

Mercury stable isotopes in fish tissue as indicators of photochemical transformations

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During the 1950s and 1960s, the U.S Department of Energy (DOE) plant Y-12, near Oak Ridge, TN, was using Hg in the production of thermonuclear weapons. During normal plant operations, large amounts of Hg were discharged into the East Fork Poplar Creek (EFPC) and its floodplain [1]. Current research aims to better understand Hg transformations that control its mobility and bioavailability.

Hg isotopes have the potential to identify and perhaps quantify certain biogeochemical reactions. Photo-reduction and -demethylation have been shown to fractionate the odd isotopes of Hg (¹⁹⁹Hg and ²⁰¹Hg), independent of their mass, due to the magnetic isotope effect [2]. Fish are assumed to be good integrators of bioavailable Hg over space and time and do not change the mass independent fractionation signature of the odd Hg isotopes. As a result, it is possible to use fish as indicators of photochemical reactions occurring in the water column. According to Bergquist and Blum [2], photoreduction of Hg(II)_(aq) creates a slope, on a $\Delta^{199}\text{Hg}$ vs. $\Delta^{201}\text{Hg}$ graph, of 1.00 ± 0.02 , methyl-Hg (MeHg) photoreduction has a slope of 1.36 ± 0.02 , and fish tissue plots on a 1.28 ± 0.03 .

Our study aims to detect and quantify Hg chemical transformations in the EFPC. Frozen fish tissues received from Oak Ridge National Laboratory were digested and analyzed on a Nu Instruments MC-ICP-MS using the Mead and Johnson [3] double-spike technique. The ²⁰²Hg/¹⁹⁸Hg ratio (reported as $\delta^{202}\text{Hg}$) was measured with a precision of $\sim 0.11\%$ relative to the NIST SRM 3133 Hg standard. Odd isotope deviations were measured with a precision of $\sim 0.04\%$ and are reported as $\Delta^{199}\text{Hg}$ and $\Delta^{201}\text{Hg}$ deviations from theoretical mass dependent fractionation values.

The $\delta^{202}\text{Hg}$ of the fish shows a weak increase increasing distance downstream from Y-12, from $-0.57 \pm 0.08\%$ (n=4) upstream to $-0.29 \pm 0.15\%$ (n=4) downstream. The odd isotope deviations also show a slight positive trend with increasing distance downstream from Y-12 (shifting $\Delta^{201}\text{Hg}$ from $-0.05 \pm 0.04\%$ to $0.05 \pm 0.04\%$ and $\Delta^{199}\text{Hg}$ from $-0.04 \pm 0.07\%$ to $0.09 \pm 0.05\%$). The slope of the data is 1.3, consistent with the slope obtained for photochemical demethylation by Bergquist and Blum [2]. Based on equations given by Bergquist and Blum [2], we can calculate, to first order, the amount of photoreduction of MeHg in the water between 4-11% using the $\Delta^{201}\text{Hg}$ values.

Fish are a good proxy for the extent of photoreduction of Hg in the water column; however, it would be beneficial to look directly at the Hg present in the water, the reactant pool. Therefore, water samples from the EFPC have been obtained and will be analyzed.

[1] Southworth *et al.* (2000) *Environmental Monitoring and Assessment* **63**, 481-494. [2] Bergquist and Blum (2007) *Science* **318**, 417-420. [3] Mead and Johnson (2010) *Analytical Bioanalytical Chemistry* **397**, 1529-1538.

Bottom Water Changes in the South Pacific Over the Last 30 ka Documented by Nd Isotopes

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North Atlantic Deep water (NADW) and the Antarctic Bottom water (AABW) are the two central supporting pillars that control deep ocean ventilation and influence atmospheric CO₂ concentrations on glacial-interglacial timescales. While much is known about past NADW changes, very little is known about variations in AABW formation and export from the Southern Ocean. Available paleo-records point at enhanced northward advection of southern sourced deep water during times of reduced NADW formation [1]. It is, however, not clear whether the observed presence of AABW in the North Atlantic is due to increased southern sourced deep water production or related to reduced NADW formation. In this study we used paleo seawater Nd isotope ratios to address the AABW formation history in the Pacific Southern Ocean for the last 30 ka.

Our study site is located in the eastern Pacific sector of the Southern Ocean [PS58/271-1; 61.24°S, 116.05°W, 5214m water depth; [2]]. Currently this site is bathed by AABW with contributions from Circumpolar Deep Water and Pacific Deep Water, and is located at the Polar Front. The Ross Sea is the nearest deep water formation area and the present-day northern limit of 'pure' Ross Sea bottom water (RSBW; defined by high salinity and density) reaches just south of our site. Thus, during times of enhanced deep water formation in the Ross Sea, RSBW would be expected to have reached the study site. Since RSBW carries the characteristic Nd isotope signal of Ross Sea sediments ($\epsilon_{\text{Nd}} = -7$; [3]), any northward expansion of RSBW should be recorded in the sediments at our core site. The Late Holocene ϵ_{Nd} value ($\epsilon_{\text{Nd}} = -6.2$) at our study site is consistent with the influence of RSBW and CDW/PDW at the core site. The downcore ϵ_{Nd} record shows that the study site was bathed by a water mass with an Nd isotopic composition of ($\epsilon_{\text{Nd}} = -5.5$) during the last glacial maximum (LGM). The ϵ_{Nd} value of the water mass gradually started to change towards more Pacific deep water-like values ($\epsilon_{\text{Nd}} = -3$) with the initiation of deglaciation around 18 ka BP. Strong Pacific deep water influence is observed at around 15.3 ka, followed by a gradual decrease to the Late Holocene value ($\epsilon_{\text{Nd}} = -6.2$). The time of maximum ϵ_{Nd} around 15.3 ka coincides with warming in the Southern Hemisphere and corresponding cooling and shut down of NADW in the Northern Hemisphere. Our data do not support increased RSBW/AABW formation at this time, rather, we observe enhanced influence of Pacific deep water. If this holds true for the entire Southern Ocean, the observed presence of AABW in the deep North Atlantic has to be explained by reduced NADW production.

[1] Lynch-Stieglitz *et al.* (2007) *Science* **316**, 66-69. [2] Jacot Des Combes *et al.* (2008) *Paleoceanography* **23**, PA4209. [3] Pahnke *et al.* (2011) *Geophysical Research Abstracts*, 13, EGU General Assembly.