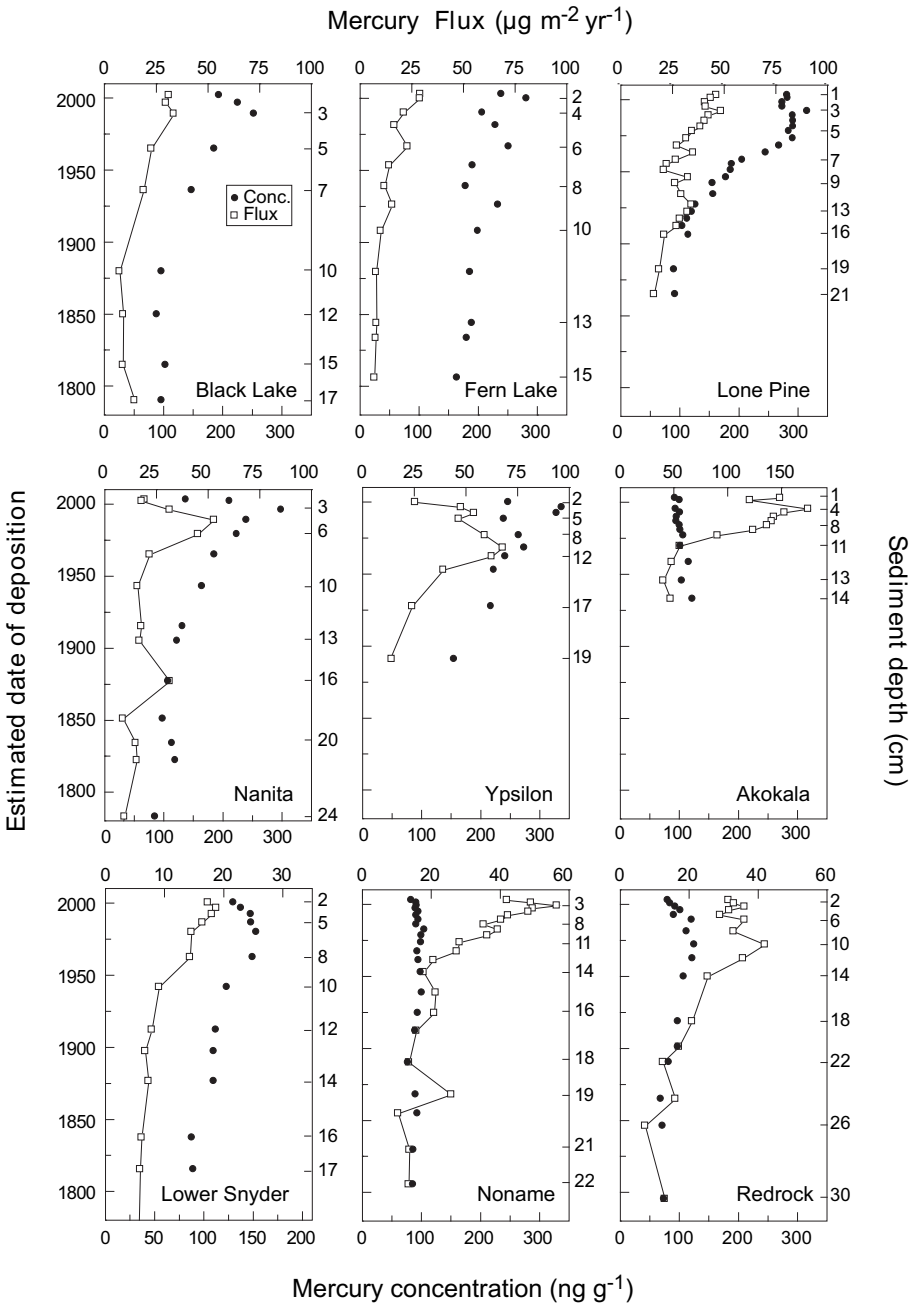

Fig. 3. Sediment-core profiles of mercury concentrations and mercury fluxes.

variable contributions from watershed weathering sources (Heyvaert et al., 2000). Normalized concentrations were computed by multiplying the metal concentration at a particular depth by the Ti concentration at that depth divided by the Ti concentration at the bottom of the core. Normalized profiles for the 8 trace elements in the Redrock core are presented in Fig. 4, including the unnormalized profile for Ti. Some elements including Co, Cr, and Ni, had relatively flat profiles, indicating they are derived primarily from weathering sources. By contrast, As, Cd, Cu, Pb, and Zn showed notable increases in concentrations during the 20th century suggesting increased atmospheric fallout from anthropogenic sources (Birch et al., 1996; Heyvaert et al., 2000).

To compare trace-element trends among lakes, mean preindustrial (pre-1875) and peak trace-element concentrations were computed for each of the four sediment cores using the normalized concentrations. Sediment-enrichment factors (SEF) were calculated from the mean concentrations, where SEF = (peak concentration − preindustrial concentration)/preindustrial concentration. The largest enrichment was observed for Cd and Pb and little or no enrichment was observed for Co, Cr, and Ni (Fig. 5). Different patterns between elements in the same lake suggest that the cores are recording trends in atmospheric fallout rather than changes in geologic source materials or post-depositional mixing and digenesis (Mahler et al., 2006).

3.4. Total carbon and nitrogen

Sediment from Akokala had the lowest average C content at 3.9%, and Ypsilon had the highest at 16.9% (Fig. 6). The LOI analyses indicated that sediment C in these lakes was almost entirely organic

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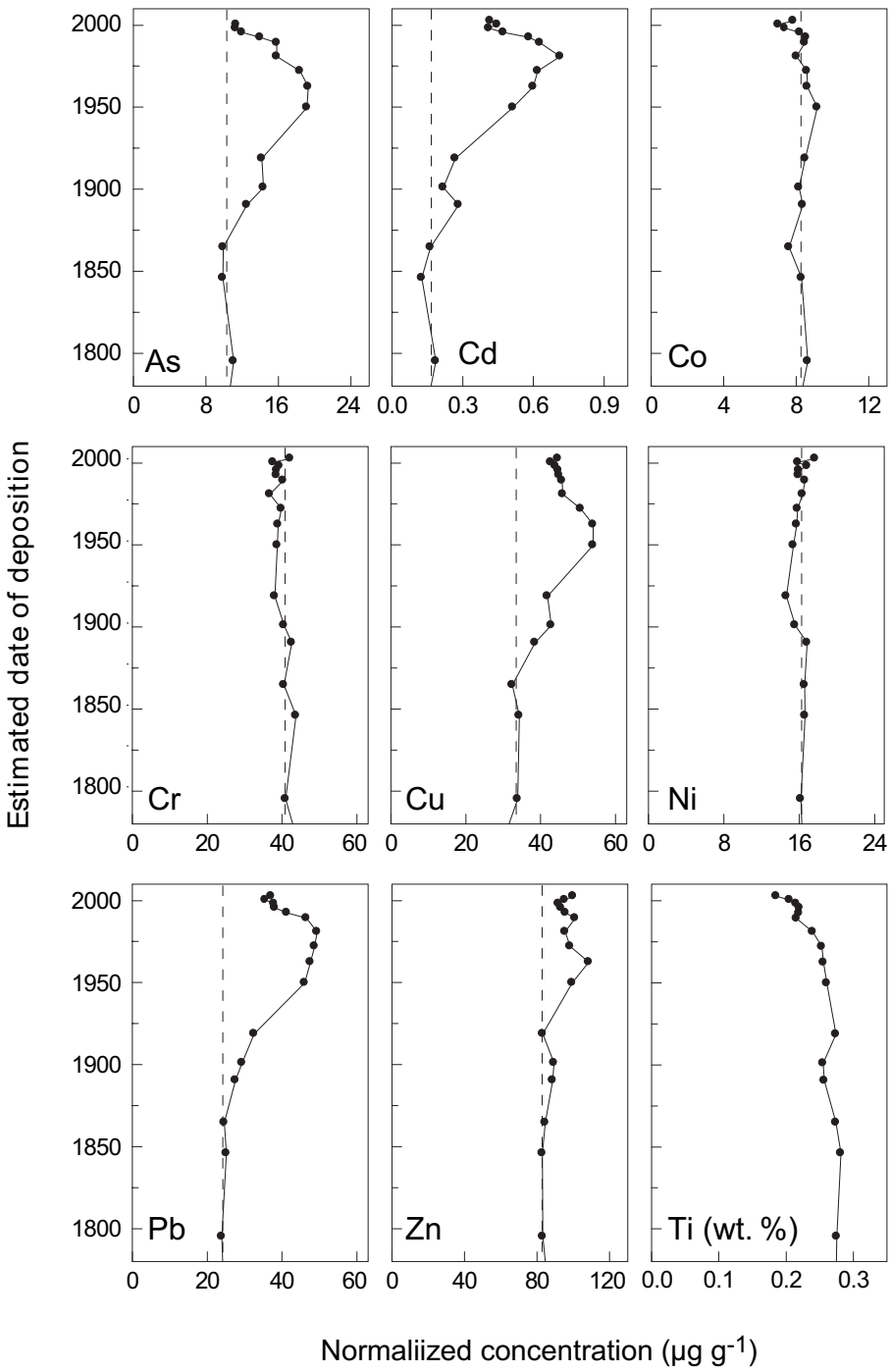

Fig. 4. Sediment-core profiles of normalized trace-element concentrations for Redrock Lake in GLAC. Also included is weight % titanium, which was used to normalize trace-element concentrations for variable contributions from weathering.

with little or no carbonate. In all the cores except Akokala, total C increased towards the surface (Fig. 6). Total N in sediment ranged from 0.34% in Akokala to 0.96% in Fern. Total N profiles generally mirrored those of total C except at Ypsilon where they diverged near the sediment surface. Average C:N ratios for the individual lakes ranged from 9.1 to 13.1. Algae have a C:N ratio between 4 and 10, whereas terrestrial organic matter has a C:N greater than 20 (Meyers, 1994) suggesting most organic matter in the lake sediments is derived from algal sources. The exception was Ypsilon which had a ratio of 21.1, which suggests a greater terrestrial input of organic carbon to this lake.

4. Discussion

4.1. Historical trends in Hg

Results from high-elevation lakes in ROMO and GLAC clearly show that Hg accumulation has increased in lake sediments over the last century. These results agree with observed sediment Hg trends from remote lakes in other parts of North America (Perry et al., 2005), and suggest that Rocky Mountain lakes also are affected by atmospheric fallout of Hg from anthropogenic sources. Another potential source of Hg to lake sediments may be from the

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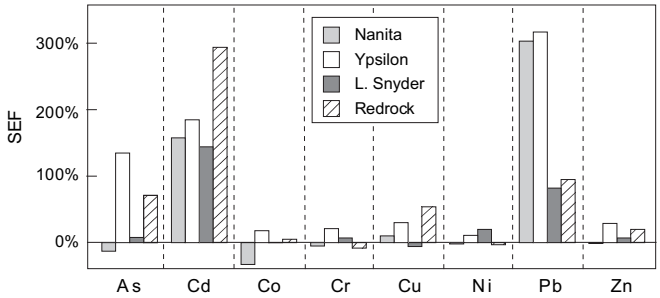

Fig. 5. Sediment-enrichment factors (SEF) of trace-element concentrations (normalized) for Nanita and Ypsilon in ROMO and Lower Snyder and Redrock in GLAC.

release of historically-deposited Hg stored in glaciers, which have been rapidly melting in some areas of North America during the last several decades. The importance of this input is difficult to evaluate; however, the similarity in temporal response among lakes, with or without glaciers in their drainage basins (Table 1), suggests that deposition is the main driver of post-industrial increases in sediment Hg.

A 270-year record of atmospheric Hg deposition in the western U.S. recently was reconstructed from an ice core collected from Fremont glacier (Fig. 1) in northwestern Wyoming (Schuster et al., 2002). Due to the high temporal resolution of the core, it recorded not only the post-industrial Hg increase as observed in the lake sediments but also peaks in 1860 and 1877 that corresponded to the California Gold Rush. There were small jumps in Hg fluxes in the Nanita, Noname, and Redrock cores around 1865; however, these were caused by higher sedimentation rates rather than by elevated concentrations. Van Metre and Fuller (2009) also did not observe a gold-rush sediment signal in a high-elevation lake located near the glacier. The lack of a signal in the study lakes may in part be due to coarser sampling intervals and lower temporal resolution in older parts of the sediment cores.

The ice-core record also indicates that Hg deposition peaked in 1980 and has since declined by as much as 50%, which the authors suggest might be due to emission reductions resulting from the Clean Air Act Amendments (Schuster et al., 2002). In some lakes (Black Lake, Nanita, Lower Snyder, Redrock, and Noname) Hg fluxes peaked in the mid-1980s, suggesting that the sediment records support the hypothesis of recent reductions in Hg deposition. In Fern, Lone Pine, and Ypsilon, however, Hg fluxes continued to increase towards the surface. One explanation for a lack of decline may be continued release of previously-deposited Hg stored in watershed soils and organic matter even as deposition declines (Perry et al., 2005). Another possibility is that Hg deposition has not declined in the Rocky Mountain region in recent years as has been observed in the eastern U.S. (Van Metre and Fuller, 2009; Butler et al., 2008). Van Metre and Fuller (2009) observed increasing Hg in recent sediments from a lake only 12 km from the Fremont Glacier and suggested that the inconsistency with the ice-core record could be due to a change in the retention of Hg deposited on the glacier rather than a reduction in Hg emissions. Another potential difference between the glacier and sediment records is that the glacier may record predominantly winter deposition, whereas lakes capture both summer and winter inputs. Modeling results of seasonal and spatial patterns in Hg deposition for the U.S. suggest domestic sources dominate mercury deposition at high latitudes in winter (Selin and Jacob, 2008). This implies that the glacier record could have a stronger domestic signal than the lakes

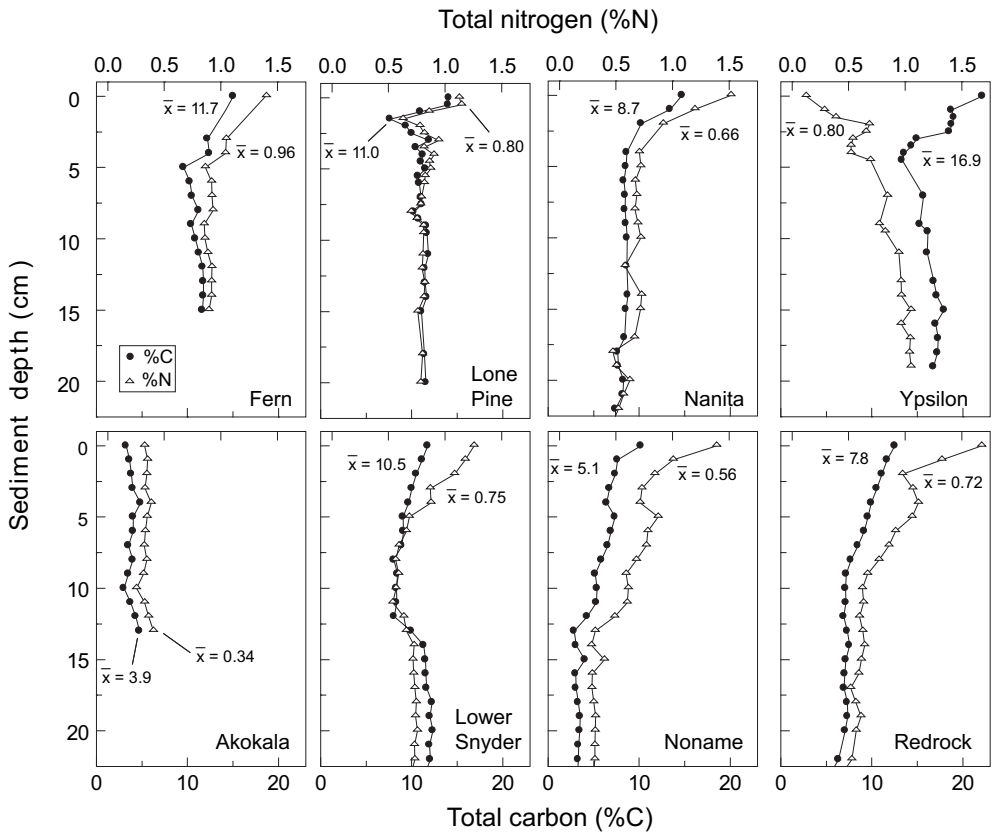

Fig. 6. Sediment-core profiles of total nitrogen and carbon content.

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and hence a different response to changes in local versus regional emission patterns.

4.2. Historical trends in other trace elements

Sediment profiles for other trace elements provide additional support that atmospheric contaminants are reaching remote lakes in the Rocky Mountains via long-range atmospheric transport and deposition. The largest post-industrial increases in sediment concentrations were observed for Pb and Cd (Fig. 5). The main source of anthropogenic Pb in the atmosphere is from use of leaded gasoline, which was introduced in the 1920s and peaked in the early 1970s (Juracek and Ziegler, 2006). Since then, anthropogenic Pb emissions in the U.S. have declined by over 95% (USEPA, 2000). Concentrations in the Redrock core are consistent with emission trends showing increases around 1920 that peaked around 1980. Although sediment Pb levels have declined since then, they remain elevated in recent (2002) sediments compared to preindustrial sediments by more than 50% despite the dramatic decline in Pb emissions (Fig. 4). Unless geologic inputs have changed, the continued accumulation of Pb in the sediment likely is due to release of previously deposited or legacy Pb stored in watershed soils (Mahler et al., 2006). Comparison of Pb increases among all four lakes reveals that enrichment factors were more than 3 times higher in the ROMO cores than in GLAC (Fig. 5). This may reflect the influence of local urban sources as ROMO is situated 40 km to the west of the most concentrated population density in the Rocky Mountain region.

Cadmium also showed notable increases over preindustrial levels in all four sediment cores. Nonferrous ore smelting, waste incineration, and fossil fuel combustion are the primary sources of Cd to the atmosphere (Pacyna and Pacyna, 2001). Although Cr, Cu, Ni, and Zn have many of the same sources as Cd, post-industrial enrichment of these trace elements was much less perceptible in the sediment records perhaps because the anthropogenic signal was small relative to natural sources. Similar to Pb, concentrations of Cd in the Redrock core increased dramatically after 1950 and peaked around 1980. Concentration decreases in recent sediments may reflect reductions in atmospheric Cd that have largely occurred as a result of declines in the smelting of zinc ores (Mahler et al., 2006). There were no notable differences in enrichment factors for Cd between the parks, indicating that, in contrast to Pb, urban areas in close proximity to ROMO did not have a strong influence on Cd relative to GLAC.

4.3. Mercury flux ratios

Flux ratios relating modern to preindustrial Hg accumulation provide a consistent measure of change in Hg deposition particularly with which to compare lake records from other regions (Wiener et al., 2006). Flux ratios in the Rocky Mountain lakes ranged from 2.9 to 3.6 with a mean of 3.2 and were quite similar to flux ratios reported for remote lakes in eastern North America (Table 3). The similarity in values across such a broad geographic area perhaps suggests that Hg accumulating in remote Rocky Mountain lakes is derived from regional rather than from local sources. This idea is further supported by the similarities in flux ratios between the two parks, which averaged 3.1 in ROMO and 3.3 in GLAC. ROMO is much closer to large urban areas and power-plants than GLAC and might be expected to have higher flux ratios if deposition were substantially elevated by local emission sources. Moreover, recent modeling results indicate only 20% of total mercury deposition in the western U.S. is from domestic sources, the remainder being derived from the global Hg pool (Selin and Jacob, 2008).

Table 3
Range of mercury flux ratios in sediment cores from remote lakes in North America.

Location	Range	*n*	Reference
Vermont/New Hampshire	2.1–6.9	10	Kamman and Engstrom, 2002
New York	1.6–5.7	8	Lorey and Driscoll, 1999
Ontario	2.2–2.3	2	Lockhart et al., 1998
Minnesota	3.2–4.9	7	Swain et al., 1992
Minnesota	2.0–5.7	5	Wiener et al., 2006
Colorado	3.0–4.4	5	Manthorne, 2002
Colorado/Montana	2.9–3.6	9	This study
Wyoming	4.6–6.5	2	Van Metre and Fuller, 2009
California	9.5–18.7	3	Heyvaert et al., 2000
California	3.3–10.8	4	Sanders et al., 2007

For remote lakes in mountainous areas of the western U.S., similar Hg flux ratios were found for lakes in Colorado but slightly ratios have been reported for lakes in Wyoming and California (Table 3) although anthropogenic watershed disturbance may have been a factor in the Heyvaert et al. (2000) study. The ice core in Wyoming also yielded higher flux ratios ranging from 5 during the California Gold Rush to as much as 20 at the peak of industrial deposition in 1984 (Schuster et al., 2002). Part of the reason for the higher peak ratio in ice is that it was determined from an individual ice-core sample representing a time interval of <2 years; such high temporal resolution is generally not attainable in cores from lakes with low sedimentation rates. The ice-core flux ratio averaged over the most recent (1986–1993) period was 11.0, which is still more than 3 times the ratio in the sediment cores. The higher ice-core ratios may in part be due to a depth-age correction made for thinning of older ice layers due to glacial flow processes (Schuster et al., 2002). If the fluxes are not depth corrected, the recent (1986–1993) ice-core ratio is reduced to 4.6 (P.F. Schuster, USGS, written commun., 2008), which is more consistent with the lake-sediment results in this study as well as Hg fluxes reported for a high-elevation lake close to the glacier (Van Metre and Fuller, 2009).

4.4. Inference of atmospheric deposition rates based on sediment records

Sediment flux rates of Hg in lake sediments have been used as a proxy for historical atmospheric deposition rates, although interpretation of individual cores can be complicated by sediment focusing and post-depositional mixing and diagenesis, and by watershed characteristics that control Hg transport (Swain et al., 1992; Kamman and Engstrom, 2002; Perry et al., 2005). Sediment focusing can be corrected for by dividing Hg flux by the focus factor for each lake (Table 2). After focus correcting, fluxes in the study lakes ranged from 3.2 to 19.3 $\mu g\,m^{-2}\,yr^{-1}$ for the preindustrial period and from 11.5 to 64.7 $\mu g\,m^{-2}\,yr^{-1}$ for the modern period. Hg flux to lake sediments has been shown to increase in proportion to the watershed to lake area (basin ratio) because some of the accumulating Hg is transported from the watershed to the lake (Swain et al., 1992; Lorey and Driscoll, 1999; Kamman and Engstrom, 2002). The study lakes showed a good relationship between basin ratio and focus-corrected modern ($r^2 = 0.69$, $p = .011$) and preindustrial ($r^2 = 0.63$, $p = .019$) Hg fluxes except for Akokala (Fig. 7). Because of high rates of sedimentation in Akokala, Hg fluxes for this lake were excluded from the regression models. Extrapolation of the linear regression to a basin ratio of 1 provides an estimate of net atmospheric deposition directly on the lake surface (Swain et al., 1992). Using this method, the direct atmospheric flux is estimated to be 3.1 $\mu g\,m^{-2}\,yr^{-1}$ for the preindustrial (pre-1875) period and 11.8 $\mu g\,m^{-2}\,yr^{-1}$ for the modern (post-1985) period. Because the slope of the relation represents the export of Hg from

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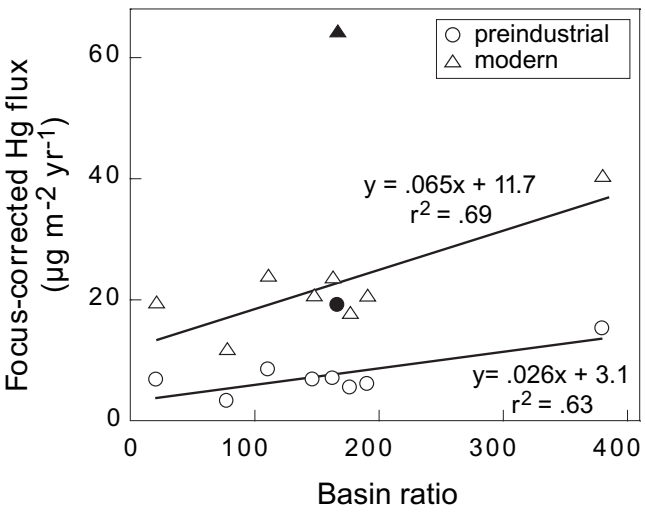

Fig. 7. Preindustrial (pre-1875) and modern (post-1985) focus-corrected mercury fluxes versus watershed to lake area (basin ratio). Solid symbols are for Akokala in GLAC, which were excluded from the regression models.

the watershed per unit increase in the basin ratio, the slope divided by the direct atmospheric flux is the fraction of the mercury load deposited on the watershed that is subsequently transported to the lake (Swain et al., 1992). For these high-elevation lakes, the ratio of the slope to intercept was about 1%, which is substantially lower than the 7–26% range reported for remote lakes in the upper Midwest and New England (Swain and others, 1992; Kamman and Engstrom, 2002). One notable difference is that basin ratios for the study lakes are much larger than in these published studies, which may suggest Hg export becomes less efficient as the distance to the lake increases. Another explanation might be that Hg export from alpine areas may be limited compared to lowland areas due to a lack of wetlands and low surface-water DOC concentrations (Table 1), which are typical of high-elevation watersheds.

The estimate of modern Hg deposition based on the sediment cores (11.7 $\mu g\,m^{-2}\,yr^{-1}$) compares well to the ice-core flux of 11.6 $\mu g\,m^{-2}\,yr^{-1}$ estimated for the period 1986–1993 (Schuster et al., 2002) but is 30% higher than present-day rates (7.8–8.6 $\mu g\,m^{-2}\,yr^{-1}$) measured in wet deposition in ROMO (Mast et al., 2005) and at a nearby MDN station in Colorado (CO96) and about twice the wet deposition rate (5.0 $\mu g\,m^{-2}\,yr^{-1}$) measured at an MDN station in GNP (MT05). The higher sediment-based rates could reflect additional inputs from dry deposition, however, the importance of dry deposition in the western U.S., particularly at high-elevations, is poorly understood. For example, a recent study in Nevada showed that dry deposition accounted for 10–90% of wet deposition inputs depending on season and estimation method (Lyman et al., 2007). The lower deposition rate at the MDN station in GNP (MT05) could partly reflect the elevation of this station, which is much lower than the study lakes and hence receives much less precipitation. The sediment-based preindustrial rate is more than 3 times higher than the flux of 0.8 $\mu g\,m^{-2}\,yr^{-1}$ estimated from the Wyoming ice core, which is more than can be accounted for by dry deposition. It is unclear why the ice-core estimate is so much lower than the sediment. It might be because the glacial record extends back farther in time than the lake sediments or because of the age-depth correction discussed previously. Although our preindustrial rate was higher than the ice-core record it was on the low end of preindustrial deposition rates (3–10 $\mu g\,m^{-2}\,yr^{-1}$) estimated for low-elevation lakes using the same graphical technique (Swain et al., 1992; Lorey and Driscoll, 1999; Kamman and Engstrom, 2002). The difference may largely reflect greater inputs from dry deposition in forested landscapes but also may provide some evidence that Hg deposition to high-elevation areas is not greatly enhanced by the process of cold condensation as has been documented for volatile organic compounds (Blais et al., 1998).

5. Conclusions

Sediment-core profiles from lakes in two National Parks provide evidence that Hg and other trace elements (Pb and Cd) are accumulating in high-elevation areas of the Rocky Mountains via long-range atmospheric transport and deposition. Although only a single sediment core was collected from a relatively small number of lakes, the similarity in timing and magnitude of Hg increases among sites indicates that lake-sediment cores provide a reliable record of atmospheric pollutant inputs to these remote areas. Hg concentrations in most of the cores began to increase around 1900, reaching a peak sometime after 1980. The average ratio of modern (post-1985) to preindustrial (pre-1875) Hg fluxes is 3.2 and is in the same range as ratios determined for remote lakes elsewhere in North America. The similarity over such a broad geographic area indicates that Hg reaching these remote lakes primarily is derived from regional sources. Moreover, deposition of anthropogenic Hg to high-elevation areas does not appear to be greatly enhanced by the process of cold condensation. Based on the ice core reconstruction from Wyoming, anthropogenic Hg emissions peaked in 1984 perhaps in response to emission controls implemented as a result of the Clean Air Act Amendments. Some of the sediment cores appear to respond to these declines while others do not. Estimates of net atmospheric deposition based on the cores were 3.1 $\mu g\,m^{-2}\,yr^{-1}$ for preindustrial and 11.7 $\mu g\,m^{-2}\,yr^{-1}$ for modern times. Current-day measurements of wet deposition range from 5.0 to 8.6 $\mu g\,m^{-2}\,yr^{-1}$, which are lower than the modern sediment-based estimate of 11.7 $\mu g\,m^{-2}\,yr^{-1}$, perhaps owing to inputs of dry-deposited Hg to the lakes.

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