

# Reliance on $^{210}\text{Pb}$ Chronology Can Compromise the Inference of Preindustrial Hg Flux to Lake Sediments

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Lake sediments are frequently used to reconstruct the rate and magnitude of human impacts on the biogeochemical cycle of mercury (Hg). The vast majority of these studies rely on excess  $^{210}\text{Pb}$  inventories in short cores to temporally constrain recent trends in Hg deposition, revealing an approximately 3-fold increase in Hg deposition since preindustrial times. However, the exhaustion of unsupported  $^{210}\text{Pb}$  and the onset of widespread global Hg pollution converge temporally in the late 19th century, raising the possibility that preindustrial Hg fluxes are poorly constrained. Here, we combine  $^{210}\text{Pb}$  and accelerator mass spectrometry (AMS)  $^{14}\text{C}$  dated lake sediment records from arctic and Andean lakes to assess the reliability of  $^{210}\text{Pb}$ -derived chronologies in the estimation of preindustrial Hg fluxes. For all four studied lakes, relying on  $^{210}\text{Pb}$  chronologies results in an overestimate of preindustrial Hg fluxes, because extrapolated basal  $^{210}\text{Pb}$  sedimentation rates are systematically overestimated in comparison to accumulation models that include  $^{14}\text{C}$  dates. In the Andes, the use of  $^{14}\text{C}$  dates is critical toward assessing the full history of Hg pollution, which extends beyond the industrial era. In the Arctic,  $^{14}\text{C}$  dating suggests that Hg deposition may have increased >10-fold since the Industrial Revolution, rather than the commonly quoted 3-fold increase. The incorporation of  $^{14}\text{C}$  dates may therefore be necessary if accurate Hg flux histories are sought from oligotrophic lake sediments.

## Introduction

Human activities have profoundly altered the global cycle of mercury (Hg) (1). However, the lack of long-term monitoring of Hg deposition limits the ability to quantify anthropogenic disruptions to the Hg cycle. Natural archives, including lake sediment cores, ice cores, and peat bogs, can provide continuous records of Hg deposition through time (2, 3).

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Lake sediments are thought to be the most reliable archive of past Hg deposition (3), and a growing number of cores record an approximately 3-fold increase in Hg deposition rates since 1850–1900 AD (3, 4).

Estimating past Hg fluxes (also known as Hg accumulation rates; typically  $\mu\text{g m}^{-2} \text{yr}^{-1}$ ) requires two independently derived measurements: Hg concentration ( $\mu\text{g g}^{-1}$ ) and dry mass sedimentation rate ( $\text{g m}^{-2} \text{yr}^{-1}$ ). Quantifying [Hg] in natural media is well developed and can be crosschecked with standard reference materials. However, sedimentation rates must be estimated using models of core chronology, for which uncertainties are propagated to the estimate of Hg flux. Accurate dating of lake sediments is thus paramount for estimating past Hg flux.

For Hg studies, sedimentation rates are most often estimated using  $^{210}\text{Pb}$  geochronology (e.g. refs 3 and 4).  $^{210}\text{Pb}$  has a half-life of 22.3 years, and its usefulness as a geochronological tool in paleolimnology is limited to the past 100–150 years (5).  $^{210}\text{Pb}$ -derived ages and sedimentation rates for each core interval are typically calculated using either the constant flux:constant sedimentation (CF:CS) or constant rate of supply (CRS) models, and the chronology derived depends (at least in part) on the model selected (5). The estimate of sediment ages (and sedimentation rates) beyond the range of  $^{210}\text{Pb}$  requires either an extrapolation of the  $^{210}\text{Pb}$ -derived chronology or the incorporation of additional geochronological tools.

Radiocarbon ( $^{14}\text{C}$ ) dating is the most widely applied geochronometer for reconstructing environmental change over the Holocene. Accelerator Mass Spectrometry (AMS)  $^{14}\text{C}$  dating allows for precise measurements on even very small sample sizes ( $\sim 0.05 \text{ mg C}$ ) and offers the opportunity to target discrete fractions within sediment horizons (6). However, AMS  $^{14}\text{C}$  dating has been rarely included in paleolimnological reconstructions of past Hg deposition (see ref 3 and references therein), despite the potential for improving the assessment of sedimentation rates beyond the limit of  $^{210}\text{Pb}$  dating. Here, we demonstrate that relying solely on  $^{210}\text{Pb}$  chronologies risks overestimating the rate of natural, preanthropogenic Hg accumulation. This in turn has ramifications for understanding the legacy of anthropogenic Hg pollution.

## Methods and Materials

**Study Sites.** We selected four remote study lakes representing different end members in their environmental setting and in potential exposure to anthropogenic Hg emissions (Figure S1; Table S1). The first two lakes, Lagunas Yanacocha 2 (hereafter LY2) and Negrilla, are located in the central Peruvian Andes. Both lakes were exposed to preindustrial Hg pollution generated by the mining and processing of cinnabar (HgS) ore at Huancavelica, Peru (7). A detailed examination of the preindustrial mining legacy preserved in both LY2 and Negrilla sediments has been presented in detail previously, showing an initial rise in Hg pollution beginning  $\sim 1400 \text{ BC}$  (7). These are contrasted with two lakes from the east coast of Baffin Island, Arctic Canada: Lost Pack and CF8. Surface cores from both lakes have been described in previous publications (8, 9). In contrast to the Peruvian lakes, the exposure of Lost Pack and CF8 to preindustrial Hg pollution should have been minimal, although arctic lakes record 20th century Hg pollution (4).

**Sediment Geochemistry.** Total sediment Hg was quantified using a DMA80 direct mercury analyzer (Milestone Inc., CT) (10); duplicates and standard reference materials were run every 10th sample. Total organic matter content of the

sediment was determined using loss on ignition (% LOI 550 °C) (11). Sediment [Hg] from LY2, Negrilla, and Lost Pack were determined at 0.5 cm intervals and 0.25 cm in the CF8 core.

**Core Chronologies.** To constrain recent sedimentation,  $^{210}\text{Pb}$  activities were measured using  $\alpha$ -spectroscopy. Supported  $^{210}\text{Pb}$  was estimated from the asymptotic activity at depth (the mean of the lowermost samples in a core) and was subtracted from total  $^{210}\text{Pb}$  activity measured at each level to derive unsupported  $^{210}\text{Pb}$  inventories. The constant rate of supply (CRS) model was used to calculate sedimentation rates and the age of each dated interval. Errors associated with  $^{210}\text{Pb}$  dates were estimated from counting uncertainties (5). To provide independent estimates of sediment age underlying excess  $^{210}\text{Pb}$ , AMS  $^{14}\text{C}$  dates were obtained on all cores. In the Andes, carbonized grass macrofossils were dated. Charcoal is terrestrial in origin and is unlikely to experience long soil-residence times and thus is a highly reliable dating target (12, 13). For CF8, aquatic moss macrofossils were dated while paired moss and humic extract samples were dated for Lost Pack. These have been shown to be appropriate for  $^{14}\text{C}$  dating in ecosystems containing little to no terrestrial vegetation (14).

Two age-depth models were subsequently developed for each core. The first relied solely upon the  $^{210}\text{Pb}$  chronologies and extrapolation to the core base. The extrapolation of  $^{210}\text{Pb}$  dates assumes *a priori* that a single, long-term value of sedimentation rate can be derived from  $^{210}\text{Pb}$  analysis of the upper core intervals (5, 17). This assumption is usually considered tenable if profiles of water content, organic matter, and sediment density remain relatively constant down-core (e.g. 18). Extrapolated sediment ages were calculated following Binford (17) using the equation

$$t_e = t_b + [(m_x - m_b) \div s_e] \quad (1)$$

where  $t_e$  is the extrapolated age at depth  $x$  in years,  $t_b$  is the age at the lowest depth with unsupported  $^{210}\text{Pb}$ ,  $m_x$  is the cumulative mass at depth  $x$  in  $\text{g cm}^{-2}$ ,  $m_b$  is the cumulative mass at the lowest depth with unsupported  $^{210}\text{Pb}$ , and  $s_e$  is the  $^{210}\text{Pb}$ -estimated sedimentation rate. If the sedimentation rate was variable over the period of unsupported  $^{210}\text{Pb}$  activity, then the lowest sedimentation rate value was used for  $s_e$ . A second age-depth model was constructed for each core using a mixed-effects model (19). This composite age-depth model uses the  $^{210}\text{Pb}$  CRS dates for the past 100 years and provides a best-fit age estimate for those intervals that are >100 years old. The composite age-depth model integrates the error associated with each individual date and between dates.

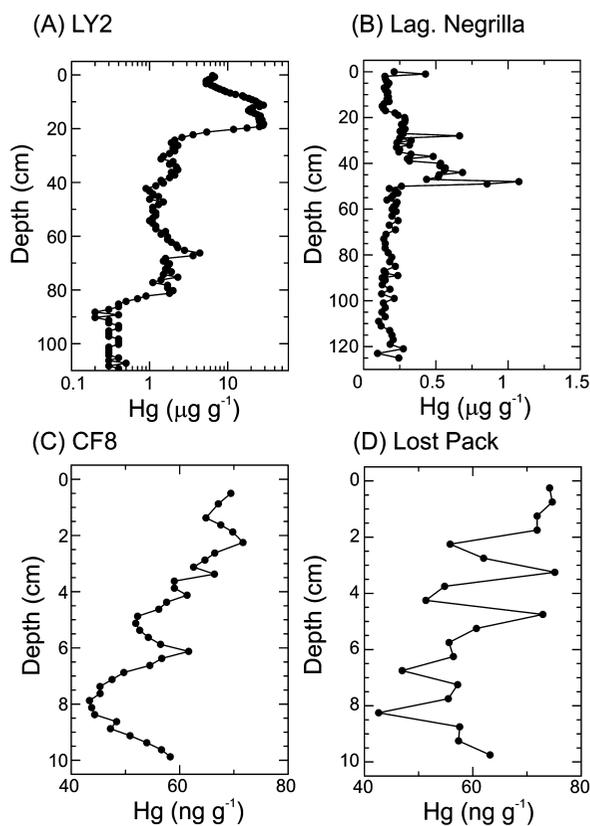
**Calculations of Hg Fluxes.** CRS sedimentation rates and Hg concentrations were used to calculate Hg flux spanning the past ~100 years. Below the limit of  $^{210}\text{Pb}$  (i.e., below the lower-most CRS date), Hg flux was estimated using the two different age-depth models developed for each core. The first estimate of Hg flux was calculated by multiplying Hg concentrations by the same sedimentation rate used to extrapolate  $^{210}\text{Pb}$  dates. This remains the most common approach used to estimate preindustrial Hg flux from lake sediment cores (e.g. refs 3 and 4). A second estimate of Hg flux ( $\text{Hg}_{\text{flux}}$ ) was calculated using

$$\text{Hg}_{\text{flux}} = s \times d \times \text{Hg}_i \quad (2)$$

where  $s$  is the sediment accumulation rate between core intervals derived from the combined  $^{210}\text{Pb}$ - $^{14}\text{C}$  chronology ( $\text{cm yr}^{-1}$ ),  $d$  is the dry density ( $\text{g cm}^{-3}$ ) at each core interval, and  $\text{Hg}_i$  is the concentration of Hg within each core interval ( $\mu\text{g g}^{-1}$ ).

## Results and Discussion

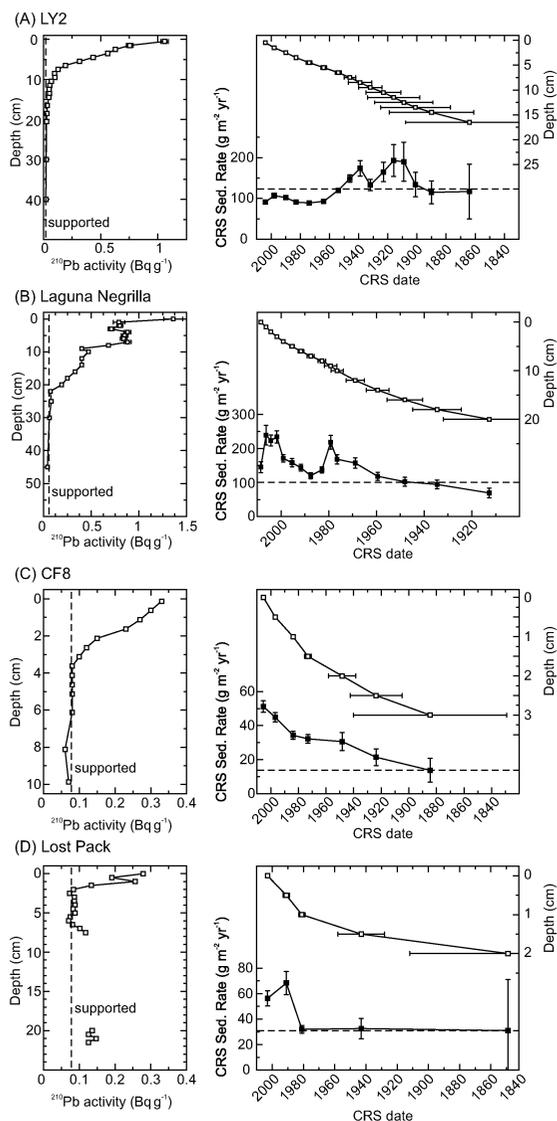
**Sediment Hg Concentrations and Core Stratigraphies.** At LY2, [Hg] is characterized by a relatively stable background



**FIGURE 1.** Down-core profiles of Hg concentration for all four study lakes.

of  $0.34 (\pm 0.06) \mu\text{g g}^{-1}$  below ~85 cm depth (Figure 1). Above this depth, [Hg] increases to  $>1 \mu\text{g g}^{-1}$ , fluctuating between  $1 \mu\text{g g}^{-1}$  and  $5 \mu\text{g g}^{-1}$  until ~20 cm when it increases abruptly again before subsequently declining toward the top of the core. At Negrilla, [Hg] is stable and low below ~50 cm, averaging  $0.18 (\pm 0.04) \mu\text{g g}^{-1}$ . [Hg] increases above ~50 cm to  $>1 \mu\text{g g}^{-1}$  and gradually declines up-core, reaching background values by the uppermost intervals. In the two arctic lakes, [Hg] displays considerable variability, superimposed on gradually increasing trends (Figure 1). At CF8, [Hg] rises from a minimum value of  $42 \text{ ng g}^{-1}$ , to a surface concentration of  $70 \text{ ng g}^{-1}$ . At Lost Pack, [Hg] displays greater variability; however, Hg concentrations are within the same range as at CF8 ( $40\text{--}80 \text{ ng g}^{-1}$ ). These [Hg] concentrations are directly comparable to other arctic lakes (4). Profiles of dry density and organic matter content are presented in Figure S2. None of the shifts in dry density are paralleled by shifts in organic content within the cores, suggesting that differences in density reflect variable water content and the effect of compaction, rather than changes in sediment composition. This is commonly thought to represent an ideal situation for the extrapolation of  $^{210}\text{Pb}$  dates (e.g. ref 18).

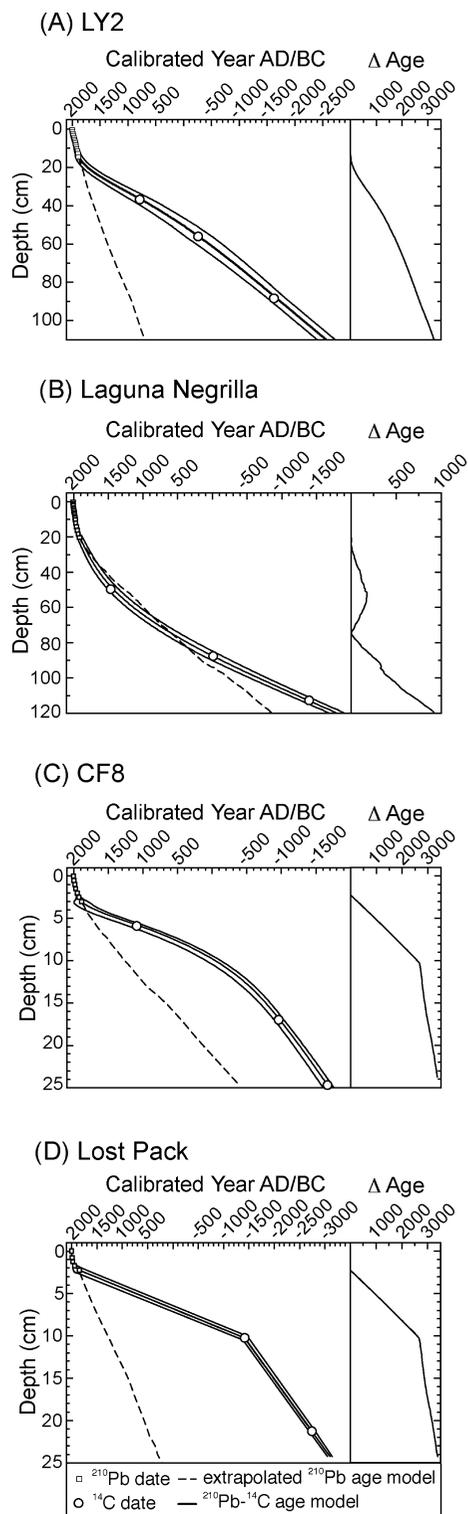
**Core Chronologies.** At all four study lakes,  $^{210}\text{Pb}$  activity declines to stable supported levels, and the CRS model was used to calculate sediment ages spanning the past century (Figure 2) (5). Below unsupported  $^{210}\text{Pb}$  intervals however, there are major discrepancies between the extrapolated and composite age models, the latter yielding much older basal dates in each case (Figure 3). This discrepancy is greatest in the two arctic lake cores. The smallest offset is observed at Negrilla, where the extrapolated  $^{210}\text{Pb}$  age model first overestimates and then underestimates the composite age model, reaching a  $\Delta^{14}\text{C}$  of ~1000 years at the core base. Thus, at all four of the study lakes presented here a difference exists between the extrapolated  $^{210}\text{Pb}$  model and the composite age-depth model suggesting changes in lake sedimentation rates with time.



**FIGURE 2.** Down-core profiles of total and supported (dashed line)  $^{210}\text{Pb}$  activities for all four study lakes. Also shown are the CRS dates and sedimentation rates for each lake. The dashed line indicates the extrapolated  $^{210}\text{Pb}$  sedimentation rates.

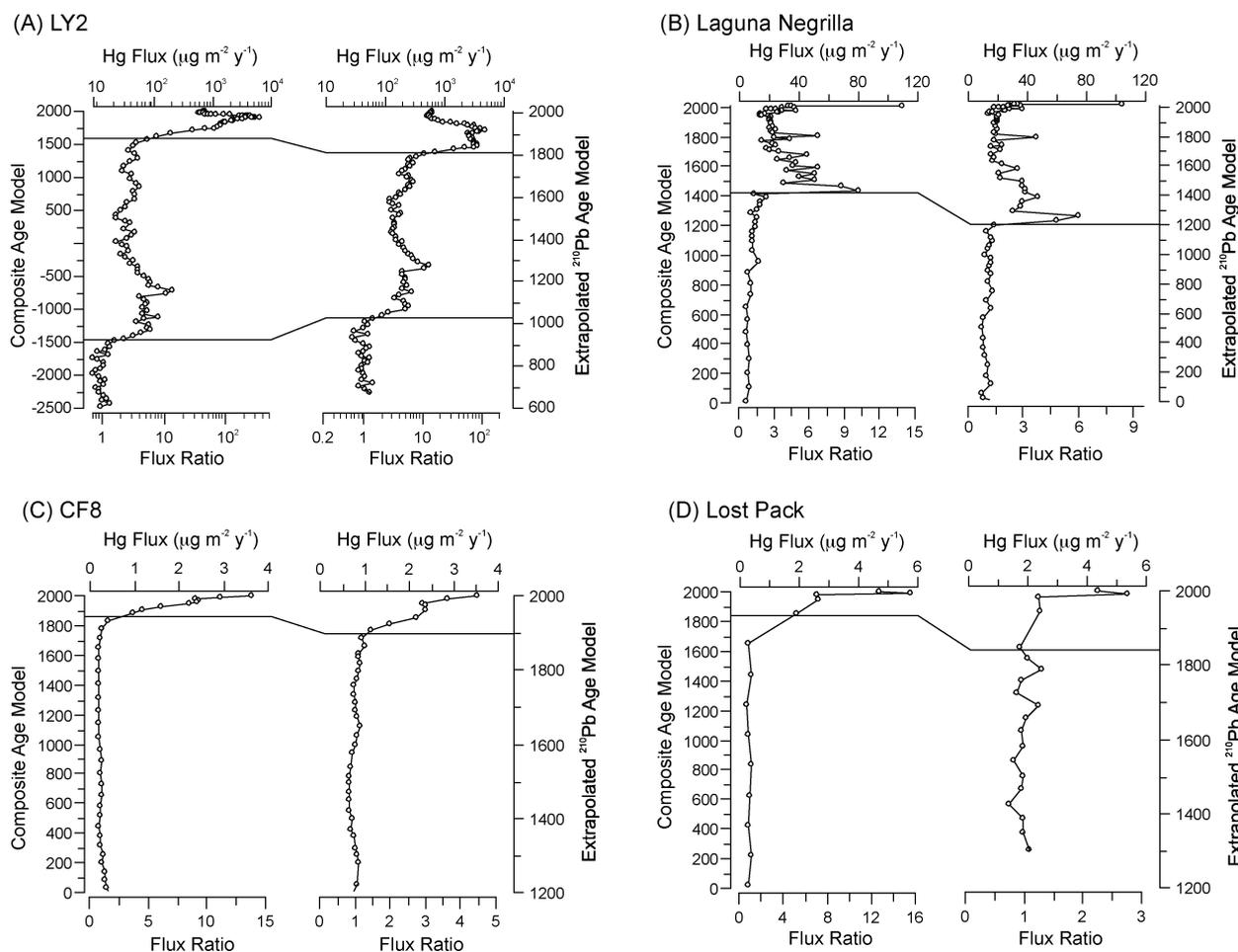
**Preindustrial Hg Flux Estimates.** Preindustrial Hg fluxes were calculated using both age-depth models (Table S2). At all four lakes, preindustrial Hg flux calculated using the extrapolated  $^{210}\text{Pb}$  age-depth model are consistently higher than those calculated using the composite age-depth model (Figure 4). The differences between the two estimates of preindustrial Hg flux reflect the incorporation of  $^{14}\text{C}$  dates into the core chronologies, and the attendant changes in preindustrial sedimentation rates. The  $^{14}\text{C}$  dates from LY2, CF8, and Lost Pack suggest a decrease in lake sedimentation rates sometime between the uppermost  $^{14}\text{C}$  date and the lowermost  $^{210}\text{Pb}$  date. While constraining the exact timing of this decrease in sedimentation rates would require additional  $^{14}\text{C}$  dates, it remains nonetheless apparent that sedimentation rates were slower pre-1900 AD than post-1900 AD.

**Implications for Preindustrial Hg Exploitation.** Profiles of Hg flux from both LY2 and Negrilla demonstrate the presence of preindustrial Hg pollution resulting from regional cinnabar mining at Huancavelica, Peru (Figure 4) (7). The earliest increase in Hg occurs in LY2 sediment at  $\sim 1400$  BC ( $\sim 80$  cm depth). A subsequent increase in Hg is preserved  $\sim 1500$  AD ( $\sim 20$  cm depth), suggesting an intensification of mining activities at this time. This latter rise in Hg is also preserved at Negrilla, reflecting the adoption of cinnabar



**FIGURE 3.** Plots of both the extrapolated  $^{210}\text{Pb}$  age model (dashed line) and the composite  $^{210}\text{Pb}$ – $^{14}\text{C}$  age model (heavy line) with 95% confidence intervals (thin lines) for all four study lakes.

smelting at Huancavelica and the long-range transport of Hg emissions (7). The recovery of long sediment records, and the incorporation of  $^{14}\text{C}$  dates, is therefore critical toward providing an accurate history of Hg enrichment in regions exposed to preindustrial Hg emissions from artisanal mining activities. Short sediment cores (e.g., a typical gravity core) that are only  $^{210}\text{Pb}$ -dated will fail to capture the true antiquity of Hg pollution in these regions and may overestimate preindustrial Hg fluxes.



**FIGURE 4.** Hg fluxes and flux ratios for all four study lakes. Fluxes and flux ratios were calculated using both the composite ( $^{210}\text{Pb}$  and  $^{14}\text{C}$ ) age model and the extrapolated  $^{210}\text{Pb}$  age model for each core. Flux ratios are unitless (sample:background) and capture the relative increase in Hg flux at each study site. Background Hg fluxes were calculated as the average Hg flux prior to the earliest evidence for Hg enrichment. Red lines join the same sediment depths across both models, and highlight the age discrepancies between the two Hg flux estimates.

**Implications for Canadian Arctic Lakes.** In the two arctic lakes, extrapolating basal  $^{210}\text{Pb}$  dates yields preindustrial fluxes of  $\sim 1 \mu\text{g m}^{-2} \text{yr}^{-1}$  and  $\sim 2 \mu\text{g m}^{-2} \text{yr}^{-1}$  at CF8 and Lost Pack, respectively (Figure 4). While these  $^{210}\text{Pb}$ -based estimates are in general agreement with previous estimates (3), none of these previous studies incorporated  $^{14}\text{C}$  dating into their core chronologies. In contrast, the composite  $^{210}\text{Pb}$ - $^{14}\text{C}$  fluxes suggest preindustrial Hg accumulation rates of  $< 0.5 \mu\text{g m}^{-2} \text{yr}^{-1}$  for both lakes, well below the  $^{210}\text{Pb}$ -based estimates. Thus, the differences between the  $^{14}\text{C}$  and  $^{210}\text{Pb}$  estimates of preindustrial Hg flux suggest that previous estimates of preindustrial Hg accumulation in the Arctic may be overestimated. Other studies have similarly concluded that sedimentation rates have increased across arctic lakes. In a recent study of 50 lakes spanning eastern and northern Canada, Muir et al. (4) found that half of the arctic lakes studied had experienced an increase of 10% or greater in sedimentation rates over the  $^{210}\text{Pb}$ -dated portion of the core. Lakes across much of this region are undergoing profound hydrological and biological changes as a result of recent warming, including increased summer evaporation (20), changes in algal community assemblages (21), and increases in both primary production (9) and inorganic sedimentation (22, 23). It seems likely that similar processes have contributed to the sedimentation histories documented here.

**Hg Flux Ratios and the Magnitude of Anthropogenic Hg Enrichment.** A critical assumption in using lake sediments to estimate past Hg deposition rates is that they provide a robust record of Hg delivery to lakes. The loading of Hg can

be influenced by watershed size and characteristics (24), catchment:lake area ratios (25), sediment focusing (26), and volatile losses of Hg prior to sequestration (27). Nonetheless, a broad array of data supports the assertion that relative changes in Hg accumulation within an individual core can be attributed to relative changes in Hg loading (28). Assuming site-specific factors remain constant over time, the relative change in Hg accumulation from modern to background times (Hg flux ratio) provides a comparable measure of increases in atmospheric Hg deposition (3). Hg flux ratios can facilitate comparisons between cores, and provide a relative measure on how Hg deposition has changed over time.

The modern Hg flux ratio at LY2 is  $\sim 45$  when the  $^{14}\text{C}$  age-depth model is used but is only 15 when the extrapolated  $^{210}\text{Pb}$  dates are used (Figure 4; Table S2). Even at Negrilla, where the extrapolated  $^{210}\text{Pb}$  dates provide a reasonable approximation of the true age-depth relationship, the modern  $^{14}\text{C}$ -based Hg flux ratio is  $\sim 5$ , versus  $\sim 2.5$  when the extrapolated  $^{210}\text{Pb}$  chronology is used. As with our lake sediment records, the Hg record from the Upper Fremont Glacier also implies a larger Hg flux ratio (2). The Upper Fremont Glacier suggests a Hg flux ratio of  $\sim 20$  during the mid-1980s followed by a decrease  $\sim 11$  during the early 1990s. Similarly, trends in [Hg] in hard tissues, including teeth, hair, and feathers from arctic animals suggest an order-of-magnitude increase in arctic marine foodweb-based animals over the industrial era (29). Our results raise the possibility that discordance between lake sediment cores, the Upper

Freemont Glacier, and arctic animal tissues may be attributable to a lack of chronological control beyond ~1850 AD in the lake records.

Both arctic lakes record an Hg flux ratio of ~12 when the  $^{14}\text{C}$  age-depth model is used (Figure 5; Table S2). In contrast, if extrapolated  $^{210}\text{Pb}$  dates are used, the flux ratio for both lakes is 2–3, at least four times lower than the Hg flux ratio implied by  $^{14}\text{C}$  chronologies. These results suggest that Hg delivery to the Arctic may have increased to a much larger degree than has been suggested previously.

The roughly 12-fold increase in Hg accumulation at CF8 and Lost Pack is dramatically higher than any other reconstructions of past Hg accumulation from the Arctic of which we are aware. In a survey of lakes from Alaska, Landers et al. (30) found Hg flux had increased by a factor of ~1, while Engstrom and Swain (31) reported flux ratios of ~2 for southeast Alaska. Fitzgerald et al. (32) reported a 3-fold increase in Hg fluxes for the same region. Bindler et al. (33) examined Hg fluxes from lakes along the west coast of Greenland, and the flux ratios were between 2 and 5. A recent summary by Muir et al. (4) includes 18 lake records of Arctic Hg accumulation, which collectively suggest an average flux ratio of ~2.

While one must exercise care when interpreting only limited numbers of records, the CF8 and Lost Pack Hg flux ratios are consistently higher than any previously published Hg flux ratios for the Arctic. This raises the possibility that previous lake sediment core studies may have underestimated both preindustrial Hg flux rates and, as a result, the degree to which anthropogenic activities have altered Hg deposition in the Arctic. Ideally, one would obtain  $^{14}\text{C}$  dates at regular intervals down the length of a sediment core. While this is rarely possible due to the availability of good dating targets, even a single date below the limit of  $^{210}\text{Pb}$  can offer some degree of additional chronological control if appropriate material exists. Whenever possible, dates on bulk sediments should be avoided, especially in regions containing carbonate rocks or clastic material derived from lignite, coal, and carbonaceous shales (34). New AMS  $^{14}\text{C}$  dates on existing Hg data sets would provide a revised appraisal of Hg enrichment and may identify spatial heterogeneity in Hg deposition over the Arctic.

**Future Efforts.** The lake records presented here place provisions on the assumption that stable sedimentation rates are reached near the base of unsupported  $^{210}\text{Pb}$  activity. At all four study lakes, preindustrial Hg fluxes are lower when  $^{14}\text{C}$  dates are incorporated into the age model. In the Andes, incorporating other means of dating is critical if the full history of preindustrial Hg emissions is to be captured. In the Arctic, our results suggest preindustrial Hg fluxes were  $<1 \mu\text{g m}^{-2} \text{yr}^{-1}$ , and the Hg flux ratio is  $>10$ . In many cases, even a rudimentary  $^{14}\text{C}$  chronology may be sufficient to confirm or refute extrapolated  $^{210}\text{Pb}$  ages and offers the opportunity to better constrain preindustrial Hg flux. While  $^{210}\text{Pb}$  dates should continue to be employed whenever possible, they should be augmented with other dating techniques to provide more accurate estimates of preindustrial sedimentation histories and hence Hg flux. If the recent increase in Hg deposition is to be considered in a long-term context, there is a need to develop regional AMS  $^{14}\text{C}$  chronologies that can be applied to both new and existing data sets.

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## Supporting Information Available

Two additional figures and three tables. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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