

1 **Mass independent fractionation of even and odd mercury isotopes during free tropospheric mercury**  
2 **oxidation**

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27 **Abstract.** Even mercury (Hg) isotope mass independent fractionation (MIF), observed in rainfall globally, is  
28 used to quantify atmospheric Hg deposition pathways. The underlying reaction and MIF mechanism are  
29 unknown however. Here we investigate the Hg isotope composition of free tropospheric gaseous elemental  $\text{Hg}^0$   
30 and  $\text{Hg}^{\text{II}}$  forms. We find that gaseous oxidized  $\text{Hg}^{\text{II}}$  has positive  $\Delta^{199}\text{Hg}$ ,  $\Delta^{201}\text{Hg}$ ,  $\Delta^{200}\text{Hg}$ , and negative  $\Delta^{204}\text{Hg}$   
31 signature, similar to rainfall  $\text{Hg}^{\text{II}}$ , and we document rainfall  $\text{Hg}^{\text{II}}$   $\Delta^{196}\text{Hg}$  to be near-zero. Cloud water and rainfall  
32  $\text{Hg}^{\text{II}}$  show enhanced odd MIF compared to gaseous  $\text{Hg}^{\text{II}}$ , indicating in-cloud  $\text{Hg}^{\text{II}}$  photoreduction. Hg MIF  
33 observations of free tropospheric  $\text{Hg}^0$  dynamics show how net  $\text{Hg}^0$  oxidation leads to opposite MIF in  $\text{Hg}^0$  and  
34  $\text{Hg}^{\text{II}}$ . A  $\Delta^{200}\text{Hg}$  mass balance for  $\text{Hg}^0$  and  $\text{Hg}^{\text{II}}$  forms suggests that measurements and models underestimate the  
35 tropospheric  $\text{Hg}^{\text{II}}$  pool.

36

## 37 **Introduction**

38 Modern anthropogenic Hg emissions ( $2400 \text{ Mg a}^{-1}$ ) outweigh natural Hg emissions by an order of magnitude  
39 (Bagnato et al., 2014; Streets et al., 2019). Hg emissions are mostly in the form of gaseous elemental Hg (GEM),  
40 which has a long atmospheric life-time against oxidation to divalent reactive Hg (RM) forms that include  
41 gaseous oxidized Hg (GOM) and particulate bound Hg (PBM) (Amos et al., 2012). RM is rapidly deposited to  
42 continental and marine ecosystems where microbial activity transforms inorganic Hg into the bioaccumulating  
43 and toxic methylmercury form (Fitzgerald and Lamborg, 2004). Predicting the impact of anthropogenic Hg  
44 emission scenarios on global Hg deposition requires detailed understanding of atmospheric Hg transformations  
45 and of GEM oxidation in particular. Two decades of atmospheric Hg research using mountain-top and in-flight  
46 observations, experimental and theoretical reaction kinetics, and coupled 3D atmosphere-ocean chemistry and  
47 transport models, have given broad understanding of atmospheric Hg dynamics (Ariya et al., 2015; Dibble et  
48 al., 2020; Donohoue et al., 2006; Holmes et al., 2010; Seigneur et al., 2004). Experimental, theoretical and  
49 modeling studies suggest Hg oxidation initiated by bromine (Br) radicals to be faster than by ozone or OH  
50 (Horowitz et al., 2017; Wang et al., 2014), yet major uncertainties in RM concentrations, oxidation and reduction  
51 mechanisms and rates remain (Jaffe et al., 2014; Saiz-Lopez et al., 2018; Weiss-Penzias et al., 2015).

52 Hg stable isotope analysis of atmospheric Hg compounds may provide new information on Hg emission  
53 sources and complex atmospheric redox cycling. During the last decade, significant advances have been made  
54 in the measurement of Hg isotope compositions of biogeochemical reservoirs (Kwon et al., 2020). Laboratory  
55 and field evidence suggests that processes controlling Hg emission such as reduction/oxidation,  
56 adsorption/desorption, or volatilization can induce significant mass dependent Hg isotope fractionation (MDF,

57  $\delta^{202}\text{Hg}$  signature)(Jiskra et al., 2015; Kritee et al., 2012; Wiederhold et al., 2010). Large mass independent Hg  
58 isotope fractionation (MIF) of odd Hg isotopes by the magnetic isotope effect has been observed in aqueous  
59 photochemical Hg reduction experiments ( $\Delta^{199}\text{Hg}$ ,  $\Delta^{201}\text{Hg}$  signatures) (Bergquist and Blum, 2007; Zheng and  
60 Hintelmann, 2009). Odd-MIF signatures imparted on inorganic Hg and methyl-Hg by photochemistry can be  
61 traced into all Earth surface environments, i.e sediments, biota, atmosphere, soils etc. Unusual even isotope MIF  
62 ( $\Delta^{200}\text{Hg}$ ,  $\Delta^{204}\text{Hg}$ ) has been observed in rainfall and snowfall globally (Chen et al., 2012; Demers et al., 2013;  
63 Gratz et al., 2010), and has been speculated to originate in GEM photo-oxidation at and above the tropopause  
64 (Chen et al., 2012). The exact even-MIF mechanism and even-MIF inducing Hg transformation(s) remain  
65 essentially unknown.

66 In this study we investigate Hg isotope composition of GEM, RM, and cloud water at the high altitude Pic  
67 du Midi Observatory (PDM, 2877m, France). The PDM regularly receives free tropospheric air masses that are  
68 enriched in RM and depleted in GEM (Fu et al., 2016a). High frequency, 12h and 24h GEM isotope observations  
69 of a free tropospheric air mass rich in GEM and depleted in GEM are investigated to derive MDF and MIF  
70 factors for net oxidation. Photoreduction experiments on rainfall are made to constrain atmospheric aqueous  
71 MDF and MIF factors. Finally, we investigated the even-MIF on the low abundance  $^{196}\text{Hg}$  isotope to help  
72 understand potential even-MIF mechanisms.

73

## 74 **Materials and methods**

### 75 **Site description and ancillary parameters**

76 The Pic du Midi Observatory (PDM, 0.14° E, 42.94° N, 2877 m a.s.l) is a high-altitude monitoring station  
77 situated on top of an isolated peak on the north edge of the central Pyrenees Mountains, Southwest France. The  
78 PDM receives free tropospheric air from the Northeast Atlantic Ocean and Europe and boundary layer air from  
79 upslope winds in Spain and southwest France (Gheusi et al., 2011; Hulin et al., 2019). The station receives  
80 predominantly southerly and southwesterly winds (> 70 %) across the main range of Pyrenees (Hulin et al.,  
81 2019). There are no major anthropogenic Hg emission point sources around the station or in the surrounding  
82 areas.

83

### 84 **Atmospheric sampling and processing**

85 Short-term (12/24h) variations in atmospheric GEM isotopic composition were investigated from 19 to 28 in  
86 Dec 2012 at PDM using large chlorine-impregnated activated carbon (CLC) traps. Traps with 600 mg CLC were

87 utilized for 24 hour sampling at a flow rate of  $\sim 10 \text{ L min}^{-1}$ ; whereas traps with 1000 mg of CLC were utilized  
88 for 12 hour sampling at a flow rate of  $\sim 20 \text{ LPM}$  (Fu et al., 2014). The sampling inlets of the CLC traps (heated  
89 at  $70^\circ\text{C}$  to avoid water condensation), preceded by a pre-burned 47mm quartz fiber filter were connected to a  
90 Tekran 1104 Teflon coated sampling manifold, operating at 100 LPM and  $70^\circ\text{C}$ , and installed into the prevailing  
91 wind direction. Sampling flow rates of CLC traps were regulated via ball flow meters installed at the outlets of  
92 the vacuum pumps, and the total sampling volumes of the traps were recorded using gas meters. Similar to  
93 Arctic studies (Berg et al., 2013; Steffen et al., 2005) we find that the Hg collected on CLC traps reflects the  
94 GEM fraction, and is not confounded by the GOM fraction. Both GOM and PBM fractions are retained on the  
95 quartz filter preceding the CLC trap. Quartz has been previously shown to efficiently scavenge GOM over time  
96 periods shorter than 24h (Lyman and Jaffe, 2011; Lynam and Keeler, 2002). CLC traps were thermally  
97 decomposed ( $25^\circ\text{C}$  to  $1000^\circ\text{C}$  over 8h) in a Hg-free oxygen flow ( $25 \text{ ml min}^{-1}$ ) in a tube furnace. Combustion  
98 products were further decomposed in a 2<sup>nd</sup> pyrolyzer tube furnace at  $1000^\circ\text{C}$ , and purged into a 10 ml 40 vol%  
99  $2\text{HNO}_3/1\text{HCl}$  oxidizing solution (Sun et al., 2013). CLC sampling efficiencies were better than 95%, mean  
100 recovery efficiencies were 87%, and full procedural blanks  $<2\%$  of Hg concentrations in trapping solutions (Fu  
101 et al., 2014).

102 Twelve samples of the atmospheric RM (RM=GOM+PBM) were obtained using Millipore  
103 polyethersulfone cation exchange membranes (CEMs, Millipore,  $0.45 \mu\text{m}$  pore size, 47 mm and 90 mm diameter  
104 (Maruszczak et al., 2017)) at the PDM from June to October 2014, with sampled air volumes between 25 and 77  
105  $\text{m}^3$ . Cloud water samples were collected from July to November 2014 with a CASCC-2 sampler at the PDM  
106 (Demoz et al., 1996). Rainfall was sampled from July to August 2014 150km downwind from the PDM at 800m  
107 altitude in the Pyrenees foothills using acid-washed polypropylene buckets and reported elsewhere (Enrico et  
108 al., 2016). Snowfall and rainfall was collected at the PDM and the Geosciences Environnement Toulouse (GET,  
109 Toulouse, France,  $43.54^\circ \text{N}$ ,  $1.48^\circ \text{E}$ ) laboratory between 2016 and 2017 using the same methods. Cloud water,  
110 rainfall and snowfall samples collected after each event were transferred into pre-cleaned Pyrex glass bottles (1  
111 and 2 L volume), then oxidized by adding 0.1 – 1 %  $\text{BrCl}$ , and kept refrigerated before Hg concentration analysis  
112 by CVAFS and further pre-concentration for Hg isotope analysis. Hg from rain and cloud water samples was  
113 pre-concentrated by reducing and purging Hg with  $\text{SnCl}_2$  and a clean argon flow and subsequent trapping in an  
114 oxidizing solution, following Sherman, et al. (Sherman et al., 2012). Recoveries of procedural standards, rainfall  
115 and cloud water samples was  $>95\%$ . RM on CEMs was leached in 20 vol%  $2\text{HNO}_3/1\text{HCl}$  with blanks  $<4\%$  of  
116 sampled RM.

117 Hg isotope fractionation factors during aqueous photochemical reduction of rainwater was studied using a  
118 solar simulator (see (Yang et al., 2019) for details). A low Hg level ( $2.6 \text{ ng L}^{-1}$ ) rainfall sample ‘GET rain 4’  
119 obtained at GET was spiked with  $103 \text{ ng L}^{-1}$  NIST 3133 and equilibrated for 48 in the dark. A 450 mL aliquot  
120 was then transferred into an acid-cleaned quartz reactor, and illuminated for 24h with the solar spectrum from  
121 a Xe lamp. After 24, the  $78 \text{ ng L}^{-1}$  dissolved Hg(II) remaining in the 450mL reactor volume was transferred to  
122 a pre-cleaned 1L Pyrex bottle, and pre-concentrated for Hg isotope analysis.

123

### 124 **Mercury isotopic analysis**

125 Hg isotope ratios were measured using cold vapor multi-collector inductively coupled plasma mass  
126 spectrometry (CV-MC-ICPMS, Thermo-Finnigan Neptune, and Neptune Plus) at the Midi-Pyrenees  
127 Observatory, Toulouse, France following the methods described in previous studies (Jiskra et al., 2019; Obrist  
128 et al., 2017). Instrumental mass bias of MC-ICPMS was corrected by standard-sample-standard bracketing using  
129 NIST3133 Hg at matching concentrations. Hg isotopic composition is reported in delta notation ( $\delta$ ) in units of  
130 per mil (‰) referenced to the bracketed NIST 3133 Hg standard (Blum and Bergquist, 2007):  $\delta^{\text{xxx}}\text{Hg} =$   
131  $[(^{\text{xxx}}\text{Hg}/^{198}\text{Hg})_{\text{sample}}/(^{\text{xxx}}\text{Hg}/^{198}\text{Hg})_{\text{NIST3133}} - 1]$ , where xxx represent Hg isotope masses 199, 200, 201, 202, 204.  
132 MIF values are expressed by “capital delta ( $\Delta$ )” notation (‰), which is the difference between the measured  
133 values of  $\delta^{199}\text{Hg}$ ,  $\delta^{200}\text{Hg}$ ,  $\delta^{201}\text{Hg}$  and those predicted from  $\delta^{202}\text{Hg}$  using the kinetic MDF law:  $\Delta^{\text{xxx}}\text{Hg} (\text{‰}) =$   
134  $\delta^{\text{xxx}}\text{Hg} - (\beta^{\text{xxx}} \times \delta^{202}\text{Hg})$ , where  $\beta^{\text{xxx}}$  is -0.5074, 0.2520, 0.5024, 0.7520, 1.493 for the 196, 199, 200, 201, and 204  
135 Hg isotopes respectively. The analytical uncertainty of isotopic analysis was assessed by repeated analysis of  
136 the UM-Almaden and ETH-Fluka standards over different analysis sessions and at Hg concentrations  
137 corresponding to the samples. The overall mean values of  $\delta^{202}\text{Hg}$ ,  $\Delta^{199}\text{Hg}$ ,  $\Delta^{200}\text{Hg}$ ,  $\Delta^{201}\text{Hg}$ , and  $\Delta^{204}\text{Hg}$  for all  
138 the UM-Almaden standards in the  $0.5$  to  $1.5 \text{ ng g}^{-1}$  range were  $-0.56 \pm 0.07 \text{ ‰}$ ,  $-0.04 \pm 0.08 \text{ ‰}$ ,  $-0.01 \pm 0.09 \text{ ‰}$   
139 and  $-0.05 \pm 0.09 \text{ ‰}$ , and  $0.04 \pm 0.19 \text{ ‰}$  (2SD,  $n = 11$ ) respectively, which agree well with previously reported  
140 values (Blum and Bergquist, 2007). The procedural standard for rainfall pre-concentration, i.e. rainfall sample  
141 ‘GET rain 4’ spiked with  $103 \text{ ng g}^{-1}$  NIST 3133 showed good recovery and no isotopic bias (Supporting Data).  
142 In the present study, the analytical uncertainty of CV-MC-ICPMS isotope analysis of RM, GEM, rainfall, and  
143 snowfall is the 2SD uncertainty of the UM-Almaden standard, unless the 2SD uncertainty on repeated analysis  
144 of the same sample over different analytical sessions was larger.

145 To attempt rainfall  $\Delta^{196}\text{Hg}$  analysis, we screened rainfall samples obtained at GET in 2016 for both high  
146 Hg concentration levels and high volume single events. Rainfall sample ‘GET rain 6’ was the only sample

147 retained as it consisted of a single thunderstorm event of 20.5 L, collected in the 8 large buckets, and had a Hg  
148 concentration of 6.0 ng L<sup>-1</sup>. The entire 20.5L volume was pre-concentrated 1200x in a single large Pyrex glass  
149 bottle to a final concentration of 8.0 ng g<sup>-1</sup> in 15.3 g of 20vol% iAR. The sample was run in duplicate during  
150 two different days using dedicated UM-Almaden and ETH-Fluka standards, also at 8.0 ng g<sup>-1</sup>. All individual  
151 sample and standard results are given in the Supporting Data. The signals obtained on the <sup>196</sup>Hg and <sup>202</sup>Hg  
152 isotopes during these sessions were 15mV and 3 Volt. We recommend the use of 10<sup>12</sup> or 10<sup>13</sup> Ω resistors on the  
153 signal amplifier of the <sup>196</sup>Hg Faraday cup. The 2σ uncertainty, based on sample, UM-Almaden, and ETH-Fluka  
154 replicates, on Δ<sup>196</sup>Hg during these analysis sessions were 0.19‰ (Supplementary Data).

155

### 156 **Ancillary parameters**

157 Atmospheric Hg speciation at the PDM, including GEM, GOM and PBM, was continuously measured off  
158 the same sampling manifold with a Tekran 2537/1130/1135 system (Tekran Inc., Canada) (Fu et al., 2016a;  
159 Maruszczak et al., 2017). Automated GOM and PBM analyses are subject to mounting criticism as the techniques  
160 lack calibration, collection efficiency control and interference correction (Jaffe et al., 2014). We partly address  
161 these issues by parallel manual sampling of RM (GOM + PBM) on CEMs (Huang et al., 2013). We find that  
162 denuder-based GOM at the PDM is systematically underestimated by a factor of 1.56 for which we correct  
163 (indicated by an asterisk hereafter, i.e. GOM\*)(Maruszczak et al., 2017). Atmospheric CO and O<sub>3</sub> concentrations  
164 were continuously measured using a TEI (Thermo Environmental Instruments Inc. USA) 48CTL gas filter  
165 correlation analyzer and 49C UV-absorption ozone analyzer, respectively, following published procedures  
166 (Gheusi et al., 2011). Meteorology, CO and O<sub>3</sub> data at the PDM were provided through the Pyrenean platform  
167 for observation of the atmosphere (P2OA, <http://p2oa.aero.obs-mip.fr>).

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### 169 **Air mass backward trajectories**

170 Seven day backward trajectories ending at PDM at a height of 3000 m above sea level were calculated  
171 every 2 hours with simulated gridded meteorological data from the Weather Research and Forecasting (WRF)  
172 model Version 3.4 with the Noah Land Surface Model, Thompson microphysics scheme, Grell-3 cumulus  
173 scheme, Dudhia radiation physics scheme, YSU scheme for PBL. The modeled domain of meteorological data  
174 mainly covered the eastern North Atlantic Ocean and European area, with a time resolution of 1 h, 400 × 800  
175 grid cells at a 12-km horizontal resolution, and vertical levels of 50 from 1000 hPa to 20 hPa. All the trajectories  
176 during the 12h, 24h of individual Hg isotope samples were grouped into an average backward trajectory to show

177 the mean air mass source region of samples.

178

## 179 **Results and discussion**

### 180 **GEM isotope compositions**

181 The nine day sampling period from 19 to 28 Dec 2012 was characterized by a shift from cloudy conditions (days  
182 1-2, samples D1-D3) to clear skies (days 3-5, samples D4-D9), and back to clouds (days 7-9, samples D10-  
183 D14). The wind direction was predominantly southwest bringing North-Atlantic Ocean air masses, over  
184 northwest Spain, to the PDM. The continuous Hg speciation observations show a pronounced increase in GOM\*  
185 to 252  $\text{pg m}^{-3}$  (48h mean), and concurrent decrease in GEM during samples D4-D6 (clear skies, Figure 1, Table  
186 S1). Back trajectory analysis, and low observed relative humidity and CO, suggest that the high GOM event  
187 represents the intrusion of a free tropospheric air mass that originated at 5000m (550hPa, Figures 1, 2). Such  
188 intrusions are typical at PDM, e.g. 61 events were registered over a one year period from Nov 2011 to Nov 2012  
189 (Fu et al., 2016a). The intrusions are of particular interest as they offer a snapshot of the free troposphere where  
190 GEM oxidation is thought to take place (Fu et al., 2016a; Lyman and Jaffe, 2011; Swartzendruber et al., 2006;  
191 Timonen et al., 2013).  $\delta^{202}\text{Hg}$ ,  $\Delta^{199}\text{Hg}$  and  $\Delta^{200}\text{Hg}$  of 12h and 24h GEM samples collected from 19 to 28 Dec  
192 2012 were in the range of 0.16 to 0.51‰ ( $\delta^{202}\text{Hg}$ , mean = 0.34‰), -0.31 to -0.11‰ ( $\Delta^{199}\text{Hg}$ , mean = -0.23‰),  
193 and -0.17 to 0.04‰ ( $\Delta^{200}\text{Hg}$ , mean = -0.07‰) (Table S1). These observations are consistent with a single two-  
194 week integrated GEM isotope sample B19, collected over the same period 19 to 28 Dec 2012 at a lower flow  
195 rate of 2  $\text{L min}^{-1}$ . with  $\delta^{202}\text{Hg}$  of 0.39‰,  $\Delta^{199}\text{Hg}$  of -0.27‰,  $\Delta^{200}\text{Hg}$  of -0.10 ‰ (Fu et al., 2016b).

196

### 197 **RM, cloud water and rainfall Hg isotope compositions**

198 In a previous study we found that rainfall Hg isotope signatures 150km east from the PDM are typical of rainfall  
199 observations globally, with a mean  $\delta^{202}\text{Hg}$   $0.17 \pm 0.33$  ‰ and significantly positive odd MIF ( $\Delta^{199}\text{Hg} = 0.72 \pm$   
200  $0.15$  ‰;  $\Delta^{201}\text{Hg} = 0.76 \pm 0.14$  ‰) and even-MIF ( $\Delta^{200}\text{Hg} = 0.21 \pm 0.04$  ‰;  $\Delta^{204}\text{Hg} = -0.33 \pm 0.10$  ‰, all  $1\sigma$ ,  $n$   
201  $= 9$ ) (Figure 3, Table S1, Enrico et al., 2016). Here we find that PDM cloud water THg concentrations and MDF  
202 and MIF signatures are not significantly different from PDM and regional rainfall ( $p=0.26$  to  $0.79$ ). For the first  
203 time we observe that RM, i.e. GOM+PBM, at PDM also has positive odd MIF ( $\Delta^{199}\text{Hg} = 0.44 \pm 0.17$  ‰;  $\Delta^{201}\text{Hg}$   
204  $= 0.44 \pm 0.10$  ‰) and even-MIF ( $\Delta^{200}\text{Hg} = 0.15 \pm 0.06$  ‰;  $\Delta^{204}\text{Hg} = -0.22 \pm 0.17$  ‰, all  $1\sigma$ ,  $n = 12$ ), similar to  
205 PDM cloud water and rainfall (Figure 3) and similar to global rainfall ( $\Delta^{199}\text{Hg} = 0.35 \pm 0.19$  ‰;  $\Delta^{200}\text{Hg} = 0.14$   
206  $\pm 0.06$  ‰;  $\Delta^{201}\text{Hg} = 0.35 \pm 0.20$  ‰ (Kwon et al., 2020). Demers et al. (2013) were the first to point out a negative

207 correlation between  $\Delta^{200}\text{Hg}$  and  $\Delta^{204}\text{Hg}$  in rainfall (Demers et al., 2013). Our work at the PDM extends this  
208 relationship to RM, cloud water, and GEM phases (Figure 3). The presence of even- and odd-MIF in RM  
209 suggests that globally observed Hg MIF signatures in rainfall are inherited from RM. Equally important, the  
210 isotopic composition of RM is in stark contrast with that of GEM (Figure 3), even though the only  
211 transformation that separates the two forms of Hg is net oxidation. This corroborates the suggestion that net  
212 photochemical oxidation of GEM is responsible for even MIF (Chen et al., 2012), but it does not identify the  
213 oxidative or reductive nature of the MIF inducing step among the myriad of possible reactions that drive  
214 atmospheric net GEM oxidation.

215 Cloud water and rainfall  $\delta^{202}\text{Hg}$  ( $0.17 \pm 0.34 \text{ ‰}$ ) and  $\Delta^{199}\text{Hg}$  ( $0.21 \pm 0.04 \text{ ‰}$ ) show significant enrichment  
216 in the heavier and in the odd Hg isotopes relative to mean RM  $\delta^{202}\text{Hg}$  ( $-0.73 \pm 0.63 \text{ ‰}$ ) and  $\Delta^{199}\text{Hg}$  ( $0.44 \pm$   
217  $0.18 \text{ ‰}$ )(both  $p < 0.001$ , all mean,  $1\sigma$ ). We investigated if this is caused by in-cloud  $\text{Hg}^{\text{II}}$  photoreduction, by  
218 incubating a rainfall sample spiked with  $103 \text{ ng L}^{-1}$  of NIST 3133 Hg. After 24h exposure to artificial sunlight  
219 from a Xe lamp, the Hg concentration had dropped to  $78 \text{ ng L}^{-1}$  and small positive shifts in  $\delta^{202}\text{Hg}$  ( $0.15 \text{ ‰}$ ),  
220  $\Delta^{199}\text{Hg}$  ( $0.10\text{‰}$ ), and  $\Delta^{201}\text{Hg}$  ( $0.11\text{‰}$ ), but not  $\Delta^{200}\text{Hg}$  ( $-0.03\text{‰}$ ) were detected. These observations are  
221 consistent with limited, slow in-cloud  $\text{Hg}^{\text{II}}$  photoreduction affecting cloud water and rainfall MDF and odd-MIF.  
222 Finally, we observe for the first time the  $\Delta^{196}\text{Hg}$  signature to be near-zero ( $-0.06 \pm 0.19\text{‰}$ ,  $2\sigma$ ,  $n=2$ ) in the ‘GET  
223 rain 6’ sample (Figure 4), which has pronounced  $\Delta^{199}\text{Hg}$  ( $0.70\text{‰}$ ),  $\Delta^{200}\text{Hg}$  ( $0.25\text{‰}$ ),  $\Delta^{201}\text{Hg}$  ( $0.82\text{‰}$ ), and  $\Delta^{204}\text{Hg}$   
224 ( $-0.45\text{‰}$ ). The observation that the least abundant  $^{196}\text{Hg}$ , and most abundant  $^{202}\text{Hg}$  isotope, both referenced to  
225  $^{198}\text{Hg}$ , show near-zero MIF, further suggests that nuclear self-shielding is unlikely to be the mechanism  
226 responsible for atmospheric Hg MIF.

227

### 228 $\delta^{202}\text{Hg}$ and $\Delta^{199}\text{Hg}$ variation during the high GOM event

229 We obtained additional evidence for odd and even MIF during net GEM oxidation from the high frequency (12-  
230 24h) GEM isotope observations during the free tropospheric air mass intrusion, enriched in GOM and depleted  
231 in GEM (Figure 1, days 4-6). The high GOM event showed GOM\* concentrations of  $252 \text{ pg m}^{-3}$  from 23-24  
232 Dec (48h mean). The GOM event was accompanied by low CO concentrations, depleted GEM concentrations,  
233 and low relative humidity (Figure 1,2), which is consistent with previous studies and indicative of GOM  
234 production by oxidation of GEM in a free tropospheric air mass (Gratz et al., 2015; Shah et al., 2016). Seven-  
235 day back-trajectories of the GOM event and of the pre- (days 1-3) and post-event (days 7-9) air masses illustrate  
236 the important control of cloudiness along the trajectory on detected GOM levels at the PDM (Figure 2). Pre/post-



237 GOM-event air masses generally travelled at 700-1000 hPa (3000m – 0m asl) over the N-Atlantic Ocean (35-  
238 50°N) with RH from 60-100% and daytime solar radiation  $<200 \text{ w m}^{-2}$  suggestive of GOM scavenging by clouds  
239 (Figure 1,2). GOM-event air masses also travelled over the subtropical N-Atlantic Ocean, though at lower  
240 latitudes (20-35°N), and higher altitudes of 500-900 hPa (5500m – 1500m asl) with RH from 0-40% and daytime  
241 solar radiation from 200-500  $\text{w m}^{-2}$  suggestive of clear skies. GOM-event mean ozone ( $47 \pm 2$  ppbv, sd), CO  
242 ( $83 \pm 3$  ppbv, sd) and relative humidity ( $34 \pm 10\%$ , sd) are typical of lower to middle free tropospheric air. Both  
243 the back trajectories and ozone, CO, RH characteristics suggest a negligible influence of stratospheric air on the  
244 observed GOM-event.

245 A negative correlation between GEM and GOM\* was observed during the 8-day study period of Dec 2012  
246 with GOM\*/GEM slope of  $-0.44 \pm 0.10$  ( $r^2 = 0.66$ ; Figure 5). It has been previously suggested that GOM/GEM  
247 slopes higher than -1 reflect the loss of newly produced GOM by scavenging processes, or the mixing with other  
248 air masses with different GEM levels (Lyman and Jaffe, 2011; Swartzendruber et al., 2006). PBM concentrations  
249 during the high-GOM event are uniformly low (mean,  $4 \text{ pg m}^{-3}$ ) and RH and solar radiation levels along the  
250 back trajectories do not support an important scavenging sink (Figure 2). A prerequisite for the GOM\*/GEM  
251 slope analysis is that the ensemble of observations has a common air mass origin, which is not the case here.  
252 The back trajectory analysis of our 8-day observations suggests overlapping altitudes for pre- and post-event  
253 (3000m – 0m asl) and GOM-event (5500m – 1500m asl) air masses. Published reviews of GEM altitude profiles  
254 suggest little variation up to 5km (Holmes et al., 2010). However, observed and modeled boundary layer GEM  
255 levels suggest maximum levels between 30-60°N, corresponding to mid-latitude emission sources, and declining  
256 levels from 30°N to the equator (1% decrease in GEM per degree latitude, Holmes et al., 2010). As mentioned  
257 above pre/post-event and GOM-event back trajectories point out different latitudinal origins of 20-35°N and 35-  
258 50°N respectively. It seems therefore plausible that the original GEM levels in pre/post-event and GOM-event  
259 levels air masses were different due to different latitudinal air mass origins. A correction for latitudinal  
260 confounding allows estimating original GEM levels to be 15% lower in the GOM-event air masses, based on  
261 the 1% drop in GEM per degree latitude, and yields a corrected GOM\*/GEM slope of -0.88 (Figure 5, gray  
262 line). The corrected slope is close to -1 and therefore suggests that all nearly GOM produced has been retained  
263 within the free tropospheric air masses observed during the high GOM-event at the PDM.

264  $\delta^{202}\text{Hg}_{\text{GEM}}$  and  $\Delta^{204}\text{Hg}_{\text{GEM}}$  during the high-GOM event were slightly but significantly higher, and  $\Delta^{199}\text{Hg}_{\text{GEM}}$ ,  
265  $\Delta^{200}\text{Hg}_{\text{GEM}}$  and  $\Delta^{201}\text{Hg}_{\text{GEM}}$  slightly but significantly lower than pre- and post-event samples during 20 - 28 Dec  
266 2012 (Figure 1; t-test all  $p < 0.05$ ). All five GEM isotope signatures are significantly correlated with GEM (Figure

267 6) and GOM concentration. Net GEM oxidation therefore seems to have caused significant MDF, odd-MIF and  
 268 even-MIF. The above analysis of the GOM event at the PDM suggests that the observed air masses represent  
 269 the reactants, products and isotope fractionation characteristics of net GEM oxidation. Because the GOM-event  
 270 was long-lived, displaying elevated GOM levels over 48 hours, we suggest that the GEM and GOM  
 271 concentration, and GEM isotope observations represent a snapshot of net GEM oxidation that has been little  
 272 influenced by further mixing with boundary layer air. This implies that the observed MDF, odd-MIF and even-  
 273 MIF has accompanied net GEM oxidation in the lower troposphere. Previous observations on even-MIF in  
 274 precipitation ( $\Delta^{200}\text{Hg}$  only;  $\Delta^{204}\text{Hg}$  not observed; Chen et al. 2012) led to the suggestion that even-MIF  
 275 originates at the tropopause or stratosphere. Our results suggest that the even-MIF mechanism also operates  
 276 within the free troposphere.

277 In Figure 6 we plot the GEM and RM ( $\sim$ GOM) isotope observations in Rayleigh diagrams, and fit MDF,  
 278 odd-MIF and even-MIF factors for net GEM oxidation. Assuming pre-/post GOM event isotope observations  
 279 as the starting point for GEM reactant in the free troposphere, we applied Rayleigh distillation equations for  
 280 residual  $\delta^{202}\text{Hg}_{\text{GEM}}$ ,  $\Delta^{199}\text{Hg}_{\text{GEM}}$ ,  $\Delta^{200}\text{Hg}_{\text{GEM}}$ ,  $\Delta^{201}\text{Hg}_{\text{GEM}}$ , and  $\Delta^{204}\text{Hg}_{\text{GEM}}$  and for cumulative product GOM to  
 281 estimate corresponding isotope fractionation factors  $\epsilon_{\text{MDF}(\text{GOM}-\text{GEM})}^{202/198}$  of  $-1.1\pm 0.2\%$ ,  $\epsilon_{\text{MIF}(\text{GOM}-\text{GEM})}^{199/198}$  of  
 282  $0.65\pm 0.11\%$ ,  $\epsilon_{\text{MIF}(\text{GOM}-\text{GEM})}^{200/198}$  of  $0.22\pm 0.05\%$ ,  $\epsilon_{\text{MIF}(\text{GOM}-\text{GEM})}^{201/198}$  of  $0.65\pm 0.10\%$ , and  $\epsilon_{\text{MIF}(\text{GOM}-\text{GEM})}^{204/198}$  of  $-0.39\pm 0.12\%$   
 283 for the net GEM to GOM conversion observed (Figure 6). It should be kept in mind that these fractionation  
 284 factor do not inform on whether oxidation or reduction is the underlying cause, i.e. they represent net oxidation.

285

### 286 **Atmospheric GEM and RM pool size**

287 GEM and RM represent the two dominant reduced and oxidized atmospheric Hg pools. The relative size of  
 288 these two pools is not very well constrained due to limited mountain-top and in-flight measurements and bias  
 289 in denuder based RM measurements (Jaffe et al., 2014). Recent global Hg chemistry and transport models  
 290 indicate that RM (500 Mg) represents 12% and GEM 88% (3600 Mg) of atmospheric Hg, most of this residing  
 291 in the free troposphere (Horowitz et al., 2017). Based on the newly observed free tropospheric RM and GEM  
 292 isotope compositions (this study), and previously observed rainfall Hg, and modeled Hg emission fluxes and  
 293 isotopic composition, we can estimate by isotopic mass balance the proportions of RM and GEM (Table 1). The  
 294  $\Delta^{200}\text{Hg}$  signature, is best suited for this, since it is not confounded by additional even-MIF in cloud water, ocean  
 295 or soil environment. Annual mean GEM  $\Delta^{200}\text{Hg}$  at the PDM of  $-0.03\pm 0.03\%$  (Fu et al., 2016b) is identical to

296 GEM  $\Delta^{200}\text{Hg}$  of  $-0.04\text{‰}$  of the pre-/post GOM intrusion air masses, representing the northern hemisphere free  
297 tropospheric GEM pool. RM  $\Delta^{200}\text{Hg}$  at PDM ( $0.15\text{‰}$ ) is similar to mean northern hemispheric rainfall  $\Delta^{200}\text{Hg}$   
298 ( $0.13\pm 0.06\text{‰}$ ), suggesting that both values represent the free tropospheric RM pool. We use a model estimate  
299 for  $\Delta^{200}\text{Hg}$  ( $0.02\pm 0.02\text{‰}$ ) of global Hg emissions (Sun et al., 2019) to constrain the mass balance, and calculate  
300 that  $30\pm 17\%$  ( $1\sigma$ ) of free tropospheric Hg should be present as RM in order to explain the rainfall, RM and  
301 GEM  $\Delta^{200}\text{Hg}$  observations. This would suggest that current RM observations and models underestimate the size  
302 of the atmospheric RM pool by a factor of two. Our assessment is potentially biased due to the lack of  
303 observations in the southern hemisphere.

304

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312

### 313 **Author contributions**

314 J.E.S conceived the study. X.F, N.M., Y.X, M.J. and J.E.S performed field sampling. X.F, N.M., Y.X, M.J, LEHB,  
315 J.C. and J.E.S performed laboratory measurements. F.G. managed ancillary data collection at the PDM. X.F and  
316 J.E.S wrote the draft manuscript, which was improved by contributions from all authors.

317

### 318 **Additional information**

319 All Hg stable isotope data measured and discussed in this study is reported in the Supplementary Data.

320

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671 **Table 1. Mean  $\Delta^{200}\text{Hg}$  signatures for Hg emissions and atmospheric reservoirs.** Mean and  $1\sigma$  for  
 672 published rainfall data represents the mean of means of remote site data points for each study in order to avoid  
 673 site type and sample number bias. Global GEM emission  $\Delta^{200}\text{Hg}$  was calculated from the listed Hg fluxes and  
 674 modeled  $\Delta^{200}\text{Hg}$ . The combined uncertainty on calculated atmospheric GEM and RM fractions was  
 675 propagated from uncertainties on observational data for emissions and RM and GEM  $\Delta^{200}\text{Hg}$ .

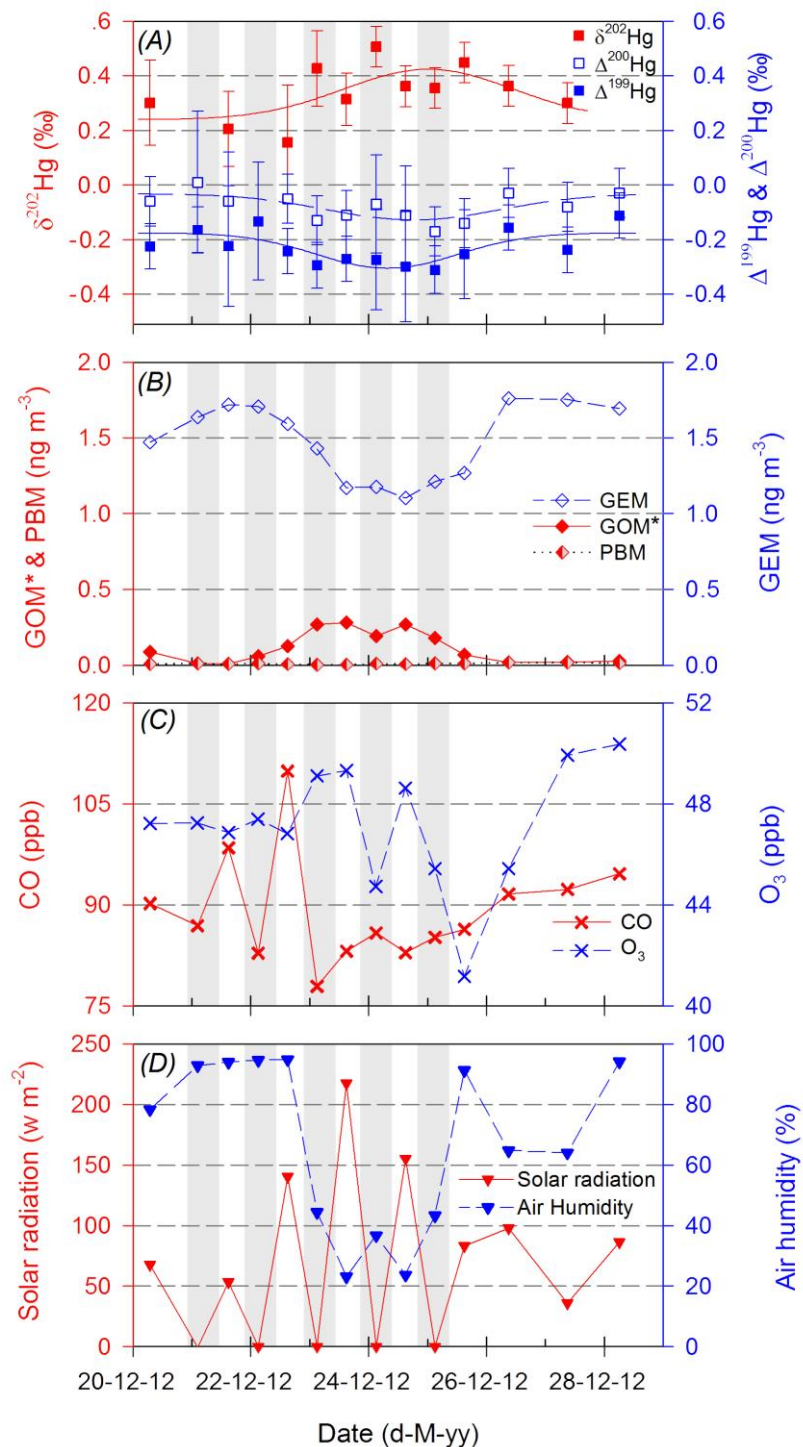
Sample type	Hg flux	$\Delta^{200}\text{Hg}$	$1\sigma$	
	$\text{Mg y}^{-1}$	‰	‰	
Pic du Midi RM		0.15	0.12	This study
Rainfall Hg		0.13	0.06	(Blum et al., 2014; Demers et al., 2013; Enrico et al., 2016; Gratz et al., 2010; Motta et al., 2019; Obrist et al., 2017; Sherman et al., 2012; Wang et al., 2015)
Pic du Midi GEM		-0.03	0.02	This study, (Fu et al., 2016b)
Ocean GEM emission	4600	0.03		(Horowitz et al., 2017; Sun et al., 2019)
Anthropogenic GEM	1470	0		(Horowitz et al., 2017; Sun et al., 2019)
Soil GEM emission	1420	-0.02		(Horowitz et al., 2017; Sun et al., 2019)
Volcanic GEM emission	250	0		(Horowitz et al., 2017; Sun et al., 2019)
Global GEM emission	7740	0.02	0.02	(Horowitz et al., 2017; Sun et al., 2019)
f(RM)		0.30 <sup>a</sup>	0.17	
f(GEM)		0.70 <sup>a</sup>	0.17	

676 <sup>a</sup> calculated from mass balance:  $\Delta^{200}\text{Hg}(\text{global GEM emitted}) = f(\text{RM}) \times \Delta^{200}\text{Hg}(\text{rainfall}) + f(\text{GEM}) \times$   
 677  $\Delta^{200}\text{Hg}(\text{PDM GEM})$ , and  $f(\text{RM}) + f(\text{GEM}) = 1$

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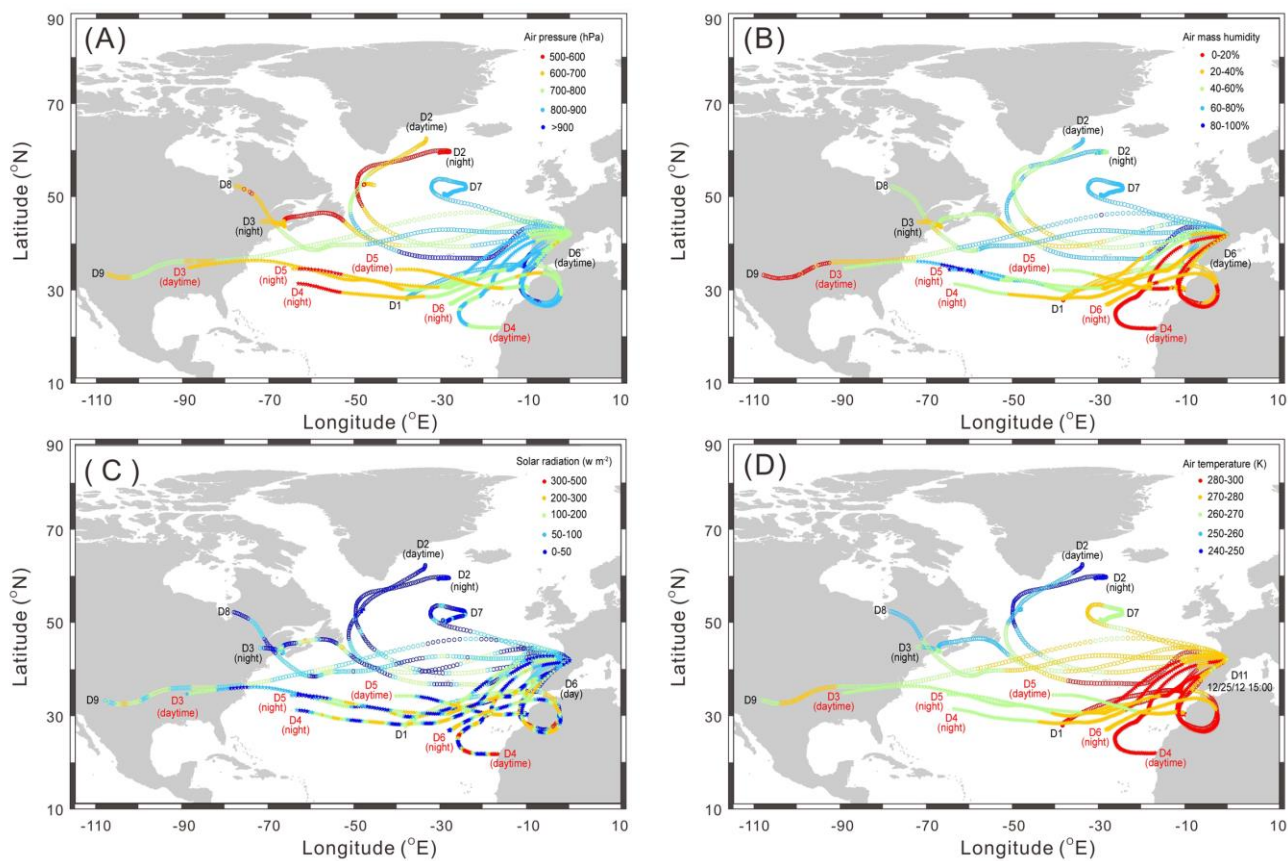
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680 **Figure 1. Hg speciation and isotope variability during a free tropospheric air mass intrusion.** From 20 to  
 681 28 Dec 2012, high frequency (12h, 24h) gaseous elemental Hg<sup>0</sup> (GEM) isotope signatures  $\delta^{202}\text{Hg}$ ,  $\Delta^{199}\text{Hg}$ ,  
 682  $\Delta^{200}\text{Hg}$  (A), CO and O<sub>3</sub> concentrations (B), atmospheric GOM, PBM and GEM concentrations (C), and solar  
 683 radiation and relative air humidity (D) showed a 48h long intrusion of a free tropospheric air mass, high in  
 684 GOM, and low in GEM and humidity.



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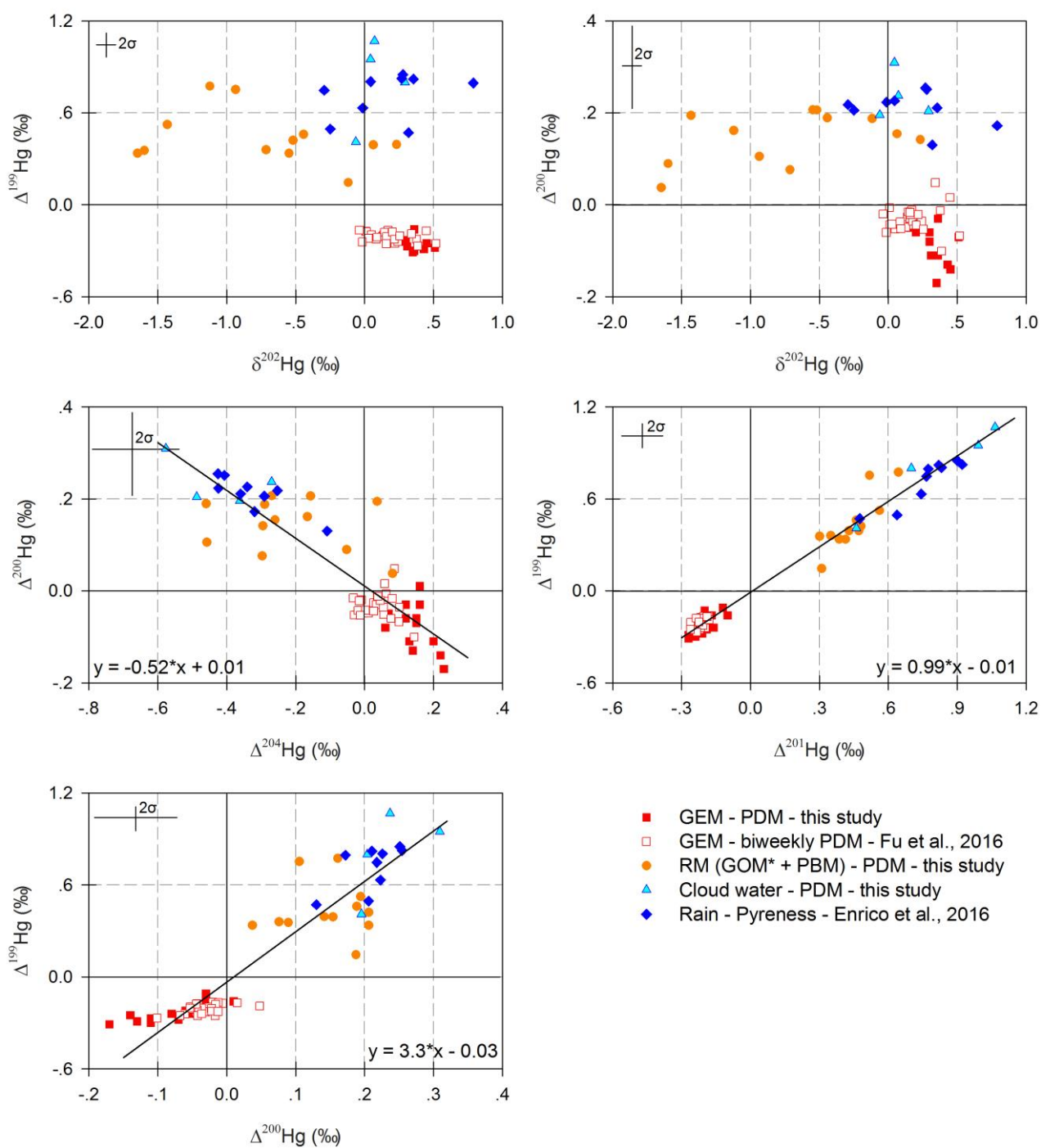
687 **Figure 2. Air mass back-trajectories of the free tropospheric air mass intrusion.** 7-day backward  
 688 trajectories of the high frequency (12h, 24h) gaseous elemental Hg<sup>0</sup> (GEM) isotope samples obtained from 20  
 689 to 28 Dec 2012: Travelling height (A, indicated by air pressure), air mass humidity (B), solar radiation (C),  
 690 and air temperature (D). Date and time labels are mid-points of 12h and 24h Hg isotope sampling windows.



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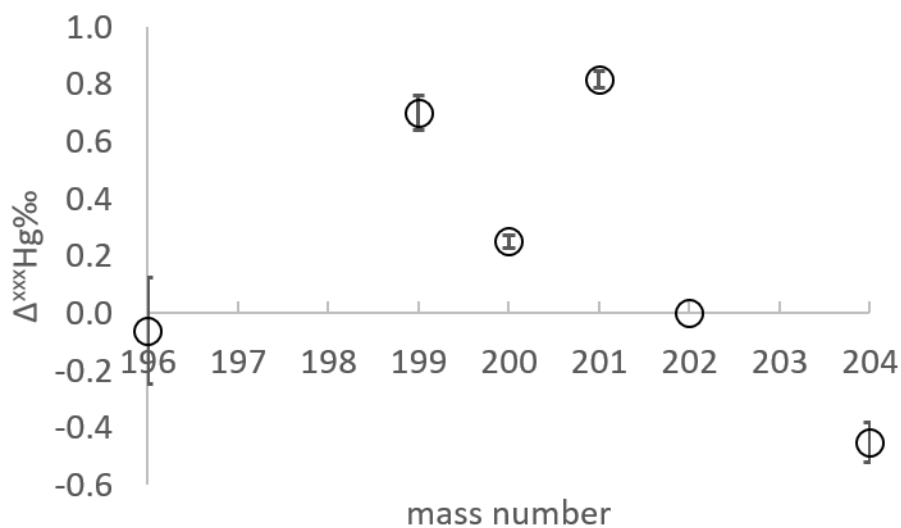
692 **Figure 3. Atmospheric Hg stable isotope variation at the Pic du Midi.** Hg mass dependent ( $\delta^{202}\text{Hg}$ ) and mass  
 693 independent ( $\Delta^{199}\text{Hg}$ ,  $\Delta^{200}\text{Hg}$ ,  $\Delta^{201}\text{Hg}$ ,  $\Delta^{204}\text{Hg}$ ) isotope signatures in reactive Hg (RM=GOM+PBM), cloud  
 694 water, 12h/24h GEM from this study, and previously published GEM (Fu et al., 2014) and rainfall (Enrico et  
 695 al., 2016).



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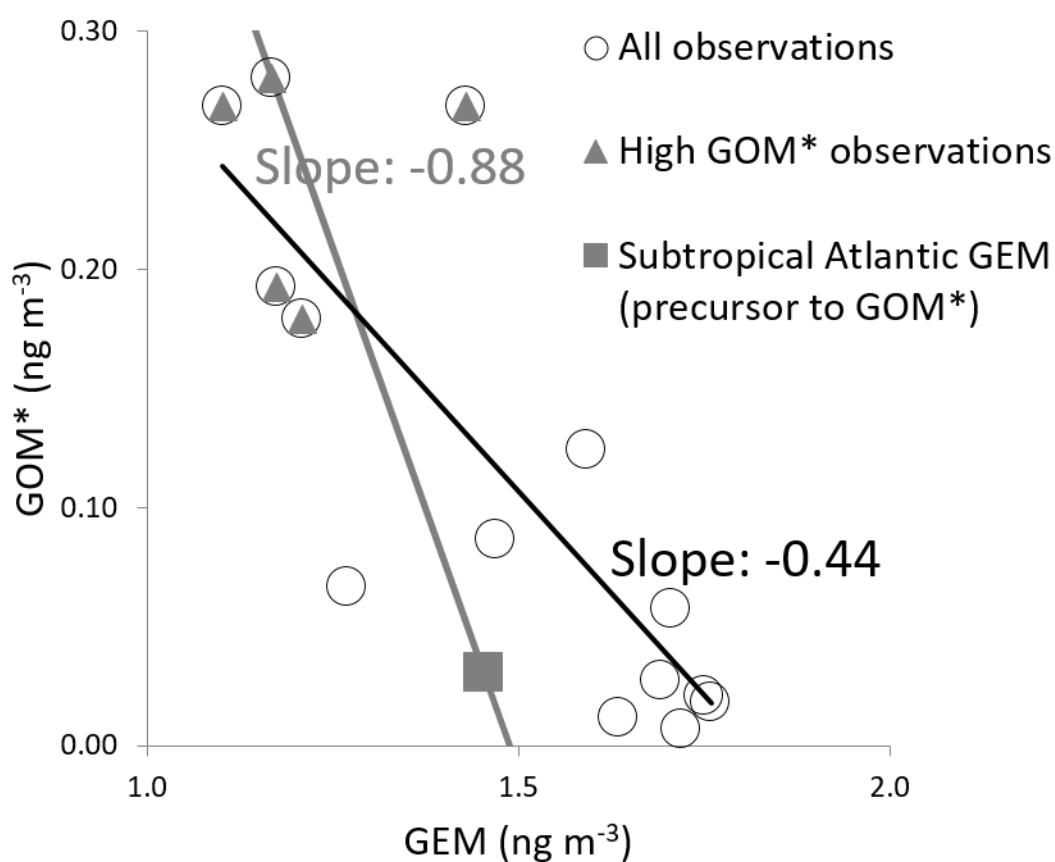
698 **Figure 4.  $\Delta^{196}\text{Hg}$  measurement of rainfall.** A 20.5L rainfall sample containing  $6.0 \text{ ng L}^{-1}$  of Hg was pre-  
699 concentrated 1200x to deliver a 0.015V signal on  $^{196}\text{Hg}$ . The resulting  $\Delta^{196}\text{Hg}$  signature is  $-0.06 \pm 0.19\text{‰}$  ( $2\sigma$ ,  
700  $n=2$ ) suggesting that nuclear self-shielding is not the underlying cause of atmospheric even-Hg MIF. A  $\Delta^{202}\text{Hg}$   
701 of 0 is indicated in the graph, since the  $\Delta^{\text{xxx}}\text{Hg}$  (where xxx are Hg isotopes masses 196 to 204) are calculated  
702 relative to  $\delta^{202/198}\text{Hg}$  ratios, themselves anchored to the  $^{198}\text{Hg}$  reference isotope.



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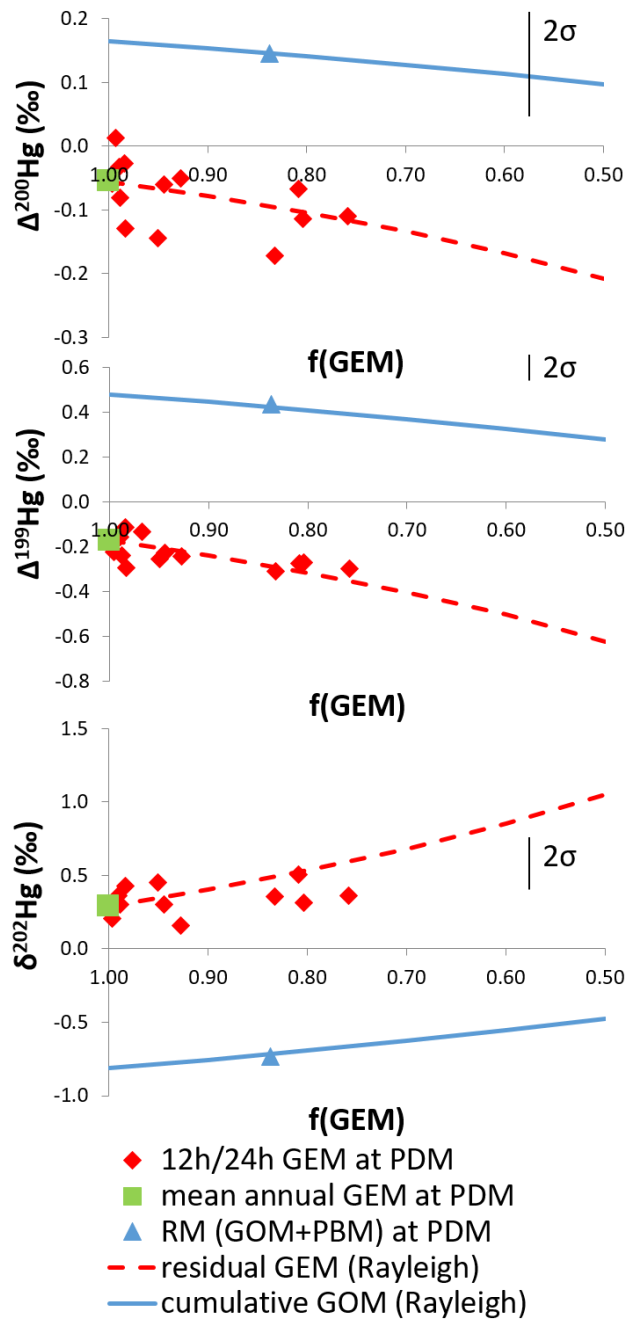
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705 **Figure 5. Hg oxidation mass balance in free tropospheric air at the Pic du Midi.** Relationship between  
706 gaseous elemental Hg<sup>0</sup> (GEM, ng m<sup>-3</sup>) and gaseous oxidized Hg<sup>II</sup> (GOM\*, ng m<sup>-3</sup>) observed during the nine day  
707 sampling campaign at PDM. Black circles and grey diamonds are Tekran GEM and GOM\* data (Extended  
708 Data), where grey diamonds represent the high GOM event only. A slope of -1 is indicative of Hg mass  
709 conservation during GEM oxidation to GOM in the observed air mass. The uncorrected GOM\*/GEM slope of  
710 -0.44 is biased low due to latitudinal bias in the GEM precursor to GOM (see main text). Latitude corrected  
711 subtropical Atlantic Ocean GEM levels (grey square) indicate a slope of -0.88, suggesting that Hg mass has  
712 been conserved in the high GOM air mass detected at PDM.



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716 **Figure 6. Rayleigh diagrams for Hg isotope fractionation during Hg<sup>0</sup> net oxidation.** This dataset is a  
717 composite of GEM isotope composition (red diamonds) recorded in the Atlantic Ocean free tropospheric air  
718 mass intrusion at PDM in Dec 2012, and mean RM (=GOM\*+PBM ~ GOM\*) isotope composition (blue  
719 triangles) at PDM recorded from June – October 2014. Isotope fractionation factors  $\epsilon_{MDF(GOM-GEM)}^{202}$  of  $-1.1 \pm$   
720  $0.2\%$ ,  $\epsilon_{MIF(GOM-GEM)}^{4199}$  of  $0.65 \pm 0.11\%$ ,  $\epsilon_{MIF(GOM-GEM)}^{4200}$  of  $0.22 \pm 0.05\%$ ,  $\epsilon_{MIF(GOM-GEM)}^{4201}$  of  $0.65 \pm 0.10\%$ , and  
721  $\epsilon_{MIF(GOM-GEM)}^{4204}$  of  $-0.39 \pm 0.12\%$  (all 1SE) were fitted by log-linear regression of Rayleigh equations for residual  
722 GEM and cumulative GOM\*. All 12h and 24h observations (blue diamonds) over the nine day period were  
723 included in the fitting. The starting isotopic composition (green square) is the mean annual GEM composition  
724 at PDM (Fu et al., 2016b).



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