Hg deposition in the tropics during the Younger Dryas

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Mercury (Hg) loadings to even the most remote aquatic ecosystems have increased by 3-fold or greater since the 20th century, greatly accelerating human exposure to this toxic trace metal. The rise in environmental Hg has been documented from a range of natural archives, including ice cores, snow deposits, peat cores, and (most frequently) lake sediment cores. A majority of these study sites are from to high- and mid-latitude locations; considerably less is known about trends in Hg deposition from low latitudes. In addition, few studies have investigated long-term variability in natural (i.e., pre-industrial) Hg deposition rates, despite evidence for changes in Hg cycling associated with environmental change. Long-term sedimentary archives of past climatic and environmental variability therefore offer a unique opportunity to asses how natural processes serve to influence natural Hg cycling in the environment. Here, we present new Hg geochemical data from a low-latitude lacustrine sediment core collected from Laguna de los Anteojos, a high-altitude (3920 m a.s.l.) cirque lake located in the Mérida Andes of Venezuela. This ¹⁴C-dated sediment core spans 14,680 to 9,350 years before present (BP), and includes multi-proxy evidence for large paleoclimatic and paleoecological shifts associated with the Bølling-Allerød, Older Dryas, and Younger Dryas climatic intervals [1].

There are two clear end-member sediment facies within the Anteojos core: clastic-rich sediments high in titanium (Ti) and low in organic matter (OM), and the opposite. Sediment [Hg] spans an order of magnitude (12-124 ng g-1), and is, to some degree, associated with OM (r^2 =0.38). [Hg] and Hg flux are lowest during the Younger Dryas, which was not only cold but also arid. Southerly migration of the intertropical convergence zone (ITCZ) during the initial stages of the Younger Dryas chronozone [2] likely decreased regional precipitation and thus Hg deposition to the lake. The return of the ITCZ and a warmer and wetter climate ~12,200 BP appears to have initiated a rapid increase in [Hg] within Anteojos sediment, as both [Hg] and Hg flux rise by >4-fold in less than a century. Alternatively, the demise of regional snowfields and glaciers, which expanded during the Younger Dryas, may have released legacy Hg into the lake. The Anteojos sediment record presented here offers a welldated and multi-proxy archive of past environmental change through a period of rapid climatic transitions.

[1] Stansell, et al. (2010) EPSL **293**, 154-163. [2] Haug, et al. (2001) Science **293**, 1304-1308.

Isotopic evidence for preindustrial mercury emissions to the atmosphere

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Lake sediment cores from the South American Andes record anthropogenic Hg emissions to the atmosphere extending as far back as 1400 BC [1]. Early Hg pollution resulted from a range of activities including cinnabar (HgS) mining [1], Hg amalgamation [2], and the smelting of non-ferrous ores [3]. While Hg may spend centuries or even millennia circulating in the environment, it remains unclear just how far early these Hg emissions were transported and to what degree they influenced the global biogeochemical cycle of Hg. Here, we present new Hg stable isotopic data from two lake sediment cores that offer insight into the magnitude and geographic extent of early anthropogenic Hg emissions. One of the cores is from the Peruvian Andes, and records clear increases in Hg associated with Andean cinnabar mining and Hg amalgamation [1]. The other sediment core is from a crater lake on San Cristobal Island (Galápagos archipelago), and thus is far removed Hg emission sources, both past and present.

Concentrations of Hg in both sediment cores increase above stable background values after ~1500 AD, signaling the onset of intensive Hg emissions and subsequent deposition resulting from Colonial cinnabar mining and Hg amalgamation. In addition, both mass dependent (MDF; δ^{202} Hg) and mass-independent fractionation (MIF; $\Delta^{201}\text{Hg})$ of sedimentary Hg is evident in both sediment cores (Fig. 1). Pre-pollution sediments (uncontaminated by even the earliest metallurgical activities) consistently record negative MDF (-2‰) and MIF (-0.2‰). However, early increases in Hg concentration are matched by a positive shift in sediment δ^{202} Hg of nearly 2‰; Δ^{201} Hg values, in contrast, remain stable across this transition. The same trends are present in both sediment cores, suggesting they record hemispheric scale processes. Moreover, the Hg stable isotopic signature of preindustrial Hg pollution overlaps with new determinations of MDF and MIF in Peruvian cinnabar, which strongly suggests that early Hg emissions can be isotopically linked to their primary mineralogical sources.

The rise of global Hg pollution during the 20th century is also recorded in both sediment cores. However, while MDF values remain constant across the preindustrial-industrial transition, MIF values shift from negative to positive. This suggests either a difference in the MIF signature of preindustrial and industrial Hg sources, or a change in the direction of photochemically-induced MIF since ~1900 AD. Collectively, these results suggest Hg stable isotopic ratios can offer insight into Hg emissions associated with both preindustrial and industrial anthropogenic activities.

[1] Cooke, et al. (2009) Proc. Nat. Aca. Sci. **106**, 8830-8834. [2] Cooke, et al. (2009) Geology **37**, 1019-1022. [3] Cooke et al. (2011) Ambio **40**, 18-25.