

METHYLMERCURY DISTRIBUTIONS IN CONTRASTED BASINS – RESULTS OF THE 2011 MEDITERRANEAN GOSHIP CRUISE

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Abstract

Toxic monomethylmercury (MMHg) accumulates to harmful levels along the marine food chain and presents a health risk at a global scale. The origin of MMHg in the marine water column is under debate. Bacterial methylation of inorganic Hg in sediments and in the oceanic water column may be in play. We investigated MMHg distributions in the contrasted basins of the Mediterranean Sea as part of the GOSHIP cruise M84/3 on RV Meteor. The 8 full depth vertical profiles cover a West-East transect from oligotrophic to ultra-oligotrophic waters. MeHg concentrations were generally higher in the more productive Western Basin. Our findings suggest that quantity and the quality of phytoplankton may influence the production of MeHg in the oceanic water column.

Keywords: Mercury, Open sea, South-Central Mediterranean, South-Western Mediterranean, South-Eastern Mediterranean

Monomethylmercury (MMHg) accumulates to harmful levels along the marine food chain and presents a health risk at a global scale. The origin of MMHg in the open ocean marine water column is under debate. Bacterial methylation of inorganic Hg in shelf sediments and subsequent advection to open ocean waters has been suggested to be the major pathway. Repeated evidences hint that in situ production in the oceanic water column may be equally if not more important. Determinations of MMHg in sea-water are still scarce mainly due to analytical limitations that did not allow detecting ultra-trace concentration levels, in the femtomolar range. Three techniques are used today to measure MMHg in sea-water and of which all imply a derivatization step: cryofocussing hydrate generation (Stoichev et al., 2002), ethylation (Bloom, 1989) and propylation (Monperrus et al., 2005).

Determination of MMHg in sea-water by species-specific isotope dilution, derivatization by propylation, and detection via gas chromatography-inductively coupled plasma mass spectrometry (ID-GC-ICP-MS) was shown to be most promising (Monperrus et al., 2005). At the GET laboratory we improved the performance of this method by optimizing the coupling between a gas chromatograph and a high resolution sector field inductively coupled plasma mass spectrometry (Element XR). We applied this method to samples from the GOSHIP cruise M84/3 on RV Meteor to the Mediterranean Sea (04/2011). A total of 83 samples were taken in pre-cleaned 250mL Savillex PFA Teflon bottles. Pre-cleaning in a class 100 clean lab involved soaking the bottles for 24h in concentrated (10N) and diluted (1N) bidistilled HCl at 120°C. Bottles were double bagged and all handling was done in an ultra-trace clean manner. On board, each bottle was rinsed 3 times with the sample from the GoFlo bottle, filled to the top, acidified with bidistilled HCl to 0.4% (v:v) and tightly capped. Acidification converts dimethylmercury (DMHg) to MMHg. The measured MMHg is therefore the sum of both species. Sub-samples were double bagged and stored in the dark at 4°C until analysis in the home laboratories. Samples were taken at 8 stations along the East-West transect. The set of samples was split in a way that the samples were analyzed in the 3 partner laboratories: 1) GET laboratory in Toulouse, France, IFREMER, 2) IFREMER Nantes, France and 3) University of Athens, Greece. Triplicates were taken at several stations to provide an intercomparison.

1) MeHg (MMHg+DMHg) was analyzed at the GET laboratory *via* isotopic dilution gas chromatography sector field inductively coupled plasma mass spectrometry (GC-SF-ICP-MS) after derivatization with propylborate and extraction into hexane. The 8 full depth vertical profiles consist of 83 samples (stations 292, 297, 306, 313, 319, 324, 331, 340). MeHg distributions show typical vertical profiles (Heimbürger et al., 2010) with very low surface concentration and highest concentration in the oxygen minimum zone and generally higher in the more productive Western Basin (mean=252±130fmol/L, range=11(LOD)-723fmol/L, n=83).

2) MeHg (MMHg+DMHg) was analyzed at the IFREMER Nantes laboratory *via* cryofocussing hydrate generation followed by cold vapour

atomic fluorescence spectrometry (CVAFS (Cossa et al., 2003; Stoichev et al., 2002)). The 4 full depth vertical profiles consist of 47 samples (stations 297, 313, 319, 340; mean=143±116fmol/L, range=40(LOD) to 467fmol/L, n=47). Those are the same samples that were measured at the GET laboratory and both measurements compare well.

3) Another 4 profiles were analyzed at the University of Greece *via* ethylation followed by CVAFS using a MERX automated analyzer (Brooks Rand).

We will present and compare the results of the different applied MeHg determination methods and put our results in context with previous work. Our findings suggest that quantity and the quality of phytoplankton may influence the in situ production of MeHg in the oceanic water column. This is important as global change may alter the trophic regime of the future Mediterranean Sea and therefore marine Hg dynamics. Changes anthropogenic Hg emissions may also alter the marine biogeochemical Hg cycling. Repeated basin wide ship surveys are required to monitor both Hg and its most toxic form, MeHg, in mediterranean waters at appropriate spatio-temporal scales.

References

- 1 - Bloom, N., 1989. Determination of Picogram Levels of Methylmercury by Aqueous Phase Ethylation, Followed by Cryogenic Gas Chromatography with Cold Vapour Atomic Fluorescence Detection. Canadian Journal of Fisheries and Aquatic Sciences, 46(7): 1131-1140.
- 2 - Cossa, D., Averty, B., Bretraudeau, J., Sénard, A.S., 2003. Spéciation du mercure dissous dans les eaux marines : Dosages du mercure total, gazeux, réactif, mono et diméthylmercuré. In: Institut Français de Recherche pour l'Exploitation durable de la Mer (IFREMER) (Editor). Quae, Nantes.
- 3 - Heimbürger, L.E., Cossa, D., Marty, J.-C., Migon, C., Averty, B., Dufour, A., Ras, J., 2010. Methylmercury distributions in relation to the presence of nano- and picophytoplankton in an oceanic water column (Ligurian Sea, North-western Mediterranean). Geochimica Et Cosmochimica Acta, 74(19): 5549-5559.
- 4 - Monperrus, M., Tessier, E., Veschambre, S., Amouroux, D., Donard, O., 2005. Simultaneous speciation of mercury and butyltin compounds in natural waters and snow by propylation and species-specific isotope dilution mass spectrometry analysis. Anal. Bioanal. Chem., 381(4).
- 5 - Stoichev, T., Martin-Doimeadios, R.C.R., Amouroux, D., Molenat, N., Donard, O.F.X., 2002. Application of cryofocusing hydride generation and atomic fluorescence detection for dissolved mercury species determination in natural water samples. J. Environ. Monit., 4(4): 517-521.