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

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Abstract :

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 (<0.45µm) 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.

Highlights

► Distribution and fluxes of total Hg have been examined in the Gulf of Lions and North Gyre of the NW Mediterranean. ► Concentrations varied from 0.6 to 4.57 pmol L^{-1} on the inner shelf, and from 0.5 to 1.5 pmol L^{-1} at open sea. ► Average Hg inputs to the Gulf are 5.7 kmol yr^{-1} from open sea, 3.2 kmol yr^{-1} from rivers, and 0.5 kmol yr^{-1} from the atmosphere. ► In the open sea, Hg and dissolved oxygen distributions are inverse.

Keywords : Mercury, Ocean margin, Coastal area, Mediterranean

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. (2015), 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,

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1991; Wollast and Chou, 2001). An early global mass balance, constructed at the scale of the ocean margins, suggested that particulate Hg from rivers 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 Tapier-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 ~12 x 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 x 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

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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 to 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 (~ 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; 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

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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, 2008b), 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,

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drifting Low Salinity Water on the shelf as well as the water column above the continental slope/rise (including the Cap de Creus canyon, Fig. 1) and in the North Gyre.

3.1.1. Atmospheric deposition

Thirteen rain events were collected for HgT determinations 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 samples were transferred into acid-washed 125 mL Teflon (FEP) bottles and acidified without filtration (0.4 % v/v HCl, SupraPur, Merck®) just 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).

3.1.2. Rhône River monitoring

Rhône River Hg monitoring was performed at Arles (Sta. SORA, Fig. 1) during two monitoring periods: (i) a period of low waters from March, 2009 to June, 2010, with only one moderate flood event (~3000 m[3] s^{-1} on December the 2nd), and (ii) during the flooding period of October-November 2008 (up to 3580 m[3] s^{-1}). Freshwater samples were collected twice a month at Station SORA by pumping through polyethylene tubing using an all-Teflon (PFA) double-bellows pump (10-LPM, ASTI®). Samples were collected in acid washed 2L 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, SupraPur, Merck[®]) and stored in acid washed 500mL Teflon (FEP) bottles.

3.1.3. Rhône delta mixing zone

Brackish water samples were collected on 16th and 17th October 2008 between Barcarin (Rhône River) and the sea using a rubber boat (Fig.1; the precise locations of the stations are indicatedi Table S1). The samples were collected, directly (by glove-covered hands) into acid washed 2L Teflon (FEP) bottles, filtered and stored as described in the previous section.

3.1.4. BIOPRHOFI cruise

During the BIOPROHFI cruise (14th – 27th May 2006), two types of water masses were sampled: (i) the productive shelf water and (ii) the mesotrophic slope water. In the first case, two Low Salinity Water lenses, originating from the Rhône River plume, were successively tracked using a Lagrangian sampling protocol: lens "1" between May 14th and 18th, corresponding to stations S1 to S68 and lens "2" between the 19th and 26th, corresponding to stations S88 to S220 (Fig. S2). In the lenses, the 0-50 m layer was systematically sampled; the height of the water column varied between 60 and 100 m during the drifting. For the second type, 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 S1.

3.1.5. CASCADE cruise

During the CASCADE cruise (1st – 23th March 2011), water was collected (i) on the inner shelf from the Rhône prodelta to the south-western end of the Gulf of Lions (Stas. A to D), (ii) at the head of Cap de Creus canyon (Stas. E and X), and (iii) by means of 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). Stations at the head of the Cap de Creus canyon and within the North Gyre water column were sampled during a storm-induced downwelling event and a convective event, respectively (Fig. 1). Two to twelve water depths were sampled for each cast, depending on the height of the water column. Sampling station locations are given in Figure 1 and their coordinates in table S1.

3.2. Sample treatment

The nomenclature used in the following text, i.e. X_{UNF}, X_F and X_P refer to the unfiltered, "dissolved" (< 0.45 µm) and particulate fractions, respectively (with X being a distinct Hg species), whereas HgT refers to total Hg (including all methylated and inorganic species).

The samples from the 0-50 m layer of the shelf water masses (BIOPRHOFI cruise) were collected by pumping with an all-Teflon (PFA) double-bellows pneumatic pump (10-2PMPFD-1, ASTI®) through polyethylene tubing, directly into a Class 100 clean 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®). Filtrates were collected in Teflon (FEP) bottles and acidified with HCl (0.4 %, v/v, Suprapur, Merck®) for HgT_F 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 (Hood et al. 2010). Deep-water samples (> 50 m) were collected during the BIOPRHOFI and CASCADE cruises by rosette-mounted 5L bottles (1010X-

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Niskin, General Oceanics®) equipped with a CTD probe. These samples were not filtered and analyzed only for HgT_{UNF}. Dissolved gaseous Hg and HgT were determined on board.

3.3. Chemical analyses

3.3.1. Total mercury

Total Hg in filtered and unfiltered samples were measured on board within a few minutes after sampling. In order to access all the Hg 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}_i 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, now known as the US-EPA standard method N° 1631, 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). 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®). 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).

3.3.2. Dissolved gaseous mercury

For analysis of DGM, 300 mL of sample was purged during 30 min with ultra-high purity nitrogen previously stripped of Hg^0 by passage through Au traps, at a flow rate of 300 L min^-

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[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, subsequently desorbed by thermo-desorption and quantified by gas-phase AFS. Dissolved gaseous Hg net production kinetics were evaluated by incubating unfiltered water samples in an incubator located on the deck of the vessel exposed to sunlight radiations under temperature control achieved 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 in the absence of light (FEP Teflon bottles, wrapped in aluminium foil) and in the presence of light (unwrapped FEP Teflon bottles). The two series of experiments allowed to identify the part of photoreduction in the DGM net production and to estimate the DGM production. Transparent FEP Teflon bottles absorbed only 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.

3.3.3. Phosphorus

Soluble reactive phosphorus (SRP) was determined in seawater with an auto-analyzer using the standard molybdate blue method (Murphy and Riley, 1962) as detailed in the protocol by Aminot and Kérouel (2007). Particulate phosphorus (P_P) determination used the same colorimetric method but after magnesium nitrate oxidation (Ormaza-Gonzalez and Statham, 1996).

4. RESULTS

4.1. Rain and aerosol

Total Hg concentrations in rain water (bulk precipitation) varied from 10 to 80 pmol L^{-1}, with a mean of 31 ± 22 pmol L^{-1} (n = 13). This range is 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). The average HgT concentration calculated here for the period 2009-2010, is more than 2 times lower than that calculated for the 40 rain events sampled between January 2002 and May 2003 in a coastal site of Corsica (Northwestern Mediterranean), namely 70 ± 100 pmol L^{-1} (Cossa and Coquery, 2005). Total Hg concentrations in the 28 aerosol samples varied between 0.1 and 35.0 nmol g^{-1} with a mean of 6.9 ± 6.7 nmol g^{-1}. Dissolved gaseous Hg was not measured in rain samples.

4.2. Rhône River and its plume

During the low flow period of the Rhône River, HgT_F and HgT_P concentrations varied in the picomolar range (Table 1). Mercury was predominantly (95%) associated with suspended particles and its solid-solution partition (KdHg) was controlled by the one of organic carbon (Fig. 2, insert). On the other hand, HgT_P depicted a negative relationship with water discharge (Fig. 2). The variation of dissolved Hg concentrations (HgT_F) during the mixing of Rhône freshwater with Gulf of Lions saltwater, between the Barcarin site and the prodelta area, is illustrated in Figure 3a. Concentrations of HgT_F varied from 0.6 to 4.2 pmol L^{-1}, and tended to be higher in freshwater than in marine water samples (HgT_F vs Salinity, $p < 0.1$). The HgT_F concentrations in Low Salinity Water lenses (1-50 m) drifting on the shelf were in a similar range (0.6-3.5 pmol L^{-1}, Table 2, Fig. 3b). Their mean concentration (1.57 pmol L^{-1}) was 36 % lower (t-test, $p < 0.01$) than the HgT_F mean concentration in the Rhône River (2.45 pmol L^{-1}). Within the water lenses, HgT_F temporal variations were roughly synchronal with the sampling depth, with a sinusoidal-type shap in lense 1 (Fig. S3). In the lenses, total Hg was equally

distributed between the dissolved and particulates phases, with an average HgT_F/HgT_P ratio of 0.49.

Dissolved gaseous Hg concentrations were measured at 5 m depth during 18 hours-long time series (20th and 21[rst] May) and on three vertical profiles within the Low Salinity Water lenses (Fig. S4). Along the DGM profiles, the concentrations varied from 0.02 to 0.45 pmol L[-1], averaging 0.09 ± 0.11 pmol L[-1] (n = 37), whereas for the time series they varied from 0.04 to 0.33 pmol L[-1], averaging 0.13 ± 0.09 pmol L[-1] (n = 10). These ranges are similar to those reported by other authors for the Mediterranean Sea and other parts of the world ocean (e.g., Mason et al., 1998; Laurier et al., 2003; Andersson et al., 2006; Wängberg et al., 2008). Vertical DGM profiles showed a downward increase in concentrations from surface to 50 m at station S88 and S95; while a surface maximum was superimposed to this tendency at S108 (Fig. S4). The time series measurements produced the classical pattern of low DGM values during the night and higher levels during the day (insert, Fig. S4). *Ex-situ* incubation experiments showed clearly higher DGM production when exposed to sun light (0.021-0.058 pmol L[-1] h^{-1}) compared to DGM production in the dark (0.006-0.032 pmol L[-1] h^{-1}). Normalized to HgT, reduction rates were 1.3-4.5 % h[-1] and 0.7-3.4 % h[-1] for light and dark conditions, respectively.

4.3. Shelf and slope

The inner shelf (Stas. A-08, B-08, C-08 and D-09, 0-100 m bottom depth) and slope edge (Stas. E-06, L-01 and M-12, 100-300 m bottom depth) water columns were explored in March 2011 (CASCADE cruise). On the shelf, average concentrations HgT_{UNF} and HgT_F were 1.52 ± 1.00 (n = 36), and 0.80 ± 0.47 (n = 37) pmol L[-1], respectively (Fig. 4a). The dissolved HgT contributed roughly 58 % of HgT_{UNF} (Table 3), yielding an average HgT_F/HgT_P ratio of 1.11.

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Concentrations were highest along the A transect, i.e. the nearest to the Rhône River prodelta, especially at surface in the brackish water plume (Table 3, Fig. 4a). Elsewhere, vertical HgT profiles (Fig. 4a) were relatively uniformous whatever the depth for both filtered and unfiltered samples. Interesting to note are the very low concentrations (< 1 pmol L^{-1}) of HgT$_F$ on the inner shelf, especially at Stas. B, C and D (Table 3). Figure 4b shows the time variations observed at the head of Cap de Creus canyon (Sta. X) during the monitored eastern storm event. Conversely to the shelf profiles, we observed a significant increase of HgT$_{UNF}$ toward the bottom for Sta. X (Fig. 4b), a feature likely linked to shelf sediment resuspension and downslope export occurring during the storm.

At the base of the continental slope (Stas. S-230, L-03 and M-10), concentrations of HgT$_{UNF}$ ranged from 0.78 to 1.53 pmol L^{-1} with no clear differences between the two cruises (Fig. S5). With the exception of two high values at the surface, HgT$_{UNF}$ was significantly ($p<0.05$) higher below than above 100 m depth, suggesting removal in upper layer and regeneration below. The few DGM concentrations (n=6) measuredin surface water from the slope ranged from 0.05 to 0.09 pmol L^{-1} and never exceeded 12% of the respective HgT$_{UNF}$.

4.4. North Gyre

Temperature and salinity transects are illustrated in Figure 5. The main oceanographical feature was the presence of a high-temperature high-salinity layer between 200 and 500 m depth corresponding to LIW, i.e. a water mass from the Eastern Mediterranean Basin. The measured HgT$_{UNF}$ concentrations varied from 0.53 to 1.45 pmol L^{-1}, averaging 1.11 ± 0.13 pmol L^{-1} (n = 96). This concentration range is similar to those measured in 2004 in the Northwestern Mediterranean (Cossa and Coquery, 2005). Figure 5 illustrates the spatial distributions of HgT$_{UNF}$ along the South-North and West-East transects in the North Gyre

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water column. Maximum and minimum HgT_{UNF} concentrations occurred within the uppermost 100 m, whereas below 500 m depth, the concentrations were rather uniformous with an average of 1.12 ± 0.06 pmol L^{-1} (n = 67). Interestingly, dissolved oxygen and HgT_{UNF} distributions showed opposite patterns, especially when stratification of the water column was well established. In fact, the high HgT_{UNF} values coincided with low dissolved oxygen levels, which develop within the high salinity LIW, due to water stratification, (Fig. 5). Two profiles (L-05 and L-10) were also analyzed for total dissolved Hg (HgT_F). Particulate Hg (HgT_P) concentrations were calculated as the difference between HgT_{UNF} and HgT_F (Table S2). The dissolved HgT fraction constituted 74 to 91 % of the HgT_{UNF}, with lowest HgT_F concentrations occurring in the uppermost 100 m (Fig. 6). As a corollary, HgT_P/HgT_F ratios were generally between 0.1 and 0.35, but reached 0.45 at the surface.

Only one profile of DGM was performed in the North Gyre (Sta. S2400), with concentrations ranging from 0.05 to 0.14 pmol L^{-1} between the surface and 500 m depth. Between 500 m and 2500 m depth, the obtained values were being relatively constant, with a mean of 0.14 ± 0.04 pmol L^{-1} (n=4). This overall distribution was similar to that reported for the NWM (Ferrarra et al., 2003).

5. DISCUSSION

5.1. Sources and sinks of Hg on the shelf

5.1.1. The open sea source

The Northern Current is the main water supplier 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 that the shelf-slope water exchange represents ~10 % of the along-slope transport, namely 0.2 x 10^6 m^3 s^{-1}. The chemical characteristics of seawater entering the shelf are well represented in the 0-100 m water layer at Sta. Antarès (Fig. 1), where HgT_{UNF} mean concentration is 0.92 ± 0.07 pmol L^{-1} (n = 3). Based on these data, the estimated mean flux of Hg entering the shelf area *via* the Northern Current, mainly as dissolved species, is 5.7 ± 0.43 kmol yr^{-1}. The comparison with other Hg fluxes (see below) clearly suggests that the open sea is the main Hg source for the Gulf of Lions. Similar conclusions have been drawn for other coastal areas, including the Gulf of Main and the Gulf of Mexico (e.g., Sunderland et al., 2012; Harris et al., 2012).

5.1.2. Gross and net river inputs

Riverine Hg inputs mainly derive from the Rhône River solid discharges. Other Gulf of Lions rivers account for less than 15% of the total riverine particulate inputs (Gairoard et al., 2012). Concentrations of HgT_P tended to decrease with increasing Rhône River discharge during the 2009-2010 monitoring period, which was characterized by the absence of large flooding events (Fig. 2). This type of relationship between Hg and water discharge has commonly been observed in rivers under various hydrological regimes (e.g., Coquery et al., 1997; Quémerais et al., 1999) and was attributed to seasonal changes in the nature of the particles carried in freshwater. For example, HgT_P is correlated with the chlorophyll content of the particles in the Loire River (Coquery et al., 1997), suggesting Hg enrichment in the phytoplankton. In the Rhône River, Hg partitioning is governed by organic carbon distribution (Fig. 2, insert) and phytoplankton is abundant

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during low summer discharge, whereas minerals (usually less enriched in Hg) dominate during floods due to erosion and bed resuspension, (Harmelin-Vivien et al., 2010).

The gross fluxes of Hg exported by the Rhône River are estimated to be 0.13 kmol yr^{-1} for the dissolved and 2.7 kmol yr^{-1} for the particulate phases (see SI 1 for calculation details). According to Gairoard et al. (2012), the Rhône River contributes 85 % of the total riverine freshwater and 83 % of the total riverine particle discharge to the Gulf of Lions. Thus, if we hypothesize that other riverine outputs into the Gulf of Lions have Hg compositions similar to that of the Rhône River, the total Hg input from riverine sources to the Gulf of Lions water can be estimated at 0.15 and 3.2 kmol yr^{-1} for the dissolved and particulate phases, respectively. There seems to be a clear temporal trend of riverine inputs to the NWM, as our calculated dissolved HgT flux value (0.15 kmol yr^{-1}) is more than 3 times lower than a previous flux estimate based on the 1994-1995 monitoring period (Cossa and Coquery, 2005) and more than 10 times lower than the estimate proposed at the end of the eighties (Cossa and Martin, 1991). This time-trend is supported by the vertical distribution patterns of HgT concentrations recorded in sediments from the Rhône prodelta (Cossa et al., this issue) or in the Pierre Blanche Lagoon (Elbaz-Poulichet et al., 2011), which all show decreasing Hg concentrations since the 1960s. It should be noted that this calculation did not take into account the submarine groundwater discharge to the Gulf of Lions, estimated to be 2-30% of the Rhône River runoff (Ollivier et al., 2008), which may be a non-negligible, yet not quantified, Hg source for the coastal water bodies (e.g., Laurier et al., 2007). For comparison purpose, it is interesting to note that the annual Hg inputs from the waste water treatment plant of the City of Marseille (850 000

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inhabitants) have been approximated to be 0.016 kmol, with 75% in the particulate phase (Jany and Zebraki, 2012).

The distribution pattern of HgT_F *versus* salinity during the freshwater-seawater mixing (Fig. 3) shows highly variable concentrations at low salinities, but fails to evoke any departure from a conservative mixing pattern, similarly with the behaviour of most other trace elements studied in the water of the Rhône Delta (Elbaz-Poulichet et al., 1996). The estuarine water escapes the mouth of the Rhône River as a turbid desalted plume that is advected, as Low Salinity Water lenses, along the Gulf of Lions shelf and the upper slope (Naudin et al., 1997). The Low Salinity Water lesnses constitute quite isolated water masses, in which the average HgT_F concentrations were 36 % lower (*t*-test, *p< 0.01*) than the HgT_F mean concentration in the Rhône River waters, 49 % higher (*t*-test, *p< 0.01*) than the HgT_F mean concentration calculated for the entire Gulf of Lions shelf water, but not significantly different (*t*-test, *p< 0.01*) from that in the prodeltaic zone (Sta. A) (Table 3). However, the Hg distribution in the Low Salinity Water lenses does not support any removal or mobilization of dissolved HgT (Fig. 3b, Fig. S3). Based on HgT partition and behavior during the estuarine mixing, occurring in the plume and in the Low Salinity Water lenses, the gross Rhône River dissolved Hg flux can be considered as similar to the net input flux into the Northwestern Mediterranean. Bearing in mind dissolved Hg species are readily available for uptake by phytoplankton, it is interesting to note from an ecological point of view that, within the Gulf of Lions shelf, the dissolved HgT flux from riverine source represents only 2.6 % of the HgT flux derived from the marine source.

5.1.3. Export and accumulation on the shelf

The fate of particulate Hg in the Rhône River plume and on the shelf, depends on the type of

suspended material involved. Generally, in rivers, the coarser particles have lower Hg concentrations (e.g., Guédron et al., 2012). Coarse material settles down near the Rhône River mouth, mostly at 4-5 m depth (Maillet et al, 2006; Marion et al, 2010; Pruski et al, 2015). Conversely, Hg-rich particles are likely present in the Rhône plume and within its well described, associated benthic nepheloid layer (Naudin and Cauwet, 1997; Durrieu de Madron et al., 2000; Many et al., 2016). The plume is transported together with the Low Salinity Water lenses, whereas the nepheloid layer progressively builds a seaward-drifting muddy sediment layer (Marion et al., 2010). Based on the burial efficiency of riverine particles in the sediment prodelta, varying from 20 to 54% under various hydrological regimes (Noël, 1996; Maillet et al., 2006; Dufois, 2008; Lansard, 2005; Pastor et al., 2011; Dufois et al., 2014), the estimated quantity of Hg currently buried in the prodelta sediments is in the range 0.64-1.73 kmol yr^{-1}. The westward Hg$_P$ export on the Gulf of Lions shelf results from sedimentation/resuspension processes primarily related to eastern storms (Ulses et al., 2008b; Marion et al, 2010; Dufois et al, 2014), and from dispersion within the benthic nepheloid layer (Lansard et al, 2006). This material eventually reaches the head of the Cap de Creus canyon at the southwestern end of the Gulf of Lions, from where it may be exported to the slope during dense shelf water cascading or downwellings induced by storms events. For example, the 3-days storm that occurred during the CASCADE cruise, on 12-15 March 2011, was recorded at Sta. X at the head of Cap de Creus canyon (Fig. 1). Based on present results and an estimated downwelling mass flux of 0.4 x 10^{12} g (Bourrin et al., 2015; Dumas et al., 2014), the amount of Hg exported this way during the recorded event was 0.2 kmol. On the other hand, the Hg associated with suspended material escaping the shelf represents around 0.32 kmol yr^{-1} or 10 % of the Rhône River inputs, according to the sedimentary budget established by Dufois et al.

(2014) and Hg concentrations determined here. Accordingly, our results suggest that one downwelling event, such as the one recorded in March 2011, can account for a large proportion (i.e., 62%) of the annual particulate Hg exported seawards from the Gulf of Lions.

The Hg accumulated in the sediments of the shelf can be roughly estimated to be ~4.5 kmol yr^{-1}, based on a mean sediment accumulation of ~0.1 g cm^{-2} yr^{-1} (Durrieu de Madron et al., 2000) and a mean Hg concentration in the surface shelf sediment of ~0.375 nmol g^{-1} (unpublish results).

5.1.4. Atmosphere/water exchanges

Based on a mean Hg concentration in rain of 31 pmol L^{-1}, a precipitation average of 332 mm yr^{-1} (Lebeaupin Brossier et al., 2012) and a surface area of 12 x 10^3 km^2 (Durrieu de Madron et al., 2003), the mean atmospheric wet Hg input to the Gulf of Lions is ~0.12 kmol yr^{-1}. According to Vincent et al. (2016), the aerosol deposition fluxes for 1-year measurements ranged from 0.9 to 7.4 g m^{-2} yr^{-1} from North to South of the Western Mediterranean. We chose the median value to calculate the Hg dry deposition on the Gulf of Lions. Using a mean Hg concentration in aerosols of 6.9 nmol g^{-1}, the mean atmospheric dry input of Hg to the Gulf of Lions is ~0.33 kmol a^{-1}, which is almost 3-times higher than the total wet deposition. According to Zagar et al. (2013) modelling Hg deposition onto the entire Mediterranean Sea, with MECAWEx model, gave also a dry to wet ratio greater than 1. More recent modelling gives a ratio close to 1 (Gencarelli et al., 2015).

Photoreduction and biologically mediated reduction appear to be the most likely DGM sources for the shelf water (Fig. S4). A photoreduction mechanism, as described by Amyot et al. (1997), is supported by the occurrence of a clear DGM maximum during the day-light period (see insert in Fig. S4). From incubation experiments we calculated DGM production

rates from 16 to 58 fmol L^{-1} h^{-1} in light and from 6 to 35 fmol L^{-1} h^{-1} in dark conditions. A 2-fold increase of reduction under light conditions, compared to dark conditions, clearly suggests that photochemistry (at least) equals biologically mediated reduction (Fig. S6), as already suggested for coastal water masses in other areas of the global ocean (e.g., Amyot et al., 1997; Fitzgerald and Lamborg, 2005). In fact, our results clearly suggest that in the present experimental conditions photochemistry (at least) equalled biologically mediated reduction.

From our measurements and using an empirical gas exchange model (Wanninkhof, 1992), — with a piston velocity of 5 m day^{-1}, a total gaseous Hg concentration in the atmosphere of 11 ± 3 pmol m^{-3} (Marusczack et al., 2015) and a mean DGM concentration in seawater of ~150 pmol m^{-3} — we calculate a Hg evasion rate from surface waters to the atmosphere of 0.6 nmol m^{-2} d^{-1}. This estimate is in the high range of the values calculated by Andersson et al. (2006) for the entire Mediterranean (0.2-0.6 nmol m^{-2} d^{-1}). Applying these values to the Gulf of Lions shelf area (12×10^3 km^2) gives an annual evasional Hg flux to the atmosphere of ~2.6 kmol yr^{-1}, which is equivalent to almost one half of the Hg inputs from marine sources to the Gulf of Lions (5.7 kmol yr^{-1}). This atmospheric evasion flux consistently accounts for the low concentrations of dissolved Hg (< 1 pmol L^{-1}) found in the shelf water at the stations B, C and D (Fig. 4). Thus, the shelf clearly is an area of intense Hg evasion to the atmosphere.

5.2. Mercury enrichment in the WMDW

The North Gyre waters are separated from coastal waters by the Northern Current, which continuously flows along the slope (Fig. 1). Water bodies in the North Gyre normally consist of WMDW underlying LIW and AW. During the first days of the CASCADE cruise

(encompassing Stas. L-05, L-08 and S2400), the water column in the North Gyre was still rather well mixed following a strong storm with northerly wind directions, and WMDW occupied the convection region (Fig 5). Then, the water column rapidly restratified due to the advection of surrounding LIW and AW over the convective region as observed for Stas. Antares, L-10, L-12, M-01, M-03, M-05, M-08, and the WMDW was confined to depths greater than 1000 m. Based on the measurements in the samples from all depths sampled in the well-mixed water column and those in the samples collected deeper than 1000 m for the stratified water columns, we obtained an average HgT_{UNF} concentration of 1.11 ± 0.06 pmol L^{-1} (n = 60). This value is slightly but significantly higher (*t*-test, *p<0.01*) than the average HgT_{UNF} concentration in the LIW, which is 1.01 ± 0.08 pmol L^{-1} (n = 18) according to Cossa and Coquery (2005). Recent measurements performed in AW collected west of the Gibraltar Strait (35° 30.82' N; 09° 09.21' W) provided HgT_{UNF} concentrations varying from 0.2 and 0.3 pmol L^{-1} (n=4) between the surface and 200 m depth, i.e. in the the water entering into the Mediterranean (Knoery et al., 2013). These low HgT_{UNF} concentrations in the AW mixed layer are likely due to both Hg evasion to the atmosphere and Hg scavenging by biological pumping in the stratified North Atlantic waters.

Thus, considering the HgT_{UNF} concentration levels in AW and LIW, there is an important addition of Hg within the Northwestern Mediterranean to reach the concentrations observed in the WMDW. According to a simulation approach, applied to the 2012-2013 period, half of the dense water is formed from the transformation of LIW and former dense water, and half from AW (Waldman et al., 2016). However, formation of WMDW is annually variable and the proportions of LIW and AW in the WMDW at

the time of our cruise are unknown. Thus, we conservatively estimate HgT_{UNF} enrichment of WMDW relative to conservative mixing of LIW and AW as ≤ 0.1 pmol L^{-1}. A simple calculation can be done for estimating the Hg flux needed to increase the North Gyre water column HgT_{UNF} concentration by 0.1 pmol L^{-1}: For a 2000 m deep water column the corresponding amount of Hg is 0.2 µmol m^{-2}. Considering a water residence time of 20 years in the Western Mediterranean basin (Béthoux et al., 2005), the minimum annual flux should be 10 nmol m^{-2} yr^{-1}. Mercury deposition from the atmosphere, diffusion from sediments and continental shelf advection are candidate sources for this addition.

A bulk atmospheric wet deposition of 10.3 nmol HgT m^{-2} yr^{-1} was calculated from the mean concentration in rain (31 pmol L^{-1}) and a precipitation average of 332 mm yr^{-1} over the Northwestern Mediterranean Sea (Lebeaupin Brossier et al., 2012). Accordingly, the required flux for the estimated HgT_{UNF} enrichment in WMDW is equivalent to the entire wet deposition or to one third of the total Hg atmospheric deposition calculated in the previous section 5.1.4.

Addition of Hg from a sediment source would be consistent with findings by Ogrinc et al. (2007), who proposed a potential Hg diffusive flux from the Northwestern Mediterranean sediment to the overlying water column in the same order of magnitude (18 nmol m^{-2} yr^{-1}). However, a diffusive flux of dissolved Hg is unlikely, since the uppermost layers of the continental rise and abyssal plain sediments in the North Gyre of the Northwestern Mediterranean are known to be oxic down to several cm below the sediment-water interface (Buscail et al, 1997). In fact, Hg diffusion out of the sediment has never been demonstrated for such oxic environments, where oxyhydroxides are thought to act as a trap for diffusing species at the benthic interface (e.g., Bothner et al., 1980; Gobeil and Cossa, 1993; Feyte et

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al., 2010). However, deep convection, such as the one occurring in winter 2011, is known to cause resuspension of deep-sea sediments, followed by vertical mixing in the whole water column (Stabholz et al., 2013; Puig et al., 2013), making a sedimentary source plausible. In the absence of any quantitative evaluation of such resuspension processes on the annual scale, the resulting Hg release to the water column remains unknown.

Mercury advection from the shelf could also contribute to the WMDW Hg enrichment. Although there is no signal in the HgT vertical profiles supporting the idea of a large continental shelf Hg advection within the North Gyre (Fig. 5), the HgT_{UNF} mean concentration in the deep profiles near the foot of the slope calculated from 2006 data (1.29 ± 0.17 pmol L^{-1}; n = 27; Fig. S5) is significantly higher (*t*-test; *p<0.01*) than the average WMDW HgT_{UNF} concentration (1.11 ± 0.06 pmol L^{-1}, n = 60). However, advection from the shelf would not affect the dissolved phase, since the lowest HgT_F concentrations occur on the shelf (Stas. B, C and D, Fig. 4a) and HgT_{UNF} distributions at the edge of the shelf point to the presence of substantial amounts of particulate HgT, especially near the bottom of the water column during the monitored stormy downwelling period (Sta. X, Fig. 4b). According to our calculation (see section 5.1.3), the amount of Hg advected from the shelf to the North Gyre deep waters, during the March 2011 downwelling event, was ~0.2 kmol, i.e., ~60% of the particulate Hg escaping the shelf each year. Atmosphere, deep-sediment resuspension and shelf are, thus, the most probable sources of the Hg enrichment in the WMDW. However, more research is needed to solve that issue. Whatever the Hg-enrichment source is, the WMDW, which is advected westward through the Gibraltar Strait, constitutes a Hg source for the North Atlantic Ocean.

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Figure Captions

Figure 1. Study site in the Northwestern Mediterranean, with main circulation patterns. Stations location during CASCADE cruise (March 2011). Station coordinates are given in the Table S1.

Figure 2. Particulate Hg (HgT_P) *versus* Rhône River water discharge at station SORA (Arles). Relationship between solid-solution partitions of HgT and organic carbon (C) expressed on the basis of their partition coefficients (Kd = conc in solid / concentration in solution, L kg^{-1}).

Figure 3. Mercury in the freshwater-seawater mixing. Dissolved total Hg (HgT_F) *versus* salinity in (a) the estuarine mixing zone, (b) the Low Salinity Water lenses (LSW) drifting on the shelf.

Figure 4. Total Hg (HgT) vertical profiles in the water of the shelf and the continental slope of the Gulf of Lions. The UNF and F subscribes refer to unfiltered and filtered samples. (a) Shelf stations, (b) station X on the slope at the head of the Cap de Creus canyon, points associated with an asterisk refer to a time series recorded during the downwelling of shelf water.

Figure 5. Transect of potential temperature, salinity, dissolved oxygen and total Hg (HgT_{UNF}) in the North Gyre water column. M-transect and L-transect refer to North-South and West-East sections, respectively (see Figure 1 and Table S1 for station localizations).

Figure 6. Mercury partition in the Northern Gyre. Vertical profiles of total Hg (HgT) at Stas. L-05 and L-10 in the North Gyre water column. F and P subscribes refer to dissolved and particulate phases, respectively.

Tables

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

	HgT_F (pmol L^{-1})	HgT_P (nmol g^{-1})
Period March 2009 – June 2010 (this study)		
Average ± SD (n)	2.45 ± 2.05 (24)	0.85 ± 0.45 (27)
Min. – Max.	0.40 – 9.25	0.20 – 2.15
Period June 1994 – June 1995 (Cossa and Coquery, 2005)		
Average ± SD (n)	5.30 ± 2.95 (24)	2.40 ± 2.00 (24)
Min. – Max.	1.40 – 16.50	0.40 – 7.50

Table 2. Low Salinity Waters drifting (Lenses 1 and 2) on the shelf and slope waters (Sta. S230) (BIOPRHOFI cruise, see figure S2 for Sta. locations). A statistical summary of HgT measurements: average ± standard deviation (number of samples) and range (Min. – Max.).

	HgT (pmol L^{-1})	
Low Salinity Waters (1-50 m layer; bottom ≤120 m) Filtered samples (<0.4μm)	1.57 ± 0.74 (84)	0.61 – 3.50
Slope Waters (< 100 m layer; bottom at 1386 m), unfiltered samples	1.22 ± 0.13 (3)	0.98 – 1.35
Slope Waters (100-900 m layer; bottom at 1386 m), unfiltered samples	1.41 ± 0.06 (4)	1.33 – 1.48

Table 3. (CASCADE cruise). Summary statistics for HgT_{UNF}, HgT_F (<0.4μm) concentrations in Gulf of Lions shelf, slope and North Gyre water samples. Average ± Standard deviation (number of samples) and range (Min. – Max.). Station locations are indicated in Figure 1 and coordinates are given in Table S1. (*) Station X, located at the head of Cap de Creus canyon, was monitored during a storm event.

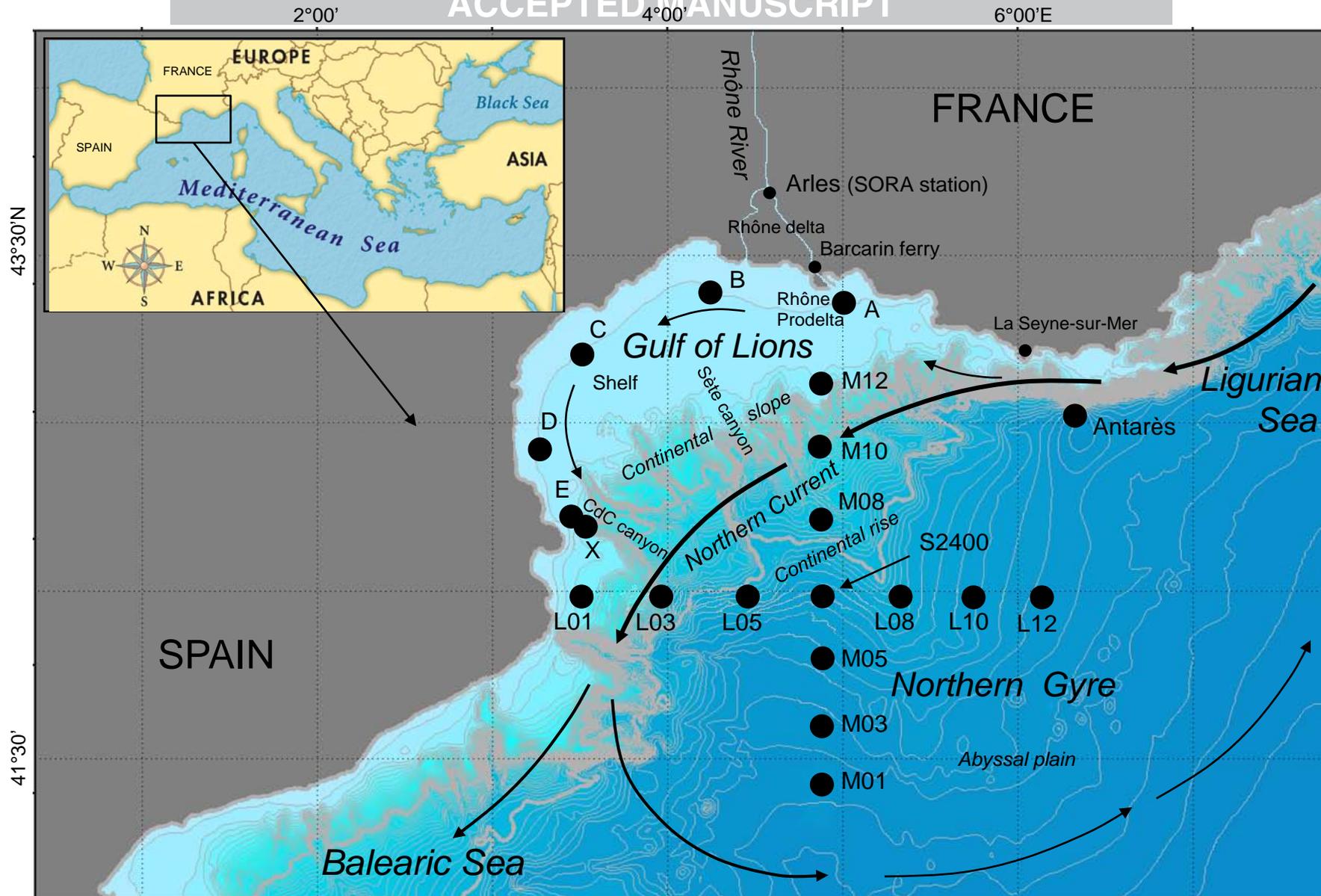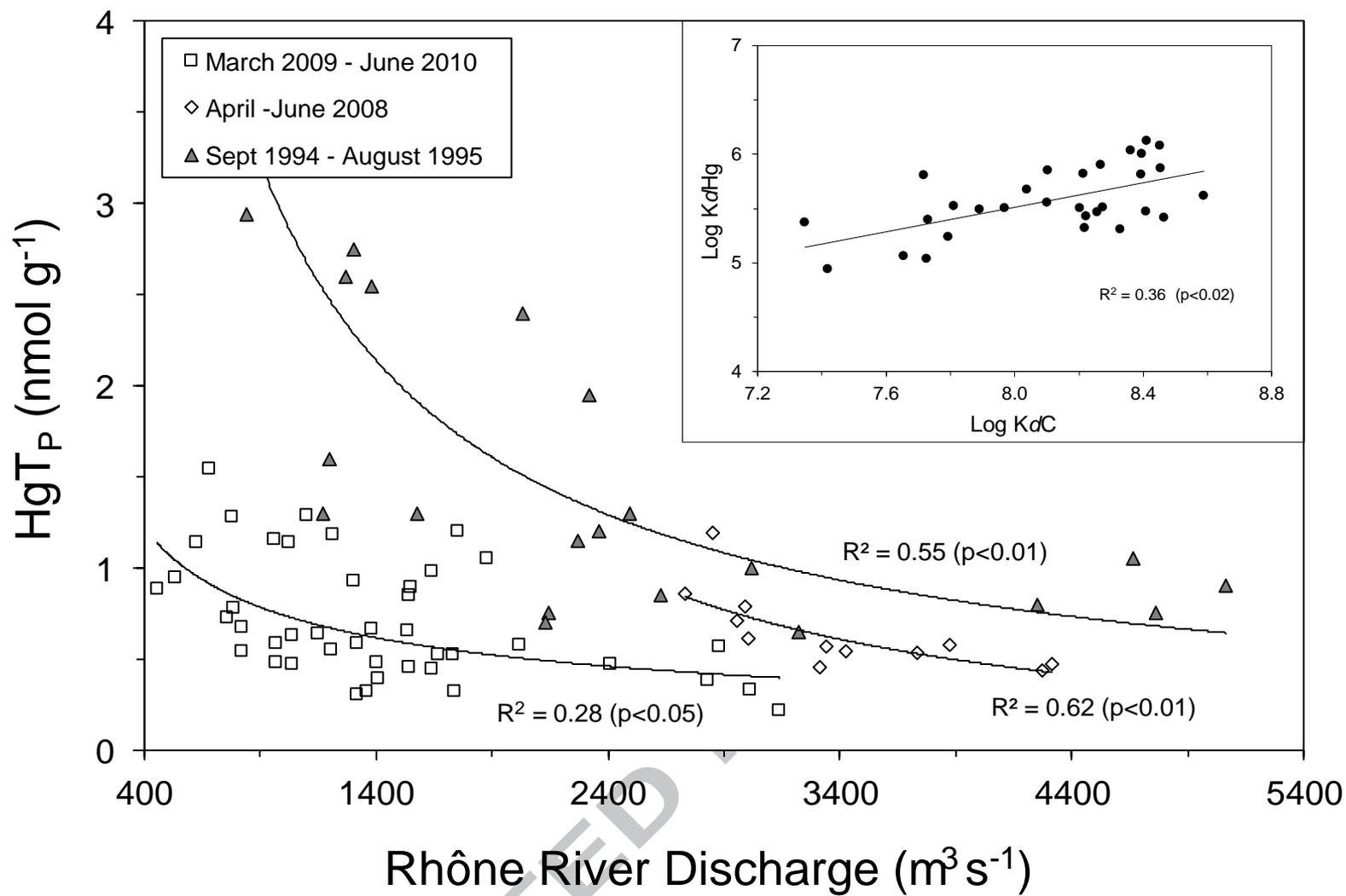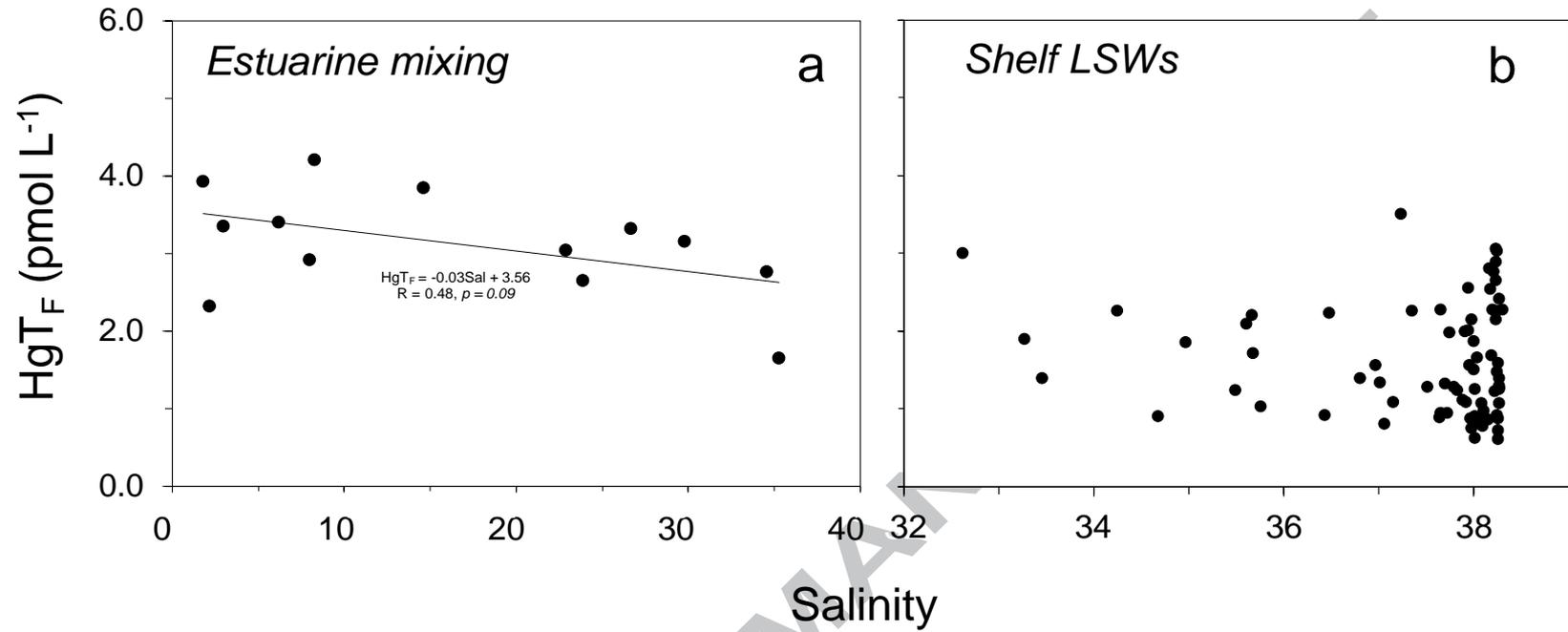| Station (water layer sampled)	HgT_F (pmol L^{-1})	HgT_{UNF} (pmol L^{-1})	HgT_F/HgT_{UNF} (%)
Inner shelf (bottom <100 m)			
A (1-90 m)	1.20 ± 0.89 (7)	2.04 ± 1.11 (7)	56 ± 12 (7)
	0.73 – 3.20	1.27 – 4.47	42 – 72
B (1-90 m)	0.65 ± 0.13 (10)	1.17 ± 0.29 (10)	57 ± 14 (10)
	0.49 – 0.88	0.78 – 1.61	43 – 89
C (1-90 m)	0.64 ± 0.26 (11)	1.40 ± 1.08 (10)	53 ± 21 (10)
	0.43 – 1.38	0.58 – 4.20	16 – 87
D (1-90 m)	0.83 ± 0.29 (9)	1.61 ± 1.23 (9)	64 ± 19 (9)
	0.66 – 1.58	0.92 – 3.80	24 - 82
A/B/C/D (1-90m)	0.80 ± 0.47 (37)	1.52 ± 1.00 (36)	58 ± 17 (36)
	0.43 – 3.20	0.58 – 4.47	16 – 89
Slope edge and head of the Cap de Creus canyon (bottom at 100-300 m)			
E (2-290 m)	0.55 ± 0.01 (2)	0.99 ± 0.52 (20)	69 ± 7 (2)
	0.54 – 0.56	0.58 – 2.94	64 – 73
X*(10-290 m)	1.11 ± 0.50 (7)	1.83 ± 0.66 (28)	63 ± 12 (7)
	1.05 – 1.16	1.00 – 2.83	45 - 80
L-01 (5-250 m)	–	1.07 ± 0.10 (6)	–
	–	1.00 - 1.26	–
M-12 (10-130 m)	1.09 ± 0.20 (4)	1.02 ± 0.12 (4)	91 ± 11 (4)
	0.85 – 1.33	0.93 – 1.14	78 – 86

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6