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

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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
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1. **Introduction**

Mercury (Hg) exists in the marine environment as elemental Hg (Hg⁰) and divalent Hg species, which include various inorganic (Hg^{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 Jernelov, 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^{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 and 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 and 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 and 2010; Luengen and Flegal, 2009; Noh et al., 2013) and waters (Mason et al., 1993; Sunderland et al., 2010; Lehnerr et al., 2011; Wang et al., 2012; Lehnerr, 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\textsuperscript{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 (Lehnheer et al., 2011). These authors found that
DMHg production from Hg^{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^{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 Tapier-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.

The Gulf of Lions receives riverine inputs mainly from the Rhône River. 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 waters. First, freshwater is rapidly mixed with seawater within the few kilometers between Barcarin and the prodelta area (Fig. 1) (Elbaz-Poulichet et al., 1996). Secondly, the Rhône River plume is driven on the shelf by changeable continental winds (the northerly Mistral, southwesterly Tramontane and southeasterly-easterly Marin) and the cyclonic Northern Current (Fig. S1) (Naudin et al., 1997). The plume is periodically broken due to wind direction changes, producing “Low Salinity Water” lenses drifting on the shelf 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 tens of centimeters per year in the proximal
delta (~ 20 m) according to 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., 2008; Guizien, 2009; Marion et al., 2010; Bourrin et al., 2015).

3. Material and methods

To summarize the nomenclature used in the following text, $X_{\text{UNF}}$, $X_F$ and $X_P$ refer to unfiltered, dissolved (< 0.45 µm) and particulate, respectively (with X being a Hg species). Detailed protocols of the sampling and analytical techniques are given in SI 1. Sampling and water sample treatments were performed using ultraclean protocols, including acid cleaning of the plastic ware, and the use of plastic gloves and high purity grade reagents (e.g., SUPRAPUR HCl from Merck®, ULTREX HNO$_3$ from J.T. Baker®).

3.1. Sampling

Sampling cruise identifications, locations and dates are summarized in Table S1.

Atmospheric deposition. Thirteen rain events were collected between April 2009 and January 2010 at a coastal site (La Seyne-sur-Mer, 43°.06.350’N; 5°53.117’E, Fig.1), located at the eastern end of the Gulf of Lions. The unfiltered samples were collected in Teflon (FEP) bottles and acidified (0.4 % v/v HCl) immediately after the water collection. The rain-collecting device (PP040, MTX®) was located 15 m above sea level. Details of the sampling are given by Castelle (2010). At the same site, 28 aerosol samples were collected on cellulose acetate membranes (0.22 µm) from July 2009 to March 2010. Each sample represents one
week of pumping at a pumping rate of 14 L min\(^{-1}\). Total gaseous Hg concentrations in the atmosphere were monitored at the same time (Marusczak et al., 2015).

**Rhône River monitoring.** Rhône River Hg monitoring was performed over two monitoring periods at Arles (Sta. SORA, Fig. 1): (i) a period of low river waters from March, 2009 to June, 2010, with only one rather weak flood event (~3000 m\(^3\) s\(^{-1}\) on December the 2\(^{nd}\)), and (ii) during the flooding period of October-November 2008 (up to 3580 m\(^3\) s\(^{-1}\)). Surface freshwater samples were collected twice a month at Station SORA in Arles (Fig. 1) by pumping through polyethylene tubing using an all-Teflon (PFA) double-bellows pump (10-LPM, ASTI\(^{®}\)). Samples were collected in Teflon (FEP) bottles then filtered through hydrophilic Teflon membranes (LCR, Millipore\(^{®}\)) with a porosity of 0.45 µm. Membranes were stored at -18°C in polycarbonate Petri dishes and the filtrates were acidified (0.4 % v/v HCl) and stored in Teflon (FEP) bottles.

**Rhône delta mixing zone.** Brackish surface waters were sampled on 16 and 17 October 2008 from a rubber boat between Barcarin (Rhône River) and the sea (Fig.1); the locations of the stations are indicated on Table S2a. The samples were collected directly into Teflon (FEP) bottles. Samples were then filtered and stored as described in the previous section.

**BIOPHOFI cruise.** During the BIOPHOFI cruise (14\(^{th}\) – 27\(^{th}\) May 2006), two types of waters were sampled: (i) the productive shelf waters and (ii) the mesotrophic slope waters. In the first type, two Low Salinity Waters, originating from the Rhône River plume, were successively tracked using a Lagrangian sampling protocol: lens “1” between May 14\(^{th}\) and 18\(^{th}\), corresponding to stations S1 to S68 and lens “2” between the 19\(^{th}\) and 26\(^{th}\), corresponding to stations S88 to S220 (Fig. S2). In the lenses, the 0-50 m layer was sampled by pumping with the all-Teflon pneumatic pump (10-2PM, ASTI\(^{®}\)) and through polyethylene tubing, directly
into a class 100 on-board clean laboratory; the water depth varied between 60 and 100 m during the drifting. Two deep casts (0-900 m) were performed on May the 26th at the slope foot (Stas. S221 and S230, Fig. S2); their coordinates are given in Table S2a.

**CASCADE cruise.** During the CASCADE cruise (1st – 23rd March 2011), water was collected (i) on the inner shelf from the Rhône prodelta to the south-western end (Stas. A to D), (ii) at the head of Cap de Creus canyon (Sta. E), and (iii) thirteen deep casts on the shelf edge (Stas. L-01 and M-12), the slope foot (Stas. L-03 and M-10) and within the North Gyre (Stas. Antarès, S2400, L-05-08-10-12 and M-03-05-08) (Fig. 1). Two to twelve water depths were sampled for each cast depending on the height of the water column (Fig. 1 and Table S2). Sediment cores were collected along the Gulf of Lions shelf, at the head of the Cap de Creus canyon and in the abyssal plain in the North Gyre area during the CASCADE cruise (Table S2b). A multicore sampler (Oktopus GmbH Multiple corer with 8 tubes of 100 mm diameter) allowing the sampling of the undisturbed benthic interface (Barnett et al., 1984) was used.

### 3.2. Sample treatment

**Water and particles.** The samples from the 0-50 m layer of the shelf waters during the BIOPRHOFI cruise were filtered through polycarbonate membranes (0.45 µm, Nuclepore®). Filtrate was collected in Teflon (FEP) bottles and acidified with HCl (0.4 %, v/v). The collection of particles from the Low Salinity Waters, for subsequent MMHgP, particulate carbon and phosphorus, and pigments determinations, was performed using in-line filtration through pre-heated glass fiber filters (GF/G, Whatman®). Deep-water samples (> 50 m) were collected during the BIOPRHOFI and CASCADE cruises by rosette-mounted 5L bottles (1010X-Niskin, General Oceanics®) equipped with a CTD probe. These samples were not filtered and were analyzed only for HgT<sub>UNF</sub> and MeHgT<sub>UNF</sub>. Total Hg was determined on board, whereas
MMHg and MeHgT analyses were performed in the laboratory within 2 months after the cruise on the acidified samples stored in the dark at +4°C in a double wrapping of polyethylene bags.

*Sediment pore water:* The sediment pore water was extracted, from below the sediment surface (-1 cm), using Milli-Q (Millipore®) water-rinsed microporous polymer tube samplers (Rhizon SMS, Rhizosphere Research Products®) attached to an acid washed all-polypropylene syringe (Guédron et al., 2012).

### 3.3. Chemical analyses

*Total mercury.* Total Hg, in filtered and unfiltered samples, was measured on board within a few minutes of sampling. The release of Hg from its ligands was achieved by addition of a BrCl solution. This technique is known as the Environmental Protection Agency from the United States of America standard method N° 1631 (www.epa.gov/sites/production/files/2015-08/documents/method_1631e_2002.pdf). The detection limit (DL = 3 times the standard deviation of the blank) was 0.1 pmol L\(^{-1}\) and the reproducibility varied according to the concentration level between 5 and 15 % (Cossa et al. 2003). The accuracy of HgT measurements was tested using the ORMS-3 water sample, which is a certified reference material (CRM) from the National Research Council of Canada. Our measurements were always within the confidence limits given for the CRM (12.6 ± 1.1 pg mL\(^{-1}\); http://inms-ienm.nrc-cnrc.gc.ca/calserv/crm_files_f/ORMS-3_f.pdf).

*Methylated Hg species.* Total methylated Hg and MMHg were measured on filtered and unfiltered samples and DMHg was calculated as the difference between MeHgT\(_{\text{UNF}}\) and MMHg\(_{\text{UNF}}\). Since DMHg is converted into MMHg at low pH (Mason, 1991; Black et al., 2009a) MeHgT was determined on acidified samples. Monomethyl Hg was determined after
bubbling samples for 40 min with argon in order to remove DMHg before acidification. Total methylated Hg and MMHg were determined as volatile MMHg hydride by purge and cryo-trapping gas chromatography and detected as elemental Hg vapor by atomic fluorescence spectrometry according to Stoichev et al. (2004). The mercury hydrides (from MMHg and Hg$^{II}$) were formed with NaBH$_4$, sparged from the sample with helium, concentrated and then separated by cryogenic chromatography before detection. During this set of analyses, the low blank (<0.01 pmol) and its reproducibility (2 %) allowed and limits of quantification (LQ) as low as 0.005 and 0.015 to 0.075 pmol L$^{-1}$, respectively. The analytical reproducibility varied with time between 6 and 15 %.

MeHgT$_P$ was determined by atomic fluorescence spectrometry after acid extraction, ethylation and chromatographic separation according to Liang et al. (1994). The analytical performances were established by analyzing a Certified Reference Material from the International Atomic Energy Agency (IAEA-142, Horvat et al., 1997). The reproducibility was 10 % and the DL 20 pmol g$^{-1}$; recovery varied from 80 to 100 %.

**Isotopic incubations.** Incubation experiments were performed onboard immediately after sampling using a $^{199}$Hg$^{II}$ stable isotope spike to study Hg methylation potentials in Mediterranean bottom water samples as described for tropical lake water incubations in Huguet et al. (2010). These experiments aimed at simulating the temporal resuspension of reducing sediments in oxic bottom water and evaluating their impact on gross methylation compared to that in bottom water without sediment resuspension. For this, we determined gross methylation in (a) unfiltered bottom water and (b) slurries of surface sediment resuspended in unfiltered bottom water as follows:
- (a) Aliquots of unfiltered seawater from the bottom of the shelf water column were transferred into acid-cleaned 125 mL Teflon (FEP) bottles, spiked with $^{199}$Hg$^{II}$ (Oak Ridge, 92 % purity) to a nominal concentration of 1000 ng $^{199}$Hg$^{II}$ L$^{-1}$ and incubated at constant temperature (12 °C) in the dark for 48, 96 and 192 hours ($n = 2$ for each time; manual shaking twice per day). Aliquots ($n = 2$) of unfiltered bottom water were spiked and methylation was immediately stopped for control. After each incubation time, methylation was stopped by adding 1 mL of 12 M HCl (INSTRa analyzed, J.T. Baker®) and the bottles were stored in double sealed polypropylene bags at 4°C and in the dark until analysis for isotopic composition of the different Hg species.

- (b) Surface sediments from the shelf at Stations A to D were added to 100 ml of unfiltered bottom water from the respective site to obtain a nominal suspended particle concentration of 100 mg L$^{-1}$; three aliquots per site) in acid-cleaned 125 mL Teflon (FEP) bottles, to simulate resuspension events. The slurries were then spiked with $^{199}$Hg$^{II}$ (Oak Ridge, 92 % purity) to a nominal concentration of 25 ng of Hg per gram of sediment slurry, including water and sediment, and incubated at constant temperature (12 °C) in the dark for 192 hours. Incubation was stopped by freezing (-20°C). The samples were stored frozen, freeze-dried and stored cool in the dark until extraction with HNO$_3$ (6M, ULTREX, J.T. Baker®) and analysis. The applied protocol including derivation (propylation with NaBPr$_4$), extraction and the analytical setup, i.e. gas chromatography (Focus GC, Thermo Fischer Scientific®) coupled to ICP-MS (X7, Thermo Fischer Scientific®) using a thermostatic interface is based on the methods described in detail elsewhere (Monperrus, 2004). The difference between the MM$^{199}$Hg measured and the MM$^{199}$Hg naturally present (calculated from the
amount of MM$^{200}\text{Hg}$ measured) represents the MM$^{199}\text{Hg}$ produced during the incubation
of the $^{199}\text{Hg}^{\text{II}}$ added. Methylation potential was estimated by dividing the amount of
MM$^{199}\text{Hg}$ formed by the amount of $^{199}\text{Hg}^{\text{II}}$ recovered after the respective incubation
periods, as described by Monperrus et al. (2007).

*Particulate organic carbon, phosphorus and pigments.* Particulate organic carbon
concentrations were measured according to Hedges and Stem (1984) with a Shimadzu®
analyzer (TOC-5000 Series). Soluble reactive phosphorus (SRP) was determined in
seawater with an auto-analyzer using the standard molybdate blue method (Murphy and
phosphorus ($P_P$) determination used the same colorimetric method but after magnesium
nitrate oxidation (Ormaza-Gonzalez and Statham, 1996). Chlorophyll pigments were
determined following the standard method by Strickland and Parsons (1972).

4. Results

4.1. Atmospheric deposition

Total Hg concentrations in unfiltered rain water varied from 10 to 80 pmol L$^{-1}$, with a mean of
31 ± 22 pmol L$^{-1}$ ($n = 13$), whereas MeHgT concentrations varied from 0.10 to 1.25 pmol L$^{-1}$,
with a mean of 0.59 ± 0.33 pmol L$^{-1}$ ($n = 13$), i.e., ~2% of the HgT. These ranges are similar
to those published for other coastal areas of the Northern Hemisphere (e.g., Hammerschmidt
et al., 2007; Marusczak et al., 2011; Weiss-Penzias et al., 2012). Methylated Hg
concentrations in the 28 aerosol samples were undetectable due to the too-small amount of
sample collected on the membrane.
4.2. Rhône River and its plume

During the low flow period MeHgF and MeHgP concentrations varied in the picomolar range (Table 1), MeHg being predominantly (90%) associated with suspended particles. The mean methylated Hg fractions (MeHg/HgT) were 4 and 2 % as dissolved and particulate, respectively.

The variations of dissolved MeHg concentrations (MeHgT_F) during the mixing of Rhône freshwater with Gulf of Lions saltwater, between Barcarin ferry and the prodelta area, are illustrated in Figure 2a. Concentrations of MeHgT_F varied from 0.02 to 0.14 pmol L^{-1} and the distribution follows a conservating mixing line (R^2 = 0.75, p < 0.01) with higher concentrations in the freshwater and lower concentrations in the seawater end-member (Fig. 2a), similarly to observations of Noh et al. (2013) in the Mekong River delta.

At the bottom of the Low Salinity Waters lenses (~50m), salinity ranged from 38.2 to 38.4, which are typical values for waters of the Northern Current. The lowest salinity in the Low Salinity Waters (32.5) at surface indicates a ~20 % dilution of marine waters with the Rhône River waters. The MeHgT_F concentrations were in the femtomolar range, with 35 % of values lower than the LQ (i.e., <0.015 pmol L^{-1}) and maximum concentration of 0.069 pmol L^{-1} (Table 2). MeHgT_F fraction varies from <0.3 to 5.5 %, averaging 1.5 ± 1.0 % of the HgT_F. The time series of MeHgT_F concentrations in the Low Salinity Waters varied little with depth (Fig. 3). Interesting to note is that high MeHgT_F concentrations occurred at the highest salinities, suggesting a marine MeHg source (Fig. 2b).

4.3. Vertical profiles along shelf and slope
On the shelf, average MeHgT_{UNF} concentrations were $0.026 \pm 0.024 \text{ pmol } L^{-1}$ ($n = 40$) (Table 3 and Fig. 4a). The MeHgT_{UNF} / HgT_{UNF} ratios averaged roughly 2 %, ranging from 0.1 to 6.3 % (Table 3).

Tables 2 and 3 summarize the results obtained for the “slope foot” (900-1800 m bottom depth) water column in May 2006 (Sta. S230, BIOPHOFI cruise) and in March 2011 (Sta. L-03 and M-10, CASCADE cruise). Concentrations of MeHgT_{UNF} ranged from 0.02 to 0.38 pmol L^{-1}, averaging 18 % of the HgT_{UNF} (Tables 2 and 3). MeHgT_{UNF} were significantly higher below than above 100 m ($p<0.05$), suggesting removal and/or photodegradation for methylated Hg in upper layer and regeneration and/or production below (Fig. 4b, Table 2).

4.4. Deep profiles in the North Gyre

Summary statistics for Hg species concentrations are given in Table 3. Methylated Hg concentrations in unfiltered samples ranged from 0.020 pmol L^{-1} at surface at Sta. S2400 to 0.478 pmol L^{-1} at 500 m at Sta. L-10 (Fig. 5a). Expressed as a fraction of the HgT, MeHgT varied between 16 to 30 % (Table 3). The MeHgT_{UNF} profiles are typical of methylated Hg vertical distribution in open ocean (e.g., Fitzgerald et al., 2007; Cossa et al., 2011; Mason et al., 2012), i.e., very low concentrations at surface increasing with depth (Fig. 5a). At five stations, MMHg was determined in addition to MeHgT, allowing calculation of DMHg concentrations by difference. Results indicate MMHg/DMHg ratios always lower < 1, varying from 0.04 to 0.81 (Fig. 5b).

4.5. Sediment pore waters

Concentrations of MeHgT_{F} in pore waters extracted from surface sediments (0-2 cm) were clearly higher (4-20 times) than in the overlaying waters and in the corresponding lower-water
column (Tables 3 and 4). Moreover, concentrations in sediment pore waters of North Gyre were one order of magnitude higher than the shelf pore waters, ranging from 2.05 to 2.18 pmol L\(^{-1}\) and from 0.07 to 0.68 pmol L\(^{-1}\), respectively (Table 4).

4.6. Ex situ methylation experiments

Concentrations of inorganic Hg in sediments ranged from 0.432 ± 0.030 nmol g\(^{-1}\) (Sta. B) to 0.598 ± 0.122 nmol g\(^{-1}\) (Sta. A), with a mean of 0.519 ± 0.084 nmol g\(^{-1}\). The results of the sediment incubation experiments showed clearly modified MM\(^{199}\)Hg/MM\(^{200}\)Hg ratios compared to both natural values (0.72 ± 0.005; n = 3) and isotope ratios observed in control samples where incubation was stopped immediately after the spike (0.76 ± 0.023; n = 3; Fig. 6a). The three replicate incubations performed for each site generally provided reproducible results, revealing clear differences between the stations. The sediment samples from Sta. A (MM\(^{199}\)Hg/MM\(^{200}\)Hg = 1.36 ± 0.06; n = 3) showed the highest methylation, whereas isotope ratios in the samples from Sta. B (MM\(^{199}\)Hg/MM\(^{200}\)Hg = 0.85 ± 0.02; n = 3) were relatively close to natural values (\(^{199}\)Hg/\(^{200}\)Hg = 0.73). Stations C (MM\(^{199}\)Hg/MM\(^{200}\)Hg = 1.05 ± 0.11; n = 3) and D (MM\(^{199}\)Hg/MM\(^{200}\)Hg = 1.11 ± 0.10; n = 3) showed intermediate and similar MM\(^{199}\)Hg/MM\(^{200}\)Hg, yet clearly different from control samples (Fig. 6a). From these isotope ratios, we estimated gross methylation rates between 0.009 and 0.083 % d\(^{-1}\) with means of 0.010 ± 0.001 % d\(^{-1}\) (Sta. B), 0.020 ± 0.005 % d\(^{-1}\) (Sta. C), 0.029 ± 0.010 % d\(^{-1}\) (Sta. D), and 0.059 ± 0.021 % d\(^{-1}\) (Sta. A). Incubations of unfiltered bottom water showed changing MM\(^{199}\)Hg/MM\(^{200}\)Hg over time, reaching values of up to 8.7 after 192 h of incubation (n = 2, data not shown). The estimated methylation potentials for unfiltered bottom water ranged from 0.00019 % d\(^{-1}\) (after 48 h) to 0.00043 % d\(^{-1}\) (after 96 and 192 hours; Fig 6b).
5. Discussion

5.1. External sources of MeHg

5.1.1. Advection from open sea

In the North Gyre, the MeHg_{UNF} concentrations varied from values below DL to 0.48 pmol L^{-1} (Table 3), which is similar in magnitude to those reported in the last ten years for the open Western Mediterranean waters (Cossa and Coquery, 2005; Kotnik et al., 2007; Cossa et al., 2009 and Heimbürger et al., 2010). The vertical MeHgT distribution patterns (Fig. 5) are consistent with the now classical oceanic MeHg behavioral model characterized by (i) a microbial net methylation within the oxycline, and (ii) a photodemethylation in surface waters. Photochemical demethylation is well documented in experimental and natural conditions (Suda et al., 1993; Black et al., 2012; Kim et al., 2016), whereas microbial methylation is supported by the occurrence of a peak of MeHg in the ODZs (e.g., Mason and Fitzgerald, 1990; Cossa et al., 2009; Sunderland et al., 2009). This model has recently been supported by isotopic Hg compositions observed in the waters of the Pacific Ocean (Blum et al., 2013). At stations L-10 and L-12, where water stratification was well established (Fig. S3), O_2-deficient Leventine Intermediate Water and maximum MeHgT concentrations were found between 200 and 400 m (Fig. 5a). For these two stations, and additionally Sta. M-10, statistically significant \( p<0.01 \) relationships between MeHgT (pmol L^{-1}) and dissolved O_2 (µmol L^{-1}) exist (Fig. 7a), with similar regression coefficients, averaging -0.0063 ± 0.0001. For other stations, which comprise coastal sites (Stas. L-01, L-03 and M-12) and/or well mixed water column (Sta. S2400), the correlations were weak or inexistent. The corresponding average regression coefficient obtained for the relationships between MeHgT and apparent oxygen utilization (AOU) is +0.0059 ± 0.0007, which is close to the value
calculated for the whole Western Mediterranean (+0.0039, $R^2 = 0.77$, $n = 40$, according to Cossa et al., 2009). In various parts of the World Ocean analogous distribution patterns have been observed, showing undetectable methylated Hg concentrations in surface waters and peaks deeper in the water column, where $O_2$ reaches a minimum due to organic carbon remineralization (e.g., Mason and Fitzgerald, 1990; Cossa et al., 2009; Sunderland et al., 2009; Cossa et al., 2011). According to the model, settling particulate organic carbon is both a source of $\text{Hg}^{\text{II}}$ to microbiologically-active waters and a source of organic matter to sustain bacterial activity. A specific gene cluster is linked to Hg methylation in a variety of microorganisms, including sulfate and iron-reducing bacteria and others (Park et al., 2013; Gilmour et al., 2013).

Furthermore, we observed here more significant regression coefficient with a steeper slope for the inverse relationship between DMHg and dissolved $O_2$ compared to that for MMHg and dissolved $O_2$ (Fig. 7b), suggesting that the organic matter regeneration is more directly connected to DMHg formation than MMHg formation. This fact is consistent with the hypothesis proposed by Fitzgerald and Mason (1996) that MMHg in marine waters is not formed directly, but is a degradation product of DMHg. The probability of this pathway is reinforced by the observation that the highest MMHg/DMHg ratios occur during the convection period (Fig. S3), when the $O_2$ depletion is limited and consequently net Hg methylation is depressed (Fig. 5b). However, recent results (e.g., Jonsson et al., 2016; Sorensen et al. 2016) leave the question of the Hg methylation pathway in the ocean open to debate.

The Northern Current is the main source of waters for the Gulf of Lions. The horizontal flux across the shelf-open sea boundary has been estimated to vary at different periods of the
year between 0.07 and 0.35 x 10^6 m^3 s^{-1} (Durrieu de Madron et al., 2003). The same authors also estimate a shelf—slope exchange as ~10 % of the along-slope transport, namely 0.2 x 10^6 m^3 s^{-1}. The chemical characteristics of waters entering the shelf are well represented by 0-100 m water layer found at Sta. Antarès. Using a MeHgT\textsubscript{UNF} mean concentration of 0.11 ± 0.02 pmol L^{-1} (n = 3), the MeHgT entering the shelf waters from the open sea \textit{via} the Northern Current can be estimated as 680 ± 120 mol a^{-1}, representing 12 % of the HgT flux.

5.1.2. Atmospheric deposition

The MeHgT contribution from the atmospheric bulk wet deposition on the Gulf of Lions, based on results from section 4.1 and a surface area of the Gulf of 12 x 10^3 km^2, can be calculated as 2.5 ± 1.4 mol a^{-1}. In the absence of quantifiable analytical determinations, we assume a MeHgT dry deposition similar to the wet (as it is for the HgT in the Mediterranean environment according to Cossa and Coquery, 2005). Thus, the total MeHgT deposition into the waters of the Gulf of Lions can be estimated at ~5 mol a^{-1}, which is 2 % of the total HgT deposition.

5.1.3. Riverine and groundwater inputs

The amount of MeHgT transported annually by the Rhône River into the Gulf of Lions waters is estimated to be 5 mol a^{-1} for the dissolved phase and 51 mol a^{-1} for the particulate phase (see S1.2 for detailed calculation). Extrapolating these figures to transports from all the Gulf of Lions rivers gives a continental surface runoff contribution of 5.8 ± 2.0 and 59.7 ± 28.1 mol a^{-1}, for the dissolved and particulate MeHgT, respectively. The conservative mixing of dissolved MeHg between fresh and marine waters (Fig. 2a) allows an estimation of the annual net MeHgT efflux to the Gulf of Lions as equal to the gross efflux calculated above. Based on previous results, and owing to the fact that the Rhône River provides 85% and 83% all
riverine dissolved and solid discharges respectively (Gairoard et al., 2012), the total riverine MeHg flux (dissolved + particulate) to the Gulf ranges within 53.3 - 77.7 mol a\(^{-1}\), with a 99 % probability. At the scale of the Gulf of Lions, this mean flux is equivalent to ~ 10 % of the MeHgT flux from marine source. To this surface runoff, the potential contribution of groundwater should be added (Black et al. 2009b; Ganguli et al., 2012). In the absence of direct measurement, a hypothetical estimate can be performed. Assuming values of groundwater discharges to the Gulf of Lions of 2-30 % of the riverine discharge (Ollivier et al., 2008), and MeHgT concentrations in groundwater similar to the only figures available to date – i.e., those measured along the Southern Californian coasts (0.2-1.0 pmol L\(^{-1}\), according to Ganguli et al., 2012) –, we can approximate the MeHgT contribution of submarine freshwater discharges to the Gulf of Lions waters to be in the range 0.2-17.4 mol a\(^{-1}\). Given the large uncertainties in this estimate, the MeHgT contribution from groundwater sources remains to be assessed based on direct measurements. However, we can conclude that the continental water contribution (gross efflux) is <95 mol a\(^{-1}\) and small compared to open sea (680 ± 120 mol a\(^{-1}\)) as a source of MeHgT for the Gulf of Lions.

5.13. Efflux from the shelf sediments

The shelf sediments can be a source of MeHgT via the diffusion of soluble phase from pore water across the sediment-water interface, via biopumping, and via the resuspension of the surficial sediments during storm events. All these processes have not been determined, however, in order to compare their magnitude with other MeHg sources, a “maximum potential efflux” of MeHg from sediment has been estimated.

The pore-waters of the shelf surface sediments are MeHgT-enriched compared to the overlying waters (Table 4). Using a simplified diffusion model (SI 3), we can calculate
potential diffusion effluxes from sediments varying from 0.2 to 2.6 pmol m$^{-2}$ d$^{-1}$ depending on the shelf stations and averaging 1.1 ± 0.8 pmol m$^{-2}$ d$^{-1}$ (n = 6). For the surface area of the Gulf of Lions shelf, which is 12 x 10$^3$ km$^2$, we estimate an annual potential diffusive flux of MeHgT from the sediment of 4.7 ± 3.5 mol, a figure similar to the dissolved riverine input (5.8 ± 2.0 mol a$^{-1}$). However, such a flux is not supported by MeHgT distribution in the water column of the shelf (Stas. A-E), since no vertical trend evoking a gradient near the bottom has been observed (Fig. 4a). In addition, a diffusive Hg flux out of the sediment may be counteracted by the presence of the oxic layer near the sediment surface, where upward diffusing Hg species may be trapped (Muresan et al. 2007). On the continental shelf of the Gulf of Lions, oxygen penetration depth in the sediments increases with water depth and distance from shore (Pruski et al, 2015). Oxidised conditions can be restricted from some millimeters to some centimeters in the proximal Rhône (20-30 m), extended down to 2-5 cm at 60 m depth (Table 4) and to 5-10 cm offshore at 100 m depth. In the sediment cores collected on the Gulf of Lions shelf during the CASCADE cruise, an oxic layer was always present at the benthic interface (Table 4). This layer should act as an efficient barrier for upward diffusion of the pore water MeHgT$_F$, by adsorption onto oxyhydroxides ($\log K_{d_{MeHg}}$ equal to 6.4 and 7.7 for FeO$_x$ and MnO$_x$, respectively, according to Muresan et al., 2007) or onto organic matter associated with oxides according to the model by Feyte et al. (2010).

If diffusion of MeHgT from sediments is unlikely, MeHg advection from sediment via bioirrigation and biopumping is more probable. Assuming this advective flux to be 3 times the diffusion flux, as calculated by Hammerschmidt and Fitzgerald (2008) for the Northeastern Atlantic coastal sediments, the biomediated MeHg efflux from sediments would be ~14.1 mol a$^{-1}$. 
Release of porewater-borne MeHgT during resuspension of surface sediment is an alternative methylated Hg source for shelf waters. Assuming a 2-cm thick layer (with a mean porosity of 0.82, according to Cathalot et al., 2010) of MeHgT-enriched pore water resuspended (0.3 ± 0.2 pmol L\(^{-1}\) according to Table 4) and 12 x 10\(^3\) km\(^2\) for the Gulf of Lions shelf surface area, the quantity of MeHgT mobilized at each storm event would be 0.07 ± 0.05 mol. According to Guizien (2009) the magnitude of the period with waves higher than 1.5 m on the Gulf of Lions shelf is around 10 % of the year. This means that a maximum of 37 days of resuspension (i.e., ~ fifteen 2.5 days-long storm events, Bourrin et al., 2012; Dumas et al., 2014) can be estimated leading to the annual injection of 2.7 ± 1.9 mol of MeHgT in the water column. Thus, the “maximum potential efflux” of MeHg from the shelf sediment of the Gulf of Lions would be ~16.8 mol a\(^{-1}\). Of course, factors such as demethylation at the sediment–water interface as well as MeHg readsorption on resuspended particles may reduce this figure. It is noteworthy that this “maximum potential efflux” is equivalent to 2.5 % of the methylated Hg entering the Gulf of Lions from the sea and 28 % of the riverine particulate MeHgT flux, from which it partially derives.

5.2. Internal MeHg production

5.2.1. Shelf and slope waters

The average of MeHgT\(_F\) concentrations in the Low Salinity Waters was low (< 0.05 pmol L\(^{-1}\)) and not different from the rest of the Gulf of Lions shelf waters (\(t\)-test, \(p > 0.01\), Tables 2 and 3). The average MeHgT\(_F\) / HgT\(_F\) ratio was 1.5 %. These low levels are consistent with active photodemethylation in the surface waters (e.g., Black et al., 2012). The highest MeHgT\(_F\) concentrations occurred where highest salinities were present at the bottom of the Low Salinity Waters lenses (Fig. 2b, Fig. 3), suggesting two possible origins for methylated Hg: its
advection from the external sources quantified above (Northern Current waters and shelf sediment) and/or its production in the shelf water column. Methylated Hg production associated with planktonic production/degradation in the mixed layer has been shown already in the Mediterranean Sea (Monperrus et al., 2007; Heimbürger et al., 2010) and elsewhere (e.g., Lehn herr et al., 2011).

In the surface waters of the Low Salinity Waters, significant relationships exist between MeHgT and particulate phosphorus ($MeHgT_{ppmol} = 0.0723P_{\mu mol L^{-1}} - 0.0048$, $R^2 = 0.44$, $0.01<p<0.05$, Fig. S4a), and between MeHgT and total pigments ($MeHgT_{ppmol} = 0.0044Pig_{\mu g L^{-1}} - 0.0078$, $R^2 = 0.43$, $0.01<p<0.05$, Fig. S4b). This relationship suggests methylated Hg accumulation in the phytoplankton of the Low Salinity Waters; however, its origin is unidentified. Interestingly, MeHgT is significantly inversely correlated with the MeHgT in Low Salinity Water surface waters ($MeHgT_{ppmol} = - 0.600MeHgT_{ppmol} - 0.030$, $R^2 = 0.46$, $p<0.05$, Fig. S5). With a regression coefficient not different from 1 (-0.600 ± 0.415; $p = 0.05$), this relationship suggests that the two phases were exchanging the MeHgT standing stock present in the water.

Along the slope (Sta. S230), MeHgT_{UNF} distribution is related to soluble reactive phosphorus (SRP) with the following relationship: $MeHgT_{UNF_{ppmol}} = 0.92SRP_{\mu mol L^{-1}} + 0.04$ ($R^2 = 0.95$, $p<0.01$). The regression coefficient is in the range of values reported for open Mediterranean waters, namely 0.89 to 1.24 (see Table 2 in Cossa et al., 2009). These values calculated for unfiltered samples are more than 10 times higher than the regression coefficient for the relationship between MeHgF and $P_F$ mentioned above (0.0723). If the mineralization of settling particules were responsible for the MeHgF versus SRP relationship, similar regression coefficients should be found for the particulate and the dissolved phases. On the other hand,
the discrepancy in the regression coefficients between MeHg_F vs SRP and MeHg_P vs P_P suggests that MeHg-enriched water is advected with Northern Current and/or that net Hg methylation occurs in the organic matter regeneration zone of the slope water column. The significant increase in MeHg_T concentrations in the slope waters when dissolved oxygen decreases (R^2 = 0.90; n = 21, p < 0.01) supports this latter interpretation (Fig. S6).

In summary, net Hg methylation seems to occur along the slope water column, whereas we find little evidence for it to occur in the Low Salinity Water lenses drifting on the Gulf of Lions shelf. This observation probably indicates that particulate organic matter degradation, which governs the Hg_II methylation, is favored when the water column is deep enough to sustain a sufficiently long residence time of settling particles. In contrast, on the shelf, where the water column depth is limited, organic matter degradation mostly occurs in the surface sediments. Incubation experiments allowed estimating the Hg methylation potentials within the Gulf of Lions water and sediment.

5.2.2. In situ Hg methylation potential

Week-long (192 h) incubation experiments suggest gross Hg methylation t rates of 0.009 to 0.083 % d^{-1} during sediment resuspension. In addition, incubations of bottom seawater sampled on the shelf during winter downwelling gave Hg methylation potentials (over 192 h) ranging from 0.0002 to 0.0004 % d^{-1}. Interestingly, the methylation rates increased during the first 96 h of incubation then remained constant at the maximum level after 96 to 192 h (Fig. 6b). Applying the above methylation potentials to the flux of inorganic particulate Hg calculated from the mean concentration of inorganic particulate Hg measured in March 2011 in the Gulf of Lions (0.519 nmol g^{-1}) and the downwelling mass flux of 0.4 x 10^{12} g per storm event (2-3 days-long; Bourrin et al., 2012; Dumas et al., 2014), the gross methylation
observed in sediment slurries may account at best for 0.02 to 0.17 mol d\(^{-1}\) MeHgT (i.e. 0.05-0.42 mol MeHgT per storm event), that is 0.7 to 6.3 mol per year for 15 storms a year. These considerations suggest that the contribution of MeHgT produced in sediment slurries resulting from sediment resuspension in bottom water and short-term settling/resuspension cycles may be similar in magnitude to MeHgT release from porewater (2.7 mol a\(^{-1}\)). If we apply the gross methylation rates obtained in bottom water (up to 0.0004 % d\(^{-1}\)) to the whole water column (with a Hg\(^{II}\) of 0.85 pmol L\(^{-1}\)), the maximum methylation rate in the entire Gulf of Lions waters (\(\sim1.8 \times 10^3\) km\(^3\)) should not exceed 2.2 mol a\(^{-1}\).

### 6. Summary and Conclusions

Reviewing the oceanic Hg biogeochemical cycle, Mason et al. (2012) sum up that, while atmospheric deposition is the main source of inorganic divalent Hg in open ocean systems, most of the MMHg accumulating in ocean fish should derive from in situ production in the upper water column. Is this model proposed for the open seas also valid for the coastal environment? Here, we have addressed the questions of the distribution and sources of methylated Hg in the waters of the Northwestern Mediterranean margin including the continental shelf (Gulf of Lions) and the adjacent open sea (North Gyre). In summary, it appears that the proportion of methylated Hg to HgT increased seaward, from the freshwaters (Rhône River waters) to the shelf waters (Gulf of Lions waters) and the open ocean (North Gyre waters). Highest MeHgT concentrations are associated with the ODZs of the North Gyre. Despite the observed in situ methylation of inorganic Hg in sediment and waters within the system (<6.3 and ~2.2 mol a\(^{-1}\), respectively), external methylated Hg sources are the largest for the Gulf of Lions. The adjacent open ocean is the dominant source, with 680 ± 120
mol of MeHg per year. Continental sources (river and groundwater) account for < 95 mol a\(^{-1}\), with MeHg being mainly associated with continental particulate matter, a phase which is not directly available for pelagic biota. Contributions from atmospheric deposition and sediment resuspension are estimated to be \(\sim 5\) and < 16.8 mol a\(^{-1}\), respectively. We conclude that (i) the methylation of inorganic Hg in the ODZs of the open sea is the main source of methylated Hg in the Northwestern Mediterranean margin waters, and that (ii) sedimentary sources have a lower influence on the distribution of MeHgT in the water column, even though high methylated Hg concentrations in the sediments may cause the exposure of organisms feeding on food webs linked to the benthic environment. Our findings underline the ecological importance of the idea that, even in coastal contaminated environments, methylated Hg transfer into food webs is driven by the efficiency of processes that determine MeHgT inputs to the water column (Sunderland et al., 2010; Chen et al., 2014). We are in favor of an approach where, in coastal ecosystems, the origin of MeHg accumulated through pelagic and benthic food webs are differentiated using stable Hg isotopes (Mason et al., 2012).

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and the MERMEX / MISTRALS project. It is a contribution to the international LOICZ program.
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mercury and methylmercury particulate distributions, methylation and demethylation rates

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**Figure Captions**

**Figure 1.** Study site in the Northwestern Mediterranean, with main circulation patterns. Stations location during the CASCADE cruise (March 2011). Station coordinates are given in Table S2.

**Figure 2.** Dissolved MeHg (MeHgT_F) *versus* salinity. (a) Estuarine mixing zone, (b) Low Salinity Water lenses. The solid line represents the linear relationship between MeHgT_F and salinity (MeHgT_F = - 0.0025*Sal + 0.1258, R^2 = 0.76), which suggests conservative mixing.

**Figure 3.** Time series of dissolved methylmercury (MeHgT_F) and salinity in the Low Salinity Water lenses (LSWs) drifting on the Gulf of Lions’ shelf and slope. Note that the LSW lenses occur mainly in the top 0-20 m depth.

**Figure 4.** Methylmercury (MeHgT) vertical profiles in the water of the shelf (a) and the continental slope (b) of the Gulf of Lions. UNF subscribes refer to unfiltered samples. Error bars correspond to standard deviations of 2 to 4 samples collected during temporal monitorings.

**Figure 5.** Vertical profiles of methylated mercury (MeHgT) in the North Gyre water column. (a) Unfiltered (MeHgT_{UNF}) water samples and (b) MMHg/DMHg ratios.

**Figure 6.** (a) Isotopic composition of MeHgT after incubation (192 h) of slurries of surface sediments in unfiltered bottom water and (b) gross methylation rates in incubations of unfiltered seawater from the bottom of the shelf water column, showing increasing methylation rates over time during the first 96h of incubation followed by the highest and constant methylation rates after 96h. Error bars represent standard deviation for multiple analyses (n=3) of the same sample. For the methylation rates, error bars estimated from multiple injections of the same sample (n=3) were smaller than symbol size.

**Figure 7.** Relationships between methylated mercury (MeHgT) and dissolved oxygen (Dissolved O_2) in unfiltered samples from the North Gyre stations. (a) Methylated mercury (MeHgT) and (b) monomethylmercury (MMHg) and dimethylmercury (DMHg). The probability threshold (p<0.01) is reached for R^2 ≥ 0.55. No dissolved O_2 measurements were available for station “Antarès”.

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Tables

Table 1. Rhône River. A statistical summary of the concentrations in dissolved ($X_F < 0.45\mu m$) and particulate ($X_P > 0.45\mu m$) HgT and MeHg, measured in the waters at Arles (Sta. SORA). HgT values measured in 1994-1995 are from Cossa and Coquery (2005). SD: standard deviation; n: number of samples.

<table>
<thead>
<tr>
<th></th>
<th>HgT$_F$ (pmol L$^{-1}$)</th>
<th>HgT$_P$ (nmol g$^{-1}$)</th>
<th>MeHg$_F$ (pmol L$^{-1}$)</th>
<th>MeHg$_P$ (nmol g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average ± SD (n)</td>
<td>2.45 ± 2.05 (24)</td>
<td>0.85 ± 0.45 (27)</td>
<td>0.100 ± 0.035 (23)</td>
<td>0.017 ± 0.008 (26)</td>
</tr>
<tr>
<td>Min. – Max.</td>
<td>0.40 – 9.25</td>
<td>0.20 – 2.15</td>
<td>0.035 – 0.185</td>
<td>0.004 – 0.032</td>
</tr>
</tbody>
</table>

Table 2. Low Salinity Water lenses (LSW) and slope foot waters (SFW, Sta. S230). A statistical summary of HgT and MeHgT (MeHgT=MMHg+DMHg) measurements during the BIOPRHOFI cruise. Average ± standard deviation (number of samples) and range (Min. – Max.). (*) mean and standard deviation were calculated with the 87 concentration values, which included 30 measurements lower than the detection limit, which have been put equal to the half of the detection limit.

<table>
<thead>
<tr>
<th></th>
<th>HgT (pmol L$^{-1}$)</th>
<th>MeHgT (pmol L$^{-1}$)</th>
<th>MeHgT/HgT (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSW (1-50 m layer; bottom ≤120 m) Filtered samples (&lt;0.4µm)</td>
<td>1.57 ± 0.74 (84)</td>
<td>0.021* ± 0.012* (87)</td>
<td>1.5 ± 1.0 (84)</td>
</tr>
<tr>
<td></td>
<td>0.61 – 3.50</td>
<td>&lt;0.015 – 0.069</td>
<td>&lt;0.3 – 5.5</td>
</tr>
<tr>
<td>SFW (&lt;100 m layer; bottom at 1386 m) Unfiltered samples</td>
<td>1.22 ± 0.13 (3)</td>
<td>0.13 ± 0.10 (7)</td>
<td>10 ± 7 (3)</td>
</tr>
<tr>
<td></td>
<td>0.98 – 1.35</td>
<td>0.026 – 0.241</td>
<td>2 – 18</td>
</tr>
<tr>
<td>SFW (100-900 m layer; bottom at 1386 m) Unfiltered samples</td>
<td>1.41 ± 0.06 (4)</td>
<td>0.32 ± 0.13 (11)</td>
<td>18 ± 1 (4)</td>
</tr>
<tr>
<td></td>
<td>1.33 – 1.48</td>
<td>0.23 – 0.38</td>
<td>16 – 20</td>
</tr>
</tbody>
</table>
### Table 3. Gulf of Lions shelf, slope and North Gyre waters (CASCADE cruise). Summary statistics for HgT<sub>UNF</sub> and MeHgT<sub>UNF</sub> concentrations. Average ± Standard deviation (number of samples) and range (Min. – Max.). Station locations are indicated on figure 1 and coordinates are given on table S2. (*) Values calculated with concentrations lower than the DL put equal to the half of the DL.

<table>
<thead>
<tr>
<th>Station (water layer sampled)</th>
<th>HgT&lt;sub&gt;UNF&lt;/sub&gt; (pmol L&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>MeHgT&lt;sub&gt;UNF&lt;/sub&gt; (pmol L&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>MeHgT&lt;sub&gt;UNF&lt;/sub&gt;/HgT&lt;sub&gt;UNF&lt;/sub&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Inner shelf (bottom &lt;100 m)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A (1-90 m)</td>
<td>2.04 ± 1.11 (7)</td>
<td>0.041 ± 0.034 (9)*</td>
<td>1.5 ± 0.9 (7)</td>
</tr>
<tr>
<td></td>
<td>1.27 – 4.47</td>
<td>&lt;0.015 – 0.119</td>
<td>0.6 – 3.4</td>
</tr>
<tr>
<td>B (1-90 m)</td>
<td>1.17 ± 0.29 (10)</td>
<td>0.034 ± 0.021 (10)*</td>
<td>3.1 ± 2.2 (10)</td>
</tr>
<tr>
<td></td>
<td>0.78 – 1.61</td>
<td>&lt;0.015 – 0.066</td>
<td>0.5 – 6.3</td>
</tr>
<tr>
<td>C (1-90 m)</td>
<td>1.40 ± 1.08 (10)</td>
<td>0.007 ± 0.009 (11)*</td>
<td>0.9 ± 1.8 (10)</td>
</tr>
<tr>
<td></td>
<td>0.58 – 4.20</td>
<td>&lt;0.015 – 0.035</td>
<td>0.1 – 6.0</td>
</tr>
<tr>
<td>D (1-90 m)</td>
<td>1.61 ± 1.23 (9)</td>
<td>0.024 ± 0.014 (10)*</td>
<td>2.2 ± 1.7 (9)</td>
</tr>
<tr>
<td></td>
<td>0.92 – 3.80</td>
<td>&lt;0.015 – 0.048</td>
<td>0.3 – 5.1</td>
</tr>
<tr>
<td>A/B/C/D (1-90m)</td>
<td>1.52 ± 1.00 (36)</td>
<td>0.026 ± 0.024 (40)*</td>
<td>1.9 ± 1.9 (36)</td>
</tr>
<tr>
<td></td>
<td>0.58 – 4.47</td>
<td>&lt;0.015 – 0.119</td>
<td>0.1 – 6.3</td>
</tr>
<tr>
<td><strong>Slope edge and head of the Cap de Creus canyon (bottom at 100-300 m)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>E (2-290 m)</td>
<td>0.99 ± 0.52 (20)</td>
<td>0.026 ± 0.048 (8)*</td>
<td>1.5 ± 2.0 (8)</td>
</tr>
<tr>
<td></td>
<td>0.58 – 2.94</td>
<td>&lt;0.015 – 0.141</td>
<td>0.3 – 4.7</td>
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<tr>
<td>L-01 (5-250 m)</td>
<td>1.07 ± 0.10 (6)</td>
<td>0.033 ± 0.023 (6)</td>
<td>3.0 ± 1.8 (6)</td>
</tr>
<tr>
<td></td>
<td>1.00 – 1.26</td>
<td>0.020 – 0.076</td>
<td>1.8 – 6.1</td>
</tr>
<tr>
<td>M-12 (10-130 m)</td>
<td>1.02 ± 0.12 (4)</td>
<td>0.049 ± 0.006 (4)</td>
<td>4.8 ± 0.8 (4)</td>
</tr>
<tr>
<td></td>
<td>0.93 – 1.14</td>
<td>0.042 – 0.056</td>
<td>4.1 – 6.0</td>
</tr>
<tr>
<td><strong>Slope foot (bottom at 900-1800 m)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M-10 (10-1100 m)</td>
<td>1.01 ± 0.15 (10)</td>
<td>0.271 ± 0.088 (10)</td>
<td>26.2 ± 6.2 (10)</td>
</tr>
<tr>
<td></td>
<td>0.66 – 1.13</td>
<td>0.092 – 0.355</td>
<td>13.9 – 33.4</td>
</tr>
<tr>
<td>L-03 (10-1860 m)</td>
<td>1.22 ± 0.12 (10)</td>
<td>0.177 ± 0.077 (8)</td>
<td>14.9 ± 6.5 (8)</td>
</tr>
<tr>
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<td>1.13 – 1.53</td>
<td>0.020 – 0.266</td>
<td>1.3 – 22.0</td>
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</table>
### North Gyre (bottom at > 2000 m)

<table>
<thead>
<tr>
<th>Station</th>
<th>Depth (m)</th>
<th>Oxygen (mL/L)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Antarès (10-2500m)</strong></td>
<td>1.05 ± 0.12 (9)</td>
<td>0.235 ± 0.107 (9)</td>
<td>21.8 ± 8.8 (9)</td>
</tr>
<tr>
<td></td>
<td>0.84 – 1.23</td>
<td>0.090 – 0.375</td>
<td>11.3 – 33.8</td>
</tr>
<tr>
<td><strong>L-05 (10-2200 m)</strong></td>
<td>1.04 ± 0.04 (10)</td>
<td>0.252 ± 0.040 (9)</td>
<td>24.3 ± 3.9 (9)</td>
</tr>
<tr>
<td></td>
<td>0.98 – 1.11</td>
<td>0.199 – 0.309</td>
<td>18.8 – 30.1</td>
</tr>
<tr>
<td><strong>L-08 (10-2150 m)</strong></td>
<td>1.07 ± 0.04 (10)</td>
<td>0.307 ± 0.045 (10)</td>
<td>28.7 ± 4.3 (10)</td>
</tr>
<tr>
<td></td>
<td>1.01 – 1.13</td>
<td>0.263 – 0.394</td>
<td>24.2 – 38.6</td>
</tr>
<tr>
<td><strong>L-10 (10-2360 m)</strong></td>
<td>1.02 ± 0.12 (10)</td>
<td>0.314 ± 0.113 (10)</td>
<td>30.2 ± 8.4 (10)</td>
</tr>
<tr>
<td></td>
<td>0.82 – 1.11</td>
<td>0.166 – 0.478</td>
<td>20.3 – 43.2</td>
</tr>
<tr>
<td><strong>L-12 (10-2500m)</strong></td>
<td>1.13 ± 0.18 (10)</td>
<td>0.237 ± 0.079 (10)</td>
<td>21.3 ± 5.1</td>
</tr>
<tr>
<td></td>
<td>0.64 – 1.23</td>
<td>0.136 – 0.398</td>
<td>13.4 – 32.4</td>
</tr>
<tr>
<td><strong>S2400 (10-2400m)</strong></td>
<td>1.11 ± 0.01 (10)</td>
<td>0.175 ± 0.123 (10)</td>
<td>15.8 ± 11.1 (10)</td>
</tr>
<tr>
<td></td>
<td>1.08 – 1.12</td>
<td>0.020 – 0.326</td>
<td>1.8 – 25.4</td>
</tr>
<tr>
<td><strong>M-08 (10-2010m)</strong></td>
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<td>0.305 ± 0.052 (10)</td>
<td>26.8 ± 5.9 (10)</td>
</tr>
<tr>
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<td>1.03 – 1.45</td>
<td>0.245 – 0.367</td>
<td>17.7 – 35.7</td>
</tr>
<tr>
<td><strong>M-05 (10-2490 m)</strong></td>
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<td>0.216 ± 0.062 (10)</td>
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</tr>
<tr>
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<td>1.05 – 1.19</td>
<td>0.106 – 0.302</td>
<td>10.0 – 26.9</td>
</tr>
<tr>
<td><strong>M-03 (10-2580 m)</strong></td>
<td>1.24 ± 0.10 (10)</td>
<td>0.276 ± 0.056 (10)</td>
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<tr>
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<td>1.09 – 1.41</td>
<td>0.137 – 0.320</td>
<td>9.7 – 27.9</td>
</tr>
<tr>
<td><strong>M-01 (10-2500 m)</strong></td>
<td>1.06 ± 0.24 (10)</td>
<td>0.278 ± 0.132 (10)</td>
<td>24.7 ± 8.7 (10)</td>
</tr>
<tr>
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<td>0.53 – 1.24</td>
<td>0.066 – 0.374</td>
<td>8.9 – 34.6</td>
</tr>
</tbody>
</table>
Table 4. Gulf of Lions shelf and North Gyre (CASCADE cruise). Summary statistics for MeHgT<sub>F</sub> (<0.4µm) in the first 2 cm of the sediment pore waters and bottom water (10 cm above the water sediment interface). The thickness of the oxidized layer (cm) is based on the redox potential value. In italic and brackets are the MeHgT concentrations (pmol g<sup>-1</sup>) in the solid phase.

<table>
<thead>
<tr>
<th>Station</th>
<th>Oxidized layer thickness (cm)</th>
<th>MeHgT&lt;sub&gt;F&lt;/sub&gt; (pmol L&lt;sup&gt;-1&lt;/sup&gt;) Pore water</th>
<th>MeHgT&lt;sub&gt;F&lt;/sub&gt; (pmol L&lt;sup&gt;-1&lt;/sup&gt;) Bottom water</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-04</td>
<td>2</td>
<td>0.071 (4.0)</td>
<td>0.022</td>
</tr>
<tr>
<td>B-05</td>
<td>3</td>
<td>0.268 (3.5)</td>
<td>0.008</td>
</tr>
<tr>
<td>C-05</td>
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<td>0.684 (3.0)</td>
<td>0.040</td>
</tr>
<tr>
<td>D-06</td>
<td>4.5</td>
<td>0.254 (3.5)</td>
<td>0.040</td>
</tr>
<tr>
<td>E-03</td>
<td>-</td>
<td>0.259</td>
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<td>E-08</td>
<td>4.5</td>
<td>0.258</td>
<td>0.040</td>
</tr>
</tbody>
</table>
Fig. 1

Fig. 2
Fig. 3

Fig. 4
Fig. 5

Fig. 6
Fig. 7
Supplementary material including Suppl. Figures (S1-S6), Suppl. Tables (S1 and S2), Suppl. Information (SI1, SI2 and SI3) and references

Supplementary Figure Captions

Figure S1. Schematic representation of the Gulf of Lions water circulation patterns.

Figure S2. Trajectories of the desalted water lenses (LSWs) drifting on the Gulf of Lions’ shelf and slope.

Figure S3. Potential temperature vertical profiles along the “L” transect (Fig. 1). Stratified stations are characterized by high temperature gradients (red zones), whereas homogenized water column are illustrated by a bleu monocolor.

Figure S4. Particulate methylmercury (MeHg\(_P\)) versus (a) particulate phosphorus, and (b) pigments at stations 221 and 230. See figure S2 for station locations.

Figure S5. Dissolved methylmercury versus particulate methylmercury in desalted water lenses (LSW) drifting on the Gulf of Lions’ shelf and slope. See figure S2 for station locations.

Figure S6. Dissolved methylmercury (MeHg\(_F\)) versus dissolved oxygen within desalted water lenses (LSW) drifting on the Gulf of Lions’ shelf and slope. See figure S2 for station locations.
Fig. S3

Fig. S4
Fig. S5

Fig. S6
Supplementary Tables


<table>
<thead>
<tr>
<th>Name of the cruise</th>
<th>Location of the sampling</th>
<th>Mode of collection</th>
<th>Date</th>
<th>Type of samples collected</th>
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<tbody>
<tr>
<td>Rhône monitoring project</td>
<td>Rhône River at Arles</td>
<td>SORA pumping station¹</td>
<td>April to June and October to November 2008</td>
<td>Particles</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>March 2009 to June 2010</td>
<td>Filtered waters and particles</td>
</tr>
<tr>
<td>Rhône delta study</td>
<td>Rhône fresh-seawater mixing zone</td>
<td>Barcarin ferry² and Zodiac</td>
<td>October 2008</td>
<td>Filtered waters and particles</td>
</tr>
<tr>
<td>BIOPRHOFI cruise</td>
<td>Shelf and slope</td>
<td>R/V Suroit³</td>
<td>May 2006</td>
<td>Filtered and unfiltered waters. and particles</td>
</tr>
<tr>
<td>CASCADE cruise</td>
<td>Shelf, slope, canyon and rise</td>
<td>R/V Atalante⁴</td>
<td>March 2011</td>
<td>Filtered and unfiltered waters and sediment cores (solid and pore waters)</td>
</tr>
<tr>
<td>Atmospheric monitoring</td>
<td>Coastal site (La Seyne-sur-Mer)</td>
<td>Rain collector</td>
<td>April 2009 to January 2010</td>
<td>Wet and dry deposition</td>
</tr>
</tbody>
</table>
### Table S2a. Water sampling stations: Cruise, coordinates and bottom depth.

<table>
<thead>
<tr>
<th>Cruise</th>
<th>Station</th>
<th>Latitude (N)</th>
<th>Longitude (E)</th>
<th>Bottom depth (m)</th>
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</thead>
<tbody>
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<td>Rhône River monitoring</td>
<td>SORA (Arles)</td>
<td>43°40.722'</td>
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<tr>
<td>Rhône mixing zone</td>
<td>I-II</td>
<td>43°15.360'</td>
<td>4°26.460'</td>
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<td>Rhône mixing zone</td>
<td>III-IV</td>
<td>43°15.012'</td>
<td>4°26.892'</td>
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<td>Rhône mixing zone</td>
<td>V-VII</td>
<td>43°15.018'</td>
<td>4°26.862'</td>
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<tr>
<td>Cruise</td>
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<td>Longitude (E)</td>
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</tr>
<tr>
<td>------------</td>
<td>---------</td>
<td>----------------</td>
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</tr>
</tbody>
</table>

Table S2b. Sediment sampling stations: Cruise, coordinates and bottom depth.
Supplementary Information

SI1. Methods

Sample treatment

**Water and particles.** The samples from the 0-50 m layer of the shelf waters during the BIOPRHOFI cruise were collected by pumping with an all-Teflon pneumatic pump (10-2PM, ASTI®) and through polyethylene tubing, directly into a class 100 on-board container, with the consequence that the seawater was never in contact with the atmosphere of the ship. All the plastic wares were previously acid-cleaned according to ultraclean sample handling protocols (e.g., Cossa et al. 2003). Discrete water samples were collected in 2L Teflon (FEP) bottles inside the container, where filtrations were then performed on sub-samples using acid washed polycarbonate membranes (0.45 µm, Nuclepore®).

Filtrate (250 mL) was collected in Teflon (FEP) bottles and acidified with HCl (0.4 %, v/v, Suprapur, Merck®) for subsequent analyses of “dissolved” fraction of total and methylmercury (HgT\textsubscript{F} and MeHgT\textsubscript{F}). The collection of particles from the Low Salinity Waters, for subsequent MMHg\textsubscript{P}, CHNP and pigments determinations, was performed using in-line filtration through glass fiber filters (GF/G, Whatman®) previously cleaned by heating at 450°C for 24h and mounted in a Teflon (PTFE)/stainless steel filter holder (Ø142 mm, Schleicher & Schuell®) within the container. Up to 60 liters of water were filtered this way in order to collect enough material for the various particulate analyses. Samples for dissolved gaseous Hg (DGM) analyses were collected in a 1L Teflon bottle (FEP) according to the traditional method used for dissolved oxygen determination in order to avoid gas evasion during the collection. Deep-water samples (> 50 m) were collected during the BIOPRHOFI and CASCADE cruises by rosette-mounted 5L bottles (1010X-Niskin, General Oceanics®) equipped with a CTD probe. These samples were not filtered and analyzed only for HgT\textsubscript{UNF} and MeHgT\textsubscript{UNF}. Dissolved gaseous Hg and HgT were determined on board, while MMHg and MeHgT analyses were performed in the laboratory within 2 months after the cruise on the acidified samples stored in the dark at +4°C in a double wrapping of polyethylene bags.

**Sediment cores:** The cores were collected along the Gulf of Lions shelf, at the head of the Cap de Creus canyon and in the abyssal plain in the North Gyre area during the CASCADE cruise. A multicore sampler (Oktopus GmbH Multiple corer with 8 tubes of 100 mm diameter) allowing the sampling of the undisturbed benthic interface (Barnett et al., 1984) was used. The pore water was drained using Milli-Q (Millipore®) water-rinsed microporous polymer tube samplers (Rhizon SMS, Rhizosphere Research Products®) fixed on an acid washed all-polypropylene syringe (Guédron et al., 2012). Collected pore water (the two first cm below the water-sediment interface) was filtered through a
hydrophilic Teflon membrane (0.45 µm, Millex-LCR, Millipore®), then acidified with high purity HCl (0.4 % v/v, Suprapur, Merck®) and stored in the dark until MMHg analysis. According to Guédron et al. (2012), Rhizon samplers preferentially recover water from the sediment macropores, containing the readily exchangeable chemical species.

**Chemical analyses**

**Total mercury.** Total Hg in filtered and unfiltered samples were measured on board within a few minutes of sampling. In order to access all the mercury chemical species, present in the sample, the release of Hg from its ligands was achieved by a BrCl solution (0.1 mL of a 0.2 M solution is added to a 100 mL sample), and then the Hg\(^{II}\) was reduced to Hg\(^0\) with an acidic SnCl\(_2\) solution (0.2 mL of a 1 M solution is added to a 100 mL sample). This technique derives from the original Bloom and Crecelius (1983) method and has been described in detail by several authors (e.g., Gill and Fitzgerald, 1988; Horvat et al., 1991; Mason and Fitzgerald, 1993) and is now known as the US-EPA standard method No 1631. The Hg\(^0\) vapor generated by the reduction is amalgamated on a gold (Au) trap then released by heating into an Atomic Fluorescence Spectrometer (2500, Tekran®). For both measurements, the detection limit (DL) was 0.1 pmol L\(^{-1}\) and the reproducibility varied according to the concentration level between 5 and 15 % (Cossa et al. 2003). The accuracy of HgT measurements was tested using the ORMS-3 certified reference material (CRM) from the National Research Council of Canada. Our measurements were always within the confidence limits given for the CRM (12.6 ± 1.1 pg mL\(^{-1}\); http://inms-ienm.nrc-cnrc.gc.ca/calserv/crm_files_f/ORMS-3_f.pdf).

**Methylated Hg species.** Total methylated Hg and MMHg were measured on filtered and unfiltered samples, whereas DMHg was not measured, but calculated as the difference between MeHgT\(_{UNF}\) and MMHg\(_{UNF}\). Total methylated Hg was determined on acidified samples, which means that both MMHg and DMHg were determined in the same time, since DMHg is converted into MMHg at low pH (Mason, 1991; Black et al., 2009a). Monomethyl Hg was determined with the same technique as MeHgT, but after bubbling 350 mL samples for 40 min with argon (Ar) at a flow rate of 250 mL min\(^{-1}\) in order to remove DMHg before acidification. Total methylated Hg and MMHg were determined as volatile MMHg hydride by purge and cryo-trapping gas chromatography and detected as elemental Hg vapor by atomic fluorescence spectrometry (AFS). The mercury hydrides (from MMHg and Hg\(^{II}\)) were formed with NaBH\(_4\), sparged from the sample with helium (He) (250 mL min\(^{-1}\)), concentrated and then separated (50 mL min\(^{-1}\)) by cryogenic chromatography before being converted in Hg\(^0\) in a furnace (800°C) and detected by the AFS detector. The hydride generation technique was initially proposed by Filippelli et al. (1992), modified by Tseng et al. (1998), and then improved by Stoichev et al. (2004) and Cossa et al. (2009). Last authors optimized the method in order to detect sub-picomolar...
levels in seawater by lowering the reagent amount (addition of only 0.6-4.0 mL of a NaBH₄ solution of 0.5 % (w/v) to a 30-200 mL water sample) and using a very stable and sensitive detector with an absolute DL of ~1 femtomol of Hg (AFS detector 2500 model equipped with a mirror-coated quartz cuvette, Tekran®). The hydrides are formed within a silanized borosilicate glass reactor (5 % DMDCS in toluene), then concentrated at low temperature (in liquid nitrogen) and separated by heating (up to 90°C) in a silanized borosilicate glass tube of 4 mm interior diameter and filled with Chromosorb WAW-DMCS (60/80 mesh impregnated with 15 % OV-3). The vector gas was Hg-free He, purified by passing through charcoal and gold filters. During this set of analyses, the blank (< 0.01 pmol) and its reproducibility (2 %) allowed DLs (calculated as 3 times the standard deviation of the blank) ranging from 0.005 to 0.025 pmol L⁻¹ depending on the volume of the sample analyzed, and limits of quantification (calculated as 10 times the standard deviation of the blank) ranging from 0.015 to 0.075 pmol L⁻¹. The analytical reproducibility varied with time between 6 and 15 %. The accuracy was not directly estimated because no certified reference seawater for MMHg was available. The calibration was performed using the dilutions of a 1 g L⁻¹ stock MMHg solution in isopropanol. The dilutions of the stock solution were performed in HCl (0.4 %, w/v, Suprapur, Merck®) water solution. Three times a day, 2 µL of saturated Hg⁰ vapor was injected into the chromatographic system through a septum in order to check the response of the instrument and verify the hydride yields. Details of the analytical system are given in a technical paper (Cossa et al. 2003).

MeHgTₚ was determined by atomic fluorescence spectrometry after HNO₃ (4M, Suprapur, Merck®) extraction, ethylation of the MMHg and Hg⁰, followed by chromatographic separation of the volatile ethylated compounds according to Liang et al. (1994). The accuracy, reproducibility and DL, established analyzing a Certified Reference Material from the International Atomic Energy Agency (IAEA-142, Horvat et al., 1997), were 80-120 % (recovery), 10 % (coefficient of variation) and 4 ng g⁻¹ (3 times the standard deviation of the blank).

Dissolved gaseous Hg. For analysis of DGM, 300 mL of sample was purged for 30 min with ultra-high purity nitrogen stripped of Hg⁰ by passage through Au traps, at a flow rate of 300 L min⁻¹, corresponding to a calculated extraction rate of 78 % (results were corrected for this yield). Volatilized Hg species were trapped and concentrated on an Au trap (Braman and Johnson, 1974), subsequently desorbed by pyrolysis and quantified by gas-phase AFS. Dissolved gaseous Hg net production was evaluated by incubating unfiltered water samples in an incubator located on the deck of the vessel exposed to sunlight radiations. Temperature was controlled by continuously pumping sea-surface water through the incubator using a through-flow system. These ex-situ incubations were performed in batch experiments during 2 to 12 h periods under the following conditions: (i) absence of light (FEP
Teflon bottles, wrapped in Al foil); (ii) presence of light (FEP Teflon bottles). Transparent FEP Teflon bottles absorbed 2.5 % of total incident radiation according to Amyot et al. (1997). Net DGM production was estimated without taking into account the possible re-oxidation of Hg$^0$.

SI2. Riverine flux calculations

In the absence of any significant relationship between “dissolved” HgT and RR water discharge the HgT$_F$ flux was calculated as the product of weighted average of Hg concentrations and average discharge (Meybeck and Ragu, 1996; Gairoard et al. 2012). On the contrary, in the case of particulate Hg, we took into account the existing HgT$_P$ dependencies upon hydrological changes (Fig. 3). Rhône river discharge and the suspended particulate matter concentrations were obtained from the Compagnie Nationale du Rhône (http://www.cnr.tm.fr/). In these conditions, the HgT discharging from the RR between June 2009 and June 2010 has been calculated to be 85 and 800 mol as “dissolved” and particulate, respectively.

Considering that during the studied period the Rhône discharge was atypically low, and using the water and particulate mean discharges calculated on the basis of the last 36 years (Gairoard et al., 2012) the annual HgT efflux from the Rhône River to the GoL would be close to 2.7 and 0.13 kmol for the particulate and “dissolved” phases respectively. Assuming average ratios of MeHg/HgT of 1.9 and 4.1 % (Table 1 of the main manuscript), the best estimates of the MeHg annual Rhône effluxes is calculated to be 51 and 5 mol for particulate and the “dissolved” phases, respectively.

SI3. Modeling the diffusive fluxes

MeHg$_F$ diffusive fluxes were estimated at the stations A to E benthic boundary layer (BBL) using Fick’s first law (Eq. 1):

$$J = - (\phi D_w / \theta^2) (\delta C / \delta x)_{BBL} \ [1]$$

Where, $J$ is the flux of the solute with concentration $C$ at depth $x$, $\phi$ is the sediment porosity (Eq. 2), $\theta$ is the tortuosity (Eq. 3), and $D_w$ is the molecular diffusion coefficient of the solute in seawater. Measuring porosity, the tortuosity was approached using Boudreau’s formulation:

$$\phi = \text{pore water volume} / (\text{solid volume} + \text{pore water volume}) \ [2]$$

$$\theta^2 = 1 - \ln(\phi^3) \ [3]$$
The $D_w$ for MeHg as MeHgCl were determined coupling the linear regressions of the infinite dilution diffusion for cations and anions against temperature (Boudreau, 1996) with the infinite-dilution diffusion for ion pairs (Applin and Lasaga, 1984). The expression was calculated for temperature salinity and pressure from an empirical equation developed by Kukulka et al. (1987). The adjustment for pore water viscosity of normal seawater was small at no more than 7% (Li and Gregory, 1974). The respective approximations for MeHg at $T = 18 \, ^\circ\text{C}, S = 35$ and $P = 2$ bar were $1.84 \times 10^{-5}$ and $8.65 \times 10^{-6}$ cm$^2$s$^{-1}$.

**Table**: MeHgT$_F$ diffusive fluxes from shelf sediments in the Gulf of Lions (Northwestern Mediterranean).

The MeHg gradient at the sediment-water interface is estimated using the difference between MeHg concentrations in surface sediment pore waters (2 cm below the interface) and bottom waters (10 cm above the water sediment interface).

<table>
<thead>
<tr>
<th>Station</th>
<th>MeHgT$_F$ (pmol m$^2$ day$^{-1}$)</th>
<th>MeHgT$_F$ (pmol L$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-04</td>
<td>0.20</td>
<td>0.049</td>
</tr>
<tr>
<td>B-05</td>
<td>1.04</td>
<td>0.26</td>
</tr>
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<td>C-05</td>
<td>2.58</td>
<td>0.644</td>
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<td>D-06</td>
<td>0.86</td>
<td>0.214</td>
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<tr>
<td>E-08</td>
<td>0.87</td>
<td>0.218</td>
</tr>
</tbody>
</table>

**References for SI1-3**


