

Methods Summary-Supplementary Material

Dissolved water samples were collected using ultra-clean techniques,¹ including the use of a largely metal-free collection system and pressure filtration to 0.45 μm of water samples directly from the sampling GO-Flo bottles. Aliquots for total dissolved Hg were collected in 250-mL, acid-washed, borosilicate glass bottles, digested with BrCl and analyzed by Cold Vapor Atomic Fluorescence Spectrometry following SnCl_2 reduction and gold-trap pre-concentration²⁻⁴.

P_{remin} was calculated according to Anderson and Sarmiento⁵ as $P_{\text{remin}} = \text{AOU} / 170 \pm 10$, where AOU is the apparent oxygen utilization and is calculated as $[\text{O}_2]_{\text{sat}} - [\text{O}_2]_{\text{obs}}$, where $[\text{O}_2]_{\text{sat}}$ is determined from depth, temperature and salinity⁶.

Particulate Hg and P were determined from subsamples of QMA or polyethersulfone (PES) filters loaded with suspended matter ($< 51 \mu\text{m}$) using McLane pumps. For Hg, the filter aliquots were digested with 2 M HNO_3 , and the digest treated as dissolved samples⁷. For P, PES filter subsamples were digested in a 3:1 sulfuric acid:hydrogen peroxide solution to oxidize and dissolve the PES filter, dried down, and then particles were digested in a 4N $\text{HCl}/\text{HNO}_3/\text{HF}$ mixture⁸. The digest was analyzed for multiple elements including P on a high resolution Inductively Coupled Plasma Mass Spectrometer and standardized using multi-element external standards (similar to Lamborg et al.⁹).

Water masses were defined primarily based on depth (as noted in Table 1), in accordance with those suggested by Talley and colleagues.¹⁰ This definition represents an approximation for more refined definitions made of the basis of temperature, salinity and basin.

Modification of CO_2 indexing

One modification to the CO_2 indexing approach must be made. As noted in Figure 1 and Table 1, the intermediate water depths of the South Atlantic and Equatorial/South Pacific appear to contain little Hg_{anth} . In the case of the Tropical Pacific, this is not surprising as relatively little anthropogenic CO_2 is observed in these waters as well. However, the intermediate water depths of the South Atlantic are thought to contain human-mobilized CO_2 . The GLODAP database estimates the amount of anthropogenic CO_2 in this water mass to be about 0.04 Pmole. Thus, CO_2 indexing overestimates anthropogenic Hg in global thermocline waters by about 1 Mmole ($0.04 \text{ Pmole } \text{CO}_2 \times 25 \text{ nmol Hg/mole } \text{CO}_2$) by including that particular water mass.

In addition, our approach could be in error if the anth-Hg/anth- CO_2 ratio in unsampled waters was significantly different than those already measured. For example, we have no data for the temperate South Pacific or the the whole Indian Ocean, which collectively contain about 47% of anth- CO_2 ¹³. If the anth-Hg/anth- CO_2 ratios for those waters were half or twice as large as those of the documented waters, then the total amount of anth-Hg in the ocean could be 15% lower or 28% higher than our current estimate. Further data are needed to test this assumption.

Lack of impact in some deep waters

To be precise, the correlation of Figure 2 does not imply that there is no anthropogenic Hg in the “un-impacted” deep waters, but just that there is a small impact. If substantial industrial or pre-industrial anthropogenic Hg had penetrated into the “unimpacted” deep ocean, then those water masses would be slightly elevated in concentration relative to their natural state, giving rise to a positive y-intercept since the perturbation would not been in effect for a full ocean mixing cycle (~ 1000 years). A pre-industrial load of Hg to deep waters could be contained in a curve such as that in Figure 2, but only if the load was relatively constant and in effect for one or more ocean mixing cycle, allowing a new steady state to be approached. It has been proposed^{11,12}

that pre-industrial inputs of Hg to the environment from gold and silver mining have been large, but these loadings would not have stretched back farther than about 600 years nor would they have been constant in time. Thus, we conclude that the Hg_{anth} from the biological pump is negligible in “unimpacted” deep waters. We have developed a very simple model of Hg accumulation in deep waters as a result of different emissions histories in Matlab, and have included that here for other to use.

```
%deepwater
% simulates the accumulation of Hg in deepwater as a result of biological
% pumping, and in particular the amount of impact that transient signals
% from anthropogenic emissions can have just from the biological pump
% (i.e., how much pollution Hg is there in the deep North Pacific?)

clear all;

load streetsemissions.mat; % an emissions history for Hg similar to that used by Streets et al.
load co2emissions.mat; % an emissions history for Hg similar in timing to that of CO2 and like
Lamborg et al., 2002

natflux=2.32; %nmole/m2/y pre-anthropogenic flux of Hg below 1000 m
z=3500; %m the depth of deep water (from 1000 m to seafloor)
c0=0; %pM the pre-anthropogenic pre-formed Hg concentration in the North Atlantic
f=0.01; %fraction of anthropogenic pulse which sinks below 1000m...assumed similar to
organic carbon

%seed the steady state, represents deep water as a vector of boxes,
%starting from the North Atlantic, and ending in the North Pacific

C=zeros(1000,1);

for i=1:1000
    C=C+natflux/z;
    C=vertcat(c0,C(1:end-1));
end

%add a transient signal, first using an emissions history similar to Streets,
%then similar to CO2
Cstreets=zeros(1000,1);

for i=1:length(streets)
    Cstreets =Cstreets +(f*streets(i)+natflux)/z;
    Cstreets =vertcat(c0,Cstreets (1:end-1));
end

Cco2=zeros(1000,1);
for i=1:length(co2)
```

```
Cco2=Cco2+(f*co2(i)+natflux)/z;  
Cco2=vertcat(c0,Cco2(1:end-1));  
end
```

```
% the plot should approximate the 1:1 if the transient has not penetrated  
% into deep water very much.  
plot(C,'b');  
hold  
plot(Cstreets,'r');  
plot(Cco2,'g');
```