

1 **Hydrochemical mercury distribution and air-sea exchange over the submarine hydrothermal**
2 **vents off-shore Panarea Island**
3 **(Aeolian arc, Tyrrhenian Sea)**
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22 **Abstract_** There is a growing concern about the mercury (Hg) vented from submarine hydrothermal
23 fluids to the marine surrounding and exchange of dissolved gaseous mercury (DGM) between the sea
24 surface and the atmosphere. A geochemical survey of thermal waters collected from submarine vents
25 at Panarea Island (Aeolian Islands, southern Italy) was carried out in 2015 (15-17th June and 17-18th
26 November), in order to investigate the concentration of Hg species in hydrothermal fluids and the
27 vertical distribution in the overlying water column close to the submarine exhalative area. Specific
28 sampling methods were employed by Scuba divers at five submarine vents located along the main
29 regional tectonic lines. The analysis of the hydrothermal fluids indicates a site-to-site variation, with
30 filtered total mercury (FTHg) concentrations ranging from 1072 to 4711 pM, as a consequence of the
31 gas bubbles partial dissolution. These **results are** three orders of magnitude higher than the FTHg
32 concentrations found in the overlying seawater column (ranging from 5.3 to 6.3 pM in the mid
33 waters), where the efficient currents and vertical mixing result in more dilution, and potentially rapid
34 transfer of the dissolved gaseous Hg to the atmosphere. Dissolved gaseous mercury (DGM) and
35 gaseous elemental mercury (GEM) were simultaneously measured and combined in a gas-exchange
36 model to calculate the sea-air Hg⁰ evasional flux. Based on the data of DGM (range: **0.05-0.22 pM**)
37 and **atmospheric** GEM (range: 1.7±0.35-6.4±2.6 ng m⁻³), we argue that the surface seawater off
38 Panarea is mostly supersaturated in dissolved elemental gaseous mercury compared to the
39 atmosphere, with a sea-air Hg⁰ net flux ranging from 0.7 to 9.1 ng m⁻² h⁻¹ (average: ~ 4.5±3.5 ng m⁻²
40 h⁻¹). Since the empirical gas-exchange model does not include the contribution of Hg⁰ released as gas
41 bubbles rising from the vents toward sea-surface, the calculated Hg⁰ evasional flux for this **location**
42 **is most likely larger.**
43

44 **Keywords:** Dissolved gaseous mercury; mercury evasion; Air-sea exchange; Hydrothermal fluids; Panarea Island;

1. Introduction

There is a general agreement in the scientific community that submarine hydrothermal activity exerts significant controls on the chemical composition of seawater, by providing major and trace-ions that have been leached from mantle rocks (Tivey, 2007; Von Damm et al., 1985). This process is particularly effective in the Mediterranean Sea, where coastal seawater is poorly flushed with respect to that of the oceans, and most of the known submarine hydrothermal venting is from shallow water (< 200 m depth) (Dekov and Savelli, 2004). Even though these contributions seem to be of a little importance on a global scale, hydrothermal submarine emissions may become significant on a local scale representing hotspots for the occurrence of accumulation dynamics of toxic trace metals along the trophic web (Andaloro et al., 2012; Astakhov et al., 2005; Von Damm et al., 1985). Mercury is known as a global pollutant which is widespread in the environment (Schroeder and Munthe, 1998). The ocean plays an important role in the complex biogeochemical cycling of this element, since once in the aquatic environment Hg can convert to methylmercury (MMHg) and bio-accumulates into the food chain (Morel et al., 1998; Fitzgerald et al., 2007; Mason and Sheu, 2002; Soerensen et al., 2010). Consumption of fish with high MMHg levels can lead to adverse health effects in humans and wildlife (USEPA, 1997). Closed marine water systems, such as the Mediterranean Basin, are very sensitive environments to Hg pollution due to limited exchange of water with the oceans. Fish harvested from the Mediterranean Sea is an important part of the diet in the region. Literature data on Hg contamination show a more marked bioavailability in the Southern Tyrrhenian Sea, the easternmost and deepest part (about 3500 m) of the Western Basin, where submarine volcanic emissions represent a local source of particular relevance able to determine great Hg enrichments in sediments and biological species (Andaloro et al., 2012). The importance of submarine hydrothermal activity as a potential long-term supplier of Hg in the marine environment has also been emphasized by previous works reporting significant Hg accumulation in bottom sediments (Dekov, 2007; Astakhov et al., 2007; Cherkashev, 2004; Prol-Ledesma et al., 2002; Ozerova, 1986, 2004; Cronan, 1972). To date, however, the extent to which Hg is released from hydrothermal vents into the ocean and its impact on bioaccumulation has been elusive (Dekov, 2007; Prol-Ledesma et al., 2004). **Generally, the hot hydrothermal fluids and gases rise up and mix with the entrained seawater concentrating and transporting Hg along the seawater column** (Varekamp and Buseck, 1984; Krupp, 1988). The speciation of soluble Hg in hydrothermal fluids is dominated by disulfide complexes (i.e., $\text{Hg}(\text{HS})_2^0$, HgHS_2^- , and HgS_2^{2-}) at a pH range of 4-8, in presence of high levels of hydrogen sulfide ($\geq 10^{-2}$ mol kg^{-1}), and under moderately reducing conditions in fairly hot fluids ($> 200^\circ\text{C}$) (Krupp, 1988). Elemental mercury (Hg^0_{aq}) can also be transported in hydrothermal fluids as water plumes with low hydrogen sulfide concentrations ($\leq 10^{-4}$ mol kg^{-1}) under strongly reducing conditions (Krupp, 1988).

81 Finally, transport of Hg in its elemental form as uncharged aqueous species Hg^0_{aq} may be also released
82 from the fluids and vented to the atmosphere directly via CO_2 -rich gas bubbles as dissolved gaseous
83 mercury (Varekamp and Buseck, 1984). Conversely, Hg complexes of Cl^- , CO_3^{2-} and OH^- ligands
84 have been demonstrated to be of no significance in the hydrothermal transport of Hg (Krauskopf,
85 1951; H.L. Barnes, 1979; Khodakovskiy and Shikina, 1983; Varekamp and Buseck, 1984).
86 In the current study, we investigated the concentration of Hg species in hydrothermal fluids and the
87 vertical distribution in the overlying water column close to the submarine exhalative area off-shore
88 2.5 km east of Panarea Island (Aeolian Archipelago). Both visual observations and geochemical
89 surveys were performed within the hydrothermal field that extends on the shallow seafloor from the
90 main Island to the group of islets located to the northeast (Fig.1).
91 Because the still limited knowledge of the magnitude of the air-sea exchange mechanisms, one of the
92 main factors affecting the overall uncertainty associated with the assessment of net fluxes of Hg
93 between the marine and the atmospheric environments in the Mediterranean region, we finally
94 propose an in-depth investigation into the production of the volatile dissolved gaseous mercury
95 (DGM) in the marine ecosystem and its subsequent transfer into the atmosphere as gaseous elemental
96 mercury (GEM or Hg^0_{g}). These measurements, the first carried out at such location, extend the
97 previous DGM records existing in literature for adjacent areas in the Mediterranean Sea (Caramanna
98 et al., 2010; Andersson et al., 2007; Kotnik et al., 2007, 2013; Gardfeldt et al., 2003; Horvat et al.,
99 2003; Lanzillotta et al., 2001), and improve the poor understanding of the submarine hydrothermal
100 discharging processes affecting Hg concentrations in the Basin, so far.

101

102 **2. Experimental method**

103 *2.1 Study area*

104 The investigated submarine hydrothermal vents are located off the eastern coasts of Panarea Island,
105 a volcanic structure belonging to the archipelago of the Aeolian Arc (Tyrrhenian Sea, Italy) (Fig. 1).
106 The most intense submarine emissions are located at the sea-bottom among five emerging reefs
107 (Dattilo, Bottaro, Lisca Bianca, Panarelli and Lisca Nera) arranged along a circular rim of about 1 km
108 in diameter, representing the remnants of an ancient volcanic center (Italiano and Nuccio, 1991;
109 Gabbianelli et al., 1986). The first geochemical surveys carried out since the beginning of the 1980's
110 (Italiano and Nuccio, 1991; Inguaggiato and Italiano, 1998;), revealed the existence of a deep
111 hydrothermal system beneath a large field of submarine gas emissions located at about 2.5 km east
112 of the Island. The deep geothermal reservoir at temperatures of 220-280 °C, is superimposed by two
113 different shallow submarine hydrothermal systems, one partially recharged by continental waters
114 from Panarea Island and the other one by marine waters (Italiano and Nuccio, 1991). Both systems

115 exhibit temperatures of about 170-210°C and feed the hydrothermal emissions at the seafloor. The
116 recent submarine volcanic activity is characterized by a widespread presence of gas vents and
117 hydrothermal seepages which are controlled by the NE-SW, NW-SE and N-S oriented fault-system
118 following with the dominant regional permeable tectonic lineaments of the Aeolian Islands (Italiano
119 and Nuccio, 1991; Gasparini et al., 1982). The discharging fluids and gases rise up and mix with the
120 entrained seawater producing chemically altered plumes (Fig. 2; Resing et al., 2004; Solomon et al.,
121 2009) which strongly modify the environmental chemical-physical parameters (mainly pH), also
122 promoting the dissolution of some benthic foraminiferal assemblages at some extent (Panieri et al.,
123 2005). Besides, most of the hydrothermal emissions are often marked by white bacterial mats
124 appearing as a white film of colloidal sulphur deposits containing numerous filaments of colourless
125 sulphur-oxidising bacteria (Gugliandolo et al., 2006) (Fig. 2).

126 *2.2 Sample collection and handling*

127 An intense geochemical survey was performed during two oceanographic cruises in 2015 (15-17th
128 June and 17-18th November, respectively) on board the Italian Research Vessel (RV) *BioForYou*, in
129 the framework of the MONSOON (MONitoraggio SOTTOMARINO per scopi ambientali ed energetici)
130 Italian research program. Samples of dry and dissolved gas, thermal waters and overlying seawater
131 column were collected from five different hydrothermal emissions identified by Scuba divers (Fig.
132 1). The selected vents, La Calcara (LC), Campo 7 (C7), Bottaro Crater (BC), Bottaro North (BN),
133 and Black Point (BP), are close each other, and located at depths between 8 and 23 m below the sea
134 level (Fig. 1). The sampling locations were selected according earlier studies reported in literature
135 (Italiano and Nuccio 1991; Caracausi et al., 2006; Gugliandolo et al., 2006). A control station (Field
136 Blank; FB) which is characterized by 25 m-bottom depth with the location at the distance of about 3
137 km from the main discharging sites and 1 km from La Calcara site, does not present any gas vent, and
138 was chosen as representative of ambient seawater not contaminated by the hydrothermal activity (Fig.
139 1). All the sampling stations were georeferenced and localized on a cartographic map as reported in
140 figure 1. Ultra-trace Hg clean techniques (USEPA, 2002) were applied during the entire cruise. To
141 collect samples of thermal waters (i.e. hydrothermal fluids), a system made of a Teflon probe and a
142 syringe connected by a three-ways valve to a pre-cleaned Pyrex bottle was used. The stopper of the
143 bottle has two holes sealed by valves. The probe was introduced into the sea floor as deep as possible
144 at each emission point in order to minimize the potential contamination by seawaters. The whole
145 sampling system was first filled by the hydrothermal gas to move out the seawaters and keep the
146 seawater contamination level as low as possible. Hence, by using the syringe, the thermal water was
147 pumped into the glass bottle through one of the valves located on the stopper. Simultaneously, the
148 same volume of gas was drawn out through the second valve and the procedure was repeated until

149 the bottle was totally filled by the thermal water (Fig. 2 a,b). At each station, the sample was brought
150 to the surface keeping both the stopper valves closed (Italiano and Nuccio, 1991). Consecutively,
151 sampling of the water column was performed over each discharging vent to determine the spatial
152 impact of local hydrothermal emissions in the marine surrounding. Seawater samples were collected
153 at three different depths of the column (surface, mid-water and bottom) using a single 10 L Niskin
154 bottle equipped with silicon seals and springs, handled by Scuba divers. All of the samples were
155 preserved in bottles previously cleaned with HNO₃/HCl (10%) and rinsed with Milli-Q water (18.2
156 MΩ cm⁻¹). Onboard, sample containers were rinsed three times by sample seawater prior to filling,
157 while environmental parameters (T, pH and Eh) were immediately determined by using portable
158 electrodes (Crison MM 40+). Samples were stored according to specific protocols used for examining
159 mercury chemical speciation (Parker and Bloom, 2005) and standard major ions determination.
160 Sampling of both thermal fluids and seawater was intended for estimating filtered total mercury
161 (FTHg), divalent reactive mercury (RHg) and dissolved gaseous mercury (DGM) determination.

162 2.3 Analytical methods

163 2.3.1 Geochemistry of hydrothermal vents

164 Analytical operations for geochemistry determinations of thermal waters and gases were all
165 performed at the Istituto Nazionale di Geofisica e Vulcanologia, sezione di Palermo (INGV-PA).
166 Standard major ions in hydrothermal fluids were analyzed by ion chromatography (Dionex 2000i)
167 with a reproducibility within ±2%, while the species HCO³⁻ concentration was determined by the
168 titration method once in the lab. These latter can be used just as indicative data, owing to the limits
169 of our HCO³⁻ analysis. The gas composition was determined by gas-chromatography (Perkin Elmer
170 8500) using argon as carrier gas and a molecular sieve 5A column for gas separation.

171 The ³He/⁴He ratios were measured by a VG 5400 TFT mass spectrometer (resolving power of 600 at
172 the 5% peak height; error <1%) and the ⁴He/²⁰Ne ratio by a quadrupole mass spectrometer VG Mass-
173 torr FX (accuracy ±5%).

174 2.3.2 Filtered total mercury (FTHg)

175 Analyses for Hg geochemistry have been carried out at both Agenzia Regionale per la Protezione
176 Ambientale (ARPA) and Dipartimento di Matematica & Geoscienze (DMG), in Trieste. Seawater
177 samples for total Hg were filtered through cellulose filters (0.45 μm), oxidized (250 μL BrCl) and
178 stored in ultra-clean washed Pyrex flasks to be kept dark and cold in double plastic zip-bags before
179 analyses. Once in the lab, excess of the oxidizer was reduced with aqueous hydroxylammonium
180 hydrochlorid followed by the reduction of mercuric ions with the addition of stannous chloride
181 solution, according to the EPA method 1631 for ultra-trace Hg analysis in natural water (USEPA,
182 2002). Hg⁰_(g) formed in the samples was purged with mercury free argon, collected on gold traps and

183 analyzed by Cold Vapor Atomic Fluorescence Spectrometry (CVAFS Mercur Analytic Jena). Before
184 the analysis, hydrothermal fluids were at first digested according to the DIN EN 1483 method in order
185 to reduce the effect of the excess of sulfur. After digestion, the reduction of mercuric ions in the
186 thermal waters was accomplished according to the EPA method 1631 and analyzed by CVAFS.

187 *2.3.3 Reactive dissolved mercury (RHg or Hg²⁺)*

188 Divalent reactive mercury (RHg) determination includes dissolved inorganic Hg species, labile
189 organo-Hg associations, and Hg that is readily leachable from any particulate matter present. In this
190 study, RHg was determined using the same apparatus (CVAFS). The only exception was that the
191 fresh, un-acidified, and un-oxidized samples were treated directly with SnCl₂ (Parker and Bloom,
192 2005) and analyzed in a few days from collection. Generally, samples for RHg determination does
193 not preserve because the acidification quickly and dramatically alters the measured Hg²⁺ level in
194 unpredictable ways. Acidification can lead either to desorption of Hg²⁺ from particulates and
195 oxidation of Hg⁰ to Hg²⁺ (Parker and Bloom, 2005). As the analysis for RHg determination was
196 performed two days later after the collection, the influence of storage time could not affect the data.
197 The system for FTHg and RHg was calibrated by running a number of certificate standard solutions
198 (NIST 3133). Based on the three times standard deviation of the system blank, the detection limit
199 (LOD) was estimated to be ~ 0.44 ng l⁻¹.

200 *2.3.4 Dissolved gaseous mercury (DGM)*

201 Samples for dissolved gaseous mercury (DGM) were collected underwater directly into 0.5 L Pyrex
202 glass flask by means of a silicon tube. Once in the laboratory of geochemistry at IAMC-CNR (sez.
203 Capo Granitola), liquid samples were purged by a flow 300-400 ml min⁻¹ of ultrapure N₂ for 10 min.
204 Volatile Hg species were collected on specific sampling gold traps and then transferred to a CVAFS
205 analyzer system supplied by the ARPA Institute, in Trieste. DGM on the sampling gold trap was
206 released by heating (500°C) for 1 min in a flow of argon to a permanent gold trap (heating for 1 min
207 at about 500 °C), released again and detected by a CVAFS analyzer. The method is described in detail
208 by Horvat et al. (2003) and Gardfeldt et al. (2003). Three blanks were prepared by conditioning traps
209 through the N₂ purge of 500 ml of ultrapure water. The method detection limit (MDL) was 0.004 pM,
210 which was defined as 3 times the standard deviation of blanks. The procedure blank equivalent
211 concentration was 0.02 pM. These levels correspond to less than 10% of the concentrations found in
212 both hydrothermal and surface seawater samples.

213 *2.3.5 Elemental mercury in bubbling gases*

214 In order to collect elemental mercury (Hg⁰) in the dry gas phase (bubbles) of the hydrothermal
215 discharge, a plastic funnel was inverted (30 cm diameter with some kilograms of ballast around the
216 lower ring) and precisely placed on the gas vent to be sampled (Fig. 2c). The funnel was connected,

217 through a silicon hose, to a Pyrex glass flask with twin valves. This flask was pre-filled with air at a
218 pressure above that of the hydrostatic pressure expected at the sampling depth in order to stop
219 seawater from entering the sampler (Italiano and Nuccio, 1991; Caramanna et al., 2005). The
220 collection funnel was filled in with the gas and the sampling glass flask was opened and allowed to
221 reach the equilibrium with the gas to be sampled. Once in the lab, the collected gaseous $\text{Hg}^0_{(g)}$ was
222 then concentrated into specific gold traps and detected by CVAFS technique. Simultaneously,
223 estimates of the gas flow rate at each submarine fumarole were computed by connecting the funnel
224 to a tank of known volume. By counting the gas filling time, it was possible to know the flow rate
225 (liters per minute) at any given vent. The filling time (seconds) was measured by filming the process
226 using a high definition video camera (GoPro Hero2). The investigated fumaroles showed
227 predominantly small degassing activity with gas flow rates ≤ 2 L/min, according to previous
228 determinations performed by Steinbruckner (2009).

229 *2.3.6 Atmospheric gaseous elemental mercury (GEM) measurements*

230 In the marine boundary layer overlying the submarine hydrothermal field of Panarea, the
231 concentration of gaseous elemental mercury (GEM) was measured in real-time along a route chosen
232 out of the main investigated discharging vents alignments (Fig. 3). The survey was carried out within
233 the first half of a very sunny and warm day of 18th November 2015, when the main hydro-
234 meteorological conditions did not change. During the survey, we measured an averaged seawater
235 temperature of 20°C (range from 18 to 22°C) by a dedicated fiber-optic sensor; while a portable
236 weather station (Xplorer 4 Skywatch) estimated a wind velocity of ~ 4 m s⁻¹ and a mean air
237 temperature of 23°C, respectively. The analysis of atmospheric GEM concentration was performed
238 using an automated real-time atomic adsorption spectrometer (Lumex-RA 915M) in the standard
239 monitoring mode (Sholupov et al. 2004). We sampled air at 1-s intervals by covering a total marine
240 distance of about 3 km at a vessels' speed of ~ 9 knots (about 16 km h⁻¹). Based on three times
241 standard deviation of the system blank, the gas analyzer has a detection limit of 2 ng m⁻³ with
242 sampling time of 1 sec at a flow rate of 10 l min⁻¹ (Sholupov et al. 2004) and an accuracy of 20%
243 checked by annual testing by the manufacturer (LUMEX, St. Petersburg). The analyzer monitored
244 GEM concentrations using differential atomic absorption spectrometry with correction for
245 background absorption via the Zeeman Effect (Sholupov et al., 2004). A zero correction resets the
246 baseline every 5 min during sampling. This approach has been successfully used in various type of
247 GEM measurements elsewhere (Ci et al., 2011; Bagnato et al., 2011; Kim et al., 2006) and showed
248 good agreement with the conventional gold trap/CVAFS system (Aiuppa et al., 2007; Bagnato et al.,
249 2014). During the cruise, the air was sampled 1 m above the topmost point of the deck of the vessel

250 (~ 3 m above the sea level overall) at its bow. The vessel-induced contamination during its motion
251 was assumed minimal in that case.

252 Additional atmospheric GEM measurements were performed closer to the sea-surface at about 1 m
253 a.s.l., by stopping the vessel over each georeferenced vent, with the aid of a GPS, and by acquiring
254 data through the Lumex analyzer for 10 minutes. This approach aimed at reducing the atmospheric
255 turbulence, an important factor that should be considered when estimating the mercury emission rate
256 from sea surface. In fact, it causes a reduction of the surface dissolved gaseous mercury (DGM)
257 concentration through the enhancement of the release process (Wanninkhof, 1992).

258 Finally, GEM concentrations in the inland subaerial fumaroles, located at the northeastern shoreline
259 of the island, were quantified as well (Fig. 1). Our intent was to discriminate the potential contribution
260 from inland degassing to the submarine hydrothermal Hg evasion flux in the marine boundary layer,
261 at least during our survey. Fumaroles were collected by placing an inverted funnel (30 cm diameter)
262 precisely on the gas vent to be sampled, connected to a glass condenser for removing water vapor
263 from the gas emission. This apparatus allowed us to convey gases directly into the Lumex mercury
264 analyzer, which actively pumped gases at 10 l min^{-1} with a sampling time of 1 sec. Each acquisition
265 lasted for about 5 min in a real-time continuous mode, waiting for the achievement of a stationary
266 concentration data signal.

267

268 **3. Results and discussions**

269

270 *3.1 Environmental parameters*

271 The presence of hydrothermal leakages affects the chemistry of the seawater surrounding the vents
272 due to the increased levels of dissolved and free gas in the water, modifying some of the main
273 parameters, such as pH and redox, with strong influences on the local environment. To verify the real
274 extent of such an effect, Scuba divers performed underwater vertical samples at different distances
275 from the five selected degassing vents. The pH was a very useful tracer of dispersion of vent
276 discharges, which showed a direct relation between proximity to the gas emission and increased
277 acidification (Table 1): the lowest pH values were measured close to the sea floor, where the
278 **concentrated**, acidic waters were constrained by their buoyancy (range: 6.08 - 7.83; Table 1). At the
279 control site (FB), pH value did not vary with depth and resulted always > 8 , while the temperature
280 showed a decreasing surface-bottom gradient from 20 to 14.7°C . Conversely, hydrothermal fluids
281 exhibited very low pH values, ranging from 4.7 to 5.7. The redox values highlighted reducing
282 conditions in both hydrothermal fluids and in the bottom waters close to the gas emissions (Eh values
283 from -235 to -80 mV and from -32 to 235 mV, respectively; Table 1), **mainly due to reduced sulphur**
284 **(H₂S) in the gas seeping from the seafloor**. Minor differences among the Eh values measured in the

285 hydrothermal fluids indicate a dilution by seawater within the discharging vents during the rising
286 toward the seafloor and/or within smaller shallower aquifers.

287 3.2 Geochemistry of the hydrothermal vents

288 Submarine vents were investigated by collecting samples of free gases and thermal waters from May
289 to September 2015; the values were averaged to obtain a general picture of the fluids composition, as
290 reported in Table 2. Data show the typical characters of the geothermal fluids, with chemical and
291 isotopic composition indicating the presence of a significant magmatic component. All the sampled
292 gases are dominated by CO₂ (94-99 vol. %), H₂S (0.2-6 vol. %) and N₂ (0.2-2 vol. %), with relatively
293 low amounts of CH₄ (0.0001-0.4 vol. %), H₂ (0.0001-0.07 vol. %) and traces of CO (3×10⁻⁵- 3×10⁻⁴
294 vol. %) (Table 2). **This composition is the result of the interaction between original deep gases and
295 seawater, at a relative low temperature (from 30 to 100°C), at equilibrium with the atmosphere. The
296 gas-seawater interaction causes both the condensation of steam and the loss of the highly soluble acid
297 species (i.e., SO₂, HCl, HF) present in the original deep gases.** Between the most abundant species in
298 the gas phase of our samples, CO₂ and H₂S, there is a negative correlation ($r^2= 0.98$), indicating that
299 the more CO₂ occurred in the dry gas phase, the less H₂S was detected (Fig. 4). By means of this
300 ratio, the five investigated sites can be distinguished from each other. The highest concentrations of
301 CO₂ together with the lowest concentrations of H₂S were determined for the BP and LC sites (Table
302 2). In contrast, the lowest CO₂/H₂S ratios were determined at the BN vent site, while gases sampled
303 at BC and C7 show ratios between both clusters (Table 2 and Fig. 4). The different CO₂/H₂S ratio
304 among the sites indicates the occurrence of gas scrubbing, whereas the extent of partial gas dissolution
305 in respect to the different solubility in seawater might be an indicator for the velocity of gas ascent
306 towards the seafloor. Therefore, the gases of large fumaroles which are probably characterized by a
307 rapid gas migration, **suffered the least** dissolution of the more soluble H₂S, which explains the lowest
308 CO₂/H₂S ratio analyzed in these gas samples. That is particularly quite conceivable for BN (Table 2),
309 the strongest and shallowest site of the studied vent areas and the only one where the gas plumes
310 reach the surface creating a “blowout” surrounded by pseudo-convective cells (Fig. 5). This effect
311 can strongly influence the mixing between the inner water more affected by the presence of CO₂ and
312 the surrounding one.

313 The helium isotopic ratio measured in the fluids, normalized to the atmosphere ($^3\text{He}/^4\text{He}_{\text{atm}} = 1.39 \times 10^{-6}$)
314 ⁶) and expressed as R/R_{air} is about 4.3±0.2, indicating that the hydrothermal reservoir feeding the
315 submarine hydrothermal field is affected by significant contribution of fluids released from a
316 magmatic body. Besides, the ⁴He/²⁰Ne isotopic ratios are up to three orders of magnitude higher than
317 the atmosphere, ranging from 67 to 210 (Table 2).

318 Chemical analyses of the discharged thermal waters show that all samples have a seawater-like Na-
319 Cl composition (Table 3; Fig. 6a), where the specific on-site parameters reveal the occurrence of
320 mixing between ambient seawater and a thermal end-member, according to previous investigations
321 (Tassi et al., 2009; Gugliandolo et al., 2006; Italiano and Nuccio, 1991; Caliro et al., 2004). Taking
322 into considerations the calculated equilibrium temperatures, the recorded thermal water compositions
323 agree with high temperature water-rock interactions inside the deep geothermal body, as proposed by
324 Tassi et al., (2009). The chemical composition of BP and LC samples shows a slight depletion in Na⁺
325 and Mg²⁺ compared to the seawater, whereas K⁺ and Ca²⁺ are more concentrated (Table 3). Several
326 authors have demonstrated that Mg can easily be removed from seawater heated by interaction with
327 hot rocks and hydrothermal fluids, through the precipitation of clays such as Mg-rich smectite and
328 chlorite (Tivey, 2007). Among the major water components, SO₄²⁻ is also only one showing a positive
329 correlation with Mg (r²=0.84; Fig. 6b), suggesting that like Mg, SO₄²⁻ is strongly depleted in the deep
330 end-member (Tassi et al., 2009). Conversely, the higher Mg and SO₄²⁻ concentrations found in the
331 lasting samples may be considered to resemble that of “concentrated seawater”, that is likely related
332 to boiling of seawater heated by the ascending hot gases (Tassi et al., 2009).

333

334 3.3 Hydrochemical mercury distribution

335 3.3.1 FTHg and RHg distribution in the seawater column

336 To elucidate the influence of mercury vented from the submarine fumaroles in the surrounding marine
337 environment, we investigated the vertical distribution of filtered total mercury (FTHg) and reactive
338 mercury (RHg) in seawater column overlying the selected vents. The mean concentration of FTHg in
339 the surface waters was 5.9±2.2 pM, with a range of values from 3.3 to 7.8 pM (Table 1). These data
340 are slightly higher than those reported for open oceans, such as the Pacific Ocean (1.15±0.86 pM;
341 Laurier et al., 2004) and the Atlantic Ocean (from 2.4±0.6 to 2.9±1.2 pM; Mason et al., 1998; Mason
342 and Sullivan, 1999), whereas are comparable to values reported in some near-shore environments,
343 such as the Black Sea (1.6-10.4 pM; Lamborg et al., 2008) and the coastal site of the Yellow Sea
344 (13.3 pM; Ci et al., 2011). Conversely, our data result somewhat higher than previous records existing
345 in literature for the Mediterranean Sea (1.46±0.41 pM, Horvat et al., 2003; 1.32±0.48 pM, Kotnik et
346 al., 2007, 2013; 2.54±1.25 pM, Cossa et al., 1997), emphasizing the importance in considering
347 submarine hydrothermal activity as an additional potential source of Hg for the Mediterranean area.
348 On the whole, the spatial distribution of FTHg with depth showed no significant variations, however
349 the bottom waters just above BC, BN and BP vents are characterized by weak Hg enrichments (Table
350 1). Probably, in this highly energetic environment the presence of efficient currents produces
351 vertically mix and uniform the water column. Furthermore, the formation of pseudo-convective cells

352 (Fig. 5), and the related current triggered by the water movement, may act as a sort of “liquid barrier”
353 which reduce the direct contact between the inner plume and the surrounding seawater (McDougall,
354 1978). As a consequence, a mixing between the more Hg-rich water inside the plume and the
355 surrounding seawater environment was reduced. In fact, FTHg concentrations measured in the near-
356 bottom seawaters of the hydrothermal vents range from 5.2 to 7 pM, with a mean value of 5.76 ± 0.7
357 pM (Table 1). The average RHg concentration in the surface waters was 5.03 ± 1.39 pM, with a range
358 of 3.5-7.3 pM, accounting for the dominant fraction of FTHg ($\%RHg/FTHg = 85\%$; Fig. 7). These
359 RHg values are generally higher than those proposed for many other open oceans elsewhere (Atlantic
360 Ocean: 0.8 ± 0.44 pM, Mason and Sullivan, 1999; Pacific Ocean: 0.47-1.85 pM; Mason and Fitzgerald,
361 1990, 1993; Antarctic Ocean: 0.6-1.25, Dalziel, 1995), and the recent records recently attained for
362 the Mediterranean Sea, as well (0.38 ± 0.29 pM, Kotnik et al., 2007, 2013; 0.02-0.97 pM, Cossa et al.,
363 1997; 0.81 ± 0.32 pM, Horvat et al., 2003). The spatial distribution of RHg with depth showed no
364 important variations, with concentrations measured in the bottom seawaters ranging from 3.5 to 5.5
365 pM (mean: 4.8 ± 0.7 pM; Table 1). Minor discrepancies in FTHg and RHg distributions observed
366 between surface and the bottom seawater may be the result of sunlight, temperature and other
367 physical-chemical parameters strongly affecting mercury speciation at shallower depths. RHg in
368 aquatic environment is generally considered as the available fraction of Hg for the biogeochemical
369 processes, such as the reduction to Hg^0 and conversion to mono-methylmercury (Morel et al., 1998;
370 Amyot et al., 1997). Hence, the measured high RHg and RHg/FTHg ratios suggest that the turnover
371 time of Hg in the investigated waters may be shorter than the other marine systems. Similar data were
372 proposed for seawater collected close to the gas seeping site of a submarine geothermal field in
373 Kagoshima Bay (FTHg: 0.25-15 pM and RHg: 0.03-7.33 pM; Tomiyasu et al., 2007), where as much
374 as 200 mg kg^{-1} of mercury was measured in the sediment near the fumaroles (Sakamoto, 1985).

375 3.3.2 FTHg and RHg in the hydrothermal waters

376 Measured FTHg concentrations in the hydrothermal fluids ranged from 1072 to 4711 pM (mean:
377 2743 ± 1455 pM), with the highest values found in the fluids collected at the BP and C7 stations (Table
378 1). In general, FTHg in these fluids was up to three orders of magnitude higher than the ambient
379 seawater (FB) (Table 1), demonstrating that the control area was not affected by the submarine
380 hydrothermal activity. FTHg contents in the hydrothermal fluids showed a clear difference from water
381 column over the vent, due to the efficient dilution. Compared with other studies, our FTHg
382 concentrations are quite higher than the results found in the thermal waters collected at the Sea Cliff
383 submarine hydrothermal field in the North-East Pacific Ocean (4-10 pM; Lamborg et al., 2006),
384 whereas they are well below than the values observed in the submarine hot fluids collected at Bahía

385 Concepción (FTHg ~10⁶ pM; Prol-Ledesma et al., 2004), one of the largest fault-bound bays in Baja
386 California, Mexico.

387 Simultaneous measurements of RHg in the hydrothermal fluids gave values in the range of 2.84-6.85
388 pM (mean: 5.21±1.9 pM), accounting for a very few portion of FTHg (%RHg/ FTHg = 0.1-0.7%)
389 (Table 1 and Fig. 7), but resulting higher than the values reported for many other open oceans
390 elsewhere (Table 4). The trivial measured RHg/FTHg ratio may indicate that in the submarine
391 hydrothermal fields significant fractions of RHg are probably involved in reducing biotic (that is
392 enzymatically catalyzed by microorganisms) and abiotic mechanisms that convert Hg²⁺ to dissolved
393 gaseous mercury form (DGM) (Ferrara et al., 2003; Mason et al., 1995; Ci et al., 2011; Dekov, 2007;
394 Fitzgerald et al., 2007; Rolfhus and Fitzgerald, 2004; Poulain et al., 2007; Fantozzi et al., 2009).
395 These processes may significantly contribute to the supersaturation of DGM found in seawaters and
396 to the emission of Hg⁰ to the atmosphere.

397 3.3.3 DGM concentrations

398 Dissolved gaseous mercury (DGM) consists of elemental and dimethyl Hg (Hg⁰ and (CH₃)₂Hg,
399 respectively). In this study, we assume that DGM, on the whole, occurs as dissolved elemental
400 mercury (DEM or Hg⁰) since, in the upper ocean, Hg⁰ is the dominant form of DGM (~ 90%,
401 Gårdfeldt et al., 2003; Laurier et al., 2004), **whereas detectable MMHg was only documented in deep**
402 **seawaters** (Amyot et al., 1997; Mason et al., 1995). The DGM in water can be transported via currents,
403 reacts chemically or biologically, or be finally released to the atmosphere. The highest DGM
404 concentrations were detected in the hydrothermal fluids (Fig. 8a), within a range of 0.2-5.6 pM (Table
405 1), accounting for a small fraction of filtered dissolved mercury (0.01-0.2% of FTHg) and
406 representing from 5 to 90% (average 28%) of the inorganic reactive dissolved mercury (RHg). These
407 results suggest that while DGM is produced in surface water mainly as a consequence of photo-
408 induced reactions (Amyot et al., 1997; Fantozzi et al., 2007, 2009; Lanzillotta and Ferrara, 2001;
409 Lanzillotta et al., 2002; Qureshi et al., 2010), in the deeper thermal waters, the photochemical
410 reduction may be excluded as a possible means of Hg⁰ formation, and the deep water hydrothermal
411 and/or bacterial activities may constitute an additional significant source of dissolved gaseous
412 mercury (Amyot et al., 1997; Costa and Liss, 1999, 2000; Gårdfeldt et al., 2001; Lanzillotta and
413 Ferrara, 2001; Lanzillotta et al., 2002; Ferrara et al., 2003; Gustin et al., 1999; Horvat et al., 2003;
414 Kotnik et al., 2007, 2013). To date, however, we cannot discriminate **mercury** contributions provided
415 by the bacterial activity in the sediment from those deriving from the **hydrothermal** activity. It seems
416 probable that they both contributed to the higher values of DGM concentration observed in the
417 collected deep thermal fluids of Panarea.

418 In shallow seawaters (~ 5mt), we measured DGM concentrations varying from 0.05 to 0.22 pM
419 (average: 0.12 ± 0.07 pM; Fig. 8b and Table 1), which account for about 2% of both total filtered
420 (FTHg) and reactive dissolved Hg (RHg). Except for LC and BC stations, which exhibited the highest
421 values of DGM in the hydrothermal fluids (5.6 and 1.6 pM, respectively), in general, our current
422 estimates are comparable to DGM presented by previous authors for the Mediterranean area (0.08-
423 0.4 pM; Cossa et al., 1997; Ferrara et al., 2003; Cossa and Coquery, 2005; Horvat et al., 2003;
424 Fantozzi et al., 2013; Table 5). Similar values are also reported for some polluted marine areas, such
425 as Tokyo Bay (0.18-0.34 pM; Narukawa et al., 2006), Yellow Sea (0.4-0.25 pM; Ci et al., 2011),
426 South China Sea (0.26-0.11pM; Fu et al., 2010), as well as most coastal regions elsewhere, such as
427 Long Island Sound (0.07-0.33 pM; Rolffhus and Fitzgerald, 2001), Chesapeake Bay (0.12-0.25 pM;
428 Mason et al., 1999), Baltic Sea (0.09 pM; Wängberg et al., 2001), and Ionian Sea (0.1-0.25 pM;
429 Andersson et al., 2007). These data are finally comparable to those reported for the North and
430 Equatorial Atlantic Ocean (0.48 ± 0.31 and 1.2 ± 0.8 pM, respectively; Mason et al., 1998; Mason and
431 Sullivan, 1999) and Equatorial Pacific (0.04-0.32 pM; Mason and Fitzgerald, 1990, 1993) (Table 5).
432 Certainly, minor differences in DGM concentrations between the above-cited marine areas may be
433 explained by the different biogeochemical, hydrodynamic and geotectonic scenarios.

434 *3.3.4 Elemental gaseous mercury in deep-rising bubbles*

435 From hydrothermal vents, mercury may be partially released as a component of hydrothermal gas
436 bubbles (gaseous elemental mercury, Hg^0_{g}), rising through the water column up to the marine surface.
437 There is a lot of interest in the role of bubbling process at the ocean surface on gas supersaturation.
438 To date, results are mainly provided from studies of gas transfer and interpretation of highly insoluble
439 trace gas concentrations (Craig and Weiss, 1971; Fuchs et al., 1987), but there is still a gap in the
440 knowledge to formulate a satisfactory theory. Recent studies, however, have shown that, at sea
441 surface, bubbles play an important role in the ocean-atmosphere exchange of gases, providing an
442 additional air-water interface for the transfer of gases, speeding the rate of equilibration (Zhang, 2012;
443 Hamme and Emerson, 2002, 2006; D'Asaro and McNeil, 2007; Vagle et al., 2010).

444 At Panarea, as a bubble rises, more soluble hydrothermal gases, such as CO_2 , rapidly will dissolve in
445 the water column in the initial few meters (Langmuir, 1977), while Hg^0_{g} will mainly transfer up to
446 the surface and it will escape into the atmosphere, due to its high volatility (Henry coefficient < 0.3 ;
447 Mason et al., 1994) and low solubility in water (60 $\mu\text{g}/\text{l}$ at 25 °C; Sarkar, 2003). Hg^0_{g} concentrations
448 in the dry gas phase (i.e. bubbles) of the thermal waters fall in the range of 624 - 7600 ng m^{-3} (~
449 7.6×10^{-5} - 9.3×10^{-4} ppm; Table 2), with the highest values measured in the samples collected at the
450 shallowest submarine vents, such as BN and BC (at 7.7 and 12.4 m depth, respectively). These data
451 confirm that the solubility of Hg^0_{g} vapor in seawater at about 20-30°C obeys Henry's Law (Fig. 9).

452 It is then justified the negative correlation between DGM and vapor Hg^0_{g} concentrations found in the
453 collected fluids suggesting that, at the same hydrostatic pressure (or related depth), the more DGM
454 occurred in the deeper hydrothermal fluids, the less Hg^0_{g} was detected. Unfortunately, since Hg^0_{g}
455 concentration in the dry gas phase vented from submarine hydrothermal activity has not been ever
456 measured to date, a comparison to other studies is not currently possible.

457

458 *3.4 Atmochemical mercury distribution*

459 *3.4.1 GEM dispersion in the marine boundary layer over the hydrothermal vents*

460 The cruise track and the atmospheric gaseous elemental mercury (GEM or Hg^0) concentration
461 measured at 3 m above the sea level are shown in Fig. 3. The overall average concentration was
462 $1.9 \pm 0.6 \text{ ng m}^{-3}$, ranging from 1.1 to 3.6 ng m^{-3} . Additional atmospheric GEM acquisitions were also
463 performed at $\sim 1.5\text{-}2$ m above the sea level and from the stationary vessel, with the aim to reduce air
464 turbulence and dilution. These additional measurements provided higher atmospheric GEM
465 concentrations over each site (range: 1.8 ± 0.5 - $6.4 \pm 2.6 \text{ ng GEM m}^{-3}$; Table 6), with the maximum
466 GEM value measured over the intensive exhaling vents BN, characterized by a strong volcanic gas
467 bubbling clearly visible at sea surface (Fig. 5). In addition, the smell of hydrogen sulphur (H_2S) was
468 significant during the sampling, confirming the rising of gas bubbles which transport Hg^0_{g} from the
469 seafloor to the shallow levels. High atmospheric GEM concentrations were also measured at the BP
470 station ($4.82 \pm 1.36 \text{ ng m}^{-3}$), while intermediate values were detected in the remaining investigated
471 vent sites (Table 6). These data resulted higher than the values measured in the marine boundary layer
472 over the selected Panarea's control site (FB, $1.7 \pm 0.35 \text{ ng GEM m}^{-3}$), and, more in general, than the
473 background GEM levels reported for the northern hemisphere ($1.58 \pm 0.04 \text{ ng m}^{-3}$, Steffen et al.,
474 2005), as well as other marine areas elsewhere (Equatorial Pacific Ocean, $1.0 \pm 0.1 \text{ ng m}^{-3}$, Kim and
475 Fitzgerald, 1986; North Atlantic Ocean, $2.1 \pm 0.8 \text{ ng m}^{-3}$, Mason et al., 1998; Baltic Sea, $1.6 \pm 0.2 \text{ ng}$
476 m^{-3} , Wängberg et al., 2001). Recent investigations performed in the Mediterranean Basin, gave
477 atmospheric GEM values lower than those reported in this study (range: 1.73 - 1.8 ng m^{-3} ; Gårdfeldt
478 et al., 2003; Kotnik et al., 2013). Finally, our new data are clearly higher than the atmospheric GEM
479 concentrations measured in the MBL overlying the submarine hydrothermal vents of the Piip volcano,
480 in the Bering Sea ($0.8\text{-}2 \text{ ng m}^{-3}$, Astakhov et al., 2011).

481 *3.4.2 GEM in the inland subaerial fumaroles*

482 Inland GEM determinations in the sub-aerial fumarolic emissions were performed during the first
483 geochemical survey on 17th June 2015. We aimed to evaluate the potential contribution of the natural
484 land's degassing to the estimated hydrothermal Hg flux at the sea-air interface. During the sampling,
485 the fumarolic emissions had a temperature of $\sim 100^\circ\text{C}$, while air temperature and wind velocity were

486 29 °C and 3 m sec⁻¹, respectively. An inverted funnel connected to the mercury analyzer was used to
487 capture gases, which were directly analyzed in the standard monitoring mode. We measured a mean
488 (±SD) GEM concentration of 2652 ± 503 ng m⁻³, with a range of 2099 to 3081 ng m⁻³. These values
489 differ a lot from those found in the diluted atmospheric marine boundary layer over the investigated
490 vents (Table 6), suggesting that the contribution of the atmospheric land's outgassing **does not impact**
491 **the calculated marine Hg evasion flux.**

492 3.5 Model for estimating Hg⁰ flux

493 3.5.1 Degree of DGM saturation (S_a)

494 The combination of photo-physical processes and the intense hydrothermal activity, leads to naturally
495 occurring, supersaturated dissolved gaseous mercury (DGM) concentrations throughout the
496 submarine degassing field east of Panarea Island and enhances the mercury evasion at the water-
497 atmosphere interface. Assuming that all of DGM is dissolved elemental mercury (DEM or Hg⁰),
498 saturation S_a is an indicator for Hg⁰ emission and it can be obtained from the following equation:

$$499 S_a = \frac{H' \times C_w}{C_a}; \quad (1)$$

500 where C_w and C_a are DGM concentrations in the seawater (pg l⁻¹) and GEM concentrations in the
501 atmosphere (ng m⁻³), respectively. H' is the dimensionless partitioning coefficient for Hg⁰ between
502 water and air (Henry's Law constant) calculated for seawater and corrected for temperature according
503 to Andersson et al. (2008) and Sanemasa (1975). The S_a value greater than 1 indicates the
504 supersaturation of Hg⁰ in surface waters with respect to Hg⁰ in air and subsequent Hg⁰ emission from
505 sea surface, otherwise the under-saturation is indicated and Hg⁰ deposition from the atmosphere to
506 the sea surface occurs.

507 Paired atmospheric GEM and DGM samples from our survey showed that most of the collected
508 surface waters were supersaturated with elemental mercury (Table 6). Similar scenarios were also
509 observed elsewhere in the Mediterranean basin, and documented by many authors (Horvat et al.,
510 2003; Amyot et al., 1997; Fantozzi et al., 2007, 2009, 2013; Lanzillotta and Ferrara, 2001; Lanzillotta
511 et al., 2002).

512 At Panarea, the degree of DGM supersaturation (S_a) was, on average, 2.5±0.4 with a range of 1.9-
513 2.8, **leading to a net emission of Hg⁰ from the sea surface to the atmosphere (Table 6).** The relative
514 variation in the saturation degree may govern the flux. At Bottaro North site (BN), for example, where
515 the S_a<1, the high atmospheric GEM value (Table 6) and the lowest DGM concentrations in surface
516 waters, indicate that most of the gaseous Hg⁰ contribution to the atmosphere is mainly given by the
517 rising of gas bubbles to the surface enhanced by the low hydrostatic pressure (i.e. low depth).
518 Conversely, the control site (FB) usually produced under saturation of DGM (S_a< 1), with low values
519 of both DGM and GEM, confirming that this area was not affected by submarine hydrothermal

520 activity and promoting a potential net Hg^0 deposition from atmosphere to sea surface. Compared to
521 other marine areas, our S_a values are lower than those reported in literature for two polluted coastal
522 areas, such as the Yellow Sea (7.8 ± 2.3 ; Ci et al., 2011) and the Tokyo Bay (~ 10 ; Narukawa et al.,
523 2006).

524 3.5.2 Air-sea exchange flux of Hg^0

525 The supersaturation of Hg^0 in the surface waters indicates that the exchange of Hg^0 would be always
526 from the sea surface to the atmosphere, at a rate dependent on the concentration of volatile forms of
527 mercury in water and air, on the water temperature and on the wind speed (Liss, 1983; Wanninkhof,
528 1992). Studies of mercury evasion from seawater have been reported in Europe and North America
529 (Cossa et al., 1997; Rolfhus and Fitzgerald, 2001; Wängberg et al., 2001; Gårdfeldt et al., 2001, 2003),
530 although mercury evasion from seawater due to extreme submarine hydrothermal impact, as reported
531 in this study, has not been observed to date.

532 To assess the potential mobilization of mercury through air-sea gas exchange, we calculated the
533 evasional Hg^0 flux from data on DGM and other factors using the two-layer gas exchange model
534 developed by Liss and Slater (1974), which assumes that the net exchange of a non-reactive gas
535 depends on the molecular diffusion on either side at the air-sea interface. This model is based on the
536 transfer coefficient and the Hg^0 gradient between vapor phase (GEM in the atmosphere) and dissolved
537 phase (DGM in the seawater), and it can be expressed as Eq. (2):

$$538 \quad F = K_w \frac{C_w - C_a}{H'}; \quad (2)$$

539
540 where F is the estimated Hg^0 flux ($\text{ng m}^{-2} \text{h}^{-1}$) and K_w is the gas exchange velocity (cm h^{-1}), which
541 primarily depends on wind speed on the sea surface and the Schmidt number representing material
542 transfer in a fluid (Wanninkhof, 1992; Nightingale et al., 2000). Wind speed is a parameter that is
543 easy to measure and it captures much of the variability in turbulence at the air-sea exchange interface.
544 The mass transfer coefficient K_w (cm h^{-1}) is calculated by Eq. (3) according to Wanninkhof (1992),
545 the most widely accepted method for determining wind-induced gas exchange fluxes, and extensively
546 used to estimate air-sea Hg^0 exchange (Wängberg et al., 2001; Rolfhus and Fitzgerald, 2001),

$$547 \quad K_w = 0.31 u_{10}^2 \left(\frac{Sc_{\text{Hg}}}{660} \right)^{-0.5}; \quad (3)$$

549
550 where u_{10} is the wind speed (m s^{-1}) 10 m above the sea surface, Sc_{Hg} is the Schmidt number of Hg^0
551 and 660 corresponds to the Schmidt number for CO_2 in seawater at 20°C (Wanninkhof, 1992). In-
552 turn, the Schmidt number for Hg^0 is derived from its definition as follows:

553

554

$$Sc_{Hg} = \frac{\nu}{D}; \quad (4)$$

555

556 where ν is the kinematic viscosity ($\text{cm}^2 \text{s}^{-1}$) of seawater and D is the Hg^0 diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$) in seawater, which was calculated by molecular dynamics simulation, as described by Kuss et al.,
557 (2009). The kinematic viscosity of seawater at the desired temperature is calculated according to the
558 method described by Wanninkhof (1992). In our calculations, we used a Sc_{Hg} value of 689, as
559 proposed by Kuss et al., (2009) for seawater at $T = 20^\circ\text{C}$.
560

561 To apply the model, the measured wind speed at 2 m above the sea surface was corrected to u_{10} using
562 the equation reported hereafter (Schwarzenbach et al., 1993),
563

563

564

$$u_{10} = \frac{10.4u_z}{\ln(z)+8.1}; \quad (5)$$

565

566 where u_z is the wind speed (m s^{-1}) measured at height z meters above the sea surface.

567 The calculated evasional fluxes of Hg^0 are listed in Table 6, together with a summary of DGM in
568 surface waters, GEM in air, wind speed at the height of 10 m above sea level (u_{10}) and saturation in
569 the investigated area off-shore Panarea.

570 Based on our data of DGM and GEM and the two-layer gas exchange model at the air-seawater
571 interface, the calculated average Hg^0 flux during the entire cruise campaign was $\sim 4.5 \pm 3.5 \text{ ng m}^{-2} \text{ h}^{-1}$
572 (range: $0.7\text{-}9.1 \text{ ng m}^{-2} \text{ h}^{-1}$; Table 6). **Given the uncertainties associated with these models, we**
573 **compared our evasional Hg^0 flux data estimated by the Wanninkhof (1992) parametrization with**
574 **those resulted by the Nightingale et al., (2000) model. We found a strong positive correlation**
575 **($r^2=0.999$) between the obtained results (as listed in Table 6), suggesting that both models may be**
576 **likely equivalent, at some extent.**

577 A summary of observed mercury fluxes presented in the literature in conjunction with averaged data
578 flux from this study is presented in Table 7. **Our data on Hg^0 flux** fall in the range proposed by
579 Andersson et al., (2007) for the Mediterranean Sea (Table 7). **Although Panarea is an important**
580 **natural source of Hg from geotectonic activity (hydrothermal) compared to the main open oceans,**
581 **similar Hg^0 flux values** were reported in literature for the Pacific Ocean ($3 \text{ ng m}^{-2} \text{ h}^{-1}$, Kim and
582 Fitzgerald, 1986; Mason and Fitzgerald, 1993), the North Atlantic Ocean ($0.4 \pm 0.3 \text{ ng m}^{-2} \text{ h}^{-1}$,
583 Andersson et al., 2011), the Arctic Ocean ($2.4 \text{ ng m}^{-2} \text{ h}^{-1}$, Andersson et al., 2008), the Baltic Sea (0.8-
584 $1.6 \text{ ng m}^{-2} \text{ h}^{-1}$, Wangberg et al., 2001), the North Sea (0.2 to $4.6 \text{ ng m}^{-2} \text{ h}^{-1}$, Baeyens and Leermakers,
585 1998), and for some polluted marine areas, such as Tokyo Bay ($5.8 \pm 5.0 \text{ ng m}^{-2} \text{ h}^{-1}$, Narukawa et al.,

2006), Minamata Bay ($5 \pm 5.8 \text{ ng m}^{-2} \text{ h}^{-1}$, Marumoto et al., 2015), the Yellow Sea ($0.88 \pm 1.38 \text{ ng m}^{-2} \text{ h}^{-1}$, Ci et al., 2011) and the Northern South China Sea ($4.5 \text{ ng m}^{-2} \text{ h}^{-1}$, Fu et al., 2010). This inconsistent analogy with the other marine areas may suggest that our Hg^0 flux calculated by the two-layer gas exchange model at Panarea has been likely under-estimated due to the data gap concerning the role of the rising hydrothermal bubbles in transporting Hg from the submarine discharging vent (see section 3.5.3). Of course, more research is needed to improve knowledge of the implications of gas bubbles as carrier for Hg^0 transport in submarine hydrothermal systems, representing a productive theme of inquiry for future studies. If we extend our calculations over the entire submarine degassing area of Panarea Island ($\sim 2.3 \text{ km}^2$), we obtain a total Hg^0 evasion flux of about 0.0001 t y^{-1} . Compared to a general overview of the results provided in literature, this value accounts for a slight proportion of the total Hg flux annually released into the atmosphere from the entire Mediterranean Basin, accounting for $60\text{-}77 \text{ t y}^{-1}$ (Andersson et al., 2007; Gardfeldt et al., 2003; Ferrara et al., 2000). In spite of this, however, this study provides new important information to expand the currently limited database on Hg released from the submarine hydrothermal activity, and allow some inferences to be made regarding the quality of previous estimates of mass balance for the Mediterranean Sea. In spite of this, as at least the annual Hg mass balance established for the Mediterranean Basin showed that exchange with the atmosphere is the most important source/sink of mercury for the water compartment (Rajar et al., 2007; Zagar et al., 2007, 2014), our preliminary results suggest that emissions from submarine hydrothermal activity could instead represent an important local source of mercury for this region. A critical assessment of the published literature highlights that previous mass balance promoting an averaged total natural submarine Hg emission in the Mediterranean Sea of $\sim 15 \text{ t y}^{-1}$ (Rajar et al., 2007; Zagar et al., 2014), is an under-estimate due to the lack of studies on Hg abundance in the submarine hydrothermal discharge affecting the Basin and its dependence on environmental factors, which have, so far, not been taken into account in the modelling. Compared to the volcanic flux from subaerial continuous passive degassing occurring in the Mediterranean region, mainly represented by Mt. Etna, Stromboli and Vulcano island, Hg^0 evasion flux from the submarine degassing system of Panarea appears less important. These three active volcanoes, in fact, account for a cumulative atmospheric Hg^0 flux of about 5.4 t y^{-1} , under quiescence degassing activity (Bagnato et al., 2011; 2014). Nevertheless, although comprising a marginal contribution to the global volcanic non-eruptive Hg emissions, these new data represent the first available assessment of Hg^0 emissions directly sampled at these locations.

3.5.3 *Uncertainties in Hg^0 flux estimate*

619 When comparing different works on estimating the air-water Hg^0 flux, it is important to keep in mind
620 that the estimated Hg^0 flux using the two-layer gas exchange model is influenced by the choice of gas
621 transfer parameterizations (K_w) and diffusion coefficient of Hg^0 (Rolfhus and Fitzgerald, 2001;
622 Andersson et al., 2007; Ci et al., 2011). As reviewed by Wanninkhof (1992), except for the wind
623 speed, a number of factors can influence K_w , such as bubbles. The release of gas from a bubble to the
624 atmosphere completes the process of air-sea gas exchange mediated by the rising bubbles (Farmer et
625 al 1993; Erickson 1993). Several attempts have been made to predict the relative importance of gas
626 exchange and bubble processes on gas supersaturation (Merlivat and Memery, 1983; Woolf and
627 Thorpe, 1991; Woolf, 1993), but evaluating bubble-mediated gas exchange flux is, however,
628 complicated by uncertainties over bubble number density, volume concentrations and depth
629 distributions (Upstill-Goddard, 2006). The gas partial pressure inside ocean surface bubbles is
630 generally higher than the partial pressure of the same gases in the atmosphere. This is because
631 hydrostatic pressure and surface curvature contribute significant extra pressure inside the gas bubbles.
632 Gas transfer mediated by bubbles is more efficient than the transfer through the air-sea interface
633 (Zhang, 2012). Very small bubbles (<0.005 cm) that are injected into deep water can totally collapse
634 under hydrostatic pressure so that their entire contents are dissolved into the water and never reach
635 the surface (Craig and Weiss, 1971; Zhang, 2012). For large bubbles, gas exchange continues until
636 bubbles reach the water surface (Fuchs et al., 1987; Woolf, 1993). The two-layer gas exchange model
637 used in this study to estimate Hg^0 emission rate does not include the contribution of rising
638 hydrothermal bubbles. To address this data gap, we performed preliminary *in-situ* Hg^0 flux estimates
639 at the sea-air interface by using the floating accumulation chamber methodology, widely employed
640 elsewhere (Bagnato et al., 2013; Wang et al., 2006; Gardfeldt et al., 2003; Covelli et al., 1999; Kim
641 and Lindberg, 1995; Zhang and Lindberg, 2001). By this approach we measured a cumulative flux
642 given by the sum of both the diffusive evasional flux from the dissolved Hg phase in surface seawater
643 (DGM) and the bubble-mediated gas component, as well. In order to assure optimal sampling
644 conditions (i.e. low wind speed and absence of waves), Hg evasional flux measurements by flux
645 chamber technique were performed only at BN station, the most shallower vent site where a strong
646 rising gas bubbling plume was clearly visible at sea surface during the survey. At this site, the gas
647 flux at sea-air surface was calculated based on the rate of concentration increase in the chamber by
648 the theoretical equation:

$$649 \quad \Phi = c_f * dC/dt \quad (6)$$

650 where Φ is the flux of a gas, dC/dt is the rate of concentration change in the accumulation chamber
651 air for each investigated gas, and c_f is a proportionality factor that, theoretically, is given by the ratio
652 between the volume of the chamber and the surface area at the bottom of the chamber (Chiodini et

653 al., 1998). These measurements gave a Hg^0 evasional flux of about $8 \text{ ng m}^{-2} \text{ h}^{-1}$, resulting up to 10-
654 fold higher than the value obtained by the model (Table 6). This result confirms the importance of
655 bubble-mediated gas exchange flux in estimating the total Hg^0 emission rate at sea-air interface from
656 the submarine thermal outgassing. By comparing this additional information with the results obtained
657 by the model and previous Hg^0 flux determinations in the Mediterranean Sea (Table 7), we can
658 suggest that *i)* data obtained by the floating accumulation flux chamber technique at BN seem very
659 reasonable; *ii)* in a scenario like that encountered at Panarea island, a large uncertainty in the
660 traditional relationship of gas transfer velocity for estimating Hg^0 evasional flux by the gas-exchange
661 model, may be ascribed to the neglect of the breaking hydrothermal bubbles effect at sea-air interface;
662 and finally *iii)* the use of the two-layer gas-exchange model to estimate the atmospheric **evasive Hg^0**
663 **flux** from the submarine hydrothermal degassing likely could have underestimated the calculation, at
664 some extent.

665 4. Conclusions

666 On a cruise campaign in the Mediterranean Sea carried out in 2015 (15-17th June and 17-18th
667 November), we investigated the concentrations of Hg species in hydrothermal fluids vented from the
668 submarine exhalative area of Panarea Island. The use of a natural laboratory, like Panarea, where
669 hydrothermally produced Hg and others major gases (such as CO_2 and H_2S) are leaking from the
670 seafloor into the overlying water column has been used to examine the vertical distribution and
671 temporal impact of these gases on marine chemistry, and to test new technologies for Hg species
672 escape monitoring. The impact of the leakages on the marine environments is clearly visible in the
673 area but with very local effects. The spatial distribution of FTHg and RHg with depth showed no
674 significant water column variations, probably due to the dilution operated by the efficient currents
675 that vertically mix and uniform the column. Anyway, more studies are needed to better define these
676 effects. Conversely, FTHg contents in the hydrothermal fluids showed a clear difference from the
677 water column over the vents. The small RHg/FTHg ratio measured in the fluids suggests that in the
678 submarine hydrothermal systems, part of RHg is probably involved in reducing biotic mechanisms to
679 produce dissolved gaseous mercury form (DGM). Dissolved gaseous mercury (DGM) and gaseous
680 elemental mercury (GEM) were simultaneously measured during the cruise and combined in a gas-
681 exchange model to calculate the sea-air Hg^0 evasional flux. The averaged Hg^0 flux of $\sim 4.5 \pm 3.5 \text{ ng m}^{-2}$
682 h^{-1} calculated at Panarea by the model, is analogous to previous values proposed by many authors
683 for the Mediterranean Sea. Given the various sources of uncertainty in models designed to assess Hg^0
684 air-sea exchange, **the time-averaged Hg^0 flux from the submarine hydrothermal activity at Panarea is**
685 **likely even larger if the bubbles contribution is considered. Of course** this area should remain a
686 productive theme of inquiry **for future studies**. Further measurement campaigns are needed in order

687 to perform more detailed studies on the parameters influencing mercury evasion at different locations
688 at the Mediterranean Sea such as season and solar radiation. The complicated cycling of Hg in the
689 marine environment indicates that the short-term field observation could not capture the integrated
690 figure of mercury cycle. In spite of this, although the water surface off-shore area of Panarea Island
691 represents only a small part of the total oceanic surfaces on the Earth, we believe that the results
692 **presented in** this study may be of help in improving the global mercury budget and cycle since such
693 measurements in large parts of the world's marine environments are still lacking.

694

695 **5. Figures captions**

696 **Figure 1_** Rough map of the investigated area east of the Panarea island. The islets of Dattilo, Bottaro,
697 Lisca Bianca and Lisca Nera have been recognized as being the remnants of a crater rim. The
698 sampling hydrothermal vent sites (BP: Black Point; LC: La Calcara; BN: Bottaro North; BC: Bottaro
699 Crater; C7: Campo 7; FB: Field Blank) and the inland fumaroles (red star) are also reported.

700 **Figure 2_** Pictures illustrating the sampling of warm thermal waters (a,b) and dry gas phase (c) for
701 mercury speciation and major chemical determinations. White bacterial mats deposits (d) often marks
702 the submarine hydrothermal emissions at Panarea Island.

703 **Figure 3_** Cruise tracks for atmospheric GEM distribution (at 3 m a.s.l) over the discharging area
704 east of Panarea during the cruise campaign in November 2015. The degassing vent sites locations are
705 also reported (black triangles) For the labels over each station, see caption of Fig.1.

706 **Figure 4_** Correlation between CO₂ and H₂S in the collected gas phase of hydrothermal fluids ($r^2=$
707 0.98). The negative correlation indicates that the more CO₂ occurred in the dry gas phase, the less
708 H₂S is detected.

709 **Figure 5_** Sea-surface manifestation of the “blowout” surrounded by pseudo-convective cells
710 created by the rising submarine gas plume from the Bottaro North discharging vent.

711 **Figure 6_** (a) Na vs. Cl⁻ and (b) Mg vs. SO₄ binary diagrams for the thermal water samples from the
712 submarine fumarolic field of Panarea Island.

713 **Figure 7_** Spatial distribution of the total filtered Hg (FTHg, unit in pM) and reactive Hg (RHg, unit
714 in pM) in (a) the surface sea-waters and (b) hydrothermal fluids, respectively.

715 **Figure 8_** Spatial distribution of DGM concentrations in the (a) surface waters and (b) hydrothermal
716 fluids, respectively along the route followed by the RV *Bio4You* during the cruise campaigns (June
717 and November 2015). (c) Elemental mercury concentrations (Hg⁰_g) in the hydrothermal dry gas phase
718 of the collected thermal waters are also reported. Labels indicate: LC, La Calcara; BP, Black Point;
719 BN, Bottaro North; BC, Bottaro Crater, C7, Campo 7; FB, Field Blank.

720 **Figure 9_** DGM and Hg⁰(bubbles) concentrations vs. depth in the collected hydrothermal fluids of
721 Panarea Island. BN: Bottaro North; BC: Bottaro Crater; LC: La Calcare; FB: Field Blank.

722

723 **6. Tables captions**

724 **Table 1_** Chemical composition of the thermal and sea water samples in comparison with local
725 seawater (Field Blank).

726 **Table 2_** Mean chemical composition (in vol %) of the gases sampled during May-September 2015.
727 The CO₂/H₂S **molar** ratios measured in the fluids are reported, together with the ⁴He/²⁰Ne isotopic
728 ratios and the helium isotopic ratios normalized to the atmosphere (R/R_{air}). Gaseous elemental
729 mercury concentrations Hg⁰ (in **ng/m³**) are also reported.

730 **Table 3_** Chemical composition of the submarine thermal waters discharged at Panarea Island. The
731 measured chemical composition of the local seawater SW (collected at the Field Blank site in June
732 2015) is also reported. Ion contents are in mg/l.

733 **Table 4_** Literature data on FTHg and RHg measured in both hydrothermal fluids and seawater
734 reported elsewhere; n.a.= not available data.

735 **Table 5_** Dissolved gaseous mercury (DGM) concentrations (in pM) for different water bodies
736 worldwide.

737 **Table 6_** Summary of station information, atmospheric GEM, surface water DGM and relevant data
738 for air-sea Hg⁰ flux calculation in the hydrothermal area east of Panarea Island during the cruise in
739 November 2015. **k_w values resulted by using both Wanninkhof (1992) (W92) and Nightingale et al.,**
740 **(2000) (N2000) parametrization have been reported for comparison, and the relative air-sea Hg⁰ flux**
741 **estimates as well.**

742 **Table 7_** Summary of observed mercury sea-air fluxes presented in the literature in conjunction with
743 averaged data flux from this study.

744

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756

757 **8. References**

758 Aiuppa, A., Bagnato, E., Witt, M. L. I., Mather, T. A., Parello, F., Pyle, D.M., Martin, R. S., 2007.
759 Real-time simultaneous detection of volcanic Hg and SO₂ at La Fossa Crater, Vulcano (Aeolian
760 Islands, Sicily). *Geophys. Res. Lett.* 34, L21307.

761 Amyot, M., Gill, G.A., Morel, F.M.M., 1997. Production and loss of dissolved gaseous mercury in
762 coastal seawater. *Environ. Sci. Technol.* 31, 3606-3611.

763 Andaloro, F., Romeo, T., Renzi, M., Guerranti, C., Perra, G., Consoli, P., Perzia, P., Focardi, S.E.,
764 2012. **Alteration of potential harmful elements levels in sediments and biota from the central**
765 **Mediterranean Sea (Aeolian Archipelago) following an episode of intense volcanic activity.** *Environ.*
766 *Monit. Assess.* 184, 4035.

767 Andersson, M.E., Gardfeldt, K., Wangberg, I., Sprovieri, F., Pirrone, N., Lindqvist, O., 2007.
768 Seasonal and daily variation of mercury on and off shore sites from the Mediterranean Sea. *Mar.*
769 *Chem.* 107 (1), 104-116.

770 Andersson, M.E., Gardfeldt, K., Wangberg, I., Stromberg, D., 2008a. Determination of Henry's law
771 constant for elemental mercury. *Chemosphere* 73, 587-592.

772 Andersson, M.E., Sommar, J., Gardfeldt, K., 2011. Air–sea exchange of volatile mercury in the North
773 Sea. *Mar. Chem.* 125, 1-7.

774 Astakhov, A.S., Wallmann, K., Ivanov, M.V., Kolesov, G. M., Sattarova, V.V., 2007. Distribution
775 and accumulation rate of Hg in the Upper Quaternary sediments of the Deryugin Basin, Sea of
776 Okhotsk. *Geochem. Int.* 45(1), 47-61.

777 Astakhov, A.S., Ivanov, M.V., Li, B.Y., 2011. Hydrochemical and atmochemical mercury dispersion
778 zones over hydrothermal vents of the submarine Piip Volcano in the Bering Sea. *Oceanology* 51, 826.

779 Bagnato, E., Aiuppa, A., Parello, F., Allard, P., Liuzzo, M., Giudice, G., Shinohara, H., 2011. New
780 clues on mercury contribution from Earth volcanism. *Bull. Vol.* 73, 497-510.

781 Bagnato, E., Sprovieri, M., Barra, M., Bitetto, M., Bonsignore, M., Calabrese, S., Di Stefano, V.,
782 Oliveri, E., Parello, F., Mazzola, S., 2013. The sea-air exchange of mercury (Hg) in the marine
783 boundary layer of the Augusta basin (southern Italy): concentrations and evasion flux. *Chemosphere*,
784 93(9), 2024-32.

785 Bagnato, E., Tamburello, G., Avard, G., Martinez, M., Enrico, M., Fu, X., Sprovieri, M., Sonke, J.,
786 2014. Mercury fluxes from volcanic and geothermal sources: an update. In: *The Role of Volatiles in*
787 *the Genesis, Evolution and Eruption of Arc Magmas.* Edited by Geological Society of London;
788 available online <http://sp.lyellcollection.org/>; doi 10.1144/SP410.2.

789 Baeyens, W., Leermakers, M., 1998. Elemental mercury concentrations and formation rates in the
790 Scheldt estuary and the North Sea. *Mar. Chem.* 60, 257-266.

791 Caliro, S., Caracausi, A., Chiodini, G., Ditta, M., Italiano, F., Longo, M., Minopoli, C., Nuccio, P.M., Paonita,
792 A., Rizzo, A., 2004. Evidence of a recent input of magmatic gases into the quiescent volcanic edifice of
793 Panarea, Aeolian Islands, Italy. *Geophys. Res. Lett.* 31, L07619, doi:10.1029/2003GL019359.

794 Cannon, G.A., Pashinski, D.J., 1997. Variations in mean currents affecting hydrothermal plumes on
795 the Juan de Fuca Ridge. *J. Geophys. Res.* 102, 24965-24976.

796 Caramanna, G. Espa, S., Bouché, V., 2010. Study of the environmental effects of submarine CO₂-
797 rich emissions by means of scientific diving techniques (Panarea Island-Italy). *Int. J. Soc. Underwater*
798 *Technol.* 29, No 2, 79-85.

799 Caramanna, G., Voltattorni, N., Caramanna, L., Cinti, D., Galli, G., Pizzino, L., Quattrocchi, F., 2005.
800 Scientific diving techniques applied to the geomorphological and geochemical study of some
801 submarine volcanic gas vents (Aeolian Islands-Southern Tyrrhenian Sea-Italy). In: *Diving for*
802 *Science: Proceedings of the 24th Symposium of American Academy of Underwater Sciences.*

803 Chiodini, G., Cioni, R., Guidi, M., Raco, B., Marini, L., 1998. Soil CO₂ flux measurements in
804 volcanic and geothermal areas. *Appl. Geochem.* 13 (5), 543–552.

805 Ci, Z.J., Zhang, X.S., Wang, Z.W., Niu, Z.C., Diao, X.Y., Wang, S.W., 2011. Distribution and air-
806 sea exchange of mercury (Hg) in the Yellow Sea. *Atmos. Chem. Phys.* 11, 2881-2892.

807 Cossa, D., Martin, J.M., Takayanagi, K., Sanjuan, J., 1997. The distribution and cycling of mercury
808 species in the western Mediterranean. *Deep-Sea Res. II* 44, 721-740.

809 Cossa, D., Coquery, M., 2005. The Mediterranean mercury anomaly, a geochemical or a biological
810 issue. *Hdb. Env. Chem.* 5, Springer-Verlag, Heidelberg.

811 Costa, M., Liss, P.S., 1999. Photoreduction of mercury in sea water and its possible implications for
812 Hg⁰ air-sea fluxes. *Mar. Chem.* 68, 87-95.

813 Costa, M., Liss, P.S., 2000. Photoreduction and evolution of mercury from seawater. *Sci. Total*
814 *Environ.* 261, 125-135.

815 Covelli, S., Faganeli, J., Horvat, M., Brambati, A., 1999. Porewater distribution and benthic flux
816 measurements of mercury and methylmercury in the gulf of Trieste (Northern Adriatic Sea). *Estuar.*
817 *Coast. Shelf S.* 48, 415-428.

818 Craig, H., Weiss, R., 1971. Dissolved gas saturation anomalies and excess helium in the ocean. *Earth*
819 *Planet. Sc. Lett.* 10, 289-296.

820 Dalziel, J.A., 1995. Reactive mercury in eastern North Atlantic and Southern Atlantic. *Mar. Chem.*
821 49, 307-314.

822 D'Asaro, E., McNeil, C., 2007. Air-sea gas exchange at extreme wind speeds measured by
823 autonomous oceanographic floats. *J. Mar. Syst.* 66, 92-109.

824 Dekov, V.M., 2007. Native Hg^{liq} in the metalliferous sediments of the East Pacific Rise (21°S). *Mar.*
825 *Geol.* 238, 107-113

826 Dekov, V.M., Savelli C., 2004. Hydrothermal activity in the SE Tyrrhenian Sea: an overview of 30
827 years of research. *Mar. Geol.* 204, 161-185.

- 828 DIN EN 1483, 2007. Water quality. Determination of mercury. Method using atomic absorption
829 Spectrometry.
- 830 Erickson, D.J., 1993. A stability dependent theory for air-sea gas exchange. *J. Geophys. Res.* 98, 8471-
831 8488.
- 832 Fantozzi, L., Manca, G., Ammoscato, I., Pirrone, N., Sprovieri, F., 2013. The cycling and sea-air
833 exchange of mercury in the waters of the Eastern Mediterranean during the 2010 MED-OCEANOR
834 cruise campaign *Sci. Tot. Environ.* 448, 151-162.
- 835 Fantozzi, L., Ferrara, R., Frontini, F.P., Dini, F., 2007. Factors influencing the daily behaviour of
836 dissolved gaseous mercury concentration in the Mediterranean Sea. *Mar. Chem.* 107, 4-12.
- 837 Fantozzi, L., Ferrara, R., Frontini, F.P., Dini, F., 2009. Dissolved gaseous mercury production in the
838 dark: evidence for the fundamental role of bacteria in different types of Mediterranean water bodies.
839 *Sci. Tot. Environ.* 407, 917-924.
- 840 Farmer, D.M., McNeil, C.L., Johnson, B.D., 1993. Evidence for the importance of bubbles in
841 increasing air-sea gas flux. *Nature* 361, 620-623.
- 842 Ferrara, R., Ceccarini, C., Lanzillotta, E., Gardfeldt, K., Sommar, J., Horvat, M., Logar, M., Fajon,
843 V., Kotnik, 2003. Profiles of dissolved gaseous mercury concentration in the Mediterranean seawater.
844 *Atmos. Environ.* 37, 85-92.
- 845 Ferrara, R., Mazzolai, B., Lanzillotta, E., Nucaro, E., Pirrone, N., 2000. Temporal trends in gaseous
846 mercury evasion from the Mediterranean seawaters. *Sci. Tot. Environ.* 259, 183-190.
- 847 Fitzgerald, W.F., Lamborg, C.H., Hammerschmidt, C.R., 2007. Marine biogeochemical cycling of
848 mercury. *Chem. Rev.* 107, 641-662.
- 849 Fu, X.W., Feng, X.B., Zhang, G., Xu, W.H., Li, X.D., Yao, H., Liang, P., Li, J., Sommar, J., Yin, R.,
850 Liu, N., 2010. Mercury in the marine boundary layer and seawater of the South China Sea:
851 concentrations, sea/air flux, and implication for land outflow. *J. Geophys. Res.* 115, D06303.
- 852 Fuchs, G., Roether, E.W., Schlosser, P., 1987. Excess ^3He in the ocean layer. *J. Geophys. Res.* 92,
853 6559-6568.
- 854 Gardfeldt, K., Sommar, J., Ferrara, R., Ceccarini, C., Lanzillotta, E., Munthe, J., Wangberg, I.,
855 Lindqvist, O., Pirrone, N., Sprovieri, F., Pesenti, E., Stromberg, D., 2003. Evasion of mercury from
856 coastal and open waters of the Atlantic Ocean and the Mediterranean Sea. *Atmos. Environ.* 37
857 (Supplement No.1), S73-S84.
- 858 Gårdfeldt, K., Feng, X., Sommar, J., Lindqvist, O., 2001. Total gaseous mercury exchange between
859 air and water at river and sea surfaces in Swedish coastal regions. *Atmos. Environ.* 35, 3027-3038.
- 860 Gasparini, P., Iannaccone, G., Scandone, P., Scarpa, R., 1982. The seismotectonics of the Calabrian
861 Arc. *Tectonophys.* 84, 267-286.
- 862 Gugliandolo, C., Italiano, F., Maugeri, T.L., 2006. The submarine hydrothermal system of Panarea
863 (Southern Italy): biogeochemical processes at the thermal fluids-sea bottom interface. *Ann. Geophys.*
864 49, 783-792.
- 865 Gustin, M.S., Lindberg, S., Marsik, F., Casimir, A., Ebinghaus, R., Edwards, G., Hubble-Fitzgerald,
866 C., Kemp, R., Kock, H., Leonard, T., London, J., Majewski, M., Montecinos, C., Owens, J., Pilote,

867 M., Poissant, L., Rasmussen, P., Schaedlich, F., Schneeberger, D., Schroeder, W., Sommar, J.,
868 Turner, R., Vette, A., Wallschlaeger, D., Xiao, Z., Zhang, H., 1999. Nevada STORMS project:
869 measurement of mercury emissions from naturally enriched surfaces. *J. Geophys. Res.* 104, 21831-
870 21844.

871 Hamme, R. C., Emerson, S. R., 2006. Constraining bubble dynamics and mixing with dissolved gases:
872 Implications for productivity measurements by oxygen mass balance. *J. Mar. Res.* 64, 73-95.

873 Hamme, R. C., Emerson, S. R., 2002. Mechanisms controlling the global oceanic distribution of the
874 inert gases argon, nitrogen and neon. *Geophys. Res. Lett.* 29 (23), 2120. doi:10.1029/2002GL015273.

875 Horvat, M., Kotnik, J., Logar, M., Fajon, V., Zvonaric, T., Pirrone, N., 2003. Speciation of mercury
876 in surface and deep-sea waters in the Mediterranean Sea. *Atmos. Environ.* 37, 93-108.

877 Italiano, F., Nuccio, P.M., 1991. Geochemical investigations on submarine volcanic exhalations to
878 the East of Panarea, Aeolian Islands, Italy. *J. Volc. Geoth. Res.* 46, 125-141.

879 Kim, K.H., Mishra, V.K., Hong, S., 2006. The rapid and continuous monitoring of gaseous elemental
880 mercury (GEM) behavior in ambient air. *Atmos. Environ.* 40, 3281-3293.

881 Kim, J.P., Fitzgerald, W.F., 1986. Sea-air partitioning of mercury in the equatorial Pacific Ocean.
882 *Science* 28, 1131-1133.

883 Kim, K.H., Lindberg, S., 1995. Design and initial tests of dynamic enclosure chamber for
884 measurements of vapour-phase mercury fluxes over soils. *Water Air Soil Poll.* 80, 1059-1068.

885 Khodakovskiy, I.L. and Shikina, N.D., 1983. The role of carbonate complexes in mercury transport
886 in hydrothermal solutions (experimental studies and thermodynamic analysis). *Geochem. Int.*, 18 (3),
887 32-43.

888 Krauskopf, K.B., 1951. Physical chemistry of quicksilver transportation in vein fluids. *Econ. Geol.*,
889 46: 498-523.

890 Kotnik, J., Horvat, M., Tessier, E., Ogrinc, N., Monperrus, M., Amouroux, D., Fajon, V., Gibičar, D.,
891 Žižek, S., Sprovieri, F., Pirrone, N. 2007. Mercury speciation in surface and deep waters of the
892 Mediterranean Sea. *Mar. Chem.* 107(1), 13-30.

893 Kotnik, J., Sprovieri, F., Ogrinc, N., Horvat, M., Pirrone, N. 2013. Mercury in the Mediterranean.
894 Part 1: spatial and temporal trends. *Environ. Sci. Pollut. Res.*, doi: 0.1007/s11356-013-2378-2.

895 Krupp, R., 1988. Physicochemical aspects of mercury metallogenesis. *Chem. Geol.* 69, 345-356.

896 Kuss, J., Holzmann, J., Ludwig, R., 2009. An elemental mercury diffusion coefficient for natural
897 waters determined by molecular dynamics simulation. *Environ. Sci. Technol.* 43, 3183-3186.

898 Lamborg, C.H., Von Damm, K.L., Fitzgerald, W.F., Hammerschmidt, C.R., Zierenberg, R.A., 2006.
899 Mercury and monomethylmercury in fluids from Sea Cliff submarine hydrothermal field, Gorda
900 Ridge. *Geophys. Res. Lett.* 33, L17606.

901 Lamborg, C.H., Yigiterhan, O., Fitzgerald, W.F., Balcom, P.H., Hammerschmidt, C.R., Murray, J.W.,
902 2008. Vertical distribution of mercury species at two sites in the western Black Sea. *Mar. Chem.* 111,
903 77-89.

904 Langmuir, D., 1977. *Aqueous Environmental Geochemistry*. Prentice Hall, New Jersey, pp.600.

- 905 Lanzillotta, E., Ceccarini, C., Ferrara, R., 2002. Photo-induced formation of dissolved gaseous
906 mercury in coastal and offshore seawater of the Mediterranean basin. *Sci. Tot. Environ.* 300, 179-187
- 907 Lanzillotta, E., Ceccarini, C., Ferrara, R., 2002. Photo-induced formation of dissolved gaseous
908 mercury in coastal and offshore seawater of the Mediterranean basin. *Sci. Tot. Environ.* 300, 179-
909 187.
- 910 Lanzillotta, E., Ferrara, R., 2001. Daily trend of dissolved gaseous mercury concentration in coastal
911 seawater of the Mediterranean basin. *Chemosphere* 45, 935-940
- 912 Laurier, F.J.G., Mason, R.P., Gill, G.A., Whalin, L., 2004. Mercury distributions in the North Pacific
913 Ocean-20 years of observations. *Mar. Chem.* 90 (1-4), 3-19.
- 914 Liss, P.W., Slater, P.G., 1974. Flux of gases across the air-sea interface. *Nature* 247, 181-184.
- 915 Marumoto, K., Imai, S., 2015. Determination of dissolved gaseous mercury in seawater of Minamata
916 Bay and estimation for mercury exchange across air-sea interface. *Mar. Chem.* 168, 9-17.
- 917 Mason, R.P., Sullivan, K.A., 1999. The distribution and speciation of mercury in the South and
918 equatorial Atlantic. *Deep Sea Research Part II: Topical Studies in Oceanography* 46 (5), 937-956.
- 919 Mason, R.P., Rolffhus, K.R., Fitzgerald, W.F., 1998. Mercury in the North Atlantic. *Mar. Chem.* 61,
920 37-53.
- 921 Mason, R.P., Rolffhus, K.R., Fitzgerald, W.F., 1995. Methylated and elemental mercury cycling in
922 surface and deep-ocean waters of the North Atlantic. *Water Air Soil Pollut.* 80, 665-667.
- 923 Mason, R.P., Fitzgerald, W.F., Morel, F.M.M., 1994. The biogeochemical cycling of elemental
924 mercury: anthropogenic influences. *Geochim. Cosmochim. Acta* 58, 3191-3198.
- 925 Mason, R.P., Sullivan, K.A., 1999. The distribution and speciation of mercury in the South and
926 equatorial Atlantic. *Deep Sea Research Part II: Topical Studies in Oceanography* 46 (5), 937-956.
- 927 Mason, R.P., Fitzgerald, W.F., 1990. Alkylmercury in the equatorial Pacific. *Nature* 374, 457-459.
- 928 Mason, R.P., Fitzgerald, W.F., 1993. The distribution and biogeochemical cycling of mercury in the
929 equatorial Pacific Ocean. *Deep-Sea Research* 40, 1897-1907.
- 930 McDougall, T.J., 1978. Bubble plumes in stratified environments. *J. Fluid Mech.* 85, Issue 4, 655-
931 672.
- 932 Merlivat, L., Memery, L., 1983. Gas exchange across an air-water interface: experimental results and
933 modeling of bubble contribution to transfer. *J. Geophys. Res.* 88 (C1), 707-724.
- 934 Morel, F.M.M., Kraepiel, A.M.L., Amyot, M., 1998. The chemical cycle and bioaccumulation of
935 mercury. *Annu. Rev. Ecol. Syst.* 29, 543-66.
- 936 Nightingale, P.D., Malin, G., Law, C.S., Watson, A.J., Liss, P.S., Liddicoat, M.I., Boutin, J., Upstill-
937 Goddard, R.C., 2000. In situ evaluation of air-sea gas exchange parameterizations using novel
938 conservative and volatile tracers. *Glob. Biogeochem. Cycles* 14 (1), 373-387.
- 939 Narukawa, M., Sakata, M., Marumoto, K., Asakura, K., 2006. Air-sea exchange of mercury in Tokyo
940 Bay. *J. Oceanogr.* 62, 249-257.

- 941 Parker, J.L., Bloom, N.S., 2005. Preservation and storage techniques for low-level aqueous mercury
942 speciation. *Sci. Tot. Environ.* 337, 253-263.
- 943 Poulain, A.J., Ní Chadhain, S.M., Ariya, P.A., Amyot, M., Garcia, E., Campbell, P.G.C., Zylstra,
944 G.J., Barkay, T., 2007. Potential for mercury reduction by microbes in the high Arctic. *Appl. Environ.*
945 *Microbiol.* 73, 2230-2238.
- 946 Prol-Ledesma, R.M., Canet, C., Melgarejo, J.C., Tolson, G., Rubio-Ramos, M.A., Cruz-Ocampo,
947 J.C., Ortega-Osorio, A., Torres-Vera, M.A., Reyes, A., 2002. Cinnabar deposition in submarine
948 coastal hydrothermal vents, Pacific Margin of central Mexico. *Econ. Geol.* 97, 1331-1340.
- 949 Prol-Ledesma, R.M., Canet, C., Torres-Vera, M.A., Forrest, M.J., Armienta, M.A., 2004. Vent fluid
950 chemistry in Bahı́a Concepcio'n coastal submarine hydrothermal system, Baja California Sur,
951 Mexico. *J. Volc. Geotherm. Res.* 137, 311-328.
- 952 Qureshi, A., O'Driscoll, N.J., Macleod, M., Meuhold, Y., Hungerbuhler, K., 2010. Photoreactions of
953 mercury in surface ocean water: gross reaction kinetics and possible pathways. *Environ. Sci. Technol.*
954 44, 644-649.
- 955 Rajar, R., Žagar, D., Horvat, M., Četina, M., 2007. Mass balance of mercury in the Mediterranean
956 Sea. *Mar. Chem.* 107, 89-102.
- 957 Rolfhus, K.R., Fitzgerald, W.F., 2001. The evasion and spatial/temporal distribution of mercury
958 species in Long Island Sound, CT-NY. *Geochim. Cosmochim. Acta* 65 (3), 407-418.
- 959 Rolfhus, K.R., Fitzgerald, W.F., 2004. Mechanisms and temporal variability of dissolved gaseous
960 mercury production in coastal seawater. *Mar. Chem.* 90, 125-136.
- 961 Sakamoto, H., 1985. The distribution of mercury, arsenic and antimony in sediments of Kagoshima
962 Bay. *Bull. Chem. Soc. Jpn.* 58, 580-587.
- 963 Sanemasa, I., 1975. The solubility of elemental mercury vapor in water. *Bull. Chem. Soc. Jpn.* 48,
964 1795-1798.
- 965 Sarkar, D., 2003. Preliminary studies on mercury solubility in the presence of iron oxide phases using
966 static headspace analysis. *Environ. Geosci.* 10, No. 4, 151-155.
- 967 Schwarzenbach, R.P., Gashwend, P.M., Imborden, D.M., 1993. *Environmental Organic Chemistry.*
968 Wiley Inter-science, New York, p. 228.
- 969 Steffen, A., Schroeder, T.W., Macdonald, R., Poissant, L., Konoplev, A., et al., 2005. Mercury in the
970 Arctic atmosphere: An analysis of eight years of measurements of GEM at Alert (Canada) and a
971 comparison with observations at Amderma (Russia) and Kuujjuarapik (Canada). *Sci. Tot. Environ.*
972 342, 185-198.
- 973 Schroeder, W.H., Munthe, J., 1998. Atmospheric mercury: an overview. *Atmos. Environ.* 32(5), 809-
974 822.
- 975 Sholupov, S., Pogarev, S., Ryzhov, V., Mashyanov, N., Stroganov, A., 2004. Zeeman atomic
976 absorption spectrometer RA-915b for direct determination of mercury in air and complex matrix
977 samples. *Fuel Process. Technol.* 85, 473-485.

- 978 Soerensen, A.L., Sunderland, E.M., Holmes, C.D., Jacob, D.J., Yantosca, R.M., Skov, H.,
979 Christensen, J.H., Strode, S.A., Mason, R.P., 2010. An improved global model for air-sea exchange
980 of mercury: high concentrations over the North Atlantic. *Environ. Sci. Technol.* 44, 8574-8580.
- 981 Steinbruckner, D., 2009. Quantification of submarine degassing of Panarea Volcano in the Aeolian
982 archipelago, Italy. *Freiberg Online Geology* 23, ISSN 1434-7512.
- 983 Tassi, f., Capaccioni, B., Caramanna, G., Cinti, C., Montegrossi, G., Pizzino, L., Quattrocchi, F.,
984 Vaselli, O., 2009. Low-pH waters discharging from submarine vents at Panarea Island (Aeolian
985 Islands, southern Italy) after the 2002 gas blast: Origin of hydrothermal fluids and implications for
986 volcanic surveillance. *Appl. Geochem.* 24, 246-254.
- 987 Tassi, F., Capaccioni, B., Vaselli, O., 2014. Compositional spatial zonation and 2005–2013 temporal
988 evolution of the hydrothermal-magmatic fluids from the submarine fumarolic field at Panarea Island
989 (Aeolian Archipelago, southern Italy). *J. Volcanol. Geotherm. Res.* 277, 41-50.
- 990 Tivey, M.K., 2007. Generation of Seafloor Hydrothermal Vent Fluids and associated Mineral
991 Deposits. *Oceanography* 20, Number 1, 50-65.
- 992 Tomiyasu, T., Eguchi, T., Yamamoto, M., Anazawa, K., Sakamoto, H., Ando, T., Nedachi, M.,
993 Marumo, K., 2007. Influence of submarine fumaroles on the distribution of mercury in the sediment
994 of Kagoshima Bay, Japan. *Mar. Chem.* 107, 173-183.
- 995 Upstill-Goddard, R.C., 2006. Air-sea exchange in the coastal zone. *Estuar. Coastal Shelf Sci.* 70, 388.
- 996 USEPA, 1997. An assessment of exposure to mercury in the United States. Mercury Study Report to
997 Congress, vol. 4.
- 998 USEPA, 2002. Method 1631. Revision E: Mercury in Water by Oxidation, Purge and Trap, and Cold
999 Vapor Atomic Fluorescence Spectrometry. EPA-821-R-02-019, United States.
- 1000 Vagle, S., C. McNeil, Steiner, N., 2010. Upper ocean bubble measurements from the NE Pacific and
1001 estimates of their role in air-sea gas transfer of the weakly soluble gases nitrogen and oxygen. *J.*
1002 *Geophys. Res.* 115, C12054, doi:10.1029/2009JC005990.
- 1003 Varekamp, J.C., Buseck, P.R., 1984. The speciation of mercury in hydrothermal systems, with
1004 applications for ore deposition. *Geochim. Cosmochim. Acta* 48, 177-186.
- 1005 Von Damm, K.L., Edmond, J.M., Grant, B., Measures, C.I., Walden, B., Weiss, R.F., 1985.
1006 Chemistry of submarine hydrothermal solutions at 21°N, East Pacific Rise. *Geochim. Cosmochim.*
1007 *Acta* 49, 2197-2220.
- 1008
- 1009 Wang, D., He, L., Shi, X., Wei, S., Feng, X., 2006. Release flux of mercury from different
1010 environmental surfaces in Chongqing, China. *Chemosphere* 64 (11), 1845-1854.
- 1011 Wangberg, I., Schmolke, S., Schgar, P., Munthe, J., Ebinghaus, R., Iverfeldt, A., 2001. Estimates of
1012 air-sea exchange of mercury in the Baltic Sea. *Atmos. Environ.* 35, 5477-5484.
- 1013 Wanninkhof, R., 1992. Relationship between wind speed and gas exchange over the ocean. *J.*
1014 *Geophys. Res.* 97 (C5), 7373-7382.
- 1015 Woolf, D. K., Thorpe, S. A., 1991. Bubbles and the air-sea exchange of gases in near-saturation
1016 conditions, *J. Mar. Res.*, 49, 435-466.

- 1017 Woolf, D. K., 1993. Bubbles and the air-sea transfer velocity of gases, *Atmos. Ocean* 31(4), 517-540.
- 1018 Žagar, D., Petkovsek, G., Rajar, R., Sirnik, N., Horvat, M., Voudouri, A., Kallos, G. and Cetina, M.,
1019 2007. Modelling of mercury transport and transformations in the water compartment of the
1020 Mediterranean Sea. *Mar. Chem.* 107, 64-88.
- 1021 Žagar, D., Sirnik, N., Četina, M., Horvat, M., Kotnik, J., Ogrinc, N., Hedgecock, I.M., Cinnirella, S.,
1022 De Simone, F., Gencarelli, C.N., Pirrone, N., 2014. Mercury in the Mediterranean. Part 2: processes
1023 and mass balance. *Environ. Sci. Pollut. Res.* 21, 4081-4094.
- 1024 Zhang, X., 2012. Contribution to the global air-sea CO₂ exchange budget by asymmetric bubble-
1025 mediated gas transfer, *Tellus B*, 64, 17, 260.
- 1026 Zhang, H., Lindberg, S.E., 2001. Sunlight and iron(III)-induced photochemical production of
1027 dissolved gaseous mercury in **freshwater**. *Environ Sci Technol.* 35(5), 928-35.