# Mercury Deposition to the Arctic over the Last Glacial Cycle

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## Final Report

### *Introduction*

Analysis of mercury (Hg) in Antarctic ice in the early 1990's indicated that large increases in Hg deposition occurred in that region during the last glacial maximum relative to the Holocene (Vandal et al. 1993). In an on-going effort to understand the mechanism behind this increase, a former WHOI Post-doctoral Scholar, Dr. Paul Drevnick, and I have been exploring the reconstruction of trends in Hg deposition across glacial/interglacial transitions using a number of archives. To date, these most notably include non-glaciated lakes (Titicaca and Baikal) as well as marine sediments. Fascinating trends have been revealed and which challenge the proposed explanation for Hg cycling in the past, and may provide the basis for using Hg as a paleo-proxy of large-scale geophysical/climate change over millennial timescales.
To further this effort, we have measured the Hg depositional changes in an Arctic analog (the Greenland Ice Sheet) to that of the Antarctic over the last 40,000 years. A number of Arctic ice cores of suitable age/length were recovered during the Greenland Ice Sheet Project #2 (GISP2), and these samples are available to outside scientists through collaboration with the National Ice Core Laboratory (NICL). Thus, we used ARI support to travel to the Core Repository in Denver, investigate which cores would be suitable, ship subsamples to the University of New Hampshire (organizational headquarters for the NICL), set up a small clean lab space within a freezer storage/workspace trailer at UNH, decontaminate our samples and analyze them for total Hg at WHOI.

Hg is an unusually volatile metal, having a relatively long-lived vapor phase in the atmosphere (nearly all $Hg^o$; Fitzgerald and Lamborg 2003). This $Hg^o$ species facilitates global dispersion of natural (especially volcanoes) and anthropogenic (especially coal combustion) emissions of Hg and allows remote natural archives (e.g., lake sediments, peat bogs, ocean sediments, glacial ice) to act as recorders of past and present global-scale cycling of this element. This $Hg^o$ form is ultimately removed from the atmosphere following oxidation to $Hg^{2+}$ by ozone, hydroxyl radical and halogen radicals. Once deposited to land and sea, some re-emission back to the atmosphere as $Hg^o$ is possible, extending the opportunity for Hg dispersion. Of particular relevance here is the reduction of $Hg^{2+}$ to $Hg^o$ in the surface ocean, facilitated by light and dissolved organic matter (DOM), resulting in supersaturation of $Hg^o$ with respect to atmospheric concentrations and subsequent evasion from the ocean. Because much of the DOM in the ocean is autochthonous, changes in ocean productivity could result in changes in $Hg^o$ evasion and therefore global redistribution of Hg from the ocean to land.

It is this last behavior that was invoked to explain the large changes in Hg deposition to Antarctica recorded in glacial ice from the Dome C site (Figure 1; Vandal et al. 1993). Vandal and colleagues analyzed ice from the Dome C core that had been scrupulously decontaminated at Caltech (Boutron and Patterson 1986) and found much lower concentrations than had been previously reported (e.g., Weiss et al. 1971; Carr and Wilkniss 1973; Appelqvist et al. 1978). Furthermore, the determinations revealed a large increase in Hg concentration and deposition to Antarctica during the last glacial maximum relative to the Holocene. By correcting their results for dust inputs (with Al) and putative volcanic inputs (with non-seasalt sulfate), they argued that the signal was entirely atmospheric, and that the only reservoir on Earth that could supply this additional material was the ocean. For the ocean to drive large increases of Hg deposition at a location of interior Antarctica would require substantial increases in $Hg^o$ evasion from the ocean and presumably an increase in ocean productivity.

Paul Drevnick (a WHOI Post-doctoral Scholar) and I have been exploring their finding by examining Hg timelines from sediment stored in the WHOI Core Repository and elsewhere. These analyses have been performed using the automated solid phase Hg analyzer in the lab of our colleague Mike Bothner of the WH USGS. Included in Figure 1 are a summary of some of Paul's findings to date from analysis of Lake Titicaca (Bolivia/Peru) and Lake Baikal (Siberia) sediments. The results from Lake Titicaca (corrected for detrital Hg inputs) are in general agreement with the extent and timing of the Hg depositional increase observed at Dome C and suggest that a wider-scale increase in Hg cycling occurred. This finding throws a wrench into the hypothesis of Vandal and colleagues, however, because there is not enough Hg in the atmosphere and surface ocean even today that could be redistributed to account for this depositional increase if it was indeed global in scale (Figure 2).

The same depositional increase in Hg was not observed in Lake Baikal (Figure 1), but we are beginning to suspect that large changes in lake productivity between glacial and interglacial states in addition to possible climatic changes in Siberia may be the reason. Thus, an additional Northern Hemisphere archive is needed to help confirm the Baikal results. Greenland ice is an attractive potential archive in this regard. Not only has such material already been collected and is available for study, but it represents an Arctic analog to the Dome C ice. Furthermore, the determination of non-seasalt sulfate and Al have already been performed, greatly simplifying our task.

The Greenland Ice Sheet Project Two (GISP2) drilled through the Greenland ice sheet in central Greenland (72° 36' N, 38° 30' W) during 1989-1993. The longest ice core that was recovered is 3053 meters in length, representing >110,000 years of Arctic paleo-environmental record, and is now archived at the National Ice Core Laboratory in Denver, Colorado. We report below what is the first ever uncontaminated determinations of Hg in this archive, in a record spanning the last 40,000 years at approximate millennial resolution.

As some of the potential samples were drilled with the aid of an n-Butyl Acetate drill fluid (to maintain bore hole integrity and lubricate the drill), we used the ultraclean and decontamination techniques already developed (e.g., Boutron and Patterson 1986; Ferrari et al. 2000; Planchon et al. 2004; Fain et al. 2008). Our targeted subsamples of GISP2-D were requested from NICL, who extracted this material using a bandsaw from the appropriate subcore. Our samples were "sticks" of ice, approximately 2 cm x 2 cm x 150 cm, and shipped frozen to Durham, NH. Our intervals were decontaminated inside a laminar-flow bench in a cold room at the University of New Hampshire (in collaboration with Mark Twickler) by shaving off several millimeters of the outside of the cores using acid-cleaned ceramic utensils. These cleaned samples were then placed into acid-cleaned borosilicate jars, allowed to thaw and processed for Hg analysis in our clean room (Watson 130) at WHOI. This processing included oxidation using BrCl for >24 hours, followed by routine total Hg analysis.

The results are summarized in Figures 3 and 4 below. The overall concentration of Hg in GISP2 was 1.2 ± 0.3 ppq (pg $g^{-1}$). These values compare well with those obtained both from Dome C (~0.25 - 2 ppq) and contemporary snow from Greenland (0.6 +/- 0.4; Boutron et al. 1998). This is encouraging as it suggests that the results are likely free from contamination bias. It is interesting to note that the most recent samples from GISP2 (ca. 5000 years before present) appear slightly higher than many of the samples reported by Boutron and colleagues. Our initial prediction was that the GISP2 Holocene samples should be lower than the contemporary samples of Boutron et al. Our Holocene data appears to be trending downwards as they get younger, suggesting perhaps that Hg deposition to Greenland was slowly decreasing during the Holocene prior to the Anthropocene. Such a trend would be required if the Greenland Ice Sheet were to contain a similar 3x increase in Hg deposition over the last 200 years as has been widely reported for temperate lakes (e.g., Lamborg et al. 2002). Other, shorter core, GISP2 archives would be a better way to assess that particular trend.

Another major feature of the new GISP2 data is the relative lack of glacial/interglacial signal. This is perhaps best illustrated in Figure 4, where the Dome C and GISP2 results are both normalized by the Holocene values and then graphed together. When presented in this way, the GISP2 record clearly lacks the same sort of feature at the Last Glacial Maximum as did the Dome C record. This is in general agreement with the lack of increase in the other Northern Hemisphere, Lake Baikal, record and strongly suggests that the two Hemispheres were differentially impacted during glacial/interglacial transitions with respect to the Hg cycle. This is not simply the result of a lack of a comparable signal in non-sea salt sulfate as suggested in Dome C, as Figure 3 shows that the LGM and deglaciation were a period of dramatic changes in nssSO4 in Greenland. In addition to the lack of coherence between Hg and sulfate, there was a similar lack of covariation with Al, an index for dust inputs to Greenland (not shown). Thus, neither dust inputs nor ocean productivity changes can be invoked as important sources of Hg to the Greenland Ice Sheet, as these would have caused large Hg signals. Thus, it appears that the source of Hg changes in the Antarctic suggested by Vandal and colleagues is not supported by Greenland data, and that our entire data set (Dome C, Titicaca, Baikal and GISP2) encourage a new mechanism be developed, and one that features very different roles for the two Hemispheres.

To add to the available data to help explain all these findings, we have also included results (Figures 5 and 6) of the determination of Hg in marine sediments from the Cariaco Basin (samples courtesy of Hughen) and the Brazil Margin (26 S; samples courtesy of Oppo and Curry). Here again, both records show relatively little change through the LGM and deglaciation, though the Brazil Margin shows dramatic changes in Hg concentration during the Holocene. These samples were subsampled from cores that had previously been processed (Cariaco) or which we subsampled from the Core Repository (Brazil Margin), were freeze-dried and measured for total Hg using Mike Bothner's automated analyzer. Unlike ice, sediment contain relatively large amounts of Hg and sample contamination is less likely to be an issue. However, these are preliminary data, presented without duplication. The results from Cariaco are perhaps not surprising as the Baikal and Dome C results suggest that the Northern Hemisphere showed little change in the last 40,000 years. However, the deep sea cores from the Southern Hemisphere at the Brazil Margin also suggest little change.

There are at least two possible explanations for all these observations. Clearly, an additional source of Hg to the system is required, and that could have been from Hg accumulated in the deep ocean (e.g., Marchitto et al. 2007) or from increased rates of volcanism (P. Huybers, Geodynamics Seminar). Marchitto and colleagues (and other groups as well) have suggested that deep water ventilation was suppressed during glacial times, which would have prevented degassing of some Hg from the ocean for several tens of thousands of years. If this water, and it's increased load of dissolved Hg were then brought back to the surface, as may have happened during deglaciation, this would represent a very large, though transient, source of Hg to the atmosphere/surface ocean. This hypothesis is superficially supported by the observation that the increase observed in Dome C and Titicaca data extends over about 10,000 years and constitutes about a factor of 7x increase in deposition. This would have been preceded by about 70,000-100,000 years of glacial state, and therefore the increase observed in Titicaca is roughly in mass balance with a preceding accumulation at normal rates in the deep sea. However, the lack of signal in deep sea sediments from the Brazil Margin circumstantially argue against this possibility. Furthermore, the peak in Hg in Dome C and Titicaca occur well before the generally accepted time for the advent of deglaciation and resumption of meridional overturning. Thus, while this mechanism might provide the proper magnitude of effect, the dynamics appear in consistent with other findings.

Turning instead to the possibility of substantial changes in volcanism as a source of increased Hg during the LGM, the new Arctic data are particularly useful. Volcanism was initially dismissed by Vandal and colleagues as a source of Hg to Dome C based on an inadequate amount of non-seasalt sulfate stored in glacial ice to explain Hg increases. However, if increased volcanism were an explanation for changes in Hg in the Southern Hemisphere, it is difficult to argue that a similar change would not been seen in the North, as the new GISP2 suggest. One possible twist on this hypothesis, however, is that an increase in just Southern Hemispheric submarine volcanism, and not global subaerial activity, might be an explanation for all the available data. During the LGM, lowered sea level could have acted to depressurize shallow volcanic and hydrothermal systems, encouraging greater activity. Submarine volcanism would add Hg to the ocean, which could later be mobilized to the atmosphere and decouple it from the sulfate and other non-volatile tracers of volcanic activity. Finally, this increased source of Hg would not require increases in deep sea burdens of Hg, but result in only atmosphere/surface ocean changes in Hg. This is unconstrained without further data and remains speculative.

Thus, at present, we are at a loss to explain the changes in the global Hg cycle across glacial states. However, the results from GISP2 were critical in helping to rule out our two initial hypotheses. Future work could include the development of more glacial-scale records of Hg deposition in the Southern Hemisphere, from both terrestrial and marine locations. The lack of coherence between atmospheric records (Dome C and Titicaca) and marine records (Brazil Margin) seems to be the best lead we have remaining for understanding these various observations.

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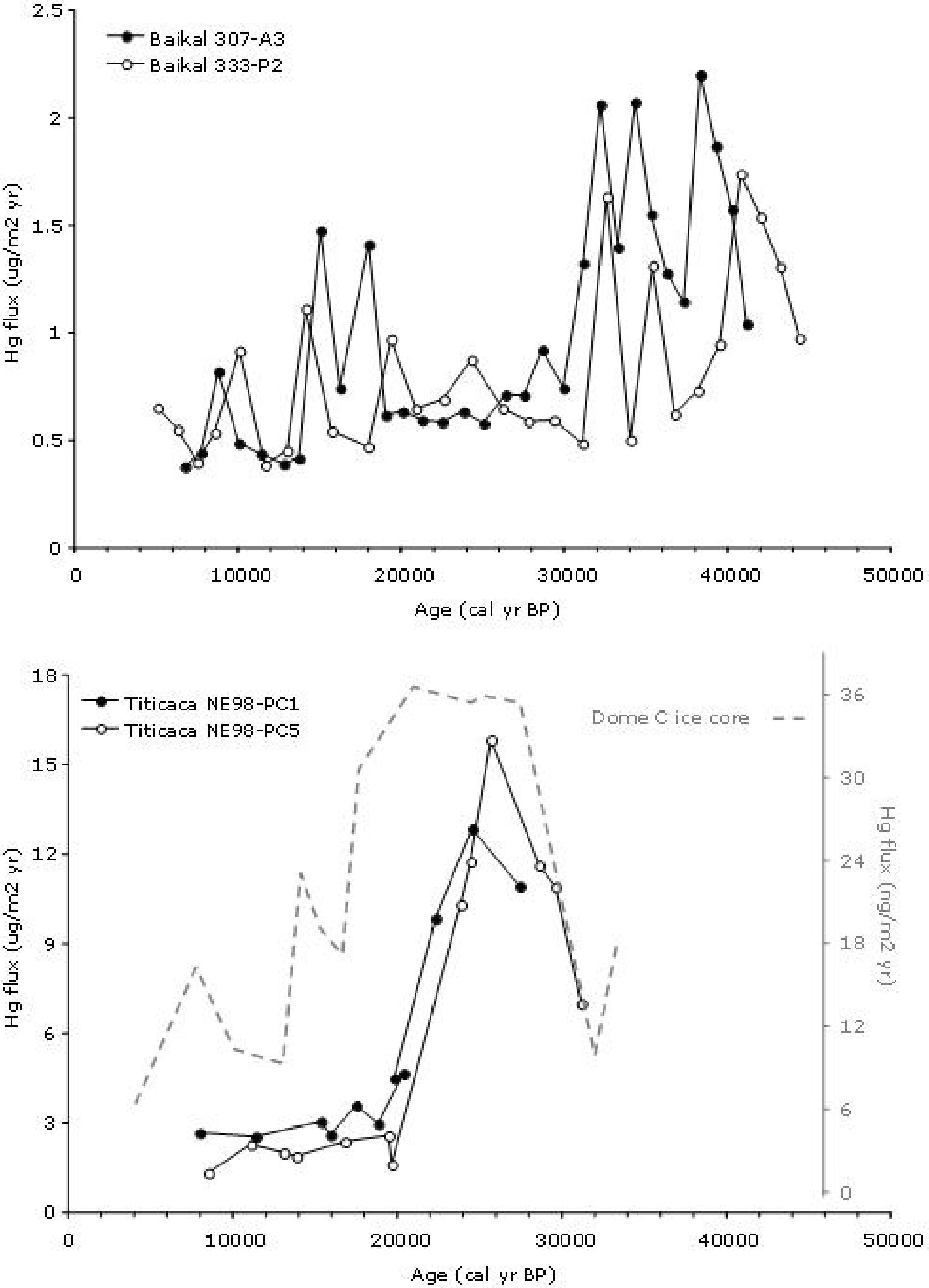


Figure 1. Changes in Hg accumulation in Lake Baikal (top), Lake Titicaca (bottom, circles and solid line) and in Dome C Antarctic ice (bottom, dashed line, Vandal et al., 1993).

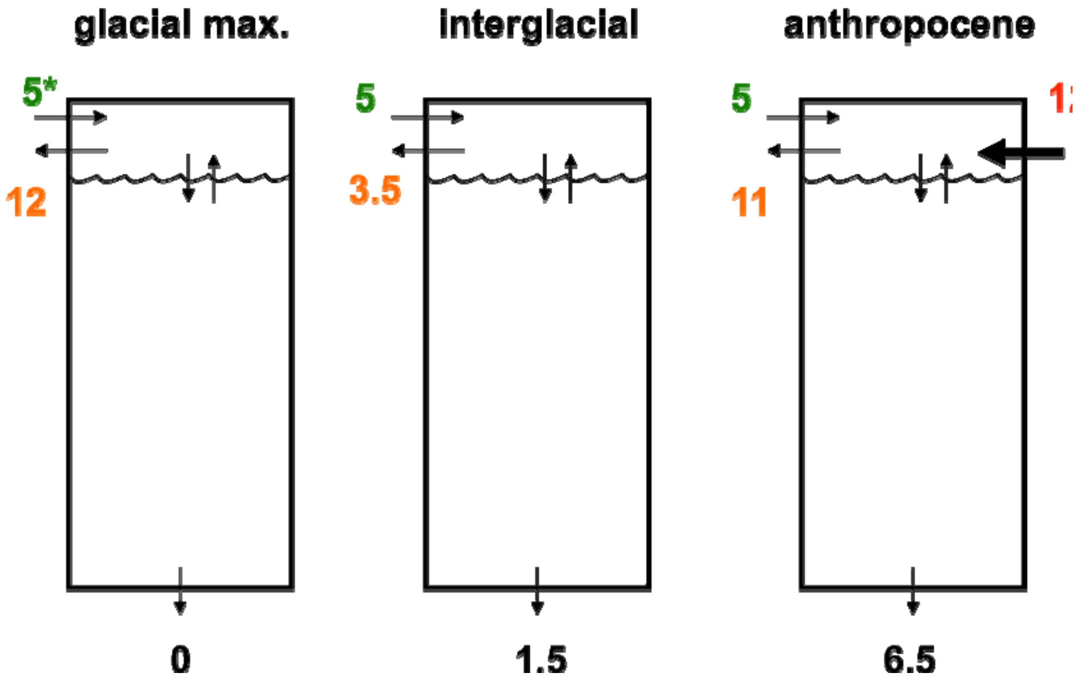


Figure 2. First-order model of Hg cycling between different periods of Earth's history (fluxes in Megamoles per year). Each one of the versions of the cycle include sources of Hg to the atmosphere from natural sources (green), deposition of Hg from the atmosphere to land (orange) and accumulation in deep sea sediments (black). In addition, the Anthropocene (modern era) includes a flux of Hg to the atmosphere from industrial sources (red). Within the model, Hg cycles between the atmosphere and ocean through the process of evasion, which allows a connection between the biology and chemistry of the ocean with transport in the atmosphere and deposition on land. The Anthropocene version of the model is based on current data and model of that system (Soerensen et al. 2010). The Interglacial (or pre-industrial era) is taken as having only natural inputs to the atmosphere, and an identical proportion of deposition to land relative to inputs. Finally, the Glacial Maximum state is set up by initially assuming that the only sources to the atmosphere are the same as in Interglacial, but with Lake Titicaca deposition rates applied to the Southern Hemisphere and Baikal deposition rates in the North. The increase in deposition during Glacial Maximum is greater than the deposition and greater than the 1.5 Mmole/y in Interglacial burial rate. This imbalance indicates that the 5 Mmole/y listed as the input to the atmosphere must be too low.

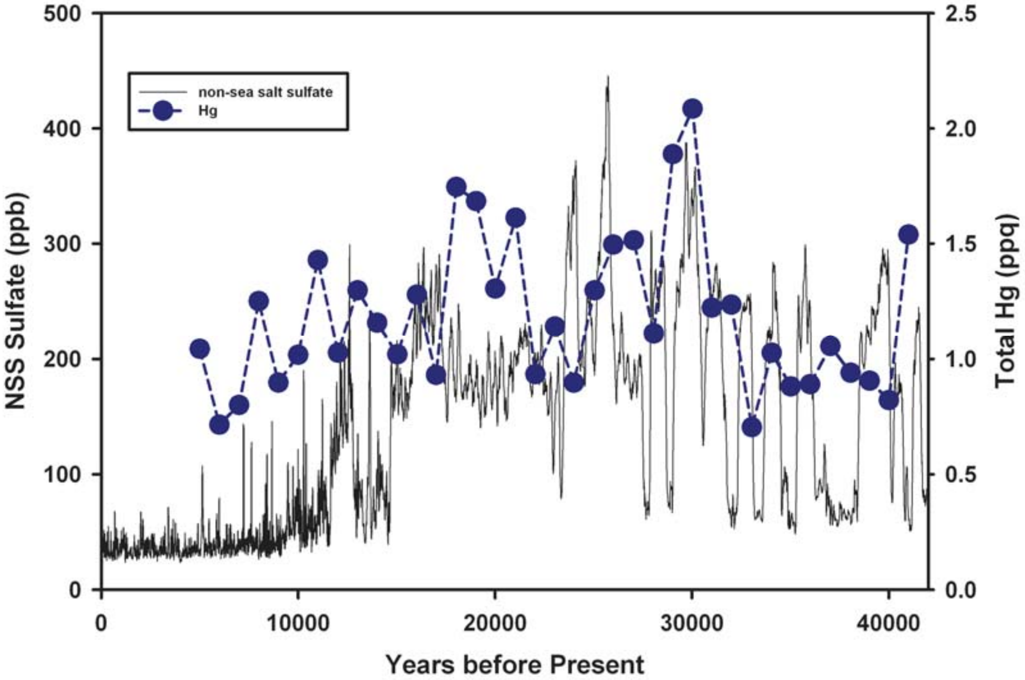


Figure 3. Results from GISP2 Hg and non-sea salt sulfate analyses. The nss-sulfate was previously determined and published.

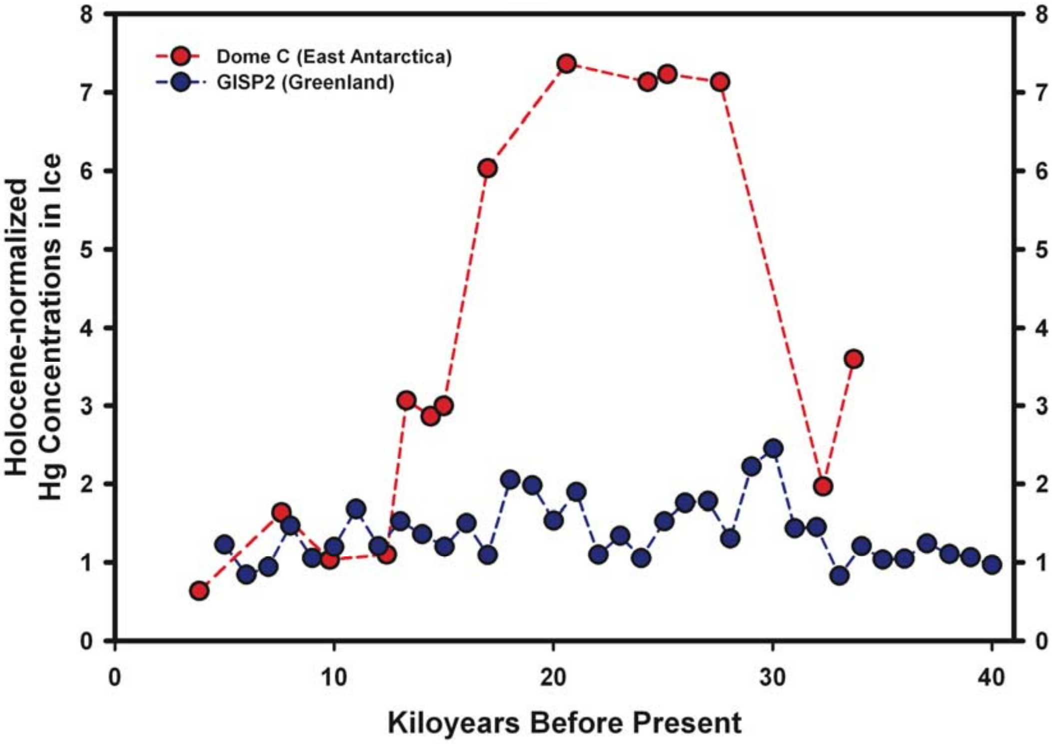


Figure 4. The concentration of Hg in glacial ice from the Arctic (blue, Greenland) and Antarctic (red, Dome C). The concentrations are normalized to their respective Holocene values so they can be compared. The Antarctic record shows a dramatic increase in Hg concentrations during the last Glacial Maximum as well as accumulation rates, while the Arctic record remained largely unchanged during the same period.

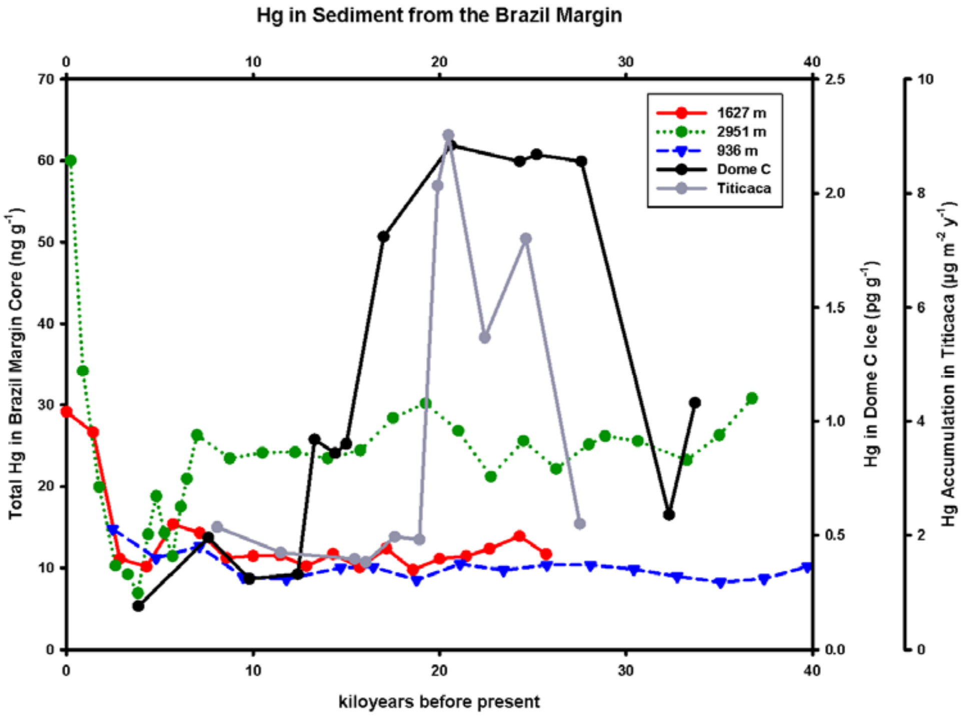
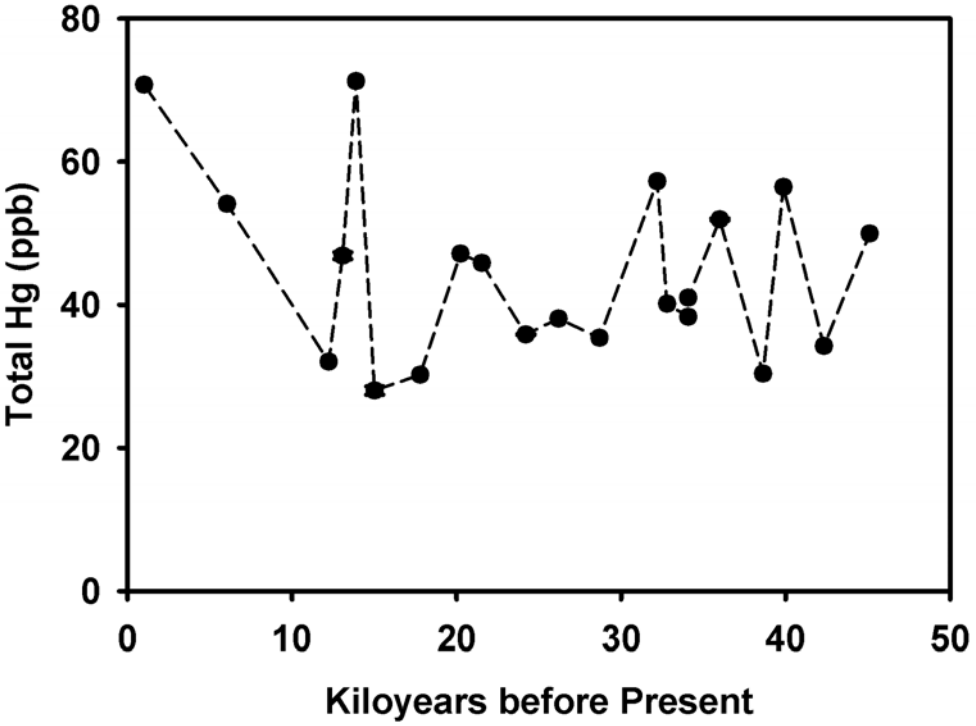


Figure 5. Comparison of Hg concentrations in Brazil Margin sediment (samples courtesy of Oppo and Curry) and Dome C ice and Titicaca lake sediment.



Fiugre 6. Preliminary data from Cariaco Basin Hg analysis (samples courtesy of K. Hughen).