Methylmercury production in the Oceans: links to physics, chemistry and biology

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Abstract

We will review and synthesize the current understanding of the marine biogeochemical cycle of mercury and how its natural cycling may have been altered by anthropogenic emissions and changing climate. The presentation will focus on potential sources of methylmercury to the marine food web, which is of most socioeconomic and health concern. Marine methylmercury production is a function of at least three variables: inorganic mercury availability, organic matter supply and bacterial assemblages. All of these variables are prone to be influenced by global changes. We will make use of recently published and unpublished data to attempt evaluating the relative importance of these variables. With this we will examine the possible impacts of the temporal variation of anthropogenic mercury emissions and warming climate on marine methylmercury production. We will also point out remaining knowledge gaps, share ideas of future research needs and potential approaches to furthering our understanding of methylmercury dynamics in the ocean.

Evidence for Open ocean Hg methylation

1. Subsurface MeHg peak in all major Ocean basins

Ever more compelling evidence for open ocean water column methylation in all ocean basins: Atlantic Ocean (Bowman et al. 2015, Bratkič et al. 2016, Heimbürger et al. unpublished), Pacific Ocean (Sunderland et al. 2009, Hammerschmidt et al. 2012, Munson et al. 2015, Bowman et al. 2016, Kim et al. 2016, Ganachaud et al. 2017), Arctic Ocean (Wang et al. 2012, Heimbürger et al. 2015), Southern Ocean (Cossa et al. 2011, Gionfriddo et al. 2016), Mediterranean Sea (Cossa et al. 2009, 2012, 2017, Heimbürger et al. 2010), Baltic Sea (Soerensen et al. 2016), and Black Sea (Rosati et al., GBC in review).

> Indian Ocean, better precision and routine analysis should be developed (GEOTRACES intercalibrations)

2. Methylation/Demethylation rates

Rate constants measurements with isotopically labeled spikes indicate net-methylation in marine waters, but have been mainly restricted to coastal studies (Bouchet et al. 2013, Sharif et al. 2014, Schartup et al. 2015, Soerensen et al. 2016).

> more open ocean and full water column needed

3. Hg isotopes

Additional evidence for open ocean Hg methylation stems from isotopic analysis of marine biota. Fish that forage at different depths in the North-Pacific Ocean show isotope gradients that can only be explained if 60-80% of MeHg is produced below the surface mixed layer (Blum et al. 2013).

> Hg stable isotope measurements for lower trophic chain, zoo-, phytoplankton, SPM, seawater

4. C isotopes

A pioneering study also explored for the first time the carbon isotope composition of the MeHg compound in tuna fish and finds similar $\delta^{13}C$ to algal derived marine organic matter (Masbou et al. 2015).

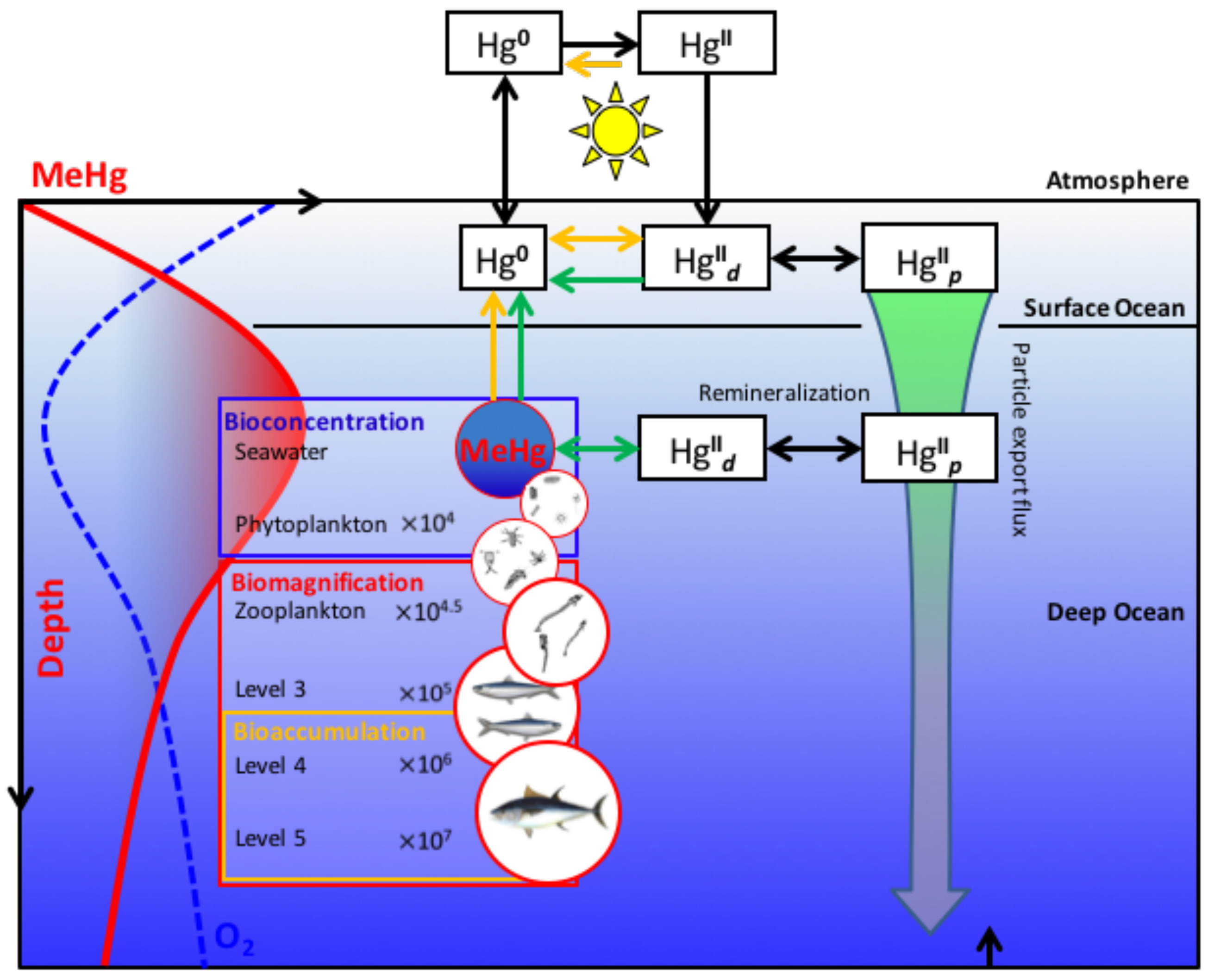
> C stable isotope measurements for lower trophic chain, zoo-, phytoplankton, SPM

5. HgcAB methylation genes

A major breakthrough has been made with the discovery of two key genes, hgcA and hgcB, that control anaerobic Hg methylation in sulfate-reducing bacteria (Parks et al. 2013). The hgcA and hgcB genes were found to be present in many anaerobic microorganisms. An analysis of publicly available microbial metagenomes found the hgcAB genes in nearly all anaerobic but not in aerobic environments (Podar et al. 2015). Genomic sequencing of the key methylating genes and identification of the microorganism community structure may help furthering our understanding of in situ MeHg production in oxic marine waters.

> More open ocean observations needed

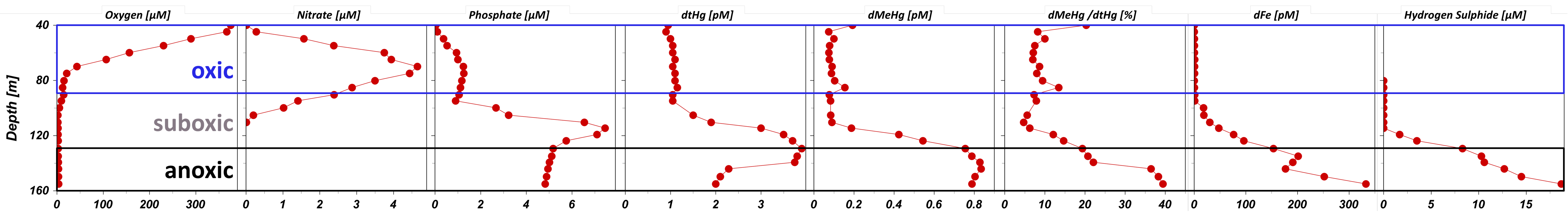
Simplified marine Hg cycle



Conclusions

- **density gradients seems to be a major controlling factor: settling particles slow down -> focus of (micro-)biotic processes**
- **oxic and anoxic waters generate similar high MeHg % (~ 30 - >50%) : MeHg can be the dominant species in seawater!**

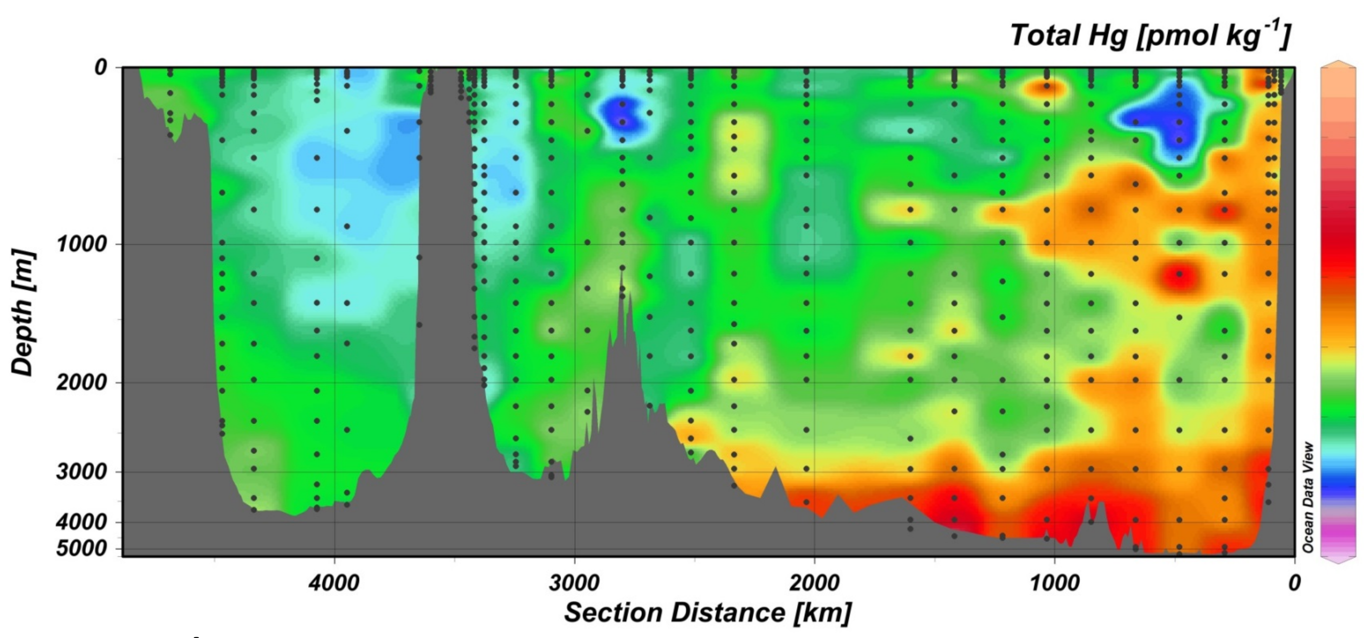
Example 1: Black Sea – MeHg production at shallow density gradient in anoxic waters (Rosati et al., GBC in review)

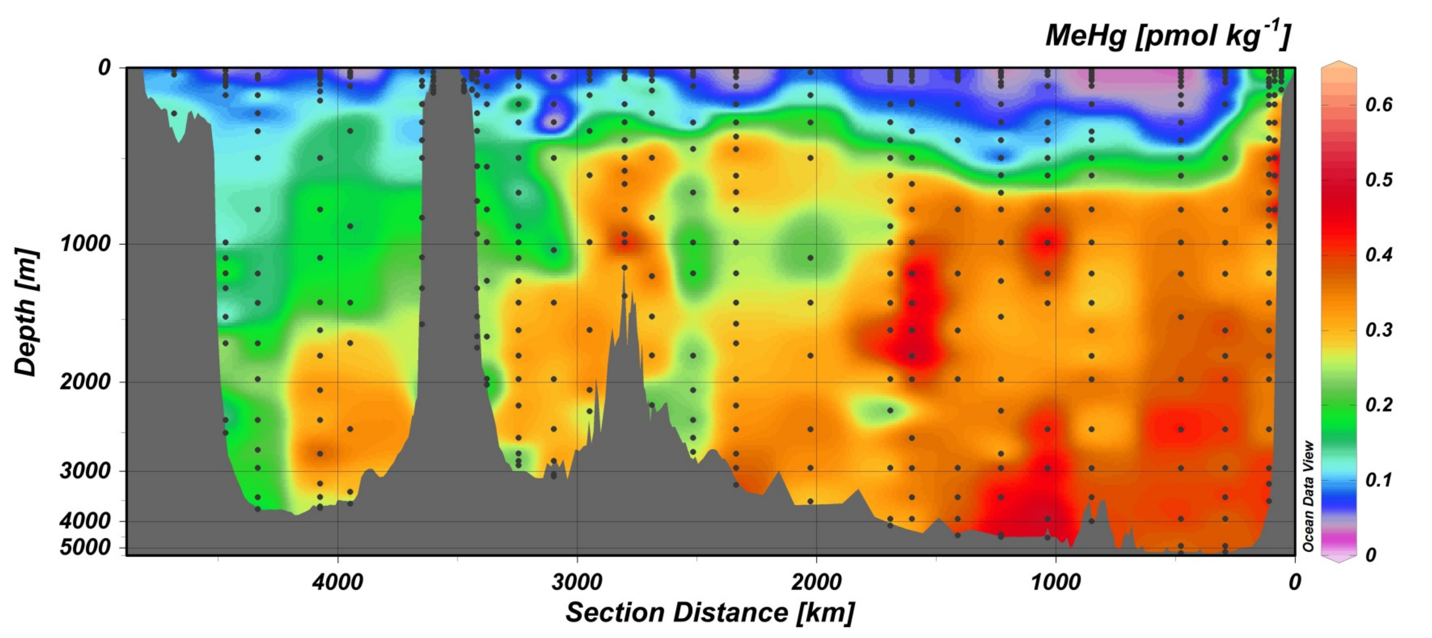


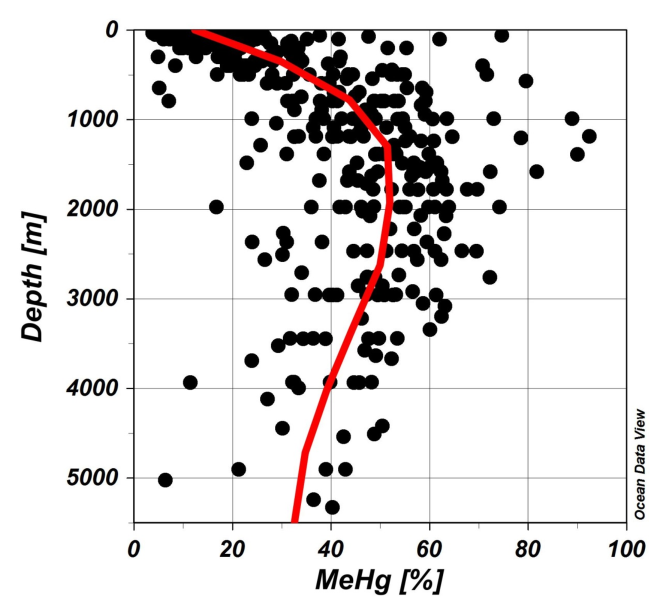
Conclusions 1

- **MeHg peaks at shallow density gradient**
- **MeHg/tHg = 40% in anoxic layer**
- other examples Wang et al. 2012, Heimbürger et al. 2015, Schartup et al. 2015, Soerensen et al. 2016

Example 2: North Atlantic Ocean – MeHg production in the deep ocean (Heimbürger et al., unpublished)







Conclusions 2

- **MeHg peaks in deep ocean (1000 m)**
- **max MeHg/tHg = >50%**
- **No clear relationship MeHg vs. tHg**

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