Indirect determination of the North-Pacific Ocean Hg MIF baseline

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The relative magnitude of Δ^{199}Hg and Δ^{201}Hg anomalies may identify different mass independent isotope fractionation (MIF) mechanisms at play. Experimental aquatic inorganic Hg (iHg) and methylmercury (MeHg) photo reduction produced $\Delta^{199/201}$Hg slopes of 1.00 and 1.36 respectively [1]. Although experimental iHg photoreduction has also produced $\Delta^{199/201}$Hg slopes of 1.2 to 1.3 [2], a review of iHg and MeHg MIF anomalies in natural samples define $\Delta^{199/201}$Hg slopes of 1.03 and 1.30 respectively. Freshwater fish MeHg contents with $\Delta^{199/201}$Hg of 1.30 are therefore thought to originate in aquatic MeHg that has been partly photoreduced [1].

Using Hg stable isotopic variations in a marine seabird biomonitor (murre eggs) we provide a window into the iHg and MeHg MIF signatures of the N-Pacific Ocean. Egg Hg (n=43, >98% MeHg) Δ^{201}Hg and Δ^{199}Hg fall within the field defined by natural iHg and MeHg MIF variations. The regression line for all egg data has a $\Delta^{199/201}$Hg slope of 1.29 ± 0.05 (SE) that suggests MeHg photo reduction to be the MIF inducing reaction. However, we also observe the hitherto unseen feature that the regression intercept with the Δ^{199}Hg axis has a significant non-zero value of -0.13 ± 0.05 ‰ (SE). The same features are present at the colony level with Gulf of Alaska colony y-intercepts of Δ^{199}Hg = -0.23, -0.14, and -0.13‰. The Gulf of Alaska regression lines intersect the natural iHg photo reduction $\Delta^{199/201}$Hg slope of 1.03 at Δ^{201}Hg = Δ^{199}Hg of +0.55, +0.45, and +0.46‰ (average of +0.49 ± 0.06‰ (SD)). We interpret these observations as follows: the inorganic iHg precursor to the MeHg that is biomagnified across the marine food chain into murre eggs already had an anomalous isotopic composition of Δ^{199}Hg = Δ^{201}Hg = +0.49 ‰. Once the iHg MIF baseline of +0.49‰ was methylated (producing MeHg with Δ^{199}Hg = Δ^{201}Hg of +0.49 ‰), subsequent photo-demethylation has evolved the MeHg isotopic compositions along the $\Delta^{199/201}$Hg slope of 1.3. We suggest here that the MIF baseline of +0.49 ‰ is in fact the anomalous iHg isotopic composition of the North-eastern Pacific Ocean. The vector-type approach to explore Δ^{201}Hg vs. Δ^{199}Hg parameter space has important consequences for Hg MIF data analysis.

[1] Bergquist & Blum (2007) *Science* **318**, 417–420. [2] Zheng W. & Hintelmann (2009) *GCA* **73**, 6704–6715.

Impact of sediments on nutrient cycling and ocean oxygen minimum zones

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Oxygen minimum zones play a key role in nutrients and elements biogeochemical cycle. These zones are believed to expand at present time [1]. An expansion of suboxic areas would increase the loss of fixed nitrogen due to denitrification or anaerobic ammonia oxidation, both in sediments and in the water column, which may have a negative feedback on export production and then reduce anoxia. At global scale, this loss in nitrate could be compensed by nitrogen fixation, which depends on phosphate and iron availability [2, 3]

An important aspect is then interactions of bottom water with sediments, as they participate in the regulation of availability of these compounds in water column. Oxic conditions favors phosphate burying in marine sediments, as phosphate is bound with insoluble iron oxides or calcium minerals. In anoxic conditions, solid phase ferric iron is reduced to soluble ferrous form, thus favorizing liberation of phosphate by suppressing burying by iron oxides. Phosphate recycling to the water column is thus greater from sediments overlaid by oxygen depleted waters [4]. Both release of phosphate and iron should lead to export increase and thus anoxia spread.

In this study we investigate the impact of sediment on phosphate and iron concentration, and then subsequently on primary production and oxygen concentration. An 'offline' transport method coupled to a biogeochemical model of intermediate complexity has been used. This biogeochemical model can either be coupled to a sediment model or to a simple flux used as a bottom boundary condition. In both case, we show that sediments has a significant impact on nutrient cycling and OMZ future evolution.

[1] Stramma *et al.* (2008) *Science* **320**, 655–658. [2] Deutsch *et al.* (2007) *Nature* **445**, 163–167. [3] Mark-Moore *et al.* (2009) *Nature Geoscience* **2**, 898. [4] Collman & Holland (2000) *SEPM Special Publication* **66.**