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Sources and exchanges of mercury in the waters of the Northwestern Mediterranean margin

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A B S T R A C T

Ocean margins are focal regions in terms of mercury (Hg) exchanges between the continent and the open sea. The aim of this paper is to describe the distribution and partition of Hg between the gaseous, dissolved and particulate phases in the waters of the Northwestern Mediterranean (NWM) margin, in order to assess the Hg sources and exchanges within the continuum between the continental shelf (Gulf of Lions) and the open sea (Northern Gyre).

Mean (±standard deviation) of total Hg species (HgT) concentrations in unfiltered water samples were 1.52 ± 1.00 pmol L^{-1} (n = 36) in the inner shelf, 1.09 ± 0.15 pmol L^{-1} (n = 30) along the slope, and 1.10 ± 0.13 pmol L^{-1} (n = 99) in the Northern Gyre. The dissolved phase (<0.45 μm) average concentrations were 0.80 ± 0.47 pmol L^{-1} (n = 37) in the inner shelf, 0.93 ± 0.20 pmol L^{-1} (n = 4) along the slope and 0.84 ± 0.10 (n = 20) pmol L^{-1} in the Northern Gyre. The particulate fraction of Hg decreased very strongly seaward from around 60% on the shelf to 10–25% above the Northern Gyre. Very low dissolved HgT concentrations occurred in the inner shelf water, consistent with the results of incubation experiments, which demonstrated that shelf water is very efficient in both production and release of dissolved gaseous Hg into the atmosphere. In the North Gyre waters column HgT presents a distribution pattern inverse to that of dissolved oxygen, and a slight Hg enrichment in the deep layer (Western Mediterranean Deep Water).

The Hg from the open sea water is the largest Hg input to the Gulf of Lions (~5.7 kmol yr^{-1}), whereas inputs from the riverine source account for ~3.4 kmol yr^{-1} and atmospheric deposition for less than 0.5 kmol yr^{-1}. The Hg accumulated in the sediments of the shelf is ~4.5 kmol yr^{-1}, including 0.6–1.7 kmol yr^{-1} in the Rhône prodelta sediments. The evasion to the atmosphere represents a Hg flux of ~2.6 kmol yr^{-1}.

1. Introduction

Mercury (Hg) is distributed in Earth's biogeochemical system between three main reservoirs: the crust (5000 Mmol), the Ocean (1780 Mmol) and the atmosphere (28 Mmol) (Mason et al., 2012; UNEP, 2013). Terrestrial emissions release volatile Hg^0 into the atmosphere and direct atmospheric deposition delivers Hg^{II} onto the ocean surface. Owing to fast redox reactions between Hg^0 and Hg^{II}, Hg is constantly exchanged between the ocean and the atmosphere (Fitzgerald et al., 2007; Mason et al., 2012). On the other hand, man-made activities have deeply modified the natural Hg cycle. According to Lamborg et al. (2014), the increase in anthropogenic atmospheric emissions, over the past two centuries, has led to doubling the oceanic Hg amount in the thermocline waters and tripling the Hg content of oceanic surface waters, compared to pre-anthropogenic conditions. In this context, what is the role of ocean margins in the oceanic Hg cycle?

Ocean margins are very important regions in terms of biogeochemical exchanges, involving organic matter and trace elements, between the continent and the open sea (Walsh, 1991; Wollast and Chou, 2001). An early global mass balance, constructed at the scale of the ocean margins, suggested that particulate Hg from rivers

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represents the largest single Hg flux but that direct atmospheric Hg deposition exceeds the dissolved Hg riverine inputs (Cossa et al., 1996). According to a more recent review, the cycling of Hg in coastal marine systems should be comparable to that in the open ocean, but with enhanced concentrations of Hg species (Fitzgerald et al., 2007). Indeed, in addition to atmospheric deposition, riverine discharge and mobilization from sediments can significantly contribute to the Hg load in coastal waters (Coquery et al., 1997; Choe and Gill, 2003; Whalin et al., 2007; Balcom et al., 2008; Muresan et al., 2008; Guédron et al., 2012; Noh et al., 2013). Other studies suggest that Hg removal processes may be boosted at the margins (Cossa et al., 1988; Gill and Fitzgerald, 1988; Cossa et al., 2004). Enhanced biological activity favors (i) scavenging removal, *via* Hg sorption on aggregating and settling biogenic particles, and (ii) atmospheric evasion, *via* microbiologically mediated Hg^{II} reduction, and consequently play an important role in regulation surface water Hg concentrations near the slope and on the shelf. In spite of the scientific progress achieved during the past decades, the Hg biogeochemical coastal specificities and their influences on the global Hg cycling remain unassessed. More precisely, according to Mason et al. (2012), there is a need for high resolution water column profiles for Hg on continental margins, especially at upper slope stations, in order to understand the processes linking the biogeochemical cycling of Hg between coastal regions and the open ocean.

Here, we address the questions of the abundance, distribution, partitioning, sources and exchanges of Hg in the water masses continuum between the continent and the open sea at the Northwestern Mediterranean (NWM) margin. A companion paper addresses methylated mercury species dynamics in the same area (Cossa et al., 2017).

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 *via* the Ligurian Sea (Millot and Taupier-Letage, 2005). This Northern Current flows as a major vein along the upper part of the continental slope and partially on the shelf (Fig. 1). Intrusions of the Northern Current on the Gulf of Lions shelf occur at different locations and in any season either as a separate vein of the main Northern Current or as a part of the main Northern Current core impinging on the shelf (Estournel et al., 2003; Petrenko et al., 2005). The North Gyre and the 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.

The Gulf of Lions covers a surface of $\sim 12 \times 10^3$ km^2 (Durrieu de Madron et al., 2003) and receives riverine inputs mainly from the Rhône River, which alone drains a watershed of 10^5 km^2 with respective mean annual liquid and solid discharges of 1750 m^3 s^{-1} and 2–20 $\times 10^{12}$ g yr^{-1} (Pont et al., 2002; Gairoard et al., 2012; Eyrolle et al., 2012; Launay, 2014). Materials present in the Gulf of Lions waters originate from allochthonous sources (rivers and atmosphere) and from autochthonous sources (bed erosion and planktonic production). The Rhône River is the major freshwater input to the western Mediterranean and its waters undergo three main processes before being diluted in the Gulf of Lions water masses. First, freshwater is rapidly mixed with seawater within a few kilometers between Barcarin and the prodelta area (Fig. 1). Secondly, the Rhône River plume is driven on the shelf by variable continental winds (the northerly Mistral and southwesterly Tramontane, and southeasterly-easterly Marin) and the cyclonic Northern Current (Fig. S1). The plume is periodically broken due to wind direction changes, engendering "Low Salinity Water" lenses drifting on the shelf as described by Naudin et al. (1997). Low Salinity Water lenses are a few kilometers in diameter and 10–50 m thick (Naudin et al., 1997; Diaz et al., 2008). Depending on meteorological conditions and on the density gradient induced by the freshwater-seawater mixing processes, Low Salinity Water lenses can accumulate along the coast or be transported towards the slope. Interestingly, these Low Salinity Water structures allow continuation of estuarine processes outside the Rhône delta area (Naudin et al., 1997). Thirdly, below the Rhône River plume, the dense riverine particles settle abruptly, generating large sediment accumulation in the prodelta area up to several dozens of centimeters per year in the proximal delta ($\sim$20 m water depth; Charmasson et al. (1998), Radakovitch et al. (1999), Maillet et al. (2006) and Cathalot et al. (2010). Finer riverine material is exported farther on the Gulf of Lions shelf, undergoing a westward net transport through sedimentation/resuspension processes generated by infrequent easterly wind storm events (Durrieu de Madron et al., 2008; Ulses et al., 2008a; Guizien, 2009; Marion et al., 2010; Bourrin et al., 2015). These easterly storms induce downwelling at the southwestern end of the Gulf of Lions, especially in the Cap de Creus canyon (Palanques et al., 2006; Palanques et al., 2009; Ulses et al., 2008a; Martin et al., 2013), and a massive export of shelf water and resuspended particulate matter to the upper slope. Furthermore, dense water, formed during winter along the coastline of the Gulf of Lions under the cooling effect of the Mistral and Tramontane winds (Fig. S1), also descends and exports fine sediments principally at the southern end of the shelf (Bourrin et al., 2008; Canals et al., 2006). These events, which may merge and concern thousands km^3 of waters (Ulses et al., 2008a, b), may coincide with the peak of the primary production on the shelf (Conan et al., 1998), probably enhancing the vertical transport of plankton-associated metals such as Hg. Dense water masses formed on the shelf usually reach 500 m depth but they can reach depth larger than 2000 m and contribute to the deep water formation of the western Mediterranean basin (Canals et al., 2006; Durrieu de Madron et al., 2013). Dense water formation during winter is also known to result from open-sea convection, which mixes surface Atlantic water (AW) with Levantine Intermediate water (LIW) within the North Gyre. This mixing may concern the entire water column and trigger strong currents during the spreading phase of the newly-formed Western Mediterranean Deep Water (WMDW) that can resuspend deep sediment and generate thick bottom nepheloid layers (Stabholz et al., 2013; Puig et al., 2013). Thus, linkages between the physical mechanisms, planktonic production, and resuspension of sediments lead to the transport of dissolved and particulate matter, including Hg, from the shelf to the slope/rise and abyssal plain.

3. Material and methods

3.1. Sampling

The water samples have been collected (i) in the Rhône River and at its mouth, (ii) on the Gulf of Lions shelf, (iii) on the continental slope, and (iiii) in the North Gyre (Fig. 1), in order to document the seasonal variations of HgT and the behavior (partitioning) of Hg species during the freshwater/seawater mixing along the continuum including the Rhône River plume, drifting Low Salinity Water on the shelf as well as the water column above the continental

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