Science of the Total Environment xxx (2012) xxx-xxx



Contents lists available at SciVerse ScienceDirect

Science of the Total Environment



journal homepage: www.elsevier.com/locate/scitotenv

The cycling and sea-air exchange of mercury in the waters of the Eastern Mediterranean during the 2010 MED-OCEANOR cruise campaign

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HIGHLIGHTS

▶ The Hg cycle in the East Mediterranean Marine Boundary Layer was examined.

Sunlight, wind and CDOM influenced dissolved gaseous mercury.

► Anthropogenic influences on concentrations and fluxes were found to be important.

ARTICLE INFO

Article history: Received 6 February 2012 Received in revised form 3 September 2012 Accepted 24 September 2012 Available online xxxx

Keywords: Dissolved gaseous mercury Mercury evasional flux Unfiltered total mercury Filtered total mercury Gaseous elemental mercury

ABSTRACT

An oceanographic cruise campaign on-board the Italian research vessel Urania was carried out from the 26th of August to the 13th of September 2010 in the Eastern Mediterranean. The campaign sought to investigate the mercury cycle at coastal and offshore locations in different weather conditions. The experimental activity focused on measuring mercury speciation in both seawater and in air, and using meteorological parameters to estimate elemental mercury exchange at the sea-atmosphere interface. Dissolved gaseous mercury (DGM), unfiltered total mercury (UTHg) and filtered total mercury (FTHg) surface concentrations ranged from 16 to 114, 300 to 18,760, and 230 to 10,990 pg L⁻¹, respectively. The highest DGM, UTHg and FTHg values were observed close to Augusta (Sicily), a highly industrialized area of the Mediterranean region, while the lowest values were recorded at offshore stations. DGM vertical profiles partially followed the distribution of sunlight, as a result of the photoinduced transformations of elemental mercury in the surface layers of the water column. However, at some stations, we observed higher DGM concentrations in samples taken from the bottom of the water column, suggesting biological mercury production processes or the presence of tectonic activity. Moreover, two days of continuous measurement at one location demonstrated that surface DGM concentration is affected by solar radiation and atmospheric turbulence intensity. Atmospheric measurements of gaseous elemental mercury (GEM) showed an average concentration (1.6 ng m^{-3}) close to the background level for the northern hemisphere. For the first time this study used a numerical scheme based on a two-thin film model with a specific parameterization for mercury to estimate elemental mercury flux. The calculated average mercury flux during the entire cruise was 2.2 ± 1.5 ng m⁻² h⁻¹. The analysis of flux data highlights the importance of the wind speed on the mercury evasion from sea surfaces.

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1. Introduction

Mercury (Hg) is a highly toxic pollutant that has become widespread throughout the worldwide environment (Mason et al., 1994; Selin, 2009). Hg is emitted from natural and anthropogenic sources and is dispersed into the worldwide atmosphere because, in contrast to other metals which tend to exist in the atmosphere in the particulate phase, Hg exists almost (>95%) in the gaseous phase and it is very stable with a residence time between 6 months and 2 years (Fitzgerald et al., 1986; Gustin and Jaffe, 2010; Slemr and Langer, 1992). Anthropogenic sources can also

0048-9697/\$ – see front matter © 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.scitotenv.2012.09.062 emit mercury as divalent mercury (RGM) and mercury associated with particulate matter (HgP) (Pacyna et al., 2006, 2010; Sunderland and Mason, 2007). The lifetime of RGM is shorter than for GEM, in some cases only a few hours (Holmes et al., 2009). Therefore, RGM is only transported tens to hundreds of kilometers before it is deposited (Schroeder and Munthe, 1998). Like RGM, HgP is deposited on local to regional scales (Sunderland and Mason, 2007).

Long-range transport of gaseous mercury, followed by wet and dry deposition, is an important process by which mercury is input to aquatic ecosystems far from its source (Sprovieri et al., 2010a). Through this process ecosystems are subjected to Hg contamination and consequential bioaccumulation in the food chain, causing negative impacts on wildlife and humans through consumption of contaminated fish (Cossa et al., 2009; Lindquist et al., 1991; Khaniki et al., 2005).

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Once in the water, mercury can be present in different forms. The main Hg forms are elemental mercury (Hg(0)), complexes of Hg(II) with various organic and inorganic ligands, and organic Hg forms, mainly as monomethylmercury cation and dimethylmercury (DMHg) (Horvat et al., 2003; Kotnik et al., 2007). The environmental fate of mercury in water is quite complex, since its toxicology, toxicity, mobility and bioaccumulation depend on its chemical form (Horvat et al., 2003). Total mercury concentrations alone do not give adequate data for understanding Hg sources and cycling in marine environments. Therefore, the study of Hg speciation in seawater is of key importance to understanding the Hg cycle in the global environment, and more specifically, its fate in the biotic and abiotic components of marine ecosystems, improving our understanding of patterns that may impact human health (Horvat et al., 2003).

A crucial part of the global mercury cycle lies in oceanic production of volatile dissolved forms of mercury, called dissolved gaseous mercury (DGM), and its subsequent transfer into the atmosphere. This transfer from water to the atmosphere occurs due to the low water solubility $(60 \ \mu g/L \text{ at } 25 \ ^{\circ}\text{C})$ and high volatility (Henry coefficient<0.3) of Hg(0) (Mason et al., 1994; Sarkar, 2003). DGM is present as Hg(0) and DMHg (Lamborg et al., 1999; Mason et al., 1995), but Hg(0) is the dominant form in the upper ocean (Gardfeldt et al., 2003; Laurier et al., 2004), while dimethylmercury may be present at greater depths (Amyot et al., 1997a). The most important sources of Hg(0) are reduction of Hg(II) by aquatic microorganisms (Mason et al., 1995; Rolfhus and Fitzgerald, 2004; Whalin et al., 2007) and photoreduction of Hg(II) (Amyot et al., 1997b; Costa and Liss, 1999; Mason et al., 2001). The presence of dissolved organic matter (DOM) may play a role in the rate of DGM formation; in particular, a photo-sensitizing role of humic substances in marine photochemical reactions has been identified (Costa and Liss, 1999). Abiotic reduction mediated by microorganisms is slower than photoreduction (Whalin et al., 2007). However, as abiotic reduction is not light dependent it can be found throughout the water column and can therefore be important in some scenarios (Qureshi et al., 2010).

Mercury is released from the ocean by evasion of Hg(0) when it is present at supersaturated concentrations in the surface waters. As most marine surface water is supersaturated in Hg(0), (Andersson et al., 2008a; Gardfeldt et al., 2003; Kim and Fitzgerald, 1986; Mason et al., 2001; Rolfhus and Fitzgerald, 2004; Whalin et al., 2007) this induces a global net upward flux.

From a global perspective, the emission of mercury from surface water to the atmosphere can account up to 50% of the mercury in the atmosphere that comes from natural processes and sources (Pirrone and Mason, 2009).

Recent studies have highlighted the importance of Hg cycling between surface water and the atmosphere in the Mediterranean region, and these studies have revealed the presence of enhanced emission rates and/or more active atmospheric transformation processes in this region (Horvat et al., 2003; Gardfeldt et al., 2003; Kotnik et al., 2007; Andersson et al., 2007; Sprovieri and Pirrone, 2008). As semi-closed sea, the Mediterranean has a distinct combination of climatological, meteorological, geographical and geological characteristics. Intense solar radiation and high temperatures characterize this basin for many months of the year, inducing the formation of Hg(0) and its emission from soil and surface waters through biological, photochemical, and photo-physical processes (Ferrara et al., 1997). Greater mercury surface emissions are also caused by the presence of extensive cinnabar deposits, as well as by volcanoes located throughout the entire region (Ferrara et al., 2003; Horvat et al., 2003). Moreover, the eastern sector of the basin is characterized by intense geotectonic activity, which may constitute an additional source of Hg(0) (Ferrara et al., 2003; Gustin et al., 1999; Gvirtzman and Nur, 2001; Horvat et al., 2003; Kotnik et al., 2007). The combination of these factors leads to naturally-occurring, supersaturated DGM concentrations throughout the region and enhances the mercury fluxes that occur at the interface water-atmosphere (Horvat et al., 2003). Ferrara et al. (2000a) estimated a value of annual mercury emissions from the entire Mediterranean to be close to 60 t per year. The magnitude of the phenomenon was confirmed by Gardfeldt et al. (2003), who calculated, using DGM data and an empirical gas-exchange model, the amount of mercury released to the atmosphere from the Mediterranean Sea during the summer to be about 66 t. Andersson et al. (2007) estimated the yearly evasion from the Mediterranean Sea surface to be 77 t, using the gas exchange model developed by Nightingale et al. (2000) and DGM data obtained during three seasonal cruise campaigns performed on the Urania Research Vessel (summer 2003, spring 2004 and autumn 2004). Hence, the Mediterranean Sea represents the main natural source of Hg released annually into the atmosphere of this region, producing an amount much higher than that $(0.6-1.3 \text{ tyear}^{-1})$ estimated for volcanoes (Ferrara et al., 2000b). These results bring out the quantitative importance of such emissions, highlighting the need for in-depth investigations into both how DGM is produced in water and into the process of volatilization.

The experimental methods currently available for making Hg(0)flux determination (flux chamber) are possible only under good weather conditions, and are therefore unsuitable for many months of the year. Mercury evasion can be also evaluated using models (Liss and Slater, 1974; Wanninkhof, 1992), but these require a good knowledge of DGM concentrations in seawater and gaseous elemental mercury (GEM) concentration in the atmosphere. Since evasion of Hg(0) from the sea surface is a particularly significant feature of the global biogeochemical cycle of mercury, more high quality ocean and atmosphere data is needed to better constrain this movement cycling, regionally and globally. To address this data gap we explored mercury exchange between seawater and the atmosphere in the Mediterranean region. Data was collected from the southern part of the Tyrrhenian Sea in the west, to the Levantine Sea in the east. The data and samples were collected in August-September 2010, on-board the Italian National Research Council's Research Vessel (RV) Urania. The vertical distribution and the spatial variation of DGM at 15 locations as well as unfiltered total mercury (UTHg) and filtered total mercury (FTHg) surface concentrations, and various chemical and physical parameters (i.e., solar radiation, water temperature, atmospheric turbulence, chromophoric dissolved organic matter proportion index) were measured. The influence of these parameters on DGM production is discussed. Moreover, we used GEM concentrations, measured continuously along with wind speed throughout the entire cruise campaign, and also along with measured DGM surface concentrations, to estimate Hg(0) evasional fluxes. For this purpose, we used the two-phase model of gas exchange proposed by Liss and Slater (1974) and employed a novel parameterization based on the most recent experimental findings.

2. Experimental

2.1. Site location and measurements

Mercury distribution and speciation in seawater and air were investigated during an oceanographic cruise carried out from 26 August to 13 September, 2010, as part of the MED-OCEANOR (Integrate Atmospheric Water Measurements to Assess the Mercury Cycle Over in the Mediterranean Sea) project. The Research Vessel Urania was equipped with meteorological and oceanographic instrumentation, including a Conductivity, Temperature, Depth (CTD) Sensors system with a cable length of 5000 m.

The Mediterranean Sea is a semi-closed basin bordered by numerous industrialized countries. A population of ~132 million live adjacent to the coast. Pollutants and contaminants released from this area have been shown to affect wildlife (de Madron et al., 2011). In addition, during the summer the area is characterized by low inversion layers and strong sunlight conditions, and this causes photochemical smog (Millán et al.,

1997). During this study atmospheric GEM, RGM and HgP concentrations were collected continuously along the route, whereas surface (1 m depth) and deep water samples (at different depths from 10 m below the surface to the bottom of the water column) were taken across 15 stations selected both at coastal and offshore locations to assess DGM, UTHg and FTHg concentrations.

2.2. Sampling and analytical methods

Both surface and deep water samples were collected using a stainless-steel rosette system on which 23 Niskin bottles with volume of 10 L were mounted. The descent and ascent speed of the system during water profile sampling was 1 m s⁻¹. Water samples for FTHg concentration measurements were filtered on-board immediately after sampling (0.2 μ m pore-size polyethersulfone (PES) filter).

2.2.1. Measurements of unfiltered total mercury (UTHg) and filtered total mercury (FTHg)

Ultra-trace Hg handling techniques were employed during the collection and the analysis of water samples (Gill and Fitzgerald, 1987; US-EPA, 2002). All containers were cleaned prior to use with acid and rinsed with Milli-Q water (N18.2 M Ω cm⁻¹). Chemical reagents were suitable for ultra-trace Hg analysis. After sampling, samples were preserved by adding 5 mL L⁻¹ of pretested 12N·HCl solution (<5 pg mL⁻¹·Hg) to the sample bottles, stored below -20 °C during the transportation and analyzed within three weeks from the end of the oceanographic campaign.

Water samples were analyzed in the laboratory for UTHg and FTHg, following the US-EPA 1631 method (US-EPA, 2002). Fifty to100 mL samples were subjected to BrCl oxidation, NH_2OH pre-reduction, $SnCl_2$ reduction, Hg-free N_2 purging, gold trap pre-concentration, thermal desorption, and Cold Vapour Atomic Fluorescence Spectrometry (CVAFS) quantification.

The CVAFS was calibrated using a gas-tight microsyringe to inject Hg(0)-saturated air from a water bath. Analytical precision was <2% (Gill and Fitzgerald, 1987; US-EPA, 2002; Ci et al., 2011b).

Every batch of samples was accompanied by at least three identically processed system blanks. Blank values ranged between 3 and 5 pg of mercury. All reported data were corrected for the mean system blank of a given batch. The detection limits based on three times the standard deviation of the system blanks were 10 pg L^{-1} .

2.2.2. Dissolved gaseous mercury (DGM)

"In situ" DGM concentrations were measured using a manual method. A detailed description of the device used in determining DGM concentrations is reported elsewhere (Ferrara et al., 2003). Immediately after sampling, 1 L of seawater was transferred into a 1.5 L glass Pyrex purging bottle supplied with a suitable light shield, in order to perform the DGM analysis under dark conditions. All handling procedures were performed using clean techniques. The DGM was stripped from seawater by purging the sample with ambient air via a membrane pump at a flow rate of 200 mL min⁻¹ for 10 min. An iodated activated carbon trap was attached to the impinger to supply Hg-free air. The volatile mercury compounds were trapped on a concentrating gold trap placed externally to a Gardis-3 atomic absorption spectrometer (Hg detection limit: 0.5 pg). A wash bottle containing 10 mL of distilled water was inserted between the purging bottle and the concentrating gold trap to remove the salts present in the seawater; this ensured that the gold trap would maintain a constant efficiency over time and with a large number of measurements. The trap was kept at a temperature of 50 °C, in order to avoid moisture condensation within the trap itself. During the stripping process, the purging air passes through the pre-concentrating gold trap and returns to the atmosphere without entering the optical cell of the spectrometer. Then, the external trap is automatically connected to the internal analytical gold trap. Mercury thermally desorbed from the concentrating trap, is then collected on the analytical trap. Following thermal desorption of the analytical gold trap mercury was determined by the atomic absorption spectrometer.

To determine the DGM concentration, consecutive measurements were made using the sample water until a constant value was reached to allow the extraction of more than 95% of the DGM. The blank was ~30% of the signal itself. The atomic absorption instrument was calibrated using a 50 μ L Hamilton gas-tight micro-syringe to inject Hg(0) saturated air from a mercury vapor generator kept at a constant temperature (4 °C) onto the concentrating gold trap. This procedure yielded very high reproducibility (2%, number of replicates = 7).

2.2.3. Atmospheric mercury speciation

Collection and analysis of GEM, RGM and HgP were performed using an integrated system that combined the analytical capability of the Tekran (Toronto, Canada) model 2537A cold vapor atomic fluorescence spectrometer (CVAFS), the Tekran model 1130 speciation unit, and the Tekran model 1135 HgP unit (Landis et al., 2002). The mercury system was mounted on the top deck of the research vessel, with the air intake at a height of approximately 10 m above the sea surface and was configured to simultaneously collect 5 min GEM samples quantified by the 2537A analyser, and 2 h RGM and HgP samples on a guartz KCl-coated annular denuder and guartz filter assembly, respectively, under total flow rate conditions of 10 l min⁻¹. After the 2 h sampling period, RGM and HgP were thermally desorbed at 500 and 800 °C respectively, and detected as GEM. This technique is based on amalgamation on gold traps, followed by thermal desorption, and then final detection by cold vapor atomic fluorescence spectrometry (CVAFS). A dual-channel design allows alternate sampling and detection, resulting in continuous sampling of the air stream. Particulate matter was removed by a 45-mm-diameter Teflon pre-filter with 0.2-µm-pore-width. The permeation tube of the Tekran 2537A instrument was calibrated using a Tekran model 2505 primary calibration unit. The calibration was conducted immediately prior and afterwards to the study, as described in Landis et al. (2002).

2.3. Chlorophyll-chromophoric dissolved organic matter (CDOM) proportion index

In order to get information on the relationship between CDOM and DGM, the CDOM-index has been used. Single spectral reflectance ratios, the ratios between 412 and 443 nm wavelengths, and 490 and 555 nm wavelengths, are sensitive to CDOM and chlorophyll, respectively. However, the former ratio is also affected by the algal content and the latter by the CDOM concentration. The band ratio technique proposed by Morel and Gentilini (2009) provides a deviation index (the CDOM-index), that represents the ratio between the actual CDOM content and the "normal" content that, on average, could be expected in case 1 waters. Case 1 waters are those oceanic waters outside of significant terrigeneous influences, and whose optical properties are chiefly determined by endogenous materials created through the biological activity. In such waters, the colored dissolved material is thus assumed to have been generated by algae and their degradation products. The CDOM index, greater or smaller than unity, denotes excess or deficit of CDOM with respect to its average, chlorophyll-dependent value. CDOM index is efficient in discriminating the chromophoric detrital material from the algal material. Indeed a value of the index higher than unity means that there is a higher proportion of chromophoric detrital material in the CDOM compared to the case 1 waters.

CDOM index values have been calculated using radiometric measurements of MODIS (moderate resolution imaging spectroradiometer) on-board an Aqua satellite, and the data are provided by the NASA Ocean Color web site (http://oceancolor.gsfc.nasa.gov/). We used level-2 data products that covered the Mediterranean region during the duration of the cruise (31 August–13 September, 2010), with a

spatial resolution of 1 km. Data files were processed using the software SeaDas 6.2, available at the NASA Ocean Color web site. The first step in processing the data was the binning of level-2 files in order to generate a level-3 product; next, the level-3 product was used to create a standard mapped image for the cruise period (the pixel resolution was 1 km). Each pixel was assigned the average of the valid CDOM index values that came from the single satellite swaths. The standard mapped image is a two-dimensional rendering of an equidistant cylindrical projection of the globe. The coordinates of the DGM sampling points were used to find the corresponding CDOM index values. Four DGM sampling points were too close to the coast, and it was not possible to retrieve a valid CDOM index value.

2.4. Numerical scheme for estimating Hg(0) flux

The Hg(0) flux at the air-sea interface, F (ng m⁻² h⁻¹), was calculated using the "two-phase" ocean model developed by Liss and Slater (1974), which assumes that the net exchange of a non-reactive gas depends on the molecular diffusion on either side at the air-sea interface. Assuming an equivalence of chemical potential across the airwater phase boundary, flux at air-sea interface is defined as the product of the gas transfer velocity and the difference between GEM and DGM,

$$F = -K_{a}(GEM - K_{H}DGM) \tag{0.1}$$

where GEM and DGM are the bulk gas phase and liquid phase mercury concentrations, respectively, and K_H is the dimensionless gas-overliquid form of the Henry's law constant. K_a (m h⁻¹) is the total transfer velocity as expressed from the point of view of the air phase, and it is composed of the two single-phase transfer velocities, one representing the rate of water-side transfer (k_w) and the other representing the air-side transfer (k_a):

$$K_{a} = \left(\frac{1}{k_{a}} + \frac{K_{H}}{k_{w}}\right)^{-1}.$$
(0.2)

The transfer velocities, k_a (m h⁻¹) and k_w (cm h⁻¹), were estimated according to the method described in Johnson (2010), which requires measurements of air temperature, water temperature, wind speed and air pressure:

$$\begin{split} k_{a} &= 0.001 + \frac{u*}{13.3S_{ca}^{0.5} + C_{D}^{-0.5} - 5 + \frac{\ln(S_{ca})}{2\lambda}} \\ k_{w} &= \left(0.222u_{10}^{2} + 0.333u_{10}\right) \left(\frac{S_{cw}}{600}\right) - 0.5 \end{split} \tag{0.3}$$

where u^{*} is the friction velocity, S_{ca} and S_{cw} are the Schmidt numbers for mercury in air and water, respectively, λ is the von Karman constant (0.4 in seawater), u₁₀ is wind speed at 10 m above the sea surface, and C_D is the drag coefficient ($C_D = (u^*/u_{10})^2$). The Schmidt number for mercury in air depends on the air's dynamic viscosity, air density, and the diffusion coefficient for mercury in air. The variation of dynamic viscosity and density of air with temperature were calculated following the Tsilingiris (2008), whereas the diffusion coefficient of mercury in air was estimated according to Fuller et al. (1966), which assumes the liquid molar volume of mercury at its boiling point to be 15.723 cm³ mol⁻¹. The Schmidt number for mercury in seawater depends on the kinematic viscosity of water and the diffusivity of mercury in water. The kinematic viscosity of freshwater was first calculated using data reported in Schwarzenbach et al. (2003) and then multiplied by a factor parameterized by Wanninkhof (1992). The mercury diffusion coefficient was calculated according to the method proposed by Kuss et al. (2009), based on molecular dynamics simulations. This method seems to be more reliable for small and heavy atoms (like Hg(0)), as opposed to other methods like the Wilke-Chang method (Wilke and Chang, 1955) and mass-based approximation (Schroeder et al., 1992). The Kuss's method has been developed with the support of experimental observations. These authors simulated the diffusion of Xenon, a monatomic small and heavy gas similar to Hg(0). Simulations for Xenon agreed well with the experimental data and it was assumed to be a reliable approach for Hg(0) as well.

The Henry's constant was estimated as:

$$K_{\rm H} = exp\left(\frac{-2404.3}{\rm T} + 6.92\right) \tag{0.4}$$

where T is the air temperature in Kelvin (Andersson et al., 2008b). The chosen parameterization for the Henry's law constant was specifically developed for mercury using experimental data.

Wind speed at 10 m was measured directly by a three-dimensional sonic anemometer (Gill HS, Gill Instruments Ltd., UK) placed at the top of the Urania's foremast. The velocity was corrected for the ship motion effect using a multi-axis inertial sensing system (MotionPak II, Systron Donner, USA), following the methodology described in Edson et al. (1998). Friction velocity was estimated as the half-hour covariance between the vertical and horizontal wind velocities, corrected for the ship motion effect. We calculated this covariance after a co-ordinate rotation to align the anemometer reference system to the mean wind velocity vector (Aubinet et al., 2000). Data from sonic anemometer and multi-axis inertial system were acquired by a real-time computer (model Compact-RIO 9014, National Instruments, USA) through a software developed using LabView 10.0 integrated programming environment (National Instruments, USA). Data corrections and flux calculations were performed by specific routines developed with MATLAB 7.0 (MathWorks, USA). Statistical analysis of data was performed by Sigmaplot 10.0 software (Systat Software Inc., USA).

The proposed numeric scheme for mercury flux estimation is a novelty because it integrates the Johnson's scheme for transfer velocities calculation and a specific parameterization for mercury.

There are approaches more detailed than the Johnson's scheme, like NOAA COARE (Fairall et al., 1996, 2003) and MESSY AIR-SEA (Pozzer et al., 2006), but they require extensive information about the physical properties of the gas and/or more detailed physical forcing data than those required in the empirical schemes. However the comparison of the Johnson scheme with NOAA COARE algorithm shows a good agreement (Johnson, 2010).

The sensitivity analysis of the Johnson's scheme indicated an overall accuracy of \pm 30% for any gas. The use of a specific parameterization for mercury diffusivity in water and for the Henry's law constant based on experimental measurements reduces the uncertainty to a level below \pm 30%. Moreover the direct measurement of wind speed at 10 m above sea surface and the estimation of friction velocity by eddy covariance technique further improve the accuracy of the scheme used in the present work with respect to schemes in which wind speed is extrapolated from measurements performed at different heights and friction velocity is modeled.

3. Results and discussion

3.1. DGM in seawater

A summary of UTHg, FTHg, and DGM surface seawater concentrations and GEM, RGM, and HgP air concentrations obtained at each sampling station is reported in Table 1, together with CDOM index and physical parameters recorded at the sampling sites. Moreover, a map of surface DGM concentrations at the 15 sampling stations is represented in Fig. 1.

High concentrations of UTHg and FTHg characterized the coastal sites whereas lower concentrations were observed at stations in the open sea. The lower concentrations were comparable to those found in other open sea environments, such as the North Atlantic (UTHg: 480 pg L^{-1}) (Mason et al., 1998), the west Black Sea (UTHg: 560 pg L^{-1}) (Lamborg

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et al., 2008), the North Pacific (UTHg: 230 ng L^{-1}) (Laurier et al., 2004), and in other parts of the Mediterranean (UTHg: 260 pg L^{-1}) (Kotnik et al., 2007). Higher concentrations were comparable to values reported in coastal environments impacted by the outflow of Hg pollution originating from terrestrial sources, such as the Gulf of Trieste (characterized by the presence of the estuary of the Isonzo river that drains the mining district of Idria) (UTHg: 5000–25000 pg L^{-1}) (Faganeli et al., 2003) and the Gulf of Baratti in the Tyrrhenian Sea (influenced by the Mt. Amiata cinnabar deposits) (FTHg: 2000 to 10,100 pg L^{-1}) (Lanzillotta et al., 2002). The highest FTHg and UTHg concentrations that we have observed during this study were recorded at Station 2, where we also measured the highest DGM concentration. Several studies indicate that the reduction of FTHg to Hg(0) is directly or indirectly mediated by photochemical reactions and that DGM photo-production, driven by the intensity of solar radiation, is the main source of volatile forms of mercury in surface water (Amyot et al., 1997a; Fantozzi et al., 2007, 2009; Lanzillotta and Ferrara, 2001; Lanzillotta et al., 2002; Qureshi et al., 2010). In our study, FTHg variation in the surface water of coastal stations followed the variations in surface DGM, suggesting that FTHg is an important controlling factor for DGM production. The analysis of the relationship between DGM and FTHg showed two different correlation patterns (Fig. 2a and b). Stations close to the coast produced a good linear correlation between DGM and FTHg ($r^2 = 0.97$, p<0.01; the intercept was not significantly different from zero). Stations in the open sea showed a low correlation ($r^2 = 0.27$, p > 0.28).

With the exception of Station 2, values of surface DGM concentrations were similar among the sampling stations (Table 1, Fig. 1). These values ranged from 16 pg L^{-1} (Station 7) to 41 pg L^{-1} (Station 4) and were comparable to those obtained in previous studies carried out in the Mediterranean Basin (Gårdfeldt et al., 2001; Lanzillotta et al., 2002; Andersson et al., 2007; Fantozzi et al., 2007).

Given the much higher values recorded at Station 2 (114 pg L^{-1}), we examined the linear relationship between DGM and FTHg for coastal sites, both including Station 2 and excluding it from the analysis. The relationship we obtained when excluding Station 2 was not significantly different from the relationship we found when including Station 2. Indeed, with Station 2 excluded, the relationship was:

DGM=0.0116×FTHg (r^2 =0.54, p<0.01), while with Station 2 included it was: DGM=0.0107×FTHg.

Station 2 is located close to the Gulf of Augusta on the southeastern coast of Sicily, one of the most industrialized and contaminated coastal environments in the Mediterranean region. This area has a relatively high influx of unregulated industrial effluents (Sprovieri et al., 2011). Its effect on DGM concentration was observed in both coastal surface waters (Station 2) and in open surface waters (Station 4). In fact, Station 4 showed the second highest DGM concentration, supporting the idea that Hg contamination impacts not only the coastal areas, but also the open sea and As observed by Kim and Fitzgerald (1988), in Tropical Pacific Oceans, DGM concentrations showed a variability in concentration, probably due to the different water masses sampled. More specifically, we hypothesize that the high DGM concentrations observed at Station 4 were due to the hydrodynamic movement and mixing of seawater, which could influence the dispersion and transport of Hg from the Gulf of Augusta to open waters in the Mediterranean. In fact, the strait of Sicily is characterized by a two layer system: the upper layer (about 200 m thick) includes Atlantic surface Waters (AW) and flows eastward; the deep layer, is composed of Levantine Intermediate Water (LIW), which flows in the opposite direction, from east to west (Gasparini et al., 2005; Kotnik et al., 2007). The relatively cool, low-salinity water from the Atlantic moves across the Mediterranean basin eastward; it warms and becomes saltier as it travels east. Atlantic water enters the eastern basin through the Straits of Sicily, meanders through the interior of the Ionian Sea and continues to flow through the central Levantine (Robinson et al., 1992). These observations are in agreement with data presented by Lacombe and Tchernia (1960), and with a circulation model developed by Zavatarelli and Mellor (1995). We argue that the movement of the upper layer water in the Strait of Sicily moves polluted water masses from the Gulf of Augusta, where Station 2 is located, eastward affecting the DGM concentration in Station 4.

To investigate the influence of DOM on DGM formation, we analyzed the relationship between DGM concentration and the CDOM index. DGM surface concentrations showed a week inverse correlation

Table 1

Summary of the analytical results for mercury species in surface water samples and in the atmosphere, physical parameters and values of the estimated mercury fluxes at the 15 sampling sites along the route followed by the RV Urania during the cruise campaign (26/08/2010–13/09/2010).

Station	LAT (N)	LNG (E)	Date of measurement	Number of sampling depths	Sea floor depth bsl (m)	Global radiation (W m ⁻²)	Wind speed (m s ⁻¹)	Water temp (°C)	Surface UTHg ^a (pg L ⁻¹)	Surface FTHg ^b (pg L ⁻¹)	Surface DGM ^c (pg L ⁻¹)	CDOM ^d index	RGM ^e (pg m ⁻³)	HgP ^f (pg m ⁻³)	GEM ^g (ng m ⁻³)	$\begin{array}{c} Hg \\ Flux^{h} \\ (ng \\ m^{-2} \\ h^{-1}) \end{array}$
1	39°41.254′	15°47.601′	28/08/2010	4	44	663	3	27	3250	1290	23	-	12.6	8.5	1.8	0.7
2	37°10.052′	15°13.686′	29/08/2010	2	<mark>16</mark>	<mark>523</mark>	<mark>3</mark>	<mark>28</mark>	<mark>18760</mark>	<mark>10990</mark>	<mark>114</mark>	-	<mark>14.1</mark>	<mark>8.5</mark>	1.7	<mark>4.1</mark>
15	40°16.724′	16°52.309′	30/08/2010	6	417	476	8	27	2880	2200	21	1.2	2.1	3.6	1.6	2.8
14.4	40°20.608′	17°09.796′	01/09/2010	4	60	685	9	26	3520	2010	24	1.5	15.2	4.5	1.4	4.3
14.8	40°21.302′	17°12.383′	01/09/2010	6	240	702	7	25	3610	2710	38	0.9	15.2	4.5	1.5	4.9
9	37°46.388′	18°16.169′	02/09/2010	10	3000	195	1	26	500	430	29	0.8	5.6	2.3	1.3	0.2
8	34°30.998′	23°53.495′	03/09/2010	11	1930	0	5	26	3510	2100	24	1.5	6.5	3.8	1.4	1.5
7	33°49.979′	27°59.991′	05/09/2010	8	2691	0	8	26	400	400	16	1.6	9.7	2.9	1.7	1.9
6	33°16.080′	29°20.264′	05/09/2010	10	2883	4	6	27	300	230	25	1.5	5.3	4.8	1.7	2.1
5	33°03.835′	26°30.411′	05/09/2010	9	2610	0	1	28	540	420	28	1.1	12.1	5.2	1.6	0.2
<mark>-4</mark>	34°42.556′	20°05.270′	07/09/2010	8	<mark>2912</mark>	<mark>829</mark>	<mark>3</mark>	<mark>26</mark>	<mark>550</mark>	<mark>480</mark>	<mark>41</mark>	<mark>1.2</mark>	<mark>2.7</mark>	<mark>5.1</mark>	1.7	1.1
<mark>3</mark>	35°58.093′	16°48.341′	08/09/2010	<mark>10</mark>	<mark>3564</mark>	<mark>242</mark>	<mark>6</mark>	<mark>26</mark>	<mark>630</mark>	<mark>590</mark>	<mark>34</mark>	<mark>1.3</mark>	<mark>5.6</mark>	<mark>3.1</mark>	<mark>1.4</mark>	<mark>3.4</mark>
<mark>19</mark>	36°09.901′	15°05.756′	08/09/2010	5	110	0	<mark>5</mark>	<mark>26</mark>	<mark>4760</mark>	3050	31	1.1	1.5	<mark>3.5</mark>	1.5	2.0
20.5	36°56.490′	14°19.839′	09/09/2010	3	110	438	3	24	4990	3200	36	-	2.4	4.4	1.4	0.8
20	37°17.019′	11°56.031′	10/09/2010	4	18	0	9	25	3030	1930	20	-	4.2	1.7	1.5	3.2

^a Total mercury concentration measured in unfiltered surface seawater samples.

^b Total mercury concentration measured in filtered surface seawater samples.

^c Dissolved gaseous mercury concentration measured in surface seawater samples.

^d Chlorophyll-chromophoric dissolved organic matter proportion index.

^e Reactive gaseous mercury concentration measured in the atmosphere.

^f Particulate mercury concentration measured in the atmosphere.

^g Gaseous elemental mercury concentration measured in the atmosphere.

^h Mercury evasional flux from the sea surface according to the numerical scheme described in paragraph 2.4.

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Fig. 1. Distribution of surface DGM concentrations along the route followed by the RV Urania during the cruise campaign (26/08/2010-13/09/2010).



Fig. 2. (a) Relationship between surface DGM concentration and surface FTHg concentration measured at the sampling coastal stations during the cruise campaign (26/08/2010-13/09/2010). (b) Relationship between surface DGM concentration and surface FTHg concentration measured at the sampling open sea stations during the cruise campaign (26/08/2010-13/09/2010).

with CDOM index (Figs. 3 and 4). CDOM index ranged from 0.8 to 1.6 whereas the DGM values ranged from 16 to 41 pg L^{-1} . The maximum value of DGM measured at Station 4 was associated with a CDOM index value of 1.2. and the DGM minimum measured at Station 7 was associated with a CDOM index value of 1.6. For four coastal stations (Station 1, 2, 20.5, and 20) it was not possible to estimate the CDOM index because of the spatial resolution of the MODIS sensor. The observed negative correlation (Fig. 3) could be due to the relative increase of detrital chromophoric dissolved organic material with respect to chlorophyll concentration, which occurs when the CDOM index rises. These findings suggest that a relative increase of chromophoric detritus concentration brings about an increase of the reaction centers, where DGM could be reduced. Others have shown that DOC is an important factor affecting mercury reduction that absorbs solar radiation and emits electrons, which are then available to reduce mercury (Lanzillotta et al., 2004; O'Driscoll et al., 2004). In addition, studies have identified humic substances playing a photosensitizing role in marine photochemical reactions (Costa and Liss, 1999). In contrast, Mason and Sullivan (1999) reported that mercury complexation by organic



Fig. 3. Relationship between the measured surface DGM concentration and the CDOM index at the sampling stations during the cruise campaign (26/08/2010–13/09/2010).

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Fig. 4. CDOM index (dimensionless) composite map for the period 31 August-13 September 2010. White crosses show the location of the of DGM sampling points where valid CDOM index values exist.

ligands reduces the concentration of Hg(II) available for reduction processes. Whether DOC is a promoter or inhibitor in Hg(0) production relies on the amount and nature of DOC, the local photo-period, and available sunlight in natural waters (Tseng et al., 2004). Additionally, aqueous light transmission varies significantly with DOC concentration. The relationship between light attenuation and DOC is the result of the chromophoric properties of DOC compounds, including humic acids (HA), fulvic acids (FA), protein amino acids, and porphyrin derivatives (Larson and Marley, 1994). In this regard, in the coastal waters of the Tyrrhenian Sea the DOC concentration was found to be twice as high (100 µM) as it was in offshore waters (Vignudelli et al., 2004), a relationship mimicked by Hg(II), 800 to 1500 pg L^{-1} (Ferrara et al., 2001) versus 40 to 360 pg L^{-1} (Horvat et al., 2001) in coastal and offshore waters, respectively. In the present study we observed higher surface DGM concentrations when the CDOM index was low (Table 1), suggesting the presence of a higher proportion of algal material in the CDOM with respect to the chromophoric detrital material. Moreover, there was no significant difference in DGM average values in coastal and open sea stations. The average DGM in coastal stations (excluding Station S2) was 27 pg L^{-1} , while in the open sea stations (excluding Station 4) it was 26 pg L^{-1} . These findings suggest that the high algal material concentrations which characterize the costal environment could reduce the Hg(II) available for reduction (Mason and Sullivan, 1999), resulting in DGM concentrations similar to those recorded at open sea locations.

In order to investigate the impact of solar radiation on DGM production, we measured DGM concentrations over short time periods (every 30 min) in coastal surface waters near Favignana Island (close to the western coast of Sicily) for two days of the cruise campaign, specifically on September 10 and 11. Both days were characterized by high solar radiation intensity that reached values of 800 to 900 W m⁻² (global solar radiation), and water temperatures of 22 to 23 °C (Table 1). During the 10th of September DGM followed the global radiation trend in the first part of the day (from 10:30 until 13:00), reaching the maximum value (31 pg L⁻¹) at noon when global radiation was 765 W m⁻². Afterwards, DGM showed a rapid decline (from 13:30 until 14:00) while the solar radiation was almost constant ranging between 803 and 820 W m⁻². DGM reached its minimum value (13 pg L⁻¹) at 15:00 when the global radiation was 331 W m⁻², afterwards it recovered its noon values. A similar pattern was observed the 11th of September when the minimum DGM value (14 pg L⁻¹) was measured at 16:30, at which time the global radiation was 365 W m⁻²; the maximum DGM value (35 pg L⁻¹) was recorded at 13:00 while the global radiation was 825 W m⁻². During the 11th of September we observed two fast reductions of DGM concentration without a significant decrease of solar radiation intensity. DGM concentration decreased from 30 pg L⁻¹ to 15 pg L⁻¹ from 11:00 to 12:00 and from 35 pg L⁻¹ to 15 pg L⁻¹ from 13:00 to 14:00, while the global radiation was always greater than 684 W m⁻².

A strict relationship between solar radiation and DGM concentration was described in Lanzillotta and Ferrara (2001), who reported the first measurements of daily-trend DGM concentrations in the coastal waters of the Mediterranean Basin. The authors observed also observed a daily variance of DGM values, that ranged from 11 to 39 pg L⁻¹ in coastal waters. These results are also consistent with numerous field observations and incubation experiments (Amyot et al., 1997a; Fantozzi et al., 2007; Whalin and Mason, 2006; Qureshi et al., 2010).

Our results suggested that there was not a consistent relationship between DGM and solar radiation patterns during the day; therefore we examined the relationship between DGM and friction velocity, since we hypothesized that atmospheric turbulent mixing was enhancing the mercury evasion process from sea surface, causing a reduction of surface DGM values. Friction velocity is related to momentum transfer along the vertical direction in the atmosphere and it is affected by the surface roughness. High values of this variable indicate a strong turbulent mixing of the atmospheric surface layer due essentially to high wind speed. Moreover, an increase of the wave motion due to wind brings about an increase of the sea surface roughness and consequently a growth of the friction velocity value. During the 10th of September friction velocity showed a rapid increase from 13:00 until 14:30, during which period it reached its maximum value (0.93 m s⁻¹). Afterward, it decreased continuously and quickly until 16:00. The increase of the u* value after 13:00 occurred simultaneously with a quick decrease of the DGM concentration. A similar pattern was observed on the 11th of September when the maximum value of friction velocity (0.55 m s⁻¹) was associated with a low DGM value (15 pg L^{-1}) at 12:00. Moreover the DGM concentration (15 pg L^{-1}) at 14:00 was also associated with

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the second highest value of friction velocity (0.40 m s⁻¹) measured the 11th of September.

These findings indicate that the atmospheric turbulence is an important factor that should be considered when estimating the mercury emission from sea surface because it causes a reduction of the surface DGM concentration through the enhancement of the release process (Wanninkhof, 1992). Solar radiation seems to be the main driver of the surface DGM under typical meteorological conditions during warm seasons, when turbulence is weak, but variation of the atmospheric turbulence regime causes rapid changes of the DGM concentration.

Regarding the DGM vertical distribution in the water column, DGM generally decreased or remained constant with depth, but in some cases slightly increased near the bottom of the water column (Station 5,

Station 8, Station 15, Station 19, Station 20) (Fig. 5), thereby highlighting the presence of a volatile mercury source. These results are in agreement with those obtained over a wider geographical scale during an international cruise campaign in the Mediterranean on-board the RV Urania in 2000 (Ferrara et al., 2003). These authors observed a general increase of DGM concentration with depth in the Mediterranean basin. In particular, they report an increase of DGM concentration from the surface until the thermocline level, then constant values down to the bottom of the water column and they suggest the presence of a source of volatile mercury in deeper waters due to bacterial activity that may produce DGM. This hypothesis is confirmed by the speciation of DGM. At the sea surface DGM is mostly represented by inorganic mercury (Hg0), whereas at the bottom of the water column a noticeable but relatively small percentage of dimethylmercury is present (Horvat



Fig. 5. Vertical profiles of DGM concentration measured along the route followed by the RV Urania during the cruise campaign (26/08/2010-13/09/2010).

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Table 2

Sea/Air Hg(0) fluxes estimated using gas exchange model in the eastern Mediterranean Sea and values reported in the literature.

Location	Time	Latitude	Longitude	$\begin{array}{c} Flux \\ (ng \ m^{-2} \\ h^{-1}) \end{array}$	Reference
Eastern Mediterranean	26 August–13 September 2010	33°N-40°N	11°E–29°E	$2.2^{a} \pm 1.5$	Present study
Yellow Sea	Four different seasons (2008–2009)	37.38°N	22.68° E	0.51± 1.29	Ci et al. (2011a, 2011b)
Northern SCS	August 2007	16°N-24°N	109°E-123°E	4.5 ^a	Fu et al. (2010)
Arctic Ocean	13 July–25 September 2005	63°N-90°N	6flux at the air-sea interface0°E-180°W	2.4 ^a	Andersson et al. (2008a)
Tokyo Bay	December 2003; October 2004; January 2005	35°N-36°N	139°E140°E	5.8 ^a	Narukawa et al. (2006)
Irish west coast	31 August-7 September 1999	59.2°N	9.5°W	2.7 ^a	Gårdfeldt et al.(2003)
East Mediterranean	17-23 July 2000	32°N-37°N	17°E–29°E	7.9 ^a	Gårdfeldt et al. (2003)
West Mediterranean	2-3 August 2000	38°N-42°N	6°E–9°E	2.5 ^a	Gårdfeldt et al.(2003)
Tyrrhenian Sea	29 July-8 August 2000	29°N-42°N	8°E–14°E	4.2 ^a	Gårdfeldt et al.(2003)
Baltic Sea	2-15 July 1997	54°N-57°N	14°W-21°W	1.6 ^a	Wängberg et al. (2001)
	2–15 March 1998	54°W– 57°W	14°W–21°W	0.8 ^a	Wängberg et al. (2001)
North Sea	May and October 1996	54.5°N	4.8°E	0.2-4.6	Baeyens and Leermakers (1998)
Equatorial Pacific Ocean	8 June–3 July 1984	4.5°S-4.5°N	93°W–155°W	3.3 ^a	Kim and Fitzgerald (1986)

^a Average values from the corresponding sampling periods.

et al., 2003; Kotnik et al., 2007). This finding is also in agreement with the results obtained by Amyot et al. (2000), who suggested that the increase in Hg(0) concentration with depth is not driven by photochemical reactions. Kotnik et al. (2007) studied the mercury speciation and its distribution in surface and deep waters of the Mediterranean Sea during two oceanographic cruises in summer 2003 and spring 2004 and they also observed that the portion of DGM typically increased towards the bottom of the water column, especially in areas with strong tectonic activity (Alboran Sea, Strait of Sicily, Tyrrhenian Sea), indicating its geotectonic origin. Our results confirm these findings as we found an increase of DGM concentration at the bottom of the water column of sampling stations (Fig. 5) that are located in correspondence to one of the major geotectonic unit in the East Mediterranean, the Serbo-Macedonian Massif within the Alpine-Mediterranean mountain belt (Meinhold et al., 2010). We cannot discriminate between the contribution of bacterial activity in the sediment and that of tectonic activity and probably they both contributed to the higher values of DGM concentration observed near the sediments at Stations 5, 8, 15, 19, and 20.

3.2. Air-sea exchange of Hg(0)

The air–water Hg(0) flux estimation is significantly affected by the choice of gas transfer parameterizations (Rolfhus and Fitzgerald, 2001; Andersson et al., 2007; Kuss et al., 2009; Ci et al., 2011b). The parameterization of the effect of wind speed and diffusion coefficient on the transfer velocity and the method used to estimate the diffusion coefficient form together the numerical scheme used to estimate both K_a and K_w .

At the air–water interface, the calculated average Hg(0) flux during the entire cruise campaign was 2.2 ± 1.5 ng m⁻² h⁻¹. This value was comparable to those previously measured in the Mediterranean Sea by Andersson et al. (2007) (1.5 to 4.9 ng m⁻² h⁻¹) and by Gardfeldt et al. (2003) (4.2 to 7.9 ng m⁻² h⁻¹), as well as to flux values observed in most of the marine environments, such as the Pacific Ocean (3 ng m⁻² h⁻¹, Kim and Fitzgerald, 1986; Mason and Fitzgerald, 1993), the Arctic Ocean (2.4 ng m⁻² h⁻¹, Andersson et al., 2008b), the North Sea (0.2 to 4.6 ng m⁻² h⁻¹, Baeyens and Leermakers, 1998), Tokyo Bay (5.8 ± 5.0 ng m⁻² h⁻¹, Narukawa et al., 2006), and the Northern South China Sea (4.5 ng m⁻² h⁻¹, Fu et al., 2010) (as shown in Table 2). Fluxes estimated in this study were significantly lower than those measured in the Atlantic Ocean (20 to 80 ng m⁻² h⁻¹) because of the extremely high DGM levels that arise via both wet and dry atmospheric deposition (130 to 240 pg L⁻¹, Mason et al., 1998).

The highest Hg(0) flux values were observed at Stations 14.8 and 14.4 (4.9–4.3 ng m⁻² h⁻¹, respectively) and at Station 2 (4.1 ng m⁻² h⁻¹) (Table 1; Fig. 6). Moreover, at Station 2 we observed the highest value of HgP (8.5 pg m⁻³). At the same station RGM was 14.1 pg m⁻³, the second highest RGM value observed during the cruise campaign. At Stations 14.4 and 14.8 we measured the highest RGM value (15.2 pg m⁻³) recorded during the cruise campaign, while the HgP was 4.5 pg m⁻³. Conversely, GEM concentrations measured during the cruise campaign did not vary substantially, and the average concentration was 1.6 ng m⁻³ (Table 1). This value is close to the northern hemispheric background of 1.7 ng m⁻³ (Slemr et al., 2003). These observed GEM concentrations are also similar to previous measurements reported in the Mediterranean Basin (Sprovieri et al., 2010b; Wangberg et al., 2008).

RGM and HgP, produced by industrial activities, are likely to be deposited at the sea surface in a relatively short time in comparison to GEM. Following deposition, RGM and HgP may be reduced and emitted into the atmosphere as GEM, which would enhance the Hg(0) flux from the sea surface near emission sources (Sprovieri et al., 2010b). The elevated values of RGM, HgP, and Hg(0) flux that we observed at Stations 2, 14.8, and 14.4 support this hypothesis. In fact, Stations 14.8 and 14.4 are located in the Gulf of Taranto, near a large steelworks factory, whereas Station 2 is close to Augusta Priolo, a town in Sicily where a chemical factory is operating. The steel plant in Taranto emitted 20.9 kg of mercury into the atmosphere during 2010. Moreover in the same area there is a power plant that emitted 15.3 kg of mercury into the atmosphere during the same year (European Pollutant Release and Transfer Register (E-PRTR) http:// prtr.ec.europa.eu/). The industrial facility nearby Augusta Priolo produces inorganic basic chemicals and mercury emission, reported in E-PRTR registry for 2010, is 56.1 kg. These data show that the mercury emission in Augusta Priolo is 55% higher than the total emission of the industrial facilities in Taranto. The presence of oxidized Hg compounds in the marine boundary layer (MBL) such as HgO and HgCl₂, that are soluble and readily deposited, could enhance the Hg(0) flux from the sea surface near emission sources (Sprovieri et al., 2010b).

We argue that tectonic activity in Station 2 is a minor contributor to mercury emission into the atmosphere because other stations placed along tectonic faults (as Station 5, Station 8, Station 15, Station 19, Station 20) showed DGM concentrations lower than that observed in Augusta Priolo and Hg(0) flux values ranging between 1.9 and 2.1 ng m⁻² h⁻¹. In Stations 6 and 7 the CDOM index was high (1.5–1.6) and this could reduce the DGM value and brings about an effect on the Hg(0) flux, but since we did not measure the CDOM index in Station 2 it is not possible to disentangle the effect of CDOM index in this station.

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Fig. 6. Map of Hg(0) flux along the route followed by the Urania during the cruise campaign (26/08/2010-13/09/2010).

DGM surface concentration at Station 2 (114 pg L^{-1}) was higher than those measured at Stations 14.4 and 14.8 (24 to 38 pg L^{-1} , respectively), but Hg(0) flux values at the two stations were comparable. This is probably due to the different wind speeds, which were 7 and 9 m s⁻¹ at Stations 14.8 and 14.4, respectively, and 3 m s⁻¹ at Station 2. As shown, high wind velocity would increase the transfer velocity and, consequently, Hg(0) flux.

The lowest Hg(0) flux values were detected at Station 9 $(0.2 \text{ ng m}^{-2} \text{ h}^{-1})$ and Station 5 $(0.2 \text{ ng m}^{-2} \text{ h}^{-1})$ where wind velocity exhibited the lowest value (1.3 m s^{-1}) . These findings highlight the Hg(0) fluxes sensitivity to wind, supporting the results obtained by Ci et al. (2011a) in the Northern South China Sea.

4. Conclusion

On a cruise campaign in the Eastern Mediterranean on-board the Italian National Research Council's Research Vessel (RV) Urania, we investigated the concentrations of UTHg, FTHg and DGM in seawater from 26 August to 13 September 2010 across 15 locations. Atmospheric concentrations of GEM, RGM, and HgP were continuously measured during the cruise. In addition, sea/air Hg(0) fluxes were estimated using atmospheric GEM concentrations, surface DGM concentrations, and meteorological parameters that we measured during the cruise campaign.

DGM, UTHg and FTHg surface concentrations ranged from 16 to 114, 300 to 18,760, and 230 to 10,990 pg L^{-1} , respectively. Higher values were recorded at coastal stations with respect to the open sea locations. In particular, the maximum values reflected the proximity to one of the most industrialized and contaminated coastal environments in the Mediterranean region (the Gulf of Augusta).

Under sunny and still conditions, the daily behavior of DGM concentrations tracked that of the solar radiation intensity, confirming the fundamental role that solar radiation plays in DGM production (Amyot et al., 1997b; Lanzillotta et al., 2002; Zhang and Dill, 2008). However, our results indicate that atmospheric turbulence can temporarily decrease DGM concentrations by increasing mercury evasion from the sea surface.

DGM distribution in the water column partially followed the distribution of sunlight and in some stations an increase of DGM concentration was recorded near the seabed, suggesting the presence of biological or tectonic activity.

All of the above-mentioned factors that affect DGM concentration highlight the difficulty in evaluating mercury evasional flux when using gas exchange models, which require a good knowledge of DGM concentration in water and GEM concentration in the atmosphere (Liss and Slater, 1974; Wanninkhof, 1992; Nightingale et al., 2000). In this study we have used a numerical scheme for estimating Hg(0) fluxes at the air-water interface (Johnson, 2010) that is based on the two-phase model (Liss and Slater, 1974), with a new parameterization based on the most recent experimental findings. In doing so, we added the Andersson et al. (2008b) parameterization for Henry's law constant and the Kuss et al. (2009) mercury diffusivity calculation to expand this flux estimation scheme. We expect to improve the accuracy of estimated fluxes because we have implemented a specific parameterization for mercury. The direct measurement of mercury fluxes by micrometeorological techniques like the Relaxed Eddy Accumulation and the gradient method will be beneficial for the validation of the proposed flux estimation scheme.

Our results provide useful information for improving our knowledge of mercury species concentrations in the MBL, the top-water microlayer, and water column, as well as for evaluating the exchange rates of gaseous Hg at the air-water interface and the spatial variability of mercury fluxes.

Further ad-hoc over-water observation programs should be carried out, to investigate the seasonal and inter-annual variability of mercury fluxes over the Mediterranean Sea. These are necessary in order to gain a better knowledge of the long-term effects of meteo-climatic drivers on mercury evasional processes, and would provide key information on gaseous Hg exchange rates at the air-water interface.

Acknowledgments

This research is part of the ongoing MEDOCEANOR program, funded by the Italian National Research Council (CNR), who we gratefully acknowledge. This research is also part of the Global Mercury Observation System (GMOS) project funded by the European Commission's 7th Framework Program (DG Research). The technical assistance of the staff of the RV Urania is also gratefully acknowledged.

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