Mediterranean Mercury Assessment 2022: An Updated Budget, Health Consequences, and Research Perspectives

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Critical Review

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ABSTRACT: Mercury (Hg) and especially its methylated species (MeHg) are toxic chemicals that contaminate humans *via* the consumption of seafood. The most recent UNEP Global Mercury Assessment stressed that Mediterranean populations have higher Hg levels than people elsewhere in Europe. The present critical review updates current knowledge on the sources, biogeochemical cycling, and mass balance of Hg in the Mediterranean, and identifies perspectives for future research especially in the context of global change. Concentrations of Hg in the Western Mediterranean average 0.86 ± 0.27 pmol L^{-1} in the upper water layer and 1.02 ± 0.12 pmol L^{-1} in intermediate and deep waters. In the Eastern Mediterranean, Hg measurements are in the same range but are too few to determine any consistent oceanographical pattern. The Mediterranean waters have a high methylation capacity, with MeHg representing up to 86 % of the total Hg, and constitute a source of MeHg for the adjacent North Atlantic Ocean. The highest MeHg concentrations are associated with low oxygen water masses suggesting a microbiological control on Hg methylation, consistent with the identification of *hgcA*-like genes in Mediterranean waters. MeHg concentrations are twice as high in the waters of the western basin compared to the ultra-oligotrophic eastern basin waters. This difference appears to be transferred through the food webs and the Hg content in predators to be ultimately controlled by MeHg concentrations of the waters of their foraging zones. Many Mediterranean top-predatory fish still exceed European Union

regulatory Hg thresholds. This underlines the necessity of monitoring the exposure of Mediterranean populations, to formulate adequate mitigation strategies and recommendations, without advising against seafood consumption. This review also points out other insufficiencies of knowledge of Hg cycling in the Mediterranean Sea, including temporal variations in air-sea exchange, hydrothermal and cold seep inputs, point sources, submarine groundwater discharge, and exchanges between margins and the open sea. Future assessment of global change impacts under the Minamata Convention Hg policy requires long-term observations and dedicated high-resolution Earth System Models for the Mediterranean region.

Introduction

Mercury (Hg) has been classified by the United Nations Environment Programme (UNEP) as a chemical element toxic to living organisms including humans[1, 2, 3]. One group of its compounds, methylated mercury (MeHg), damages the human nervous system[4, 5, 6], and has been linked to cardiovascular disease[7]. Exposure of top predators to MeHg is caused by its high biomagnification potential within aquatic food webs[2, 8,]. Marine fish consumption is the main source of MeHg to humans[2, 8, 9, 10]. Hg is of global environmental concern, because of the major perturbation of its natural cycle by human activities, its long-distance transport *via* the atmosphere resulting in its ubiquity in terrestrial and marine ecosystems, and finally because of its long persistence in biologically-crucial zones of the aquatic environment[11, 12, 13]. The global issue of Hg has begun to be confronted by the adoption of the Minamata Convention, which entered into force in 2017 under the auspices of UNEP to reduce human and ecosystem Hg exposure.

The recent Global Mercury Assessment (GMA 2018)[1] highlighted key policy-relevant findings and includes an updated inventory of anthropogenic Hg releases: artisanal and small-scale gold mining, fossil fuel and biomass burning, waste incineration, smelters, and from the re-mobilization of anthropogenic Hg deposited in the past to soils, sediments, water bodies, dumping grounds, and mine-tailings. Anthropogenic Hg emissions have been substantial since the Industrial Era, and have left a detectable environmental imprint for more than 2000 years[14]. Moreover, it has been estimated that 95 % of Hg emissions occurred in the last 500 years and that they have increased by 1.8 % per year during the 2010-2015 period[15, 16]. The global Hg budget, updated in 2018[13], states that current Hg concentrations in the global

atmosphere, surface, and deep marine waters have increased respectively by 450, 230, and 12-25 % above levels prevailing during the pre-Colombian period[11], i.e., before ~1450 CE. This budget however presents large uncertainties, in particular, local differences are to be expected, due to specific geographical, geological, biological, and anthropogenic factors.

The GMA 2018[1] also stresses that Mediterranean (MED) populations tend to have higher Hg levels than people from Asia, North America, and Europe. Already, 50 years ago, high Hg levels were observed in MED fish and marine mammals[17, 18], and these findings have been confirmed several times[19, 20, 21]. It has been recently suggested that Hg accumulation rates in bluefin tuna are the highest in the individuals from the MED[22] and that certain birds linked to the marine ecosystem could be at risk of suffering long-term, Hg-related effects[23]. These observations suggest specific features and a particular vulnerability of this region and emphasize the need to reassess, there, the state of the art on Hg. The present Critical Review aims to summarize and update current knowledge on the biogeochemistry of Hg in the MED, including its main implications for human health, and to identify perspectives for future research activities in this field.

1. The marine mercury cycle and relevant Mediterranean-specific features

The main chemical reactions within the Hg cycle in the environment may be roughly summarized by the interconversions of elemental Hg (Hg^0), inorganic divalent Hg (Hg_i^{II}), and organic divalent, including mono- and dimethylated species (CH_3Hg^+/MMHg and CH_3HgCH_3/DMHg, hereafter collectively abbreviated as MeHg). Mobility through the atmosphere is favored by volatile Hg^0, and through the hydrosphere by the solubilities of various Hg^{II} species. A summary of the latest scientific advances on the global Hg biogeochemical cycle is available in a recent paper[24]. Due to its volatility, Hg is dispersed in the global atmosphere. Part of it is redeposited onto continental and sea surfaces, where it is incorporated into biota mainly as MeHg. MeHg biomagnification along the food web is its main source of Hg for top predators, with a bioconcentration factor up to 10^7 (Ref. 25). The result is that some marine predators eaten by human populations or other animals are the main sources of their exposure to MeHg and as such a major risk of Hg poisoning[8]. A more detailed summary of the biogeochemical Hg cycle is given in the Supporting Information (SI.1).

The MED is a semi-enclosed sea (Fig. 1), with a water residence time of around 100 years, characterized by marked North-South and East-West gradients, mainly driven by the different physiographies of the two basins, the different terrestrial nutrient loadings, and the cyclonic and anticyclonic wind-driven current structures[26, 27]. The geological context, the contrasting hydrodynamic regimes, and the biogeochemical functioning of the MED have several characteristics important to the MED Hg cycle. In addition, the MED has been identified as a climate change hotspot[28, 29].

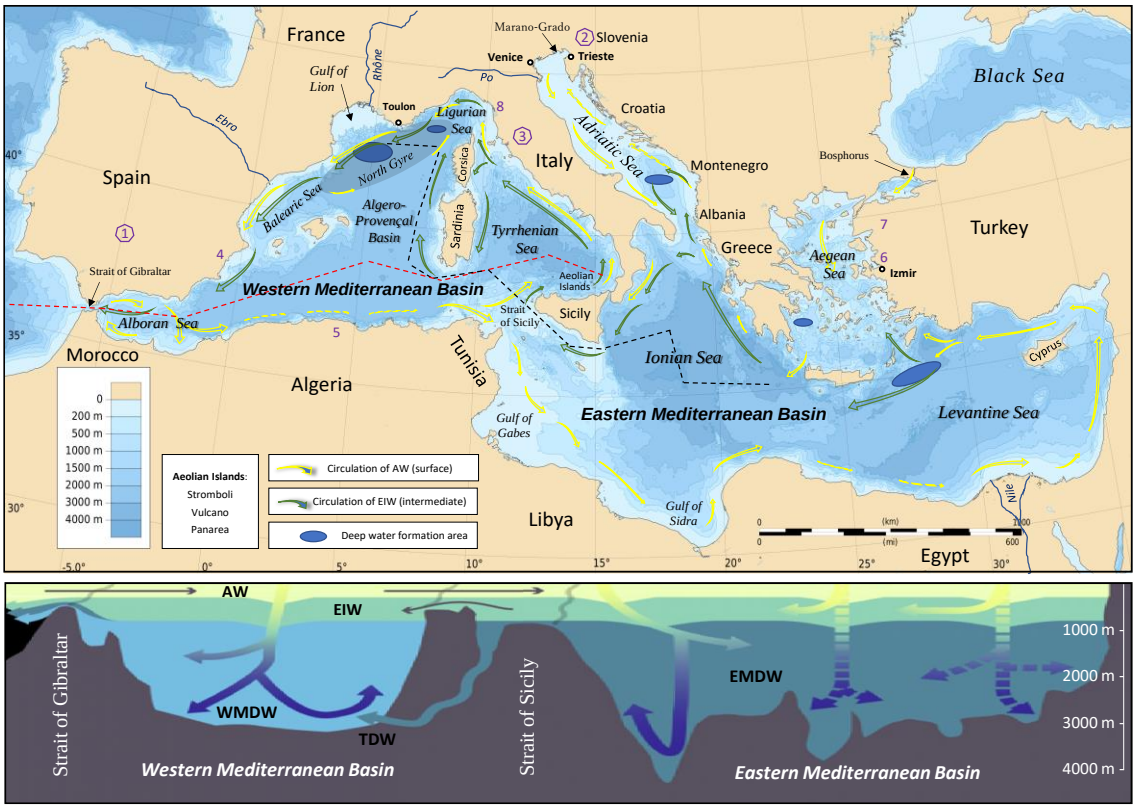


Figure 1. *The Mediterranean Sea with its main rivers and a schematic of water circulation. Purple numbers refer to Hg ore deposits: (1) Almaden, Spain, (2) Idrija, Slovenia, and (3) Monte Amiata are the main ones; other minor Hg deposits include (4) Azogue Valley (Pulpi), Spain, (5) Numidia, Algeria, (6) Karaburn, Turkey, (7) Kuçukyenice, Turkey, and (8) Levigliani, Italy. The red dash line refers to the Figure 2 transect. The black dash line refers to the Figure 3 transect. Dash arrows refer to seasonal circulation paths. The lower part of the figure is modified from Ref. 27. www.ifremer.fr/lobtln/COURANTS/SCHEMA_3D_MED_LABELS_EN.jpg.*

The Iberian Hg belt, where cinnabar (HgS) is the principal Hg ore, is found along the edges of the MED. It extends from Spain (Almaden) to Italy (Monte Amiata), Slovenia (Idrija), Algeria (Numidia belt), and Aegean Turkey (Karaburun) (Fig. 1). In addition to these natural sources, mining and other anthropogenic activities have mobilized large quantities of Hg that are now buried in coastal sediments. Among the

most relevant anthropogenic legacy Hg hotspots in the MED, are the Gulf of Trieste (with 13 000 Mg of anthropogenic Hg accumulated in the sediments[30, 31]), Marano Grado Lagoon (271 Mg[32]), Venice Lagoon (20 Mg[33]) in the Eastern MED (EMED), and the Toulon Bay (26 Mg[34]) in the Western MED (WMED) (Fig. 1). These Hg reservoirs can maintain steady inputs to the water column. Also, Hg-laden sediments may be remobilized and transported off-shore during floods or storms. Mercury inputs to the MED from hydrothermal vents are suspected but are not yet constrained[35]. Elevated Hg concentrations have been found in shallow hydrothermal fluids[36] and terrestrial volcanoes[37]. Subaerial volcanic Hg emissions in the Mediterranean region are dominated by the Aeolian Island volcanoes Vulcano and Stromboli, and by Mt Etna in Sicily[38] (Fig. 1).

Since it has become possible to determine accurately ultra-trace levels of Hg in ocean waters, several mass budgets for Hg in the MED have been established[39, 40, 41]. The first budget concludes that Hg entered through the Gibraltar Strait as inorganic Hg and was exported to the North Atlantic Ocean with a larger proportion of MeHg[39]. Another conclusion was that atmospheric exchanges are the main source and sink of Hg in the MED[41]. Hg exchanges at the sediment/water interface and the influence of hydrothermal vents are currently much less well constrained. The ultimate sources of water-column MeHg are currently under debate[42, 43]. The experimental estimates of Hg methylation rates[44, 45] suggest that the consequence of even a small change in these transformation rates would have a major impact on the levels of MeHg, which is the main factor governing the entry of Hg into the food webs. Continental Hg sources, namely rivers and groundwaters, have not yet been considered with sufficient attention in the karstic MED environment. Large discrepancies also exist between estimates of Hg transport in water masses, due to variations in Hg water column concentrations over the last 30 years[39, 40, 41]. These variations in Hg flux estimates may be due to (i) the observed decrease in Hg concentrations in North-Atlantic surface waters which can be over 50 % between 1989 and 2012[46], but also to (ii) variations in the surface water inflow estimated at Gibraltar[47]. Furthermore, the residence time of water in the WMED is shorter than 50 years and biogeochemical conditions and Hg fluxes may vary over a decadal time scale[27, 29]. In summary, the steady-state Hg fluxes in the different MED biogeochemical compartments are far from being well-established, warranting a revisit of Mediterranean Hg dynamics and budget. Moreover, Hg accumulation in biota is a multi-causal

process[21, 48] that is ultimately determined not only by past Hg emissions and their temporal evolution, but also by changes in biogeochemical, climate-induced, and biologically mediated processes[49]. Thus, the ecological and health consequences of the present Hg cycle in the MED will likely further evolve with the climate changes expected over the next decades.

2. Updating the Mediterranean Hg cycle

2.1. Emissions, evasions, and deposition

An early assessment of the total anthropogenic Hg emissions of countries bordering the MED was about 100 Mg for the year 1995 (i.e., equivalent to a third of European or 5% of global anthropogenic emissions)[50]. Thirty (30) Mg resulted from the burning of fossil fuels, 29 Mg from the incineration of household wastes, 28 Mg from cement production, and 10 Mg from the production of chlorine and lye. In addition, the total amount of Hg released to the atmosphere from forest fires in the Mediterranean region accounted for 4.3 Mg y^{-1} (Ref. 51) and 7 Mg y^{-1} from volcanoes (see section 2.5.). The GMA 2018[1] indicates that between 2010 and 2015 anthropogenic emissions from the (then) EU28 (EU28 was the abbreviation of the 28 countries of the European Union) decreased by 12.5 % while those from North Africa increased slightly (+15.8 %). Both EU28 and North Africa increased in large-scale gold production, and while the EU28 countries reduced emissions from the oil industry and power plants, North Africa increased emissions from domestic and industrial fossil fuel combustions. The phasing out of Hg in chlor-alkali plants in EU28 led to a two-thirds reduction in emissions from chemical industries.

Since the year 2000, numerous oceanographic and more local near-coast measurement campaigns have been carried out to determine Hg species concentrations in the marine boundary layer and the water column[52, 53, 54, 55, 56]. Evasion fluxes of Hg are calculated using measured dissolved gaseous mercury (DGM) and $Hg^0_{(g)}$ concentrations, wind speed, and sea surface temperature, and several approaches can and have been used to estimate MED efflux/volatilization/atmospheric rates[57, 58, 59, 60]. Details about the medalling approaches to calculate gas transfer velocities at the air-sea interface are given in Supporting Information (SI.2)[61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71].

Averaged Hg evasion fluxes for the MED are reasonably consistent across the literature, 2-8 ng m^{-2} h^{-1}, with higher values typically found in summer and autumn (up to 20 ng m^{-2} h^{-1} was reported[60] for a short period), and for the Eastern Basin compared to the Western Basin[57, 58, 59, 60]. The higher values obtained for the Eastern Basin stem possibly from tectonic activity. These fluxes lead to estimates of annual evasion of Hg^0 to the atmosphere between 50 and 100 Mg y^{-1} (Table 4 in Ref. 71). While the estimated average fluxes are close between the studies, all the above studies indicate that the Hg^0 flux to the atmosphere can be extremely variable over space and time. Indeed, they depend on DGM concentrations, temperature, and exponentially on wind speed, which are all highly variable. There are also several Hg "hot spots" in the MED, both due to tectonic activity and regions impacted by anthropogenic activities where significantly higher evasion fluxes can occur[72, 73]. A description of atmosphere surface exchange measurement techniques can be found in a recent review[74].

Mercury deposition to the MED is a combination of Hg^{II} wet deposition (rainfall), dry deposition of gaseous, and particulate oxidized Hg^{II} forms. There are several "European Monitoring and Evaluation Programme" sites that measure Hg wet and/or dry depositions. Unfortunately, only 3 of these are in or near the MED basin, and measure wet deposition only: Iskrba, Slovenia, at 500 m a.s.l., Longobucco, in Southern Italy, at 1358 m a.s.l., and Ostriconi, in Corsica, at 100 m a.s.l. Annual Hg wet deposition at these sites is 6.7, 1.7, and 3.0 µg m^{-2} y^{-1} respectively[75, 76]. The paucity of representative measurement data for the MED is an issue that needs to be addressed. Hg deposition to the MED has therefore been estimated from knowledge of the concentration of Hg^0 and its oxidants in the region, the rate of atmospheric oxidation processes which lead to the formation of Hg^{II}, and wet and dry deposition processes. Gencarelli et al.[77] used a version of WRF-Chem to estimate dry and wet deposition fluxes to the MED. They found that the modeled contributions to deposition were almost equal, 19.6 and 18.1 Mg y^{-1} dry and wet, respectively. No observational data exist for Hg dry deposition. Combined with modeled annual evasion of Hg^0 from the sea surface of 67.5 Mg y^{-1} (in agreement with most of the estimates from the studies above), the model budget gives a net annual evasion flux of 30 Mg. A further model study showed that dry deposition accounted for more than half the Hg deposited to the MED in the summer months, and between 40 and 50 % of the annual total deposition, depending on the atmospheric Hg oxidation mechanism employed in the model[78]. Synoptic scale wet

deposition of Hg contributes roughly ten times more to the total Hg deposition than convective wet deposition and is the dominant source of Hg to the MED from Autumn through to Spring. Most Hg deposition to the MED is due to transport from distant sources, except in the summer when sources from countries surrounding the MED have a greater influence due to the prevailing meteorological conditions. This is reflected in the change in the total modeled deposition to the MED when using anthropogenic emission databases for 2005 and 2010, where a 33 % reduction of in-domain emissions resulted in a 12 % deposition decrease. A global modeling study[79] suggested that slightly more than 20 % of Hg deposited to the MED comes from primary anthropogenic sources. A recent study[80] estimates that a 50 % reduction in EU emissions, would only lead to a 17 % decrease in Hg deposition to the MED.

The recent advances in understanding the processes driving atmospheric Hg redox chemistry[81, 82, 83, 84], and also in coupling ocean and atmosphere models[69, 71], suggest that it would be an appropriate time for high-resolution MED modeling studies to be conducted again. Potentially the photolytic reduction of Hg^{II} compounds in the atmosphere[82] could have a significant role in the cycling of Hg between the atmosphere and seas. Gas-phase reduction of Hg^{II} could decrease model estimates of both Hg^{II} wet and dry deposition to the MED, by a proportion that needs yet to be modeled. Given the dominance of Hg long-range transport and the synoptic rain fluxes, the chemical reduction of gaseous Hg^{II} likely has a small impact. Gas-phase reduction of Hg^{II} could decrease model estimates of both Hg^{II} wet and dry deposition to the MED, by a proportion that needs yet to be modeled, and that is supported by recent Hg stable isotope observations of Hg in the MED[85].

Despite the questions remaining regarding the exact nature of atmospheric Hg redox pathways, there is little doubt that the MED is a net source of Hg to the atmosphere, with roughly 60 - 80 Mg y^{-1} is emitted to the atmosphere while it is estimated that dry and wet deposition amount at around 20 Mg y^{-1} each.

2.2. The waters of the Mediterranean Sea

2.2.1. Geographical distribution of total mercury (THg)

The vertical structure of the WMED water column can be schematically subdivided into three major water masses: (i) Atlantic Water (AW), (ii) Eastern Intermediate Water (EIW), and (iii) Western Mediterranean Deep Water (WMDW)[27] (Fig. 1). AW (from the

surface to ~ 250 m) is a low salinity water mass entering the MED at Gibraltar, and spreading eastward into the entire basin. EIW is a high salinity water mass, located just below AW and down to ~600 m, originating in the EMED. Below that depth and down to the seabed is the WMDW formed in the WMED during winter convection periods, which fills the entire basin. In addition, in the Tyrrhenian basin, Tyrrhenian Deep Water (TDW) is formed as the result of the deep mixing of waters from eastern and western MED (Fig. 1).

Figure 2 illustrates a recently measured distribution of THg across the western basin (WMED). Summarized statistics of THg concentrations (pmol L^{-1}) in the WMED waters measured between 2000 and 2017 are given in the Supporting Information (SI.3). In open waters, the <0.45 μm fraction represents 89% of the THg in waters. High and low THg concentrations are present in the AW (0.21-2.01 pmol L^{-1}) averaging 0.86 ± 0.27 pmol L^{-1}. Within the EIW and WMDW, the concentrations vary over a narrower range (0.51-1.62 pmol L^{-1}) averaging 1.02 ± 0.12 pmol L^{-1}. The highly variable concentrations in AW are the consequence of air-sea exchange dynamics which govern the balance between Hg deposition and evasion from the sea surface, and primary production, which governs the downward Hg biological pump. In places where deep convection occurs (i.e., the Ligurian Sea and the Gulf of Lion), transferring the surface layer and its Hg level to depth, a local Hg-enrichment (or depletion) of the WMDW can be observed compared to the rest of the Western Basin. By comparison, the THg concentrations in the waters of the WMED margins (Gulf of Lion) are slightly higher: 1.52 ± 1.00 pmol L^{-1} in the inner shelf, 1.09 ± 0.15 pmol L^{-1} along the slope, and 1.10 ± 0.13 pmol L^{-1} in the Northern Gyre. These higher concentrations result from the higher particulate Hg load of shelf waters[86] rather than dissolved Hg species. In the open waters of the eastern basin (EMED) Hg measurements are scarce. The first "oceanographically consistent" profile showed little vertical THg variation (mean = 1.01 ± 0.08 pmol L^{-1}, n = 22)[75]. Note that "oceanographic consistency" means, among other criteria, that vertical profiles should be smooth and relatable to established oceanographic features[87]. In contrast, more data are available from the Adriatic Sea. This region, consisting of a large continental shelf, exhibits high THg concentrations and strong geographical gradients due to Hg mining and industrial sources[88].

No temporal trend has been detected in the THg concentrations listed in the Supporting Information (SI.3). However, a significant decrease in concentration in the

Alboran Sea and the adjacent Northeast Atlantic waters was observed over a 20-year period[46]. Based on the results of THg in water columns on both sides of the Strait of Gibraltar between 1989 and 2012, it was proposed that a 30 % decrease of THg has occurred in the deep layer which flows out of the MED, whereas a 50 % decrease has occurred in the Atlantic waters entering the MED.

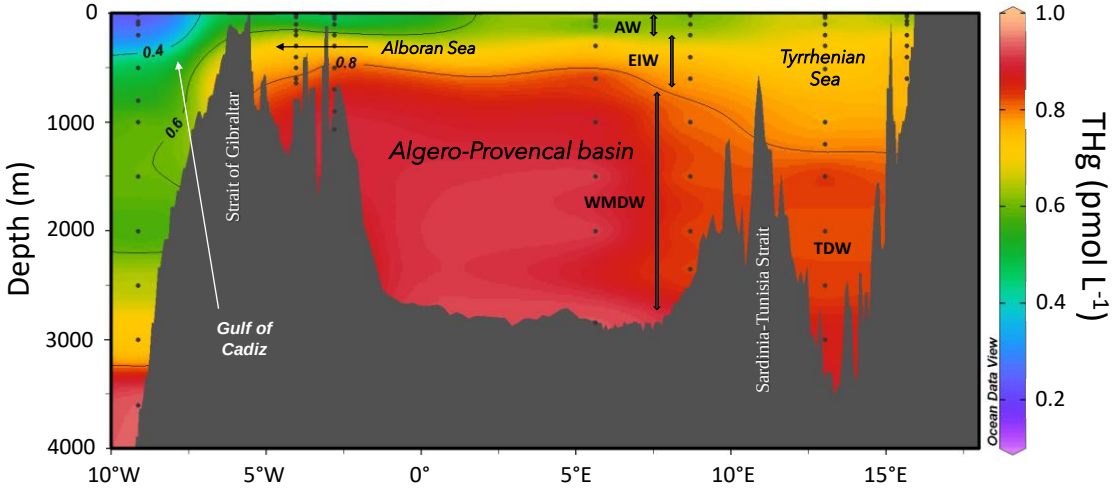
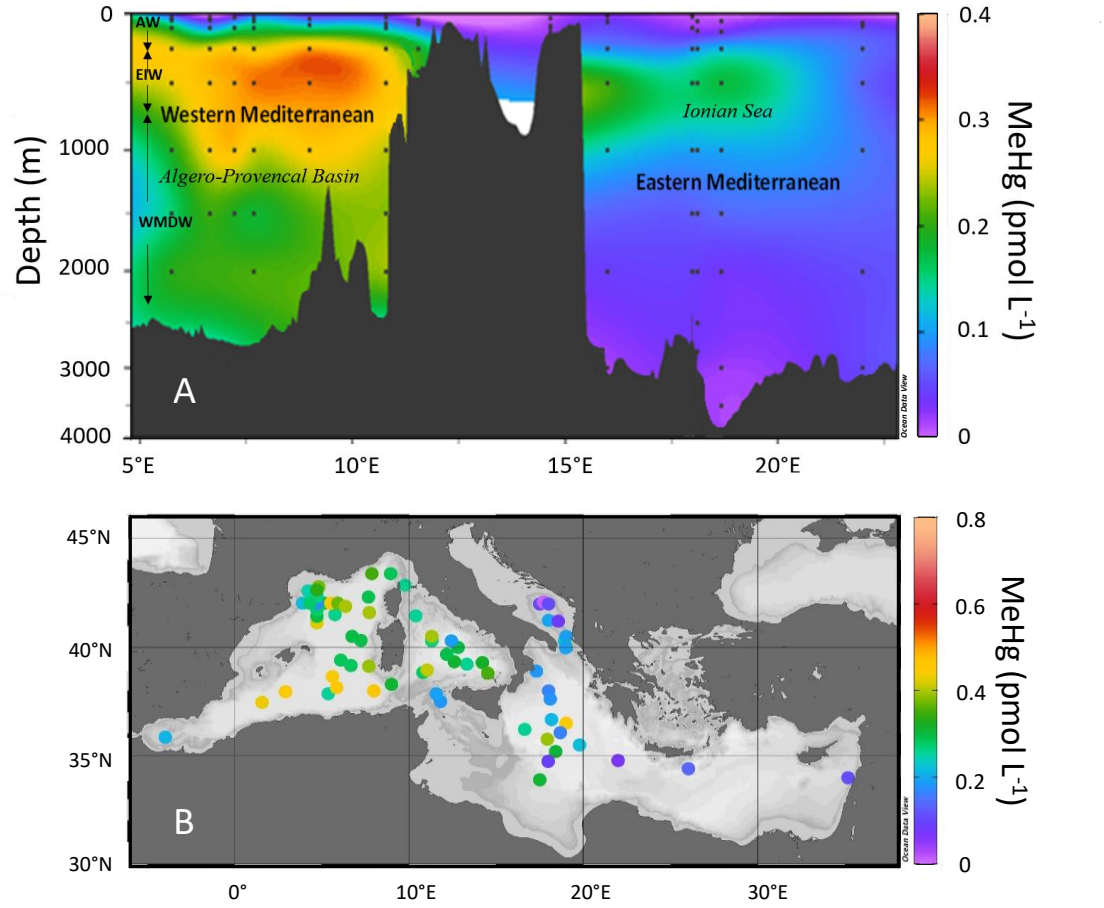


Figure 2. *Distribution of total Hg in unfiltered samples (THg) distribution across the WMED during FENICE cruise (2012). AW: Atlantic Water, EIW: Eastern Intermediate Water, WMDW: Western Mediterranean Deep Water, TDW: Tyrrhenian Deep Water. The path of the transect is the red dash line in Figure 1.*

296 *2.2.2. Geographical distribution of methylated mercury (MeHg)*



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298 ***Figure 3.*** *Panel A: Methylated Hg (MeHg) in unfiltered samples during* ALDEBARAN *cruise*
299 *(June 2009). AW: Atlantic Water, EIW: Eastern Intermediate Water, WMDW: Western*
300 *Mediterranean Deep Water, TDW: Tyrrhenian Deep Water. The path of the transect is the black*
301 *dash line in Figure 1. Panel B: MeHg in unfiltered samples from 400 m during* MEDSHIP *cruise*
302 *(2011).*

303

304 Recent MeHg measurements[89, 90] display concentration ranges from <0.02 pmol L^{-1}
305 up to 0.71 and up to 0.23 pmol L^{-1} for the WMED and EMED waters, respectively. The
306 MeHg:THg ratios vary from 0.01 to 0.86. The highest values are found in the oxygen
307 minimum zones (OMZ). These ranges are similar to other ocean basins (Supporting
308 Information, SI.4). MeHg concentrations vary spatially (Fig. 3) with higher levels in the
309 WMED compared to the EMED, and over-time as shown by time-series in the Ligurian
310 Sea (WMED)[91]. MeHg was positively correlated with oxygen consumption (Fig. 4),
311 especially within aphotic layers, namely EIW and DMW ($MeHg_{pM}$ = 0.004 $AOU_{\mu M}$ –
312 0.017 (R^2 = 0.58, n = 301, p< 0.001). Regression coefficients (molar ratios) of MeHg *vs*

apparent oxygen utilization (AOU) relationships, assumed to be a proxy for the Hg methylation capacity of a water mass, varied between 2.1 x 10^{-3} and 6.6 x 10^{-3} during a number of Mediterranean cruises. Compared with values obtained in the North, Equatorial, South Pacific[92, 93], the Southern Ocean[94], and the North Atlantic[95], the methylation capacity of intermediate waters of the MED is the highest. Methylation in the OMZ results from microbiological activity in association with OM regeneration[92, 96, 97, 98]. Low MeHg concentrations were found in waters overlying the continental shelves of the Northern Adriatic and Gulf of Lion[43, 88].

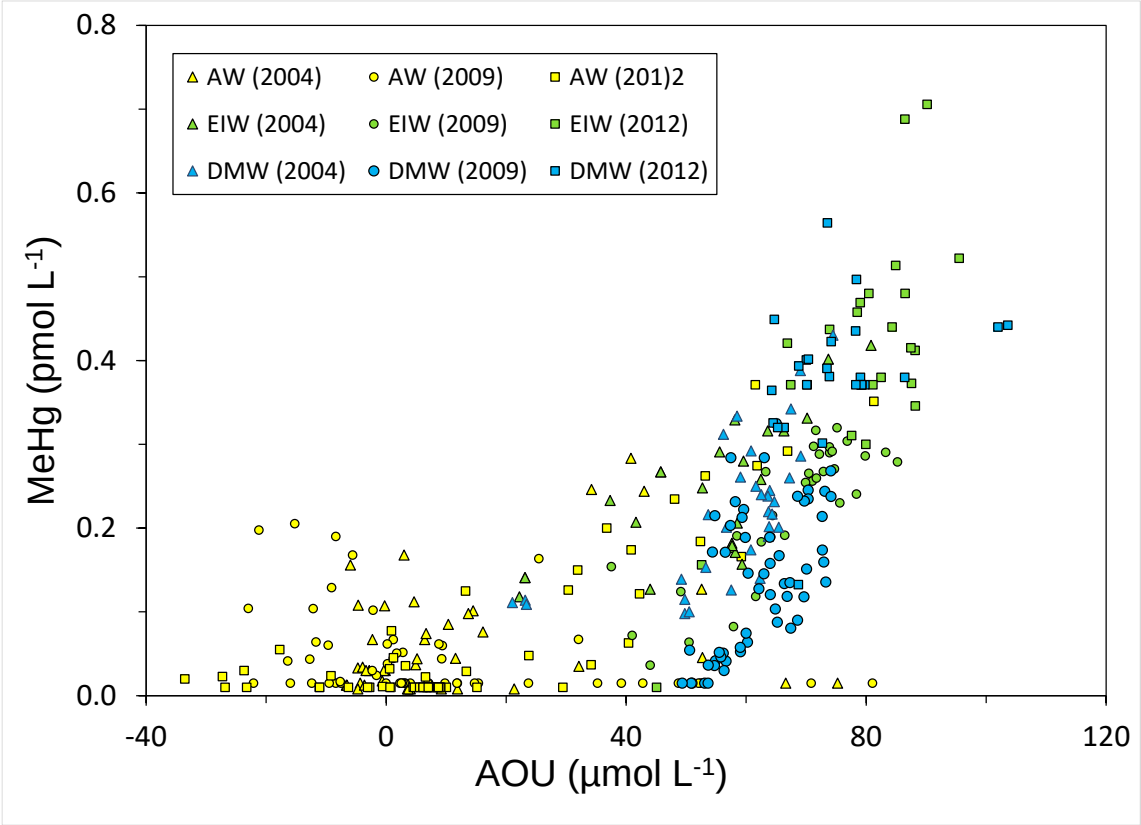

Figure 4. *Methylated Hg (MeHg)* vs. *Apparent Oxygen Utilization (AOU) during MEDOCEANOR-3 (April 2004), ALDEBARAN (June 2009), and FENICE cruises (August 2012). Colors refer to various water masses (yellow for AW, green for EIW, and blue for DMW, Fig. 1). The shapes of symbols refer to the different cruises.*

Mono- and dimethylmercury have been identified in Mediterranean waters[39, 43, 99]. However, observed MMHg:DMHg ratios vary inexplicably in space and time. This possibly indicates a very fast interconversion of the two Hg methylated species or more likely analytical difficulties. Thus, the first step to address this issue would be to acquire additional quality-controlled data on Hg speciation. The second step would be to further

explore the mechanisms for Hg_i^{II} methylation in oxic oceanic waters. Suboxic/anoxic microzones of the marine snow may be suitable environments for microbiological Hg methylation, as has been suggested for settling particles in lakes[100]. In marine oligotrophic waters, such as those of the EMED, findings suggest an important role for a noncellular or extracellular methylation mechanism[101].

2.2.3. Dissolved gaseous Hg

Generally, DGM represents 1/5th of the THg in Mediterranean waters and it would consist, mostly of dissolved Hg^0 if DMHg data are correct. Vertical profiles of DGM presents large spatial and temporal variations from a few tenths to 1.4 pmol L^{-1}, with high concentrations found in intermediate and deep waters (e.g., EIW, WMDW, and EMDW) compared to AW[88], and frequent increases in the hypoxic layer. This is coherent with a microbially-mediated Hg reduction to DGM species. Finally, a possible geotectonic origin for DGM exists in the hydrothermal zones of the MED[102]. In coastal areas of the Adriatic Sea, the influence of anthropogenic Hg on DGM has been suggested[88].

2.3. The sediments of the Mediterranean Sea

Sediment cores were collected on the abyssal plain of the MED[42, 75, 103]. Some THg vertical profiles in sediment cores from the abyssal plain of the MED are shown in Figure 5. The use of Hg stable isotopes allowed us to suggest anthropogenic sources for Hg in Mediterranean surface sediments[104]. A recent paper[105] shows that Hg accumulation rates rose from 0.4 to 8.6 µg m^{-2} y^{-1} in the last 6000 years, with a maximum deposition in the last 120 years. According to the same authors, the accumulation rate for the year 2001-2002 measured with a sediment trap, located 20 m above abyssal sediments, was 3.1 ± 0.5 µg m^{-2} y^{-1} and suggests to Hg fluxes to the deep WMED sediments of 4.2 Mg y^{-1}. The rare MeHg determinations in open MED sediments indicate that it would represent between 0.5 to 2 % of the THg[42, 106]. A MeHg diffusive flux from deep sediments to the water column was estimated between 0.2 and 2.3 µg m^{-2} y^{-1} (Ref. 42), which represents more than 50% of the deposition; these are probably largely overrated. For the EMED deep sediments, we based our calculation on a sedimentation rate ratio of 0.68 between EMED and WMED[107] and a Hg concentration in EMED surface sediment of half of the WMED (Fig. 5). With these assumptions, the Hg accumulated each year in the deep sediment of the EMED is ca. 1.6 Mg. Mercury accumulation on MED coastal sediments is more documented particularly on the shelves

of the Gulf of Lion (WMED)[86] and of the Adriatic Sea (EMED)[88, 108] where Hg hotspots were identified. Extrapolating these data, the Hg accumulated each year on the shelf is 3.6 and 3.2 Mg for Western and Eastern basin shelf sediments, respectively. However, the shelf sediments may not be a permanent sink, and turbiditic currents and cascading phenomena may export part of the sediment to the abyssal plain trough canyons[109].

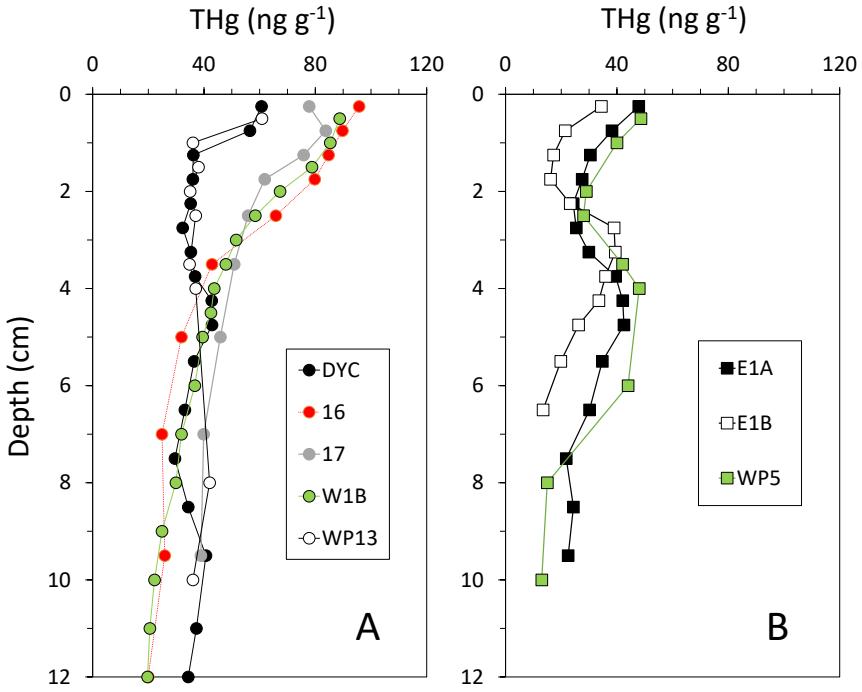

Figure 5*. Total Hg concentration (THg) profiles in sediment cores from the abyssal plain (bottom > 2000m) of the Western Mediterranean (A) and Eastern Mediterranean (B). (DYC) Ligurian Sea[103]; (WP13, WIB, 16 and 17) Algero-Provençal basin[42, 75]; (EIA and E1B) Ionian Sea[75]; (WP5) Levantine Sea[42].*

2.4. Exchanges with the Atlantic Ocean

Using water mass fluxes and updated THg concentrations from Table 1, the Hg inflow entering the MED at the Strait of Gibraltar is 2.54 ± 0.26 Mg y^{-1}. This estimation is more than 3 times lower than the 7.5 Mg y^{-1} estimated in the previous budget[41]. On the other hand, Hg outflow to the North Atlantic Ocean is 3.99 ± 0.76 Mg y^{-1}, a value also smaller than the preceding estimate (6.5 Mg y^{-1})[41]. The largest difference of this budget compared to the previous transport calculation at the Gibraltar Strait is the net export of "Mediterranean Hg" to the adjacent North Atlantic Ocean of ~1.9 Mg y^{-1}. This export is consistent with the Hg-enriched Mediterranean water lenses found at the salinity maximum in the North-East Atlantic Ocean water column[110]. Thus, the MED is a source

386 of Hg for the adjacent Eastern North Atlantic Ocean, as it is also for lead[111], another
387 anthropogenic trace metal still abundant in the MED. Considering the MeHg fluxes, the
388 excess of Mediterranean export to the Atlantic is more marked, since MeHg is maximum
389 at depth (with outflowing waters at Strait of Gibraltar) and demethylation of MeHg
390 occurs in inflowing surface waters. Using the water fluxes at Gibraltar of 0.85 Sv and
391 the MeHg concentrations of 0.25 pmol L^{-1}, this export of Mediterranean MeHg to the
392 North Atlantic Ocean is 1.35 Mg y^{-1}.

393 ***Table 1.*** *Average concentrations (± standard deviation) of total Hg (THg) and methylated Hg*
394 *(MeHg) and derived fluxes at the Strait of Gibraltar. 1 Sv = 10^6 m^3 s^{-1}. (*) at Espartel sill*
395 *according to Ref. 112. THg concentrations from Ref. 46. MeHg concentrations from Ref. 90.*

Water mass	Water flux* (Sv)	THg (pmol L^{-1})	Hg flux (kmol y^{-1})	MeHg (pmol L^{-1})	MeHg flux (kmol y^{-1})
Atlantic inflow	0.89 ± 0.12	0.45 ± 0.05	12.6 ± 2.3	<0.05	<1.4
Mediterranean outflow	0.85 ± 0.13	0.83 ± 0.13	22.3 ± 3.8	0.26 ± 0.09	6.9 ± 1.2

396 ***2.5. Volcanic and hydrothermal emissions***

397 Subaerial volcanic Hg emissions in the Mediterranean region are dominated by the
398 Aeolian volcanoes Vulcano and Stromboli, and by Mt Etna in Sicily. A cruise campaign
399 to the south-western sector of the Mediterranean Basin during summer 2015 studied the
400 potential impact of continuously active volcanoes of the Aeolian arc on observed
401 atmospheric Hg concentrations[113]. Increases in GOM (Gaseous Oxidized Mercury)
402 concentrations, often during night time (30 pg m^{-3} with peaks of 129 pg m^{-3}), were
403 observed close to Stromboli volcano in the air originating from it, simultaneously with
404 an increase in both SO_2 and GEM (Gaseous Elemental Mercury). There are currently
405 many difficulties in quantifying the Hg flux from volcanic emissions due to the spatial
406 and temporal variabilities in the activity from one volcano to another[37, 114], or from
407 different emission sites on the volcano[115].

408 Ferrara et al.[37] measured Hg/SO_2 ratios at Vulcano and used these to calculate
409 passive Hg emissions ranges for Vulcano (1.3 – 5.5 kg y^{-1}), Stromboli (7.3 – 77 kg y^{-1}),
410 and Etna (0.06 – 0.54 Mg y^{-1}) by multiplying with field-based SO_2 emission estimates.
411 Here we use a mean global volcanic Hg/SO_2 ratio of $7.8 \pm 1.5 \times 10^{-6}$ (n = 13, Ref. 116)
412 and modern satellite-based SO_2 emissions for Stromboli and Etna[117] between 2005-2015
413 to estimate passive degassing Hg emissions of 0.5 ± 0.3 Mg y^{-1} for Stromboli and 5.8 ±

1.8 Mg y^{-1} for Etna. Remote sensing SO_2 data is not available for Vulcano, so we cannot refine its budget here. Global eruptive volcanic SO_2 emissions, estimated by remote sensing, are indicated to be one order of magnitude smaller (8.8x) than passive degassing[117]. We, therefore, estimate the sum of passive and eruptive aerial volcanic Hg emissions in the MED region to be 7.0 ± 2.3 Mg y^{-1}.

Two recent GEOTRACES cruises found elevated Hg levels crossing the Mid Atlantic Ridge and no distinct Hg signal crossing the East Pacific Rise in the vent plumes[118, 119]. The results and implications are either contradictory or point to strong site-specificity and temporal dynamics. Some contradictory data exists for hydrothermal systems in the deep ocean (Ref. 35 and references therein), but no deep vents exist in the MED. Hydrothermal systems in shallow (less than 200 m-depth), near-shore environments have been largely ignored, and their contribution to the global Hg cycle remains unknown[13]. In the MED several shallow sites are known (e.g., Milos). A first investigation of the Panarea site (Italy) shows significant Hg inputs, especially Hg^0 (Ref. 36). The study finds that the Hg^0 evasion flux is negligible in the MED budget. The authors state that previous assessments of total hydrothermal inputs to the MED ~15 Mg y^{-1} (Refs. 40, 41), are underestimations. This possibly important source is far from being well-constrained; obviously, more data are crucially needed in this field.

2.6. Riverine and submarine groundwater discharge

According to a recent paper, riverine discharge from European rivers into the MED is 2.9 Mg y^{-1} (Ref. 120); this input is highly seasonal due to the Mediterranean hydrological regime[75]. However, the inputs from rivers into the eastern and southern parts of the MED shore are not included in this inventory. The way we have chosen to assess the total Hg riverine influxes to the MED is by extrapolating the mean Hg concentrations (2.45 pmol L^{-1}, 0.85 nmol g^{-1}, for dissolved and particulate Hg, respectively) of the Rhône River, for which multi-year time-series exist[43], to the total MED river discharge. We arrive at a total Hg input of 6 Mg y^{-1}, which is divided into 2.3 and 3.7 Mg y^{-1} for the Western and Eastern basins, respectively. Hydrological data used for these calculations are from Refs. 121, 122, 123. These calculated fluxes are in the same order of magnitude that the Hg accumulated annually in shelf sediments (see Section 2.3.). This observation suggests that most of the Hg associated with riverine particles settles into shelf sediments.

For submarine groundwater discharges (SGD) the available data are even more limited. The Hg load of SGD has been studied in the Marseille region (NWMED): THg concentrations were in the picomolar range and often < 3 pmol L^{-1} (Ref. 124). For a 20 km long coastline an annual mean of THg discharge of 0.14 ± 0.12 kg was calculated. Extrapolating this figure to the total MED shoreline and assuming constant submarine discharge point and flux density gives a total Hg flux from SGD of ~0.32 Mg y^{-1}. However, this figure could be largely underestimated. Trace element SGDs in the WMED have been estimated to be roughly in the same range as riverine discharges[125]. Assuming a similar behavior for Hg would give a total Hg discharge from submarine groundwaters an order of magnitude higher, namely ~6 Mg y^{-1}. In summary, Hg inputs from continental exoreic water sources to the MED can be estimated at ca. 12 Mg y^{-1}. Here again, this flux is not well constrained, and more studies are needed on rivers and especially SGD.

2.7. Mercury budget in the Mediterranean Sea

The diagram in Figure 6 sums up the Hg exchanges at the boundaries of the system and the Hg species inventory of the two MED basins. Precision concerning the Hg measurements, their natural variability, as well as that of the hydrodynamic and particulate fluxes, make this an exercise with major uncertainties. However, information that can be gained by such a mass balance calculation is to reveal the relative magnitudes of various sources and sinks and to test the hypothesis of a steady-state of Hg in the MED waters. In terms of balance, Hg output exceeds input by ~15 Mg y^{-1}, which is ~17% of the total export flux. Considering the uncertainties, the present Hg budget is close to balance. However, if we consider the excess of Hg export as real, this means that the Hg quantity in the MED is decreasing at the time scale of the residence time of Hg (2 % y^{-1}). This is consistent with the observations of a ~30% decreasing Hg concentrations in the MED over the last 20 years[46].

In summary, the achievements of the updated budget are:

- It is confirmed that the exchanges between surface water and the atmosphere dominate the Mediterranean Sea Hg transport; however, the excess of evasion compared to the deposition, currently given by the models, is still insufficiently supported by the observations to be fully reliable;

- In absence of a robust quantification of diffusive Hg flux from sediment, the Hg buried in deep sediment is estimated around 5.8 Mg y^{-1};
- The rate Hg accumulated in shelf sediments is ~6.8 Mg y^{-1}, which is similar to the Hg flux from rivers; part of it is probably temporarily trapped in coastal sediments before a possible transfer to the deep sea *via* submarine canyons;
- The finding that Hg efflux to the Atlantic Ocean, with intermediate and deep waters at Gibraltar, dominates the Atlantic input in surface water (by a factor ~2), with Hg entering the MED as inorganic species and escaping substantially as MeHg; MED is a site of MeHg production and a point source of MeHg for the adjacent Northeastern Atlantic Ocean (~1.4 Mg y^{-1});
- The estimation of a Hg (MeHg) content of the MED ~680 Mg (~150 Mg), with 0.7 % being associated with biota (6 % of which is annually removed by fisheries) (see section 4 below);
- The estimation of a residence time of Hg in MED waters < 10 years, which is roughly 5 to 10-times less than the residence time of waters; thus, decreasing the atmospheric Hg deposition (i.e., a decrease of anthropogenic emissions) over the MED region would more rapidly decrease the Hg concentration in MED waters than in other parts of the World Ocean.

The present budget remains poorly constrained about several Hg inputs especially those from geotectonic origins, coastal erosion, SGD, sedimentary mobilization, and point sources. These uncertainties are added to that of the imbalance in the Hg air-sea exchanges between evasion and deposition. Seasonal variation of numerous inputs needs to be assessed. In addition, the transport of particulate Hg inputs from terrigenous origin to the deep open sea through canyons is not quantified. For example, which part of riverine Hg inputs (associated with particulate material) remains in the margin sediments, which part reaches the abyssal sediments *via* canyons or is released in the water column, and may become available to benthic food webs? Such questions need answers for refining the Hg budget in order to use it to manage the near-shore areas where fishing and aquaculture activities are located.

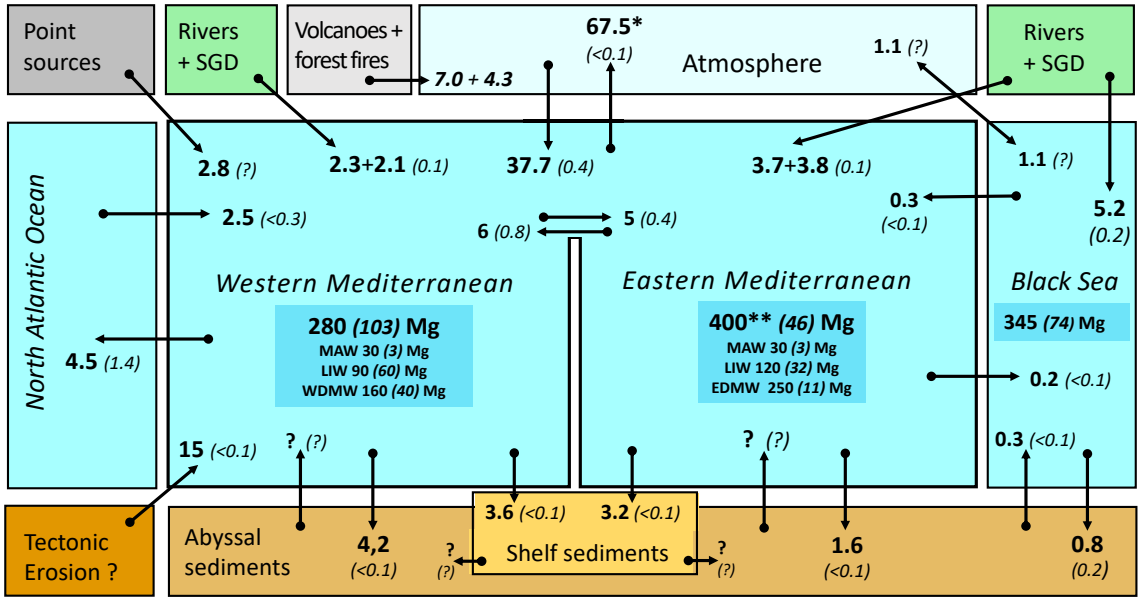

Figure 6*. Total Hg (THg in bold) and methylated Hg (MeHg in brackets) annual mass fluxes in the Mediterranean Sea (Mg y^{-1}). In the dark blue rectangle are the Hg inventories (Mg) in sub-basins and water masses. Fluxes from modeled air-sea exchanges are discussed in Section 2.1, Gibraltar exchanges are from Section 2.4, volcanic inputs from Section 2.5, and sediment deposition from Section 2.3; point sources are taken from Refs. 32, 33, 40, and 126; tectonic fluxes from Ref. 40 (probably an underestimation), are not differentiated according to basins; erosion fluxes are not quantified; fluxes from/to the Black Sea are from Ref. 45. The seawater fluxes at the Sicily Strait are from Ref. 123. Mediterranean areas and volumes are from Ref. 127. *Range: 50-100 Mg y^{-1}; **THg concentrations in the EMED used for calculation are limited to 24 measurements on only one profile in the Ionian Sea acquired in 2004 during* MEDOCEANOR*-3 cruise.*

3. Biological mercury transformations: state of the art for MED

The net amount of MeHg formed in the ocean is controlled by three processes: (i) the methylation of Hg_i^{II} to MMHg, (ii) MMHg demethylation to Hg_i^{II}, and (iii) interconversion between DMHg and MMHg. Abiotic methylation of Hg_i^{II} is possible if suitable methyl donors are present, but research efforts have mostly been concerned with biologically mediated Hg methylation. The biological methylation of Hg_i^{II} to MeHg can be performed by microorganisms carrying the *hgcA* and *hgcB* gene clusters[128, 129, 130, 131]. A detailed description of the gene clusters is given in Supporting Information (SI.5). Some *Nitrospina hgcA*-like genes in one of three MED water samples were also detected[132]. In particular, those gene copies were detected in surface waters and were not detected at the deep chlorophyll maximum of the MED. Three samples are not representative of the vertical and horizontal variability of the MED but, based on previous knowledge, it can be speculated that *hgcA* might be more abundant in surface waters and

at the OMZ of the MED. Due to the lack of data, a more extensive evaluation of the presence and activity of *hgcA* in the MED is needed to determine the position in the water column where these microorganisms are active, and thus responsible for biological MMHg formation in the MED water column, and to unveil their different metabolic capacities.

Besides the occurrence of potential Hg_i^{II} methylators in the ocean, the amount of Hg_i^{II} available for methylation plays an important role in determining the rate of this process. In this context, Hg_i^{II} reduction, which might decrease Hg_i^{II} bioavailability for methylation, and MMHg demethylation, which might increase it, are both critical processes to consider. Both Hg_i^{II} reduction and MMHg demethylation can be biotically[133, 134] and photochemically mediated[135, 136, 137, 138]. As mentioned above, although rates of photochemical transformations have never been reported for the MED, it is logical that these processes are limited to the photic zone and thus to the AW. Similarly, there is no information concerning biological Hg_i^{II} reduction. Two pathways of MMHg demethylation have been identified: an oxidative pathway yielding Hg^{II} and CO_2, and a reductive pathway yielding Hg^0 and CH_4. Since the Hg^0 produced from reductive demethylation can diffuse out of the cell, it has been proposed that reductive demethylation is a cellular detoxification mechanism[134], which would dominate at high Hg concentrations, whereas the oxidative pathway, which is an unknown, would be more important at low Hg concentrations[139]. MMHg demethylation is biologically mediated by the *mer* operon[134, 140]. Lastly, the interconversion between DMHg and MMHg is still poorly understood but has been suggested to be potentially abiotic[141, 142]. In the MED the lack of knowledge regarding metabolic pathways and the organisms involved in these processes has limited the possibilities to further understanding of Hg biogeochemical cycling.

4. Biological transfers in food webs

In the MED, top-predator fish often exceed EU regulatory Hg thresholds[75, 143, 144, 145, 146, 147, 148] and contribute to the increase in MeHg exposure of seafood consumers[10, 149]. Also, for over 50 years, Hg-enrichment in Mediterranean fish compared to other oceanic regions at the same latitudes has been observed (e.g., Refs. 17, 18, 148), with the result that Aston and Fowler[20] describe these findings as a real “mercury enigma” in MED biota. After debates about the possible importance of biological factors[20, 75], a comparison

565 of Hg content in hake and its food web elements from the MED and the adjacent North
566 Atlantic Ocean suggests a multi-causal explanation for this issue[21], namely (i) the
567 location of the MeHg maximal concentration in the water column, (ii) the growth rates of
568 the fish, and (iii) the structure of the food webs.

569 Most available information on Hg concentrations in Mediterranean organisms, from
570 primary producers to marine mammals and birds, recorded between 1969 and 2015 was
571 compiled into a large database[148]. Among Animalia about 80 % of samples concern
572 Actinopterygii (mainly teleost fish) and Bivalvia (mainly mussels), while among Plantae
573 87 % of the data concern the seagrass *Posidonia oceanica*, highlighting the lack of
574 knowledge on Hg content in important small organisms, such as phytoplankton
575 producers, zooplankton consumers, and benthic invertebrates. More information is
576 available from the northern than the southern part of the MED and the western rather than
577 the eastern basin[148]. Hg transfer in biota involves three complex multifactorial processes
578 (bioconcentration, bioaccumulation, and biomagnification) interacting at different levels
579 of the food webs, which need to be taken into account for a true understanding of
580 Mediterranean specificities and to facilitate geographical comparisons.

581 ***4.1. Bioconcentration***

582 Bioconcentration is the absorption of contaminants in organisms directly from water
583 through cell membranes. This is the first and most important step in Hg transfer, which
584 occurs mainly at microorganisms levels. Bioconcentration depends not only on the
585 bioavailable Hg concentration in seawater, but also on the specific composition of
586 phytoplankton communities, their abundance, and size, which govern Hg sorption and
587 uptake in the first trophic level of food webs[150]. It has been demonstrated that MMHg is
588 preferentially integrated into the cell cytoplasm whereas Hg_i^{II} is adsorbed on
589 phytoplankton membranes[151]. As a consequence, MeHg is assimilated by zooplankton
590 four times more efficiently than Hg_i^{II} (Ref. 150). For a given Hg concentration in
591 seawater, absorption is negatively related to phytoplankton abundance (dilution by
592 biomass), and uptake is negatively related to cell size (higher surface/volume ratio in
593 smaller cells) and their rates vary among species[152, 153]. As the base of the food web is
594 mainly made up of pico- or nano-bacteria and phytoplankton in oligotrophic
595 Mediterranean seawaters[154], the combination of low phytoplankton abundance and small-
596 sized cells increase both sorption processes resulting in higher Hg concentrations of the
597 first trophic level in the MED than in the northeastern Atlantic[21]. At a smaller spatial

scale in the MED, higher Hg bioconcentration in phytoplankton is also found in oligotrophic offshore waters than in mesotrophic coastal waters due to similar processes[21]. In the MED, the higher proximity at mid-depth of both chlorophyll (~40 m)[155] and MeHg maxima (~250-400 m)[21] increases Hg bioavailability for phytoplankton incorporation. In contrast, these two zones are more separated in the Northeastern Atlantic, where the MeHg maximum is located in deep waters (800 m)[21] and the chlorophyll one in shallow waters (5-40 m), contributing to reduce bioconcentration at the base of the food webs in this region. In the Black Sea, MeHg maximum occurs in permanently anoxic waters[45]. The strong stratification of the water column between the oxic and anoxic layers precludes the exposure of higher living organisms to elevated MeHg concentrations. In addition, the high primary production of the Black Sea adds a bio-dilution effect and may contribute to explaining the lower Hg bioconcentration observed[156].

Studies in the Gulf of Lion provide evidence of higher Hg concentrations in the smaller (6-60 µm), rather than the larger (60-200 µm), phytoplankton fractions analyzed[157], consistently with the results obtained experimentally and by modeling[150, 158]. However, in these small-size fractions, detrital organic particles and numerous associated bacteria are mixed with autotrophic and heterotrophic plankton. That raises the question of the relative role of living and non-living particles, and of the different types of plankton in Hg transfer in food webs. Which species or size fractions are the most significant for Hg transfer in food webs? It seems that Hg could be more readily assimilated by copepods when they are feeding on ciliates (protozoa) than on phytoplankton or heterotrophic dinoflagellates[159].

4.2. Bioaccumulation

Bioaccumulation refers to a contaminant increase in an organism during its lifetime from both the environment and food consumption. Hg bioaccumulation in consumer organisms during their lifetime is mainly due to prey consumption[160, 161], and differs widely according to species, and the organs or body parts considered[148, 157, 162]. Thus, the Hg content of prey is one of the major parameters for explaining bioaccumulation in organisms, and a positive correlation between Hg content in food and consumer is generally observed[163]. In the MED as elsewhere, whole organisms are analyzed for plankton, benthic invertebrates, and fish larvae due to their small size, whereas muscle tissues are generally analyzed in larger marine consumers (crustaceans, cephalopods, and

631 fish) due to their consumption by human populations[10, 146]. Other tissues are analyzed for
632 larger Mediterranean predators, such as skin biopsies for mammals[164] or blood for
633 seabirds[165]. Higher Hg concentrations are generally found in the liver, compared to
634 muscle and the gonads in MED fish[157, 166, 167], while this pattern may differ according to
635 species, higher Hg content is found in muscle than liver of hake[168] and shark[169].
636 Conversely, a higher MeHg percentage (85-97 %) is recorded in muscle than in the liver
637 (30 %)[162] due to the slower elimination rate from muscle than liver (2 % and 60 %
638 respectively)[167]. In addition to organ differences, bioaccumulation is modulated at the
639 individual level by a series of interacting biological (species, size, weight, sex, age, life
640 duration, growth rate, reproduction, metabolism, proximal composition, detoxification
641 mechanisms, diet, etc.) and environmental (depth, habitat, temperature, primary
642 production, etc.) factors, as described in studies of the European hake *Merluccius*
643 *merluccius*[21, 170, 171] and small pelagic fishes in the Gulf of Lion[157]. The synergistic and
644 antagonistic effects of all these factors, which vary in space and time for a given species,
645 explain the high variability of the vast amount of data published on Hg concentrations in
646 MED organisms and the complexity of fully understanding and explaining local and
647 regional differences (e.g., Ref. 148 and references therein). Generally speaking, a positive
648 correlation is observed between Hg concentration and individual size, weight, age,
649 trophic level and depth, and a negative correlation with growth rate (Hg dilution by an
650 increase in organism biomass) in MED fishes and mammals, with numerous exceptions
651 according to species or populations. For example, a higher Hg content was found in male
652 than female hakes of similar size in the Gulf of Lion but not in the Bay of Biscay, as
653 males grow more slowly than females in the MED, but not in the Atlantic[21]. Hg content
654 was correlated with size in *Mullus surmuletus* in the Ligurian Sea[172] and south of Spain[168]
655 but not in the Gulf of Lion[156]. A recent study also demonstrates the importance of the
656 proximal composition (mainly protein and lipid contents) of organisms on Hg
657 concentration in MED fish[168]. Besides, as the whole life history determines Hg
658 accumulation in organisms, the inter-individual variability would be higher in the older,
659 often also the larger, individuals in a population, a pattern observed in MED fishes[170, 173]
660 and marine mammals[164]. Most authors agree however on the higher Hg bioaccumulation
661 in MED benthic fish species compared to pelagic fish, and in individuals within species
662 occurring at deeper than in shallower waters[, 166, 173, 174, 175, 176], while exceptions are also
663 observed[177].

Regional comparisons of Hg concentrations in marine organisms are thus complicated by the combination of the high number of factors involved in contaminant bioaccumulation and may differ according to the organisms studied[178]. Mediterranean organisms, from sponges to fish, marine mammals, and seabirds, are known for their higher Hg concentrations than their Atlantic counterparts[21, 48, 164, 165, 179, 180, 181, 182] . Within the MED, some geographic regions such as the North Adriatic Sea, the Tyrrhenian Sea, and the Sea of Marmara[174, 180, 181] are known hotspots for Hg bioaccumulation, while the Aegean Sea[183], Ionian Sea[174], the Black Sea[156], and the Tunisian coast[162] appear to be less contaminated. Locally, Hg concentration in one species may vary by an order of magnitude, as observed for mussels on French MED coasts[184]. The exceptionally high spatial variability in MED organisms is highlighted by all studies, both between western and eastern basins, northern and southern coasts, and among habitats and depths. An example of the WMED-EMED difference of Hg content in fish is provided by the red mullet *Mullus barbatus*, a much-used species in monitoring surveys, from the Gulf of Lion[170] and the coast of Turkey[183]. *M. barbatus* of the same size range (11-19 cm TL) exhibit a ~2 times higher mean Hg content in the WMED (0.190 ± 0.013 µg g^{-1} wet weight in muscle, n = 94) than the EMED (0.090 ± 0.017 µg g^{-1} ww, n = 52) (Fig. 7). The regression logHg *vs* size presents a significantly higher intercept in the WMED than in the EMED, suggesting a higher Hg concentration at the base of the food web in WMED, while slopes do not differ due to the high variance of data indicating similar Hg bioaccumulation rates in the two fish populations. Such regional differences in fish Hg content could be related to the higher MeHg concentration in WMED than EMED waters (Fig. 3), which could induce more pronounced bioconcentration processes and thus higher Hg content in all trophic levels in WMED food webs. Consistently, the relatively high Hg bioaccumulation observed in Mediterranean hakes[21] could be essentially related to the environmental specificities of the MED compared to the adjacent NE Atlantic, including slightly higher MeHg concentrations in waters where predators are foraging. This latter hypothesis is supported by recent results on bluefin tuna, for which very high Hg levels have been observed[22]. Indeed, Tseng et al. (2021)[22] showed that this long-lived apex predator has Hg accumulation rates (defined as a change in muscle Hg concentration per unit change in either size/weight or age) which reach the highest level in the MED and decrease as North Pacific > Indian Ocean > North Atlantic. The authors argue that the Hg accumulation rate in tuna can be used as a Hg contamination index in the oceans. This

interesting hypothesis deserves further testing and it is probably related to the high methylation capacity of MED waters (see section 2.2.2).

In addition, the higher temperature of the MED and its oligotrophic waters would induce an increase in metabolic activity[185, 186] and a decrease in the growth of the organisms[187, 188], leading to a smaller size at a given age, which, along with a lower Hg elimination rate[167], would induce higher bioaccumulation of Hg in Mediterranean organisms[21, 48].

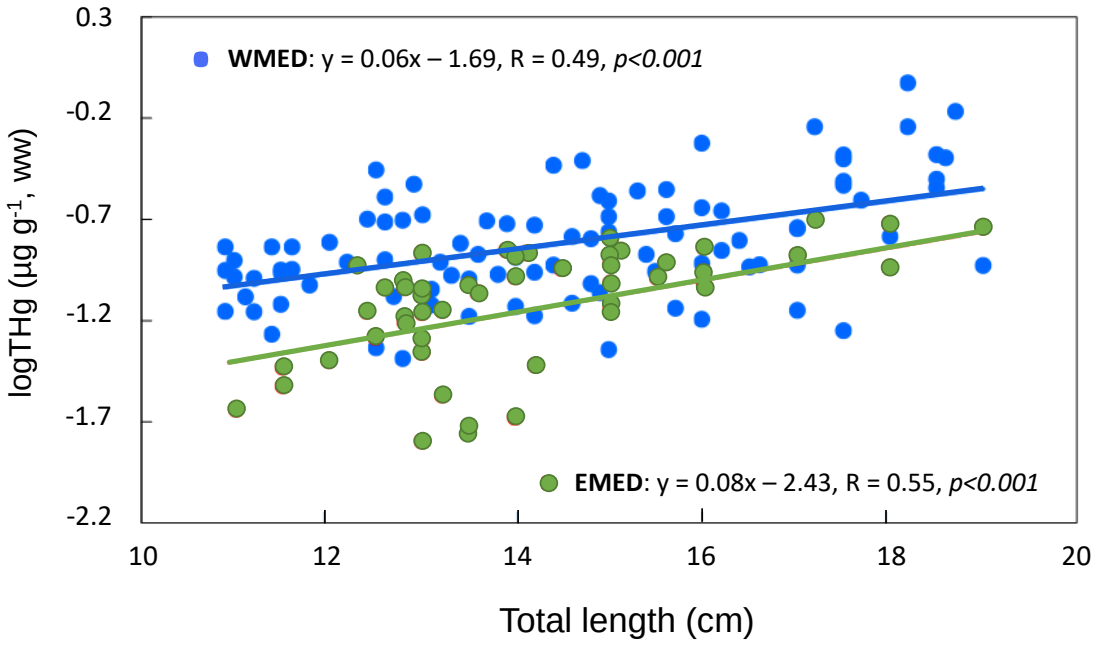

Figure 7. *Log-log relationships between THg and total length in the red mullet* (Mullus barbatus) *from the Gulf of Lion, France (WMED) and the Gulf of Izmir, Turkey (EMED).*

4.3. Biomagnification

Biomagnification is defined as the increase in Hg concentration in organisms from prey to predator throughout food webs from primary producers to high trophic level predators. Some studies provide data on Hg biomagnification along Mediterranean food webs from primary producers to various consumers at different trophic levels[21, 157, 176, 178]. Most often the food webs analyzed were comprised of only a few trophic levels as highlighted in the worldwide meta-analysis[189] in which the food webs analyzed ranged across a mean of only 1.7 trophic levels, but a few studies recently analyzed entire food webs from phytoplankton to marine mammals[153]. All studies provide evidence of an exponential

716 increase of total Hg concentration with the trophic level increase, and a steeper slope for
717 MeHg which presents a higher retention efficiency due to its lower elimination rate.

718 Mercury biomagnification in food webs is generally quantified either by the trophic
719 magnification slope (TMS) (also called biomagnification power), corresponding to the
720 slope (b) of the regression between logHg or logMeHg *vs* trophic level or $\delta^{15}N$ of the
721 organisms, or by the trophic magnification factor (TMF) calculated as $TMF = 10^b$ (see
722 Ref. 190 for a critical discussion). Trophic magnification slope generally ranges from
723 0.11 to 0.22 for total Hg and 0.14 to 0.36 for MeHg in the food webs studied from polar
724 to tropical ecosystems, which corresponded to TMFs ranging from 1.29 to 1.66 for Hg
725 and from 1.38 to 2.29 for MeHg[153, 184, 189]. The TMFs calculated for Hg in Mediterranean
726 food webs are within this range with a lower value in Sicily (1.22, Ref. 175) than in the
727 Gulf of Lion (1.68, Ref. 171) or the Bay of Marseille (1.25 - 1.58, Ref. 177), but reaches
728 2.40 (TMS = 0.38) for MeHg in the Gulf of Lion[21]. A higher biomagnification power for
729 MeHg was calculated in the hake food web in the MED than in the NE Atlantic (2.40
730 and 1.95 respectively)[21], while no difference in MeHg biomagnification power between
731 the MED and the Atlantic was found for deeper fish species occurring in deeper
732 waters[48], such as the sharks *Scyliorhinus canicula* and *Galeus melastomus.* Currently,
733 due to the scarcity of relevant data, it is not possible to account for a particular Hg
734 biomagnification in MED food webs. However, a possible hypothesis is that the smaller
735 size of individuals in the MED induces longer or more complex food webs, which may
736 result in a higher Hg biomagnification factor. It is proposed that longer food chains
737 induce a decrease in energy transfer and an increase in contaminant retention[191, 192].
738 During summer, when nutrients become limiting, changes in trophic conditions could
739 modify the importance of the microbial loop as well as the role played by mixotrophic
740 organisms in the trophic transfer of Hg. It is not known if there are differences in the
741 processes involved in Hg transfer and biomagnification in pelagic and benthic-
742 dominated food webs or a difference in the magnitude of similar processes. Few data are
743 available on Hg and MeHg concentrations in the benthic invertebrates which constitute
744 important prey sources for higher trophic level consumers. The specificity of the MED
745 food web functioning itself may well influence Hg transfer[193].

746 The use of different trophic markers (carbon and nitrogen stable isotopes, fatty acids,
747 amino-acids, compound-specific stable isotope analyses) and stable Hg isotopes may
748 improve the comprehension of trophic transfer in the first levels of the food web and

thus refine the estimation of Hg and MeHg transfers under varying environmental conditions. Ecosystem models such as ECOPATH with ECOSIM, ECOSPACE, and ECOTRACER[194, 195] take into account all food web interactions. Applying such models here should allow better quantification of the trophic transfers of Hg and MeHg in MED ecosystems and their temporal and spatial variability. Regional food web models accounting for bioaccumulation need to be implemented to simulate the spatial variability, as well as the population-variability, of Hg concentration in organisms, and refine the estimation of total Hg and MeHg content in MED biota. All these questions require accurate knowledge of organism biology, physiology, and ecology, to determine how they differ in the MED from adjacent areas.

4.4. Quantification of Hg content in Mediterranean biota and fisheries harvest

From the data compiled in the Supporting Information (SI.6), we estimated the THg and MeHg content in MED biota. Detailed methodological and calculation details are also given in the Supporting Information (SI.7). The estimate indicated that MED marine biota contains ~ 4.7 Mg of THg and ~2.2 Mg as MeHg. Due to the uncertainty associated with the initial biomass estimation, a range between 3.0 and 6.4 Mg of THg in MED biota can be approximated using the standard deviation of the biomass compartments[196]. These results illustrate not only the importance of primary producers, which represent 13 % of THg in MED biota, as already observed in other mass balance inventories[197] but also the chief importance of the benthos, a too often neglected compartment, which accounts for ~50 % of THg (32 % of the MeHg) in MED biota. Cetaceans also constitute an important Hg reservoir (10 % of THg and 18 % of the MeHg present in MED biota). However, THg in biota represents only a small part (0.7 %) of the general Hg budget in the MED. An estimation of Hg removed from the MED by fishery catches was performed using the observed data of catches for the year 2011[196]. A total of 0.30 Mg THg y^{-1} and 0.26 Mg MeHg y^{-1} is extracted from the MED by fisheries, which is similar to the value of 0.29 Mg MeHg y^{-1} calculated by Žagar et al.[41] using a different method. However, in contrast to these authors, total aquaculture products were not included in our estimation, which could therefore be considered as a minimum value. Catches therefore annually remove ~6 % of the THg and ~12 % of MeHg held in living biomass in the MED. Sharks and small pelagic fishes (including sardine and anchovy) constitute the main quantities of MeHg (20 % each) removed by MED fisheries, followed by large pelagic (13 %) and large

demersal (11 %) fishes. These estimations should be treated with caution as a large degree of uncertainty is associated with all steps of the calculations.

5. Human exposure

Mercury is one of the ten most important pollutants of global concern for human health[198]. The major toxic effects of MeHg, a naturally occurring organic form of Hg prevalent in fish, are on the central nervous system, with the developing fetus being most vulnerable[1]. Consumption of fish is considered a major source of Hg exposure to Europeans. Other sources are well described, but their contributions are minor in comparison with fish consumption[199].

Human exposure to mercury and its compounds can be assessed through the measurement of Hg concentrations in many different biological sample types. The most commonly used biomarkers are the concentrations of mercury in hair, urine, blood, and cord blood, and their selection can depend on factors such as the potential source of exposure, chemical form, and exposure life stage. An extensive recent review indicated that the individuals with the highest reported Hg levels were those living in the Arctic, Pacific, MED, and Atlantic coast regions who consume the highest amounts of fish, seafood, and marine mammals[200]. It has been shown that several species of fish from the MED have higher levels of Hg in their tissues compared with the same species from the Atlantic Ocean[201, 202,] and references cited in section 4.3. An extensive review of mercury levels in biota is presented by Cinnirella et al.[148] and indicates that among all the species considered, *Diplodus sargus*, *Sardina pilchardus*, *Thunnus thynnus*, and *Xiphias gladius* show trends of mercury concentration higher than safe limits defined by WHO and EU.

Human exposure to Hg in Europe, and in particular, the question of whether MED populations are more exposed to this contaminant than other European populations has been addressed in the literature. Two studies have evaluated Hg concentrations in blood, urine, and hair, widely used biomarkers to evaluate Hg human exposure, of populations from European Countries[199, 203]. Both studies agreed on the fact that there are significant differences in MeHg exposure across the EU and that exposure is highly correlated with the consumption of fish and marine products, as well as the availability of large fish species from the MED. Whether human exposure to Hg is higher in the MED than in

North European countries still needs to be elucidated through a well-designed comparative study.

The results of studies in the MED countries are provided in the Supporting Information (SI.8)[199, 203]. The highest levels are found in coastal regions with local seafood consumption (Spain, Morocco, Tunisia, and Greece) which is consistent with other studies around the world. In the framework of the EU-funded DEMOCOPHES project[204], the dietary habits and consumption frequency of fish and other marine products showed great variations among the 17 EU countries, which was also reflected in the high variability of Hg levels in the hair of mothers and children. Among the MED countries participating in DEMOCOPHES the highest values (geometric means) were found in Spain (1.59 μg g^{-1}), whereas Cyprus and Slovenia showed much lower values (0.43 μg $g^{-1}$and 0.26 μg g^{-1}, respectively).

In the MED region, two cohort studies aimed to link prenatal Hg exposure and health outcomes in newborns. The prenatal exposure in both studies was based on cord blood mercury measurements. In Spain, the "Environment and Childhood" (INMA) study implemented in the period 2004 to 2008 included several regions, and 1883 cord blood samples were analyzed for THg[205]. The highest concentrations expressed as geometric means were found in samples collected in Valencia (9.5 μg L^{-1}) and Asturias (10.8 ng mL^{-1}) and were strongly related to fish consumption, especially large oily fish and tuna. The second MED cohort study included coastal regions in Italy, Slovenia, Croatia, and Greece[206, 207] in the period between 2007 and 2011. This cohort study included 1308 mother-child pairs enrolled in the Public Health Impact of long-term, low-level, Mixed Element exposure in a susceptible population (PHIME). The highest levels of cord blood samples were found in the Greek population with geometric means of 7.7 ng mL^{-1}, followed by Italy with 5.6 ng mL^{-1}, Croatia with 5.1 ng mL^{-1}, and the lowest in Slovenia with 2.1 ng mL^{-1}. These levels were strongly correlated with fish consumption, and in Greece primarily due to locally caught fish. The Valencia and Asturias region in the INMA and Greek PHIME prenatal exposure values are comparable to regions with high fish intake in Japan, Honk Kong, Korea, and Polynesia[205]. These two studies confirm the data presented in Supporting Information (SI.8) that indicate high variability of Hg exposure in the MED region reflecting variation in the frequency of fish consumption, their sources, and type. Similar findings were reported in a recent publication of Petrova et al.[10], where mean Hg levels in hair for women of childbearing age on the French

Mediterranean coast were higher than for women of childbearing age from other European countries. This trend is in accordance with the higher annual fish consumption *per capita* in various European countries. Besides, it has to be noted that fish from aquaculture often have lower Hg levels compared with wild fisheries. For example, levels of Hg in seabass (*Dicentrarchus labrax*) from wild fisheries in the MED were, on average, approximately 10 times higher than in aquaculture seabass[207].

While fish consumption is an important element of human health, especially in the early stages of life[208, 209], higher MeHg exposure during pregnancy is associated with a poorer metabolic profile. Both MED epidemiological studies, INMA and PHIME, also indicated that there is a growing awareness of inter-individual differences in the toxicokinetics of mercury and the resulting biomarker measurements may be influenced by genetic polymorphisms[210, 211]. Since the symptoms of MeHg exposure are subtle and multi-causal, there is still no consensus on a health-based guidance value for MeHg exposure despite the large number of studies trying to connect low exposure levels to actual risk[209, 212]. However, there is a general recommendation that pregnant women, children, and women of childbearing age should be protected as much as possible from Hg exposure. Therefore, it is important to know what the actual exposure to MeHg is in the general population and what the sources of exposure are to formulate adequate mitigation strategies and recommendations. For example, an attempt was made for the Italian population[213] with the formulation of advice regarding food habits that could maximize the benefits, whilst reducing the risks of MeHg intake in sensitive groups without compromising seafood consumption. This should allow a better understanding of the food risk associated with mercury, particularly in highly polluted sites. Overall, the Minamata Convention on Mercury sets guidelines for limiting human exposure to Hg. Article 22 of the Minamata Convention calls for parties to monitor mercury in the environment as well as in people (biomonitoring) as a way of assessing the effectiveness of the convention.

6. Modeling the Hg cycle in the Mediterranean

Numerical biogeochemical models are effective tools to investigate the fate and transport of Hg in the environment. Synthesizing available knowledge into a rigorous framework, they help to highlight gaps in process understanding and data availability[32, 33, 45, 214, 215, 216, 217, 218, 219, 220, 221, 222, 223]. Moreover, models can be used to predict the

879 evolution of a system under different Hg emission scenarios, trophic conditions, and
880 climate change, supporting the evaluation of alternative management strategies[218, 219, 224,
881 225, 226, 227]. Reviewing modeling studies for the marine Hg cycle in the Mediterranean
882 area, we found that only one paper has sought to model the Hg cycle in the MED at the
883 basin scale[41], pointing out uncertainties in Hg input to the basin and a poor
884 understanding of Hg methylation and demethylation processes at that time. Other
885 modeling efforts in the MED are local scale studies focusing either on transport and
886 transformation processes of Hg species in regional seas[69] and coastal sites[32, 224, 228, 229,
887 230, 231], as well as on the bioaccumulation and biomagnification processes[21, 232]. Most of
888 these models still presented several limitations, namely, the use of the quasi-steady state
889 approach, coarse spatial resolutions, and the lack of full coupling between physical and
890 biogeochemical processes.

891 Small-scale assessments are relevant to provide estimates of Hg fluxes from coastal
892 and former industrial areas[233] since a comprehensive assessment of Hg point sources and
893 legacy Hg for the MED is lacking. However, existing modeling studies for Hg in the
894 MED are also geographically biased as they have been carried out in the areas where
895 more data have been collected over the years: either the Northern Adriatic Sea, or the
896 NWMED. Significant differences in the distribution and fluxes of Hg species are
897 observed[46, 88], in these two sub-basins, driven by contrasting oceanographic and
898 biogeochemical features, (i.e. the Northern Adriatic Sea is a shallow shelf with depth <
899 50 m and high river discharge, while the NWMED a deep system with seasonal
900 upwelling events), but a complete understanding of the MED system as a whole is
901 missing.

902 Remarkable research efforts in the last decades to unveil the mechanisms
903 underlying Hg methylation in the ocean pointed out organic matter remineralization as a
904 key process that triggers the release of dissolved Hg and fuels the activity of
905 heterotrophic bacterioplankton[96, 97, 234 , 235, 236]. Phytoplankton phenology patterns have a
906 large impact on MeHg production and bioaccumulation, as the cell size affects both the
907 ability to bioaccumulate Hg[152,158] and the sinking velocity after death, with small slow-
908 sinking plankton favoring water column Hg methylation in the water column[91, 237], and
909 large fast-sinking plankton acting as a fast vector for Hg sequestration through
910 scavenging and transport to the seafloor[238]. These pieces of evidence are fostering new
911 efforts aimed at developing integrated modeling tools that couple the biogeochemistry of

912 Hg species with that of organic matter and nutrients and with hydrodynamic transport[219, 223]. At the state of the art, coupled physical-biogeochemical models for the MED, can simulate the key processes of nutrients (i.e., nitrogen, phosphorus, silica, iron) carbon, and oxygen in the water, sediments, and in the food web from heterotrophic bacteria to phytoplankton and zooplankton, reproducing the observed spatial gradient and seasonal variations of chlorophyll and primary production at a spatial resolution up to 1/64 degree[239]. Validated model outputs for the BFM-OGSTM model, a biogeochemical model coupled to the physical model NEMO-OceanVar, are freely available at the Copernicus Marine Service site (https://resources.marine.copernicus.eu), with a spatial resolution of 1/24 degree, for 125 depth levels, for forecast simulations and 20-year reanalysis. Given the high standard attained in physical-biogeochemical models, a full physical-biogeochemical-Hg coupling will likely add insights into the cycling of Hg in the MED and its possible future evolution.

To improve our ability to model the Hg cycle, a better mechanistic understanding is also needed. A few measurements are available for Hg methylation and demethylation rates in the MED waters, as well as for the formation of Hg^0 and DMHg[43, 44, 240]; but rates of photochemical transformations have never been assessed in the MED[137, 138], nor has a full mechanistic understanding been achieved for any of these processes. Moreover, a recent review highlighted significant uncertainties in assessing potential seawater Hg methylation and demethylation rates[241]. Given the relevance of DMHg in the open ocean[39, 43], more observations and modeling experiments are needed to constrain transformation kinetics between DMHg, MeHg, and inorganic Hg^{II} (Ref. 237). Further investigation of Hg species transformations in sub-basins of the MED with different trophic status could provide more reliable site-specific rates to be used in the models and could help to elucidate how different controlling factors, such as primary production, dissolved organic matter, oxygen, temperature, and chlorides affect transformations kinetics. The continuous availability of data of Hg species in water and plankton, the latter being particularly scarce in MED[148], is also crucial for model validation and to improve our ability to deal with the challenges posed by climate change.

7. Overview of recent advances

Compiling the oceanographically consistent THg data obtained in the open WMED waters between 2000 and 2017 allowed us to draw a consistent pattern of Hg distributions (Fig. 2). The THg concentrations of the upper layer (AW) are rather variable (as a result of Hg evasion and biological pumping) averaging 0.86 ± 0.27 pmol L^{-1}, whereas, in the intermediate and deep waters (EIW+WMDW), they are more homogenous with a mean of 1.02 ± 0.12 pmol L^{-1}. In the EMED, the available THg measurements are in the same range as those of the WMED but are far too few to determine any consistent oceanographical pattern. MeHg represents around 10, 40, and 13 % of THg in AW, EIW, and DMW, respectively. The highest MeHg values are found in the OMZ with high AOU (Fig. 4). The methylating, *hgcA*-like genes from different microbial groups have even been identified in MED waters. The MeHg distribution seems likely to be ultimately governed by the intensity of primary production and the associated OM degradation. Consistently, MeHg concentrations in the mesotrophic WMED average twice those in the oligotrophic EMED. In addition, the methylation capacity of MED waters is high compared to other parts of the World Ocean. The THg (MeHg) inventories in waters are ~280 (100) Mg and ~400 (50) Mg for the WMED and EMED, respectively. Air-sea exchanges dominate the Hg fluxes, and Hg evasion largely exceeds atmospheric deposition (~30 Mg y^{-1} net). However, the excess of evasion, given by the models, is still insufficiently supported by the observations to be fully reliable. The MED is a net exporter of Hg to the adjacent Atlantic Ocean (~2 Mg y^{-1}, with ~1.4 Mg y^{-1} as MeHg), and MED abyssal sediments are a net sink for Hg (~6 Mg y^{-1}), whereas shelf sediments retain (at least temporarily) ~7 Mg y^{-1}. Most of this latter input originates from rivers (~6 Mg y^{-1}). This budget is, however, still far from being well constrained. For example, our estimations of submarine groundwater discharges, coastal erosion, submarine tectonic inputs, and point sources are rather coarse. High Hg concentrations were observed in Mediterranean predator organisms.

The MED is not only a bioreactor for MeHg production but also one of the places in the World Ocean where the methylation capacity of the Hg is highest. The difference in MeHg water concentrations between the MED basins (and other oceanic basins) appears to be transferred through the food webs and the Hg content in predators to be ultimately controlled by the MeHg concentrations of the waters of their foraging zones. Mediterranean top-predator fish still exceed European Union regulatory Hg thresholds. Since fish are the main vector of MeHg to humans, the current knowledge of the actual

exposure of MED populations to MeHg is still needed to formulate adequate mitigation strategies and recommendations without compromising seafood consumption. Mitigation of MED ecosystem exposure to Hg requires a full coupling of physical-biogeochemical-Hg models based on a better assessment of anthropogenic Hg sources; such coupling will likely add insights into the possible future evolution of the Hg cycling in the MED, as a result of climate changes and variations in Hg atmospheric deposition.

8. Perspectives

8.1. Hg cycle, climate change, and human coastal management in the MED

MED shares most of the uncertainties with other parts of the global ocean concerning the Hg cycle and its possible modification due to climate change. Non-Mediterranean-specific changes in Hg cycling are expected from climate change, such as those listed for a global perspective[242], including changes in atmospheric Hg oxidation and deposition and wildfires. Also, climate change is expected to induce modifications in the hydrological regime that would consequently affect the Hg atmospheric wet depositions, input regime from rivers, and submarine groundwater discharges. More specifically, the MED is very vulnerable to future climate change scenarios[28], which are expected to induce an increase in vertical stratification, a depletion of oxygen in deep layers, and a reduction of primary productivity. Shallow and deep-water mixing would affect the efficiency of Hg transfer to the bottom sediments. A possible decrease in plankton productivity may slow down the uptake and subsequent Hg scavenging. Depletion of oxygen may favor the MeHg formation. However, the multi-causal drivers of Hg methylation and demethylation rates add complexity to any attempts to predict future effects. Besides, a reduction in European atmospheric emissions would lead to a decrease in Hg deposition to the MED, and the short Hg residence time in waters should favor a rapid decline of Hg concentrations in waters. Climate change may induce in the MED not only a reduction of primary productivity but changes in phytoplankton community composition and likely a decrease in cell size, as already observed in different geographic zones[243, 244, 245]. Human coastal management may also impact terrestrial inputs, such as the decrease of phosphorus inputs to the Mediterranean rivers in recent decades inducing a decrease in plankton size[246]. An increase in oligotrophy and a decrease in cell size may thus increase Hg bioconcentration processes at the base of food webs. At higher trophic

levels, an increase in temperature would increase the metabolic demand of organisms[186] and affect their behavior[185], leading to a decrease in their growth rate and size that could cause an increase of MeHg bioaccumulation and a decrease in its elimination rate[167]. A decrease in organism size generally leads to longer and less efficient food webs, along which Hg biomagnification would be increased, while the effects of temperature on food web length are complex and may vary spatially[192, 247, 248]. Thus, the three Hg transfer processes in biota, bioconcentration, bioaccumulation, and biomagnification could be enhanced by different climate change scenarios in the MED[158], but its intensity would probably be highly spatially heterogeneous. An increase in Hg concentrations in marine organisms would be problematic for seafood consumers in the MED region.

8.2. The unknowns of the Mediterranean Hg cycle and research needs

Despite the numerous scientific advances described in this review paper, several uncertainties in the MED Hg distribution, cycling, and budget persist.

- Measurements of THg and MeHg in the Southern MED and the Levantine Basin waters are insufficient for mapping oceanographically consistent distributions of Hg species in the water column of the EMED.
- The revised Hg budget for the MED remains poorly constrained relatively to several Hg inputs especially because of the almost total absence of spatial and seasonal data series, including speciation, and fluxes at the air-sea interface, hydrothermal vents, cold seeps, SGD, and point sources. Monitoring systems for seasonally quantifying continental inputs have to be implemented.
- Notwithstanding a general agreement for a net Hg evasion flux (~30 Mg y^{-1}) to the atmosphere, taking into account the photolytic reduction of Hg^{II} compounds in the atmosphere could modify this figure. Gas-phase reduction of Hg^{II} would reduce dry and wet deposition to the MED, however by how much, requires further modeling studies to be performed. In addition, at-sea monitoring of seasonal and spatial variability (coastal upwelling) of Hg deposition and evasion is needed to explore to what extent atmospheric deposition is the primary factor controlling evasion of Hg^0 to the atmosphere. Such data will provide the basis for models and for validating them.
- The transport of particulate Hg inputs from terrigenous origin to the open sea through canyons is not adequately quantified. For example, which part of riverine Hg inputs (associated with particulate material) remains in the margin sediments,

which part reaches the abyssal sediments *via* canyons, which part is released in the water column, and which part may become available to benthic food webs?

- Some aspects of Hg speciation in waters are still questionable. For example, published observations on MMHg/DMHg ratios diverge widely in space and time and show little coherence or rationale. The ratio between the two methylated forms has consequences for MeHg fate and distribution between the atmosphere, water, and biota.
- Further work is also needed to elucidate Hg methylation mechanisms. The biogeochemical factors which promote net Hg methylation are still being identified. The importance of the nutrient status (and associated plankton communities) appears to be a determining criterion. Indeed, we know that the oligotrophic EMED waters are less loaded with MeHg than the WMED. To what extent is the heterotrophic activity responsible for Hg methylation, especially in phosphate-limited environments? Is there a place for abiotic methylation?
- The main challenge to advancing the understanding of Hg transfer in MED marine food webs resides in the clarification, and quantification, of bioconcentration processes at the base of the food chain, by far the largest "quantum" leap in Hg concentration in biota. This challenge comes with several questions:
    - What are the relative roles of food web length, plankton size and nature, and detritus in the transfer efficiency of MeHg?
    - How would differences in biomass of the various groups of viruses, bacteria, autotrophic and heterotrophic pico, and nanoplankton cells affect Hg bioaccumulation in zooplankton consumers?
    - Could the oligotrophic conditions modify the importance of the microbial loop as well as the role played by mixotrophic organisms in the trophic transfer of Hg?
    - Rather few data are available on Hg and MeHg concentrations in the benthic invertebrates which constitute important prey sources for higher trophic level consumers. Are there different processes involved in Hg transfer and biomagnification in pelagic and benthic-dominated food webs?

To sum up, a strategy for building a comprehensive understanding of the Hg cycle in the MED, allowing future assessment of global change impacts in conjunction with

the Minamata Convention Hg policy, should be based on long-term time-series observations, the use of new markers (e.g., Hg isotopes), and high-resolution Earth System Models dedicated to the MED area. Understanding, representing, and quantifying the interlinked processes involved in the Hg cycle, from earth system physics to microbial transformations, is far from trivial. Although the levels of uncertainty associated with individual processes are still high, models can be useful in dealing with such uncertainty through scenario analyses[45, 78, 224]. Coupled physical-biogeochemical numerical models can help in investigating the impacts of climate change on marine ecosystems focusing on Hg biogeochemistry and its interconnections with transport and transformation phenomen[33, 218, 219, 224] allowing different hypotheses and scenarios to be tested. Future efforts should be made in coupling Hg models into integrated regional and/or earth system models, able to describe Hg cycling through the ocean, atmosphere, and biosphere, and to properly consider contamination hot spots, and impacts on regions of particular interest, such as coastal areas[249, 250]. Such a challenge calls for a combination of modeling refinement, from the use of variable spatial mesh and/or downscaling, to a better parameterization of transport and transformation processes, aerosols, and Hg bioaccumulation and magnification in terrestrial and marine ecosystems. Such integrated modeling is the ultimate step in building realistic scenarios of Hg cycle evolution in the Mediterranean environment. New spatial and dynamic end-to-end ecosystem modeling which relates trophic transfer and Hg and MeHg transfer, based on field data should be developed to relate observations of physical and biogeochemical processes to marine resource exploitation and consumption. Such integrated models are required to test scenarios and to be used as mitigation and management tools.

ACRONYMS

AOU: Apparent oxygen utilization
AW: Atlantic Water
DGM: Dissolved gaseous mercury
DMHg: Dimethyl mercury
DMW: Deep Mediterranean Water
EIW: Eastern Intermediate Water
EMED: Eastern Mediterranean
EU: European Union
GEM: Gaseous elemental mercury
GMA: Global mercury assessment

GMOS: Global mercury observation system
GOM: Gaseous oxidized mercury
Hg: Mercury
INMA: Environment and Childhood Project (ISGlobal, Spain)
MED: Mediterranean
MeHg: Methylated mercury (MMHg+DMHg)
MMHg: Monomethyl mercury
NWMED: Northwestern Mediterranean
OM: Organic matter
OMZ: Oxygen minimum zone
PHIME: Public Health Impact of Long-Term, Low-level Mixed Element Exposure in Susceptible Population Strata (USA Department of Agriculture)
SGD: Submarine groundwater discharge
TDW: Tyrrhenian Deep Water
TMF: Trophic magnification factor
TMS: Trophic magnification slope
UNEP: United Nations Environment Programme
WHO: World Health Organization
WMDW: Western Mediterranean deep water
WMED: Western Mediterranean

Supporting Information

SI.1. Summary of the biogeochemical Hg cycle; SI.2. Calculation of the gas transfer velocities at the Mediterranean air-sea interface; SI.3. Summary statistics on total Hg concentrations in the western Mediterranean waters; SI.4. Methylated mercury in various oceanic basins; SI.5. Biological methylation and demethylation mechanisms; SI.6. Calculations of total and methylated Hg masses in Mediterranean marine biota; SI.7. Total and methylated Hg content in Mediterranean biota; SI.8. Mercury levels in exposure biomarkers in humans in the Mediterranean countries.

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