

# Caribbean Lead and Mercury Pollution Archived in a Crater Lake

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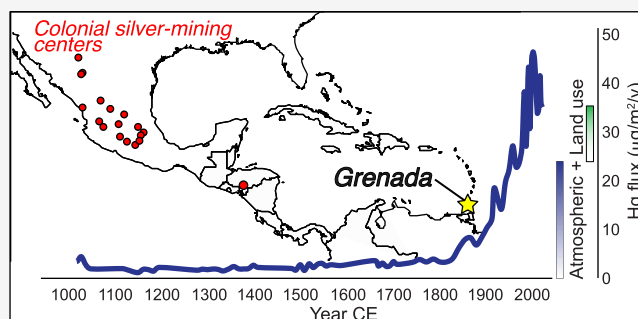
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Supporting Information

**ABSTRACT:** Lead and mercury have long histories of anthropogenic use and release to the environment extending into preindustrial times. Yet, the timing, magnitude, and persistence of preindustrial emissions remain enigmatic, especially for mercury. Here, we quantify tropical lead and mercury deposition over the past ~3000 years using a well-dated sediment core from a small crater lake (Lake Antoine, Grenada). Preindustrial increases in lead and mercury concentrations can be explained by varying inputs of watershed mineral and organic matter, which in turn reflect climate-driven changes in the lake level. We find no evidence that preindustrial lead and mercury use raised deposition rates in this remote ecosystem, and our results underscore the need to carefully evaluate common normalization approaches for changing lithogenic inputs and sedimentation rates. Industrial-era lead and mercury accumulation rates in Lake Antoine have been accelerated by land use and land cover change within the crater rim, yet global industrial pollution remains evident. After correcting for watershed inputs, we find that recent atmospheric lead and mercury deposition rates averaged 2925 and 24  $\mu\text{g}/\text{m}^2/\text{y}$ , respectively, which are in close agreement with monitoring data. Our results challenge recent assessments suggesting preindustrial mercury use raised atmospheric deposition rates globally, highlighting the unique nature of 20th Century industrial pollution.

**KEYWORDS:** paleolimnology, heavy metals, tropics, mercury, lead, pollution, Grenada



## INTRODUCTION

Human activities release a broad spectrum of heavy metals to the environment. Among these metals, special concern exists for both lead (Pb) and mercury (Hg). This concern reflects the health impacts associated with both metals,<sup>1</sup> their long histories of anthropogenic use and emissions,<sup>2–4</sup> and the degree to which anthropogenic emissions of both elements continue to exceed natural emissions.<sup>4,5</sup> During the industrial era, these two toxic heavy metals have been emitted to the atmosphere from different anthropogenic activities: Pb emissions resulted primarily from the combustion of leaded gasoline<sup>5</sup> and mercury emissions from the combustion of coal.<sup>6,7</sup> However, prior to the industrial era, emissions of both metals resulted primarily from one activity: the extraction of silver from ores.<sup>2,8</sup>

Lead emissions occur mainly as particulates, while Hg emissions are dominated by gaseous elemental Hg (GEM). These differences result in different atmospheric transport pathways. Atmospheric Pb is more readily deposited as aerosols or scavenged in rainfall. In contrast, GEM is characterized by long atmospheric residence times with hemispheric to global circulation. Following deposition, Pb is sequestered in soils and sediment;<sup>9</sup> Hg, in contrast, can be reemitted and recycled among air, soils, and surface waters for centuries.<sup>4</sup> The recycling of legacy Hg is one reason environmental Hg concentrations exceed current emissions.<sup>4</sup>

Constraining legacy emissions from natural and anthropogenic sources is necessary to understand the current global Hg budget.

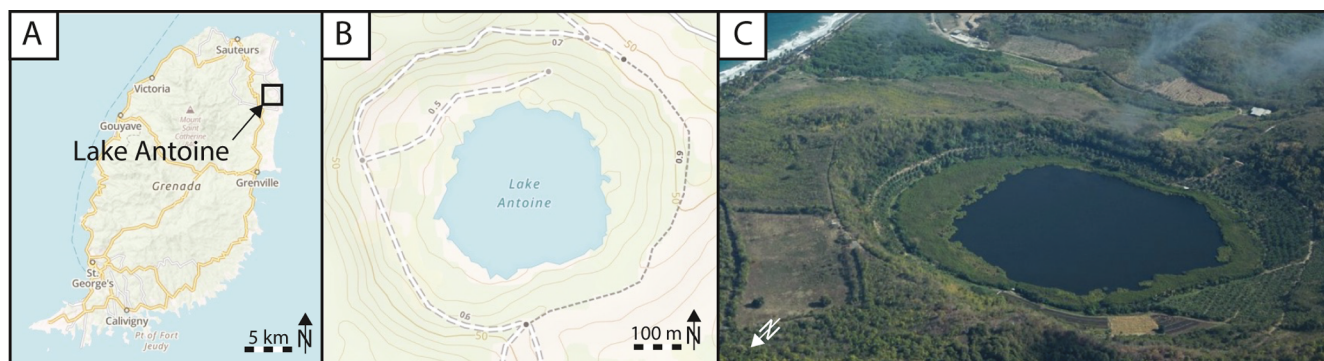
Considerable releases of both Pb and Hg occurred prior to the industrial era, before ~1850 CE.<sup>2</sup> Early mining and smelting first raised atmospheric Pb burdens across Europe and the Arctic during the first millennium BCE.<sup>2</sup> This Pb pollution was then deposited in soils and lake sediments across northern latitudes.<sup>2,10</sup> Preindustrial Pb pollution is also evident in lake sediments located near metallurgical centers in both North<sup>11</sup> and South<sup>10,12–14</sup> America. In the Andes, the mineral galena (PbS) was used as a flux during the smelting of silver-bearing ores creating an environmental legacy of local (<10 km) to regional (10–50 km) Pb pollution since ~500 CE. Globally, the smelting of ores has resulted in atmospheric emissions of 640,000–1,280,000 metric tons of Pb from 1500 to 1895 CE.<sup>8</sup>

Mercury was also mined and used prehistorically.<sup>3,15</sup> In the Andes, cinnabar (HgS) has been mined since ~1500 BCE.

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**Figure 1.** Maps of Grenada (A) and Lake Antoine (B) alongside a photograph (C) looking from the northwest clearly showing the results of land use and land cover change within the watershed.

These activities raised local rates of Hg deposition into nearby lakes.<sup>13</sup> Later, during the 16th Century, large quantities of liquid elemental Hg were used in the patio amalgamation process to extract silver from Andean ores.<sup>16</sup> The environmental impact of Hg used prior to the industrial era remains debated.<sup>17–20</sup> To understand the degree to which human activities impacted the global biogeochemical cycle of Hg, we must determine the environmental fate of atmospheric Hg emissions from historical silver and cinnabar mining.<sup>4,21</sup>

Quantifying historical Pb and Hg emissions requires the use of natural archives, including peat, lake sediment, ice, and tree rings.<sup>22</sup> Lake sediments are the most widely used of these archives, and they suggest a 3- to 5-fold increase in Hg deposition during the industrial era.<sup>19,22,23</sup> Well-dated records extending into the preindustrial era are required to quantify potential impacts of preindustrial anthropogenic Hg emissions. Unfortunately, relatively few lake records have been published from low latitude tropical regions, which were loci of preindustrial Hg mining and use.<sup>16,24,25</sup> Of those that have, many have studied sediment cores collected from lakes located near major historical mining and metallurgical centers.<sup>10,22</sup> In addition, not all lakes are equally sensitive to atmospheric deposition because they also receive Hg from direct deposition on their surfaces and from watershed inputs. Variability in rates and amounts of watershed inputs may confound reconstructions of past atmospheric deposition rates.<sup>26,27</sup> Lakes occupying extinct volcanic craters are ideal because watershed inputs are minimized. If preindustrial Pb and Hg emissions were circulated globally, then increased deposition rates of those heavy metals should be evident in well-dated lake sediment records. We present a new record of Pb and Hg deposition from Lake Antoine, a small crater lake located near Central and South American centers of preindustrial Hg mining and use.

## METHODS

**Study Site.** Grenada is an island nation located ~125 km northeast of the Venezuelan coast (Figure 1). Extensive volcanism produced basalts, andesitic flows, and ashes that dominate the island's geology. Higher elevations (>800 m asl) in the center of the island support tropical rainforest, with dry secondary forest at lower elevations. Grenada lies in the belt of the northeast trade winds with highly seasonal rainfall. Most precipitation occurs between June and November. Rainfall totals range from ~4000 mm/y in mountainous areas to ~1000 mm/y in lowland regions.<sup>28</sup>

Lake Antoine occupies an extinct volcanic crater that formed ~16,000 years ago.<sup>29</sup> The lake is small (~0.1 km<sup>2</sup>), >6 m deep, and occupies a ~0.4 km<sup>2</sup> watershed with no surface inlet or outlet. A hiking trail circles the lake and the Lake Antoine watershed has been cultivated intensively (Figure 1).<sup>30</sup> Banana plantations occur within the crater rim and outside of the crater sugarcane plantations (for rum production) are extensive. Two parallel sediment cores with a maximum length of 8.5 m were collected near the lake's depocenter in 2008.<sup>31</sup> These cores, including a surface core with an intact mud-water interface, were described previously in a published record of past variations in pollen and phytolith assemblages and charcoal concentrations.<sup>31</sup> We sampled these same sediment cores for geochemical analyses.

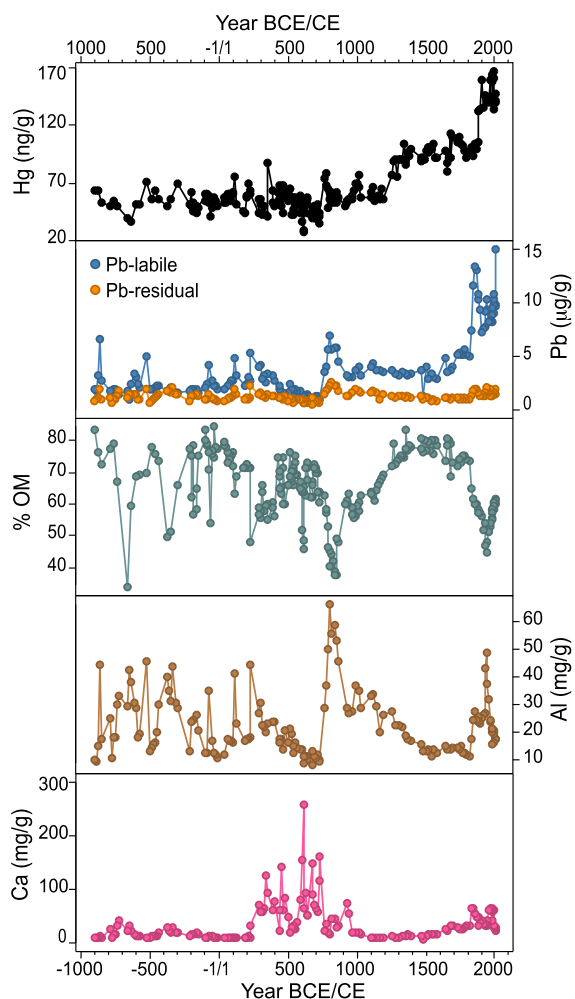
**Sediment Geochemistry.** A previous publication of these sediment cores relied upon <sup>14</sup>C dates to develop an age-depth model for the 8.5 m long core, which spans ~9000 years.<sup>31</sup> We made new measurements of excess <sup>210</sup>Pb activity and obtained additional <sup>14</sup>C dates to develop an updated age-depth model for the uppermost ~4.5 m, which encompasses the past ~3000 years (Tables S1 and S2). The age-depth model was developed using the CLAM package in R.<sup>32</sup> Discrete horizons of tephra or highly inorganic slump deposits, noted in previous cores,<sup>29</sup> are evident as abrupt decreases in the organic matter (OM) content and increases in dry bulk density (Figure S1). These horizons represent instantaneous depositional events in our updated age-depth model for the core (Figure S2).

These sediment cores were first used for a paleoenvironmental and paleoclimatic study.<sup>31</sup> Thus, our sampling for this project was opportunistic, targeting intervals where sufficient sediment remained. Total Hg was measured using EPA Method 7473 using a DMA80.<sup>33</sup> Percent OM was measured as the mass loss during combustion on the DMA80.<sup>34</sup> Trace element concentrations were quantified after undergoing a two-stage sequential extraction.<sup>35</sup> Labile elements were first extracted using ~6 mL of 1 M nitric acid added to ~200 mg of freeze-dried sediment. The sample was shaken overnight, centrifuged, and the extract poured off and measured by ICP-MS. This extraction method, which typically includes any anthropogenic pollutants, targets trace elements weakly bound to OM and to the outside of inorganic particles.<sup>35–37</sup> To extract the lithogenic (i.e., residual) component, the remaining sediment was then rinsed three times using milli-Q water, centrifuged, and then freeze-dried again before being digested using hydrofluoric acid before being quantified by ICP-MS. Total trace element concentrations are the sum of the labile and residual fractions.

Analytical uncertainty and recoveries were assessed using duplicates and certified reference materials (see the Supporting Information; Table S3).

## RESULTS AND DISCUSSION

**Preindustrial Hg and Pb Deposition.** Between 1000 BCE and 700 CE, the concentrations of both Hg and Pb<sub>labile</sub> in Lake Antoine sediment were relatively stable, averaging ( $\pm 1\sigma$ )  $53 \pm 9$  ng/g (Hg) and  $2 \pm 1$   $\mu$ g/g (Pb) (Figure 2). Pb and Hg



**Figure 2.** Concentrations of mercury (Hg), labile and residual (lithogenic) lead (Pb), organic matter (OM), aluminum (Al), and calcium (Ca) in Lake Antoine over the past 3000 years.

concentrations were stable during this period despite changing sediment composition, evidenced by the fluctuating % OM, Al concentrations, and markedly higher Ca concentrations from ~200–700 CE. Previous studies of Lake Antoine have documented large climate-driven changes in the lake level, which in turn drove changes in sediment<sup>30,32</sup> and diatom-community composition,<sup>29</sup> charcoal concentrations,<sup>32</sup> and pollen and phytolith assemblages.<sup>31</sup> Geochemical changes occurred during this period as well. The presence of sediment Ca on volcanic islands lacking carbonate bedrock reflects the precipitation of authigenic calcite. Calcite precipitation occurs when arid conditions result in decreased water levels (and volume), thereby increasing lake-water ionic concentrations above the maximum solubility for the ambient conditions.

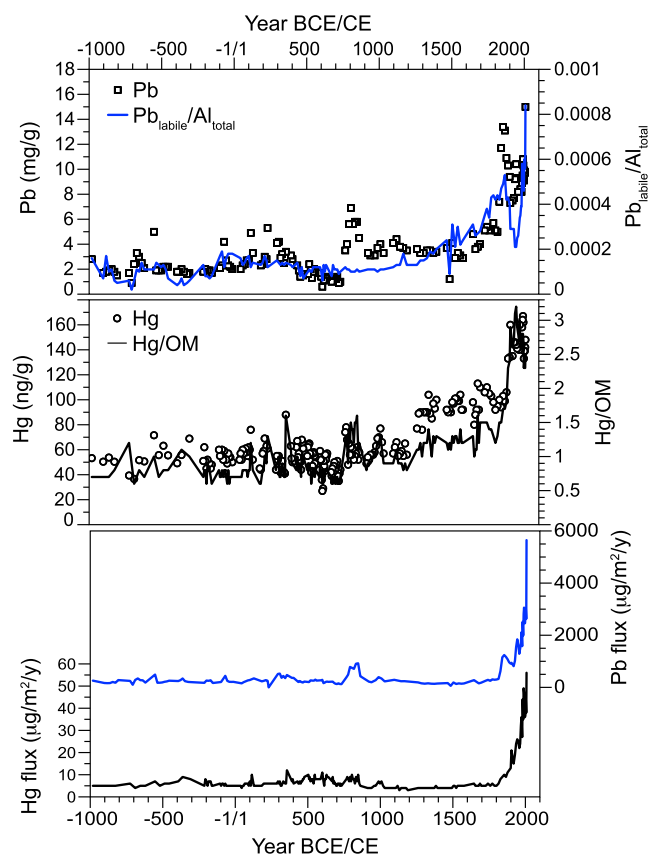
According to the age-depth model, varying intensities of aridity occurred between ~200 and 700 CE. Fritz et al. came to a similar conclusion in their study of changing diatom assemblages and sedimentology using a different set of sediment cores from Lake Antoine.<sup>29</sup> However, despite climate-driven changes in the lake level and sediment composition, Hg and Pb concentrations in Lake Antoine remained relatively low and stable for nearly 2000 years.

This period of aridity appears to have ended ~700 CE, when the concentrations of Ca and OM decreased and Al increased. The influx of Al reflects the erosion of terrestrial (mineralogenic) sediment, due either to rising lake levels or precipitation-driven watershed erosion, or both. Pb<sub>labile</sub> concentrations increased briefly at this time to ~7  $\mu$ g/g before returning to ~4  $\mu$ g/g (Figure 2). Hg concentrations also increased, but, unlike Pb, they returned rapidly to background concentrations. Another increase in Hg (but not Pb) concentrations occurred after ~1200 CE during a period of rising % OM and declining Al. During this period, Hg concentrations increased to roughly 2 $\times$  background levels, averaging  $95 \pm 8$  ng/g from 1200 to 1850 CE. Finally, rapid increases in both Pb and Hg concentrations occurred after ~1850, during the industrial era. Hg concentrations were approximately 3 $\times$  background values (average:  $141 \pm 17$  ng/g) and Pb concentrations were ~5 $\times$  higher than background (average:  $10 \pm 2$   $\mu$ g/g). These industrial era increases in Pb and Hg were coeval with a decrease in OM and an increase in Al. Elevated Al concentrations may have coincided with the introduction of sugarcane plantations within the Lake Antoine watershed or with another smaller drop in the lake level, as suggested by increasing Ca concentrations to ~500 mg/g.

Concentrations of Pb and Hg in lake sediment archives reflect natural and anthropogenic-driven changes in rates of atmospheric deposition, shifting watershed inputs (i.e., changes in soil and bedrock erosion amounts and rates), and changing sedimentation rates within the basin. To separate these factors and help distinguish between natural and anthropogenic inputs, Pb and Hg may be normalized to the amounts of organic or inorganic sediments or other indicators of bedrock or soil erosion, including such lithogenic elements as Al.<sup>38</sup> Changing sedimentation rates within a lake basin can either increase or decrease sediment Hg concentrations even as atmospheric Hg deposition remains constant. Calculating accumulation rates can account for potential changes in the sedimentation rate. We normalized the Hg to OM content and Pb<sub>labile</sub> to Al<sub>total</sub> to distinguish natural from anthropogenic inputs. The same results were obtained using other lithogenic elements (Figure S3). Hg was normalized to OM rather than Al because Hg associates more closely with organic rather than inorganic particles in lakes and watershed soils. Accumulation rates (fluxes) were also calculated for Hg and Pb<sub>labile</sub> (Figure 3).

Normalizing Pb<sub>labile</sub> to Al<sub>total</sub> and Hg to OM eliminates some of the key features of the preindustrial Pb and Hg concentration curves (Figure 3). For example, the abrupt increase in Pb concentrations ~700 CE appears to have been driven entirely by an influx of lithogenic Pb (and Al), evidenced by the constant Pb/Al ratio at this time. Similarly, the rise in Hg concentrations ~1200 CE is not evident in the Hg/OM profile. Steady increases in % OM (Figure 2) and progressively wetter conditions were documented in this part of the Caribbean by ~1200 CE.<sup>29</sup> The preindustrial rise in Hg concentrations likely resulted from increased in-lake primary





**Figure 3.** Changes in Pb and Hg after normalization to Al and organic matter (OM), respectively, and Hg and Pb accumulation rates (fluxes) over the past 3000 years.

production and/or wash-in of terrestrial OM rather than increases in atmospheric Hg deposition. The same interpretation applies to the steady rise in Pb/Al ratios after  $\sim 1300$  CE. While a steady rise in the Pb/Al ratio may indicate a new source of Pb pollution,<sup>37</sup> the increasing Pb/Al ratio observed here is a product of decreases in Al rather than increases in Pb concentrations (Figure 2). Much of the preindustrial variability in Pb and Hg concentrations is therefore attributable to climate-driven changes in the limnology of Lake Antoine.

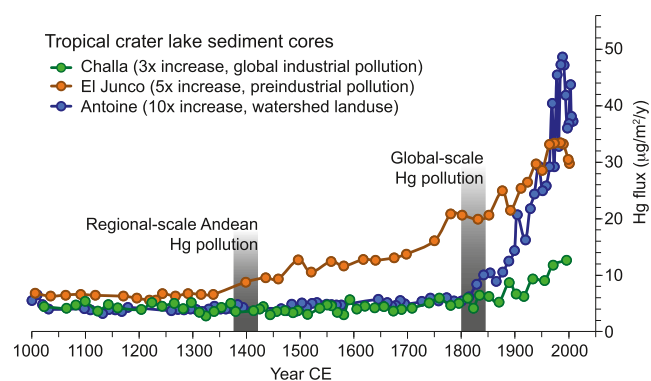
Any indication for a preindustrial rise in Pb or Hg deposition disappears with the calculation of Pb and Hg fluxes (Figure 3). Preindustrial (1000 BCE to 1800 CE) Pb and Hg fluxes averaged  $275 \pm 178$  and  $6 \pm 3 \mu\text{g}/\text{m}^2/\text{y}$ , respectively. Both flux profiles are characterized by several brief increases (e.g., both Pb and Hg  $\sim 200$  CE and Pb  $\sim 800$  CE). These increases in Pb and Hg flux are products primarily of the sedimentation rate ( $\text{cm}/\text{y}$ ) rather than increases in Pb, Hg, or dry density (Figure S1). The Pb and Hg flux increases appear to be resulting from near-instantaneous inputs of terrestrial material rather than episodes of high atmospheric Hg deposition due to such factors as volcanic events.

**Industrial Era Pb and Hg Pollution.** While the Lake Antoine sediment core lacks evidence for preindustrial Pb and Hg pollution, both Pb and Hg fluxes rise rapidly after  $\sim 1800$  CE, reaching  $>3500$  and  $\sim 45 \mu\text{g}/\text{m}^2/\text{y}$ , respectively. These values are 18-fold (Pb) and 10-fold (Hg) higher than the preceding  $\sim 800$  years, increases that are greater than typical for lakes not directly impacted by local Pb and Hg emission sources.<sup>10,22</sup> The establishment of banana and sugarcane plantations within the Lake Antoine watershed may account

for the elevated Pb and Hg fluxes (Figure 1). Changing land-cover and land-use within the crater rim would have increased soil erosion rates during a period of increasing atmospheric deposition of Pb and Hg pollution. The Hg/OM ratio only increased by a factor of  $\sim 3$  during this same period, suggesting atmospheric Hg deposition also increased by  $\sim 3$ -fold at this time. The correlation between Pb and Al and between Hg and OM also allows us to estimate separately the current rates of atmospheric deposition and watershed (erosional) inputs (see the Supporting Information).<sup>37</sup> Our calculations suggest that between 2000 and 2008 CE, Pb and Hg atmospheric deposition rates have averaged 2925 and 24  $\mu\text{g}/\text{m}^2/\text{y}$ , respectively. These estimates agree closely with measured wet Pb and Hg deposition rates elsewhere in the Caribbean. In Cuba, atmospheric Pb deposition averaged 2336  $\mu\text{g}/\text{m}^2/\text{y}$  between 2014 and 2016 CE.<sup>39</sup> Hg deposition in Puerto Rico has averaged 25  $\mu\text{g}/\text{m}^2/\text{y}$  since monitoring began in 2014 CE.<sup>40</sup> Correcting for watershed inputs allows for the calculation of the atmospheric fraction of Pb and Hg deposition to Lake Antoine.

**Pb and Hg Deposition in the Tropics.** Relative to mid- and high-latitude locations, relatively few records of late Holocene tropical Pb and Hg deposition have been published. Kamenov et al. studied a peat core from the El Triunfo mire in the Colombian Andes.<sup>41</sup> They noted an increase in Pb/Sc ratios and a shift in Pb isotope ratios to document the appearance of enigmatic Pb pollution around 2000 years ago. They suggested this Pb resulted from local mining activities. While we lack measurements of Pb isotopes in Lake Antoine, we see no evidence that this early, northern Andean Pb pollution was transported as far north as the Caribbean. In addition, while European Pb emissions have been deposited in Greenland ice<sup>2,42</sup> and across Europe<sup>9,10</sup> since the first millennium BCE we do not observe any evidence for this early Pb pollution in Grenada. Thus, preindustrial Pb emissions do not appear to have circulated globally.

Two other low latitude crater-lake sediment Hg records were collected from El Junco (Galapagos Islands)<sup>13</sup> and Lake Challa (Kenya).<sup>19</sup> Those sediment cores were also dated by both  $^{210}\text{Pb}$  and  $^{14}\text{C}$ . Unlike Lake Antoine, the watersheds of both El Junco and Challa were not impacted by human activities during the industrial era. All three crater lakes are characterized by similar preindustrial Hg fluxes (Figure 4). These are crater lakes located in watersheds largely



**Figure 4.** Profiles of Hg concentration and accumulation rate (flux) over the past 1000 years from three low-latitude crater lakes including Lake Antoine (this study), El Junco Lake in the Galapagos Islands (Ecuador),<sup>13</sup> and Lake Challa (Kenya, Africa).<sup>19</sup>

undisturbed by preindustrial activities. Therefore, we conclude that preindustrial atmospheric Hg deposition rates in the tropics were likely very close to  $5 \mu\text{g}/\text{m}^2/\text{y}$ . Of the three records, only El Junco records a preindustrial increase in both Hg concentration and Hg flux beginning  $\sim 1450$  CE.<sup>13</sup> This preindustrial Hg pollution was carried atmospherically from emission sources in the Peruvian Andes, raising Hg deposition rates downwind. Based on measurements of Hg isotopes, Cooke et al.<sup>13</sup> suggested the most likely emission source was cinnabar mining activities at Huancavelica, Peru. Huancavelica has been one of the most important sources of Hg throughout history, and recent historical assessments of Hg pollution through time suggest cinnabar mining and retorting may have been the single largest source of preindustrial Hg emissions.<sup>8</sup> Elevated Hg values are not evident in the sediment record from Lake Challa (Figure 4), suggesting these emissions were not circulated across the Southern Hemisphere.

Our results contribute to a growing body of evidence suggesting that preindustrial Hg emissions were smaller in magnitude than has been previously proposed.<sup>19,22</sup> Furthermore, the Lake Antoine data support suggestions that preindustrial and much of the 20th Century Hg emissions were deposited locally near urban and industrial centers of Hg use and release.<sup>6,13</sup> However, recent assessments of preindustrial Hg emissions have come to a different conclusion. Amos et al.<sup>43</sup> and Li et al.<sup>20</sup> suggested preindustrial Hg emissions raised global atmospheric GEM concentrations and Hg deposition rates to terrestrial archives. Those conclusions relied primarily on statistical summaries of published peat and lake sediment cores extending into the preindustrial era. Two biases need to be considered in assessing the presumed preindustrial Hg pollution. First, the reliability of peat cores as faithful archives of past Hg deposition is questionable.<sup>22,23,44</sup> Multiple studies have documented postdepositional mobility of Hg in peat. Thus, peat core records of past GEM concentrations or past Hg deposition rates should be interpreted with caution. The second area of bias results from confounding local versus global Hg pollution in lake sediments. Many of the sediment cores included in these syntheses were collected from lakes directly downwind (often  $<50$  km) of major preindustrial Hg emission sources.<sup>20,43</sup> While these records serve as useful histories of local mining, metallurgy, and emissions, they are not representative of global patterns in Hg deposition.

Our Lake Antoine sediment core represents the first well-dated record of late Holocene Pb and Hg deposition in the Caribbean. We observed no evidence that preindustrial mining and metallurgy in Europe and the South American Andes increased the deposition of Pb or Hg pollution to Grenada. The lack of any preindustrial increase in these two elements contrasts with locations directly downwind and downstream of the emission sources. Thus, preindustrial anthropogenic activities did not elevate global atmospheric Pb and Hg burdens. This finding for Pb and Hg contrasts with carbon, which may have been impacted by deforestation and animal husbandry during the mid-Holocene.<sup>45</sup> Ice cores from both the Arctic and Antarctic record increasing atmospheric  $\text{CO}_2$  and  $\text{CH}_4$  concentrations since the mid-Holocene. Indeed, carbon may prove to be the only element impacted at a global scale by preindustrial anthropogenic activities.

With the industrial era, global-scale impacts extend to heavy metals (Pb, Hg), nitrogen,<sup>46</sup> and even radionuclides.<sup>47</sup> While the use of leaded gasoline was phased out beginning in the

1970s resulting in declining lead emissions to the atmosphere, Pb burdens remain well above background levels in geographically remote lake sediment records like Lake Antoine. We see no evidence for a decline in Pb deposition in Lake Antoine. Indeed, Pb concentration and fluxes are the highest in the uppermost sediments. This may reflect either the continued export of industrial-era Pb pollution from the watershed<sup>27</sup> or the continued supply of anthropogenic Pb from the recent combustion of leaded gasoline in regions upwind like Africa, or both. Algeria became the last nation to phase out leaded gasoline in 2021.<sup>48</sup> Additional sediment cores from crater lakes offer opportunities to refine spatial and temporal patterns in local and global scale industrial and preindustrial heavy metal emissions.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.est.1c06791>.

Additional methods and materials; profiles of % OM, dry bulk density, and Hg concentration in the Lake Antoine sediment core; age-depth model for the Lake Antoine sediment core integrating both  $^{210}\text{Pb}$  and  $^{14}\text{C}$  ages; plots of the labile and residual fractions of Pb and Al as well as Pb/Zr and Pb/Ti ratios;  $^{210}\text{Pb}$  results for the Lake Antoine sediment core; radiocarbon ( $^{14}\text{C}$ ) dates in years before present used as part of this study; and results of QC samples included as part of the Hg and trace element measurements (PDF)  
Cooke EST Data (XLSX)

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### Notes

The authors declare no competing financial interest.

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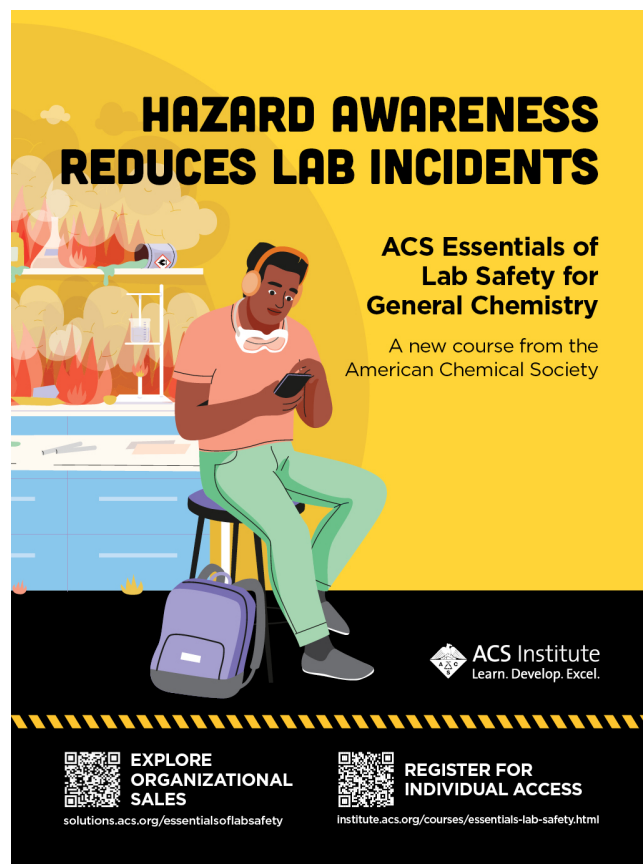
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