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The open sea as the main source of methylmercury in the water column of the Gulf of Lions (Northwestern Mediterranean margin)

Daniel Cossa [a,b,*], Xavier Durrieu de Madron [c], Jörg Schäfer [d], Laurent Lanceleur [d], Stéphane Guédron [b], Roselyne Buscail [c], Bastien Thomas [e], Sabine Castelle [a], Jean-Jacques Naudin [f]

[a] *Ifremer, Mediterranean Centre, BP 330, F-83507 La Seyne-sur-Mer, France*
[b] *Université Grenoble Alpes, ISTerre, BP 53, F-38041 Grenoble, France*
[c] *Université de Perpignan, Cnrs-Cefrem, 52, Ave. P. Alduy, F-66860 Perpignan Cedex, France*
[d] *Université de Bordeaux, Epoc, F-33615 Pessac, France*
[e] *Ifremer, Atlantic Centre, BP 21105, F-44311 Nantes Cedex 03, France*
[f] *Université P. et M. Curie, Lobb, F-66651 Banyuls-sur-Mer, France*

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Abstract

Despite the ecologic and economical importance of coastal areas, the neurotoxic bioaccumulable monomethylmercury (MMHg) fluxes within the ocean margins and exchanges with the open sea remain unassessed. The aim of this paper is to address the questions of the abundance, distribution, production and exchanges of methylated mercury species (MeHgT), including MMHg and dimethylmercury (DMHg), in the waters, atmosphere and sediments of the Northwestern Mediterranean margin including the Rhône River delta, the continental shelf and its slope (Gulf of Lions) and the adjacent open sea (North Gyre).

Concentrations of MeHgT ranged from <0.02 to 0.48 pmol L^{-1} with highest values associated with the oxygen-deficient zone of the open sea. The methylated mercury to total mercury proportion (MeHgT/HgT) increased from 2% to 4% in the Rhône River to up to 30% (averaging 18%) in the North Gyre waters, whereas, within the shelf waters, MeHgT/HgT proportions were the lowest (1–3%). We calculate that the open sea is the major source of MeHgT for the shelf waters, with an annual flux estimated at 0.68 ± 0.12 kmol a^{-1} (i.e., equivalent to 12% of the HgT flux). This MeHgT influx is more than 80 times the direct atmospheric deposition or the *in situ* net production, more than 40 times the estimated "maximum potential" annual efflux from shelf sediment, and more than 7 times that of the continental sources. In the open sea, ratios of MMHg/DMHg in waters were always <1 and minimum in the oxygen deficient zones of the water column, where MeHg concentrations are maximum. This observation supports the idea that MMHg could be a degradation product of DMHg produced from inorganic divalent Hg.

Keywords: Mercury; Methylmercury; Ocean margin; Coastal area; Mediterranean

* Corresponding author at: Université Grenoble Alpes, ISTerre, CS 40700, 38058 Grenoble Cedex 9, France.
E-mail address: dcossa@ifremer.fr (D. Cossa).

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1. INTRODUCTION

Mercury (Hg) exists in the marine waters as elemental Hg (Hg^0) and divalent Hg species, which include various inorganic (Hg_i^{II}) species (e.g., chlorocomplexes) and the two methylated species: monomethylmercury (MMHg) and dimethylmercury (DMHg). Monomethylmercury is a neurotoxin that bioaccumulates in aquatic organisms and biomagnifies through trophic webs (e.g., Jensen and Jernelöv, 1969; Clarkson and Magos, 2006). However, despite the ecological and economical importance of coastal areas, especially in terms of fish and shellfish production and capture, the distributions, sources and fluxes of methylated Hg species in the waters of the ocean margins are still poorly explored.

Methylated Hg sources for coastal waters include (i) inputs from upwellings, rivers, groundwaters, atmospheric deposition and waste water point sources, and (ii) *in situ* Hg_i^{II} methylation in coastal waters and sediments (Cossa et al., 1996; Fitzgerald et al., 2007). The river-watershed contribution can be large due to direct inputs of MMHg to coastal waters (Coquery et al., 1997; Choe and Gill, 2003; Balcom et al., 2008, 2015; Muresan et al., 2008; Guédron et al., 2012; Buck et al., 2015) and continental groundwaters *via* submarine estuaries (Ganguli et al., 2012). Contribution of the open ocean to the methylated Hg load of oceanic margin waters has also been evidenced: DMHg is conveyed, *via* upwellings, from ocean interior to surface coastal waters (Conaway et al., 2009). Atmosphere has been reported as external methylated Hg sources, but available data are limited (e.g., Weiss-Penzias et al., 2012, 2016). *In situ* Hg methylation has been observed in both coastal sediments (e.g., Gobeil and Cossa, 1993; Hammerschmidt et al., 2004; Hammerschmidt and Fitzgerald, 2006; Balcom et al., 2008; Hollweg et al., 2009, 2010; Luengen and Flegal, 2009; Noh et al., 2013) and waters (Mason et al., 1993; Sunderland et al., 2010; Lehnherr et al., 2011; Wang et al., 2012; Lehnherr, 2014; Schartup et al., 2015). Experimental MMHg production from incubation of settling particles (“marine snow”) or water strongly suggests that water column methylation may be important worldwide (Monperrus et al., 2007; Ortiz et al., 2015). In summary, numerous internal and external sources of methylated Hg in coastal waters exist; however, their relative importance is not well established.

Pathways of Hg methylation in both oceanic and coastal waters are still poorly described, despite the oceanographically-consistent measurements of methylated Hg performed for three decades in the waters of the Atlantic Ocean (Mason et al., 1998; Mason and Sullivan, 1999; Bowman et al., 2015), the Pacific Ocean (Mason and Fitzgerald, 1990; Hammerschmidt and Bowman, 2012; Munson et al., 2015), and the Mediterranean Sea (Cossa et al., 1994, 1997 and 2009; Horvat et al., 2003). The highest concentrations of methylated Hg are consistently found in the oxygen deficient zones (ODZs). The generally significant correlation between methylated Hg and oxygen consumption (or organic carbon regeneration rates) have been interpreted as the result of net microbiological Hg_i^{II} methylation at these depths (e.g., Mason and Fitzgerald, 1990; Cossa et al., 2009; Sunderland et al., 2009). The MMHg/DMHg molar ratios in the ODZs vary broadly (0.2 to >10) depending on location, even in the same oceanic region. Early North Atlantic data suggests that MMHg is a degradation product of DMHg in the water column (Fitzgerald and Mason, 1996; Mason et al., 1998; Mason and Sullivan, 1999). However, production rate measurements, performed on Arctic waters, found contradictory results (Lehnherr et al., 2011). These authors found that DMHg production from Hg_i^{II} was two orders of magnitude less than MMHg production, but faster than the rate of DMHg production from MMHg methylation. Consistent with these findings, recent results show that MMHg is the dominant form of methylated Hg in deep waters of the North Atlantic (Bowman et al., 2015). More recently, Jonsson et al. (2016) suggest that MMHg can be methylated on sulfide mineral surfaces, a pathway potentially responsible for much of the DMHg in oceanic waters. In summary, data on MMHg and DMHg distributions in marine waters are still scarce (especially in coastal areas), and, consequently, the methylation mechanism of Hg_i^{II} remains uncertain.

In the present work, we address questions of abundance, distribution, production and exchanges of methylated Hg in the waters of the Northwestern Mediterranean margin including the Rhône River delta, the continental shelf and its slope (Gulf of Lions), the continental rise and the adjacent open sea (North Gyre) (Fig. 1). The objective is to assess the relative importance of internal and external sources of methylated Hg in the context of marine Hg cycle. For this, we have (i) monitored atmospheric deposition and riverine inputs of total methylated Hg (MeHgT = MMHg + DMHg), (ii) studied the MeHg distribution within the Rhône River plume, the freshwater–sea water mixing zone, the continental shelf-slope-rise system, and the adjacent open sea, and (iii) estimated the MeHg exchanges across various interfaces, including water/sediment and coastal/off-shore water interface. Additional data of total Hg (HgT = all the Hg species) were also collected in order to estimate the importance of MeHg fraction.

2. STUDY AREA

The Northwestern Mediterranean is characterized by the presence of a large continental shelf and the associated slope, both constituting the Gulf of Lions (Fig. 1). The water circulation in the Gulf of Lions is influenced in the South by the Northern Current, which is a part of a current system going from the Tyrrhenian Sea up to the Alboran Sea (Millot and Taupier-Letage, 2005). This Northern Current flows as a major vein along the upper part of the continental slope intruding onto the shelf (Fig. 1). The North Gyre and Gulf of Lions have contrasting hydrological and biological properties. The North Gyre is a typical oligotrophic open Mediterranean environment experiencing strong winter mixing of the surface and intermediate water masses, whereas the Gulf of Lions constitutes one of the few mesotrophic coastal regions within the Mediterranean Sea (Morel and André, 1991) largely influenced by the Rhône River freshwater inputs.