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X. Fu, N. Maruszczak, Lars-Eric Heimbürger-Boavida, B. Sauvage, F. Gheusi, E. Prestbo, E. Sonke

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1        Atmospheric mercury speciation dynamics at the high-altitude Pic du Midi  
2                                  Observatory, southern France  
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4        X. W. Fu<sup>1,2</sup>, N. Maruszczak<sup>1</sup>, L.-E. Heimbürger<sup>1,3</sup>, B. Sauvage<sup>4</sup>, F. Gheusi<sup>4</sup>, E. M.  
5                                  Prestbo<sup>5</sup>, J. E. Sonke<sup>1</sup>,  
6                                  <sup>1</sup>Observatoire Midi-Pyrénées, Laboratoire Géosciences Environnement Toulouse, CNRS/IRD/Université de  
7                                  Toulouse, 14, avenue Édouard Belin, 31400 Toulouse, France  
8                                  <sup>2</sup>State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences,  
9                                  Guiyang, China.  
10                                  <sup>3</sup>Mediterranean Institute of Oceanography, Campus de Luminy, 13288 Marseille, France  
11                                  <sup>4</sup>Observatoire Midi-Pyrénées, Laboratoire d’Aérodologie, CNRS/IRD/Université de Toulouse, 14, avenue Édouard  
12                                  Belin, 31400 Toulouse, France  
13                                  <sup>5</sup>Tekran Research and Development, 330 Nantucket Blvd., Toronto, ON, Canada M1P2P4  
14                                  Correspondence to:\*Xuewu Fu    E-mail : [fuxuewu@mail.gyg.ac.cn](mailto:fuxuewu@mail.gyg.ac.cn)  
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16        Abstract: Continuous measurements of atmospheric gaseous elemental mercury (GEM),  
17 particulate bound mercury (PBM) and gaseous oxidized mercury (GOM) at the high-altitude Pic  
18 du Midi Observatory (PDM, 2877 m a.s.l) in southern France were made from Nov 2011 to Nov  
19 2012. The mean GEM, PBM and GOM concentrations were  $1.86 \text{ ng m}^{-3}$ ,  $14 \text{ pg m}^{-3}$  and  $27 \text{ pg m}^{-3}$ ,  
20 respectively and we observed 44 high PBM (up to  $98 \text{ pg m}^{-3}$ ) and 61 high GOM (up to  $295 \text{ pg m}^{-3}$ )  
21 events. The high PBM events occurred mainly in cold seasons (winter and spring) whereas high  
22 GOM events were mainly observed in the warm seasons (summer and autumn). In cold seasons  
23 the maximum air mass residence times (ARTs) associated with high PBM events were observed in  
24 the upper troposphere over North America. The ratios of high PBM ARTs to total ARTs over North  
25 America, Europe, the Arctic region and Atlantic Ocean were all elevated in the cold season  
26 compared to the warm season, indicating that the middle and upper free troposphere of the  
27 Northern Hemisphere may be more enriched in PBM in cold seasons. PBM concentrations and  
28 PBM/GOM ratios during the high PBM events were significantly anti-correlated with atmospheric  
29 aerosol concentrations, air temperature and solar radiation, suggesting in situ formation of PBM in  
30 the middle and upper troposphere. We identified two distinct types of high GOM events with the  
31 GOM concentrations positively and negatively correlated with atmospheric ozone concentrations,  
32 respectively. High GOM events positively correlated with ozone were mainly related to air masses  
33 from the upper troposphere over the Arctic region and middle troposphere over the temperate  
34 North Atlantic Ocean, whereas high GOM events anti-correlated with ozone were mainly related  
35 to air masses from the lower free troposphere over the subtropical North Atlantic Ocean. The  
36 ARTs analysis demonstrates that the lower and middle free troposphere over the North Atlantic  
37 Ocean was the largest source region of atmospheric GOM at PDM Observatory. The ratios of high  
38 GOM ARTs to total ARTs over the subtropical North Atlantic Ocean in summer were significantly  
39 higher than that over the temperate and sub-arctic North Atlantic Ocean as well as that over the  
40 North Atlantic Ocean in other seasons, indicating abundant in situ oxidation of GEM to GOM in  
41 the lower free troposphere over the subtropical North Atlantic Ocean in summer.  
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## 43 1 Introduction

44 Transformations of mercury (Hg) in the atmosphere play a crucial role in the global Hg cycle  
45 (Selin et al., 2007; Driscoll et al., 2013). Gaseous elemental mercury (GEM) is the predominant  
46 form emitted by anthropogenic and natural sources (Pirrone et al., 2010). GEM is then  
47 transformed to gaseous oxidized mercury (GOM) and particulate bound mercury (PBM) by  
48 oxidation. Atmospheric Hg deposition occurs by wet deposition and dry deposition pathways.  
49 Models suggest global GEM dry deposition to be potentially important, yet lack broad  
50 observational evidence (Selin et al., 2008). On the other hand, GOM and PBM are readily  
51 scavenged from the atmosphere by cloud droplets followed by wet deposition, and by dry  
52 deposition. Hence, conversion of GEM to GOM and PBM is a crucial process in the removal of  
53 Hg in the atmosphere, which in turn affects the loading of Hg to terrestrial and marine ecosystems.

54 Conversion of GEM to GOM and PBM is potentially occurring throughout the global  
55 atmosphere, but the rates of conversion are thought to vary and are dependent on the levels of  
56 atmospheric oxidants and environmental factors. Current modeling studies suggested that  
57 conversion of GEM to GOM and PBM produces approximate 8000 tons of GOM and PBM  
58 annually, which explains at least 90% of the total sources of GOM and PBM in the atmosphere  
59 (Holmes et al., 2010). However, it is still unclear where the majority of the conversion takes place,  
60 by what mechanism and what the major oxidants and environmental factors are involved. Over the  
61 last decade, studies have been carried out to measure atmospheric Hg speciation at high-altitude  
62 sites in the USA and Asia and on research flights. A study at the Mount Bachelor observatory  
63 (MBO, USA) showed elevated GOM (up to 600 pg m<sup>-3</sup>) and low GEM in the free troposphere,  
64 suggesting in situ oxidation (Swartzendruber et al., 2006). Observations at Storm Peak laboratory  
65 (SPL, USA) and Lulin Atmospheric Background Station (LABS, Taiwan) showed similar, though  
66 less elevated, GOM events in free tropospheric air masses (Fain et al., 2009; Sheu et al., 2010).  
67 Long-term Hg speciation observations at MBO suggest GEM oxidation to be enhanced in  
68 long-range Asian pollution plumes, but also in marine boundary layer (MBL) air masses  
69 originating over the Pacific Ocean (Timonen et al., 2013). INTEX-B in-flight observations of  
70 GEM in the tropopause region (8-12km) have shown low GEM levels, sometimes down to zero,  
71 indicative of rapid oxidation (Talbot et al., 2007). CARIBIC in-flight observations of total gaseous  
72 Hg (TGM ~ GEM+GOM) showed lower TGM levels in the southern hemisphere, TGM depletion  
73 in the extratropical lowermost stratosphere and a general positive correlation between TGM and  
74 ozone (Slemr et al., 2009; Slemr et al., 2014). In-flight, in-situ analyses of stratospheric aerosols  
75 suggest that the upper troposphere and lower stratosphere depletion in GEM is balanced by  
76 abundant PBM (Murphy et al., 1998; Murphy et al., 2006). Recent in-flight measurements  
77 provided the first simultaneous observations of both GEM and the combined GOM+PBM



78 fractions at an altitude above 6 km (Lyman and Jaffe, 2012). The study showed elevated  
79 GOM+PBM levels in stratospheric air masses and confirmed the importance of stratospheric  
80 GEM oxidation. The findings of all these studies indicate that the free troposphere and lower  
81 stratosphere are important regions for conversion of GEM to GOM and PBM.

82 A recent study reviewed mountain-top studies of free troposphere Hg dynamics and  
83 compared observations to the GEOS-Chem atmospheric Hg chemistry and transport  
84 model (Weiss-Penzias et al., 2015). The model intercompared Hg oxidation by Br against  
85 OH-ozone pathways and was able to only marginally reproduce observations, indicating the need  
86 to improve both measurement techniques and models. Additional long-term observations of GEM,  
87 GOM, and PBM are therefore necessary to map out regions and altitudes that favor GEM  
88 oxidation, and provide insight into the oxidation mechanisms. In the present study, we carried out  
89 one year of continuous measurements of speciated atmospheric mercury at the Pic du Midi (PDM)  
90 Observatory, a high-altitude site (2877 m a.s.l) in the French Pyrenees mountains. This is the first  
91 year-around study of atmospheric Hg speciation at a mid-latitude high-altitude site. This study  
92 may help to better understand the seasonal patterns of high GOM and PBM events and the  
93 mechanisms underlying the transformations of atmospheric Hg in the free troposphere over the  
94 lower, middle and high latitudes.

95

## 96 **2 Materials and methods**

### 97 **2.1 Site description**

98 The Pic du Midi (PDM) Observatory (0.142° E, 42.937° N, 2877 m a.s.l) is a high-altitude  
99 monitoring station situated on top of an isolated peak (elevated approximately 1300 m relative to  
100 the surrounding terrain) on the northern edge of the central Pyrenees mountains, Southwest France.  
101 It is approximately 150 km to the east of the North Atlantic coast and 210 km to west of the  
102 Mediterranean Sea. The PDM Observatory frequently receives free tropospheric air from the  
103 North Atlantic and Europe (Henne et al., 2010). The station may also be partly influenced by  
104 boundary layer air transported by plain-to-mountain winds from southwest France or through  
105 regional transport from Spain under southerly or south-westerly synoptic wind conditions (Gheusi  
106 et al., 2011; Tsamalis et al., 2014). There are no source points around the station or in the  
107 surrounding areas. The two nearest cities are Pau and Tarbes which are respectively located 60 and  
108 30 km northwest to the station and may influence the observations via upslope transport.

109

### 110 **2.2 Measurements of speciated atmospheric mercury and Ancillary parameters**

111 Speciated atmospheric Hg is continuously measured at PDM Observatory using the Tekran  
112 2537/1130/1135 system (Tekran Inc., Canada). The period analyzed in this study goes from 18<sup>th</sup>



113 Nov 2011 to 17<sup>th</sup> Nov 2012. The Tekran system has been widely used and described in detail  
114 elsewhere (Landis et al., 2002; Lindberg et al., 2002). Briefly, GOM, PBM, and GEM in ambient  
115 air were collected onto KCl-coated annular denuder, regenerable quartz fiber filter and dual gold  
116 cartridges in sequence. The system was programmed to collect GOM and PBM at 1-h intervals at  
117 a volumetric flow rate of 10 L min<sup>-1</sup>; and GEM was collected at 5-min intervals at a volumetric  
118 flow rate of 1.07 L min<sup>-1</sup>. Once collected, Hg is thermally decomposed from each unit and  
119 detected by cold vapor atomic fluorescence spectroscopy (CVAFS) as Hg<sup>0</sup>. KCl-coated denuder,  
120 Teflon coated glass inlet, and impactor plate were replaced bi-weekly and quartz filters were  
121 replaced monthly. Denuders and quartz filters were prepared and cleaned before field sampling  
122 following the methods in Tekran technical notes. The Tekran 2537B analyzer was routinely  
123 calibrated using its internal permeation source at a 47 h interval, and was also cross-calibrated  
124 every 3 months against an external temperature controlled Hg vapor standard. Due to the frequent  
125 extreme weather conditions at PDM Observatory, the system was installed inside a  
126 temperature-controlled laboratory. Ambient air was introduced into the Tekran unit using the  
127 Tekran 1004 Teflon coated manifold, which is similar as that used at the MBO,  
128 USA (Swartzendruber et al., 2006). The inlet of the Tekran 1104 manifold was about 0.5 m from  
129 the outside wall of the laboratory and oriented to the southwest (the local predominant wind  
130 direction) of the laboratory. Temperature of the Tekran 1104 manifold was kept at 70 °C and air  
131 flow through the manifold was about 100 L min<sup>-1</sup>. Blanks of Tekran unit and manifold were  
132 quantified at the beginning and end of each maintenance (bi-weekly) using Hg-free ambient air.  
133 The annual mean GEM blank of the Tekran unit was 0.04 ± 0.03 ng m<sup>-3</sup> (1SD) and detection limit  
134 of GEM was estimated to be 0.1 ng m<sup>-3</sup>.

135 Measurement of GOM and PBM is challenging due to the typical low part per quadrillion  
136 (ppq) concentrations, reactivity and potential for species interconversion, and the need to  
137 pre-concentrating on a surface. In addition the lack of understanding of the specific forms and  
138 accepted calibration standards of GOM and PBM hinders the ability to obtain in-field quality  
139 assurance measurements, like dynamic spiking under changing atmospheric conditions. Recently,  
140 uncertainties regarding the accuracy of GOM measurements have been discovered related to O<sub>3</sub>  
141 and water vapor levels suggesting a potential for low GOM bias under certain atmospheric  
142 conditions (Lyman et al., 2010; Gustin et al., 2013). Another study using cation exchange  
143 membranes suggested that on average KCl-coated denuders may create up to a 50% low bias in  
144 the humid air, but was only a comparison of two differing methods, with neither one challenged in  
145 real time by standard spiking under atmospheric conditions (Huang et al., 2013). On the other  
146 hand, the potential for the PBM to be biased has not been thoroughly studied and understood, for  
147 the reasons mentioned above, however the bias would likely be positive due to GEM uptake as the



148 regenerable filter ages and becomes more reactive. At PDM Observatory, similar to other high  
149 altitude studies, we do not observe simultaneous increases of PBM during high GOM events  
150 suggesting no significant GOM breakthrough or GEM uptake on the filter (Malcolm and Keeler,  
151 2007;Swartzendruber et al., 2006;Fain et al., 2009). Similarly GOM loss from denuders has been  
152 suggested to relate to high humidity levels (McClure et al., 2014). The elevated free tropospheric  
153 PBM and GOM events discussed in this study occur predominantly in low humidity air masses  
154 (median humidities of 21 and 28 % respectively) limiting GOM losses. Therefore, as most of the  
155 discussion in the present study is based on the relative variations of GOM and PBM, we assume  
156 the potential sampling artifacts may bring a minimal uncertainty to the overall findings. Most  
157 importantly, the method used in this study and others is “state of the art” at this time and has  
158 resulted in profound discoveries that are scientifically coherent (Schroeder and Munthe,  
159 1998;Laurier et al., 2003;Lindberg et al., 2002;Swartzendruber et al., 2006;Steffen et al.,  
160 2008;Sprovieri et al., 2010;Fu et al., 2015). Currently, there is no better method to routinely  
161 separate and quantify low, part-per-quadrillion concentrations of the mercury fractions with hourly  
162 time resolution, than the use of a fully heated sample train that rejects large particles(>2.5 μm) by  
163 impaction, capture of “sticky” GOM species on a laminar flow, coated annular denuder, which  
164 rejects both PBM and GEM, followed by a quartz fiber filter to collect PBM, which rejects GEM  
165 so it can pass to a sensitive monitor for continuous detection. The operationally defined method to  
166 quantify atmospheric mercury fractions is similar to well established methods used for other  
167 “sticky gases” ammonia and nitric acid.

168 Atmospheric CO and ozone concentrations were continuously measured using the TEI  
169 48CTL gas filter correlation analyzers and 49C Ozone analyzer (Thermo Environmental  
170 Instruments Inc. USA), respectively. Detailed information regarding the principle of the  
171 instruments, calibrations, and measurement uncertainties can be found in a previous study (Gheusi  
172 et al., 2011).The standard uncertainties associated with CO and ozone datasets (15-min averaged  
173 data) were reported to be 6.6 and 1.2 ppbv, respectively (Gheusi et al., 2011). Atmospheric aerosol  
174 number concentration in PM<sub>10</sub> particles (i.e. of diameter<10 μm) was measured at PDM  
175 Observatory using a condensation particle counter (CPC), Model 3010 by TSI Inc. The particles  
176 are detected by condensing butanol vapor onto the particles, causing them to grow into droplets.  
177 These particles (in the droplet form) are then counted by optical absorption (Gheusi et al., 2011).  
178 CO and ozone mole fractions, as well as atmospheric aerosol number concentration and standard  
179 meteorological variables at PDM Observatory were obtained as 5-min averages from the PAES  
180 (French acronym for atmospheric pollution at synoptic scale; <http://paes.aero.obs-mip.fr/>)  
181 network.

182



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### 183 2.3 Simulations of back trajectories, air masses residence times and potential source regions

184 In the present study, we calculated 10-day back trajectory for high PBM events and 7-day  
185 back trajectory for high GOM events, respectively using the NOAA Hysplit trajectory model and  
186 gridded meteorological data (Global Data Assimilation System, GDAS1) (Draxler and Rolph).  
187 The GDAS1 has a horizontal resolution of 1 degree (360×180 grid cells) with 23 vertical levels  
188 from 1000 hPa to 20 hPa. The trajectories ended at the PDM Observatory at a height of 3000 m  
189 a.s.l. (approximately 100 m above the sampling site). In addition, we also used the Flexpart  
190 Lagrangian particle dispersion model version 9.0 (Stohl et al., 2005) to simulate the 20 days back  
191 trajectories for two special events (high PBM event #12 and #19 ) and to make a comparison with  
192 Hysplit. The Flexpart model is driven by wind fields provided by the European Centre for  
193 Medium-range Weather Forecast (ECMWF) with a temporal resolution of 3 hours (analyses at  
194 00:00, 06:00, 12:00, 18:00 UTC; forecasts at 03:00, 09:00, 15:00, 21:00 UTC) and with horizontal  
195 resolution of 32 km. The model output refers to the time, in seconds, the released particles spent in  
196 each output grid box before reaching the PDM Observatory. Flexpart residence times are output  
197 every 3 h on a uniform grid of 0.5° latitude × 0.5° longitude in 40 vertical layers from mean sea  
198 level to a height of 20 km above sea level. In the present study, we analyzed how air masses from  
199 different sublayers in the troposphere affect atmospheric PBM and GOM concentrations at the  
200 PDM Observatory. We subdivide the troposphere into 4 sublayers: boundary layer (> 900 hPa),  
201 lower free troposphere (700-900 hPa), middle free troposphere (500-700 hPa) and upper free  
202 troposphere (200-500 hPa).

203 Air mass residence times (ARTs) were calculated on the basis of the simulations of 7-day  
204 backward trajectories ending at PDM Observatory. The studied domain covered by the trajectories  
205 was divided into 3590 grid cells of 2.5° latitude × 2.5° longitude. To reduce the “central  
206 convergence” effect and highlight the long-range transport processes (Cuevas et al., 2013), we  
207 adjusted the residence times using the geometric adjustment factor as proposed by Poirot and  
208 Wishinski (1986).

209 The potential source regions of PBM and GOM were simulated using a Potential Source  
210 Contribution Function (PSCF) approach (Zeng and Hopke, 1989). The PSCF value indicates the  
211 probability that a source area contributed to the receptor site and is defined as:

$$212 \text{PSCF}_{ij} = \frac{M_{ij}}{N_{ij}} \times W_{ij} \quad (1)$$

213  $M_{ij}$  is the total number of endpoints in a grid cell associated to PBM and GOM  
214 concentrations at PDM Observatory higher than the annual means,  $N_{ij}$  is the total number of  
215 endpoints in a grid cell, and  $W_{ij}$  is a weighting function used to minimize the uncertainties of a  
216 small  $N_{ij}$  and described by Polissar et al (2001). For the PBM and GOM PSCF analysis, 7-day  
217 back trajectories ending at PDM Observatory were calculated every 2 hours throughout the whole





218 study period. The total trajectory endpoints in the boundary layer, lower free troposphere, and  
219 middle and upper troposphere in the studied domain were 152025, 285726, and 250557,  
220 respectively. The studied domain was divided into 5566 grid cells of  $2.0^\circ$  latitude  $\times$   $2.0^\circ$  longitude.  
221 Areas with high PSCF values are likely enriched in atmospheric PBM and GOM and probably  
222 contribute to the elevated PBM and GOM concentrations at PDM Observatory.

223

### 224 **3 Results and discussion**

#### 225 **3.1 Annual, seasonal, and diel trends**

226 Averaged atmospheric GEM, PBM, and GOM concentrations at PDM Observatory during  
227 the study period were  $1.86 \pm 0.27$  ng m<sup>-3</sup>,  $14 \pm 10$  pg m<sup>-3</sup>, and  $27 \pm 34$  pg m<sup>-3</sup>, respectively (time  
228 series of GEM, PBM and GOM concentrations are in Figure S1). The level of GEM at PDM  
229 Observatory was slightly higher than the previous observations at remote sites in Europe (means:  
230  $1.66 - 1.82$  ng m<sup>-3</sup>) (Slemr and Scheel, 1998; Lee et al., 1998; Kock et al., 2005) and North America  
231 (means:  $1.32 - 1.72$  ng m<sup>-3</sup>) (Kellerhals et al., 2003; Lan et al., 2012), but lower than that observed  
232 in Asia (means:  $1.60 - 3.98$  ng m<sup>-3</sup>) (Fu et al., 2015). Continuous measurements of atmospheric  
233 Hg speciation at high-altitude sites are limited worldwide. The mean PBM concentration at PDM  
234 Observatory was approximately 7 times higher than at LABS ( $2$  pg m<sup>-3</sup>,  $23.5^\circ$  N, 2862 m asl)  
235 (Sheu et al., 2010), and also higher than the summertime means at SPL ( $9$  pg m<sup>-3</sup>,  $40.5^\circ$  N, 3230 m  
236 a.s.l) and MBO ( $5$  pg m<sup>-3</sup>,  $44.0^\circ$  N, 2700 m a.s.l) (Swartzendruber et al., 2006; Fain et al., 2009).  
237 The annual mean GOM concentration at PDM Observatory was relatively higher than at LABS  
238 ( $12$  pg m<sup>-3</sup>) and SPL ( $20$  pg m<sup>-3</sup>) (Fain et al., 2009; Sheu et al., 2010), but lower than at MBO ( $40$   
239 pg m<sup>-3</sup>) (Swartzendruber et al., 2006). The difference in atmospheric PBM and GOM  
240 concentrations among high-altitude sites may partially reflect measurements uncertainty, but also  
241 be due to the different regional and long-range Hg transport, atmospheric Hg transformations, and  
242 intrusions of air from the upper troposphere and lower stratosphere.

243 Differences in GEM concentrations for different seasons were not statistically significant (t  
244 test  $p = 0.73$ , Figure 1). The monthly mean PBM concentrations were relatively higher ( $p < 0.05$ )  
245 in winter (December to February) and spring (March to May) than in summer (June to August)  
246 and autumn (September to November), with the highest monthly mean of  $21$  pg m<sup>-3</sup> in February  
247 and the lowest monthly mean of  $7$  pg m<sup>-3</sup> in October. This seasonal pattern is similar to the  
248 observations at LABS as well as low-altitude sites in North America and China (Lan et al.,  
249 2012; Fu et al., 2012; Sheu et al., 2010). Elevated winter PBM concentrations are common at  
250 low-altitude sites in the Northern Hemisphere, which is likely linked to emissions from residential  
251 heating, and low temperature facilitating gas-particle partitioning of atmospheric mercury, and  
252 decreasing wet scavenging processes (Lan et al., 2012; Rutter and Schauer, 2007; Selin et al., 2007).



253 Monthly mean GOM concentrations were relatively higher ( $p < 0.05$ ) in summer (mean:  $38 \text{ pg m}^{-3}$ ),  
254 followed by winter (mean:  $25 \text{ pg m}^{-3}$ ), autumn (mean:  $25 \text{ pg m}^{-3}$ ), and spring (mean:  $23 \text{ pg m}^{-3}$ )  
255 (Figure 1). In general, in-situ oxidation of GEM and long-range transport of GOM-enriched air  
256 from the free troposphere, rather than anthropogenic emissions are the dominant sources of  
257 atmospheric GOM at high-altitude sites (Sheu et al., 2010; Swartzendruber et al., 2006; Fain et al.,  
258 2009). The summer maximum GOM at PDM Observatory may indicate these processes are more  
259 dominant in summer than during other seasons .

260 Atmospheric GEM, PBM, and GOM displayed well-defined diel trends at PDM Observatory  
261 (Figure 2). GEM concentrations (2-hour means) were relatively higher during daytime with the  
262 maximum observed in the later afternoon (around 17:00) and minimum observed in the early  
263 morning (around 5:00), and positively correlated with CO ( $r^2 = 0.70$ ,  $p < 0.01$ ). The diel trends in  
264 PBM and GOM contrast with that of GEM, with the maximum PBM and GOM concentrations  
265 (2-hour means) observed in the early morning (around 7:00) and the minimum concentrations in  
266 the later afternoon (around 17:00) (Figure 2). PBM and GOM concentrations were significantly  
267 anti-correlated with GEM concentrations ( $r^2_{\text{GEM-PBM}} = 0.91$ ,  $r^2_{\text{GEM-PBM}} = 0.87$ ,  $p < 0.01$  for both)  
268 and CO concentrations ( $r^2_{\text{GEM-PBM}} = 0.74$ ,  $r^2_{\text{GEM-PBM}} = 0.75$ ,  $p < 0.01$  for both), and positively  
269 correlated with each other ( $r^2_{\text{GOM-PBM}} = 0.91$ ,  $p < 0.01$ ) and with ozone concentrations ( $r^2_{\text{ozone-PBM}} =$   
270  $0.93$ ,  $r^2_{\text{ozone-GOM}} = 0.88$ ,  $p < 0.01$  for both). The diel trends of atmospheric Hg species at PDM  
271 Observatory were similar to those at MBO and LABS (Sheu et al., 2010; Swartzendruber et al.,  
272 2006), but in contrast with the GOM diel trend at SPL which showed relatively higher values in  
273 the afternoon (Fain et al., 2009). The PDM Observatory is frequently impacted by upslope, valley,  
274 and plain-to-mountain breezes (Gheusi et al., 2011; Tsamalis et al., 2014). Elevated GEM  
275 concentrations during daytime were likely related to upward transport of GEM enriched boundary  
276 layer air, whereas elevated PBM and GOM concentrations at night were attributed to long-range  
277 transport of PBM and GOM-enriched air in the free troposphere (see below).

278

### 279 3.2 High PBM events

280 We observed 44 high PBM events, which were defined as the peak concentrations higher than  
281  $31 \text{ pg m}^{-3}$ , which are the 95<sup>th</sup> percentile PBM levels for the entire study. The maximum PBM  
282 concentration was  $98 \text{ pg m}^{-3}$ , and was the highest value among the maximum PBM concentrations  
283 ( $33 - 40 \text{ pg m}^{-3}$ ) observed at high-altitude sites (Sheu et al., 2010; Swartzendruber et al., 2006; Fain  
284 et al., 2009; Timonen et al., 2013).

285 For the 44 high PBM events, 30 events showed significant anti-correlations between PBM  
286 and GEM concentrations (Supplementary Table S1). Also, the GEM levels during the 30 high  
287 PBM events when peak PBM concentrations were observed were generally low with



288 concentrations less than the annual mean GEM concentrations of  $1.86 \text{ ng m}^{-3}$ . This phenomenon is  
289 in contrast with PBM and GEM observations impacted by anthropogenic and biomass burning  
290 emissions which showed simultaneous increases of PBM and GEM concentrations (Manolopoulos  
291 et al., 2007; Song et al., 2009; Fu et al., 2011; Obrist et al., 2008). The air masses related to the 30  
292 high PBM events mainly originated from the upper free troposphere over North America, Europe  
293 and the Arctic (supplementary Figure S2). For the 30 high PBM events, 20 events had PBM/GOM  
294 ratio higher than 1, indicating a significant proportion of depleted GEM in the upper free  
295 troposphere was in the form of PBM rather than GOM. We acknowledge that PBM/GOM ratios  
296 may be affected by bias in denuder GOM measurements (Gustin et al., 2013). Nevertheless our  
297 observations on high PBM events appear different from previous studies at high-altitude sites  
298 (note that these studies were conducted in the warm season or in the tropics) (Sheu et al.,  
299 2010; Swartzendruber et al., 2006; Fain et al., 2009). A possible explanation is that most of the high  
300 PBM events at PDM Observatory were observed in the cold season which may favor the  
301 production and/or accumulation of PBM in the upper free troposphere.

302 Six out of the 44 PBM events (supplementary Table S1) were probably related to direct  
303 anthropogenic pollution. These events were accompanied by elevated GEM (mean =  $1.96 \pm 0.13$   
304  $\text{ng m}^{-3}$ ) and CO concentrations (mean =  $141 \pm 26$  ppb) and low GOM concentrations (mean =  $22 \pm$   
305  $15 \text{ pg m}^{-3}$ ). Also, the changes in PBM concentrations, in most cases, were positively correlated  
306 with GEM and CO and anti-correlated with GOM. The back trajectory analysis suggests that the  
307 air masses of these 6 PBM events were likely mixed with boundary layer air over Europe prior to  
308 ending at the PDM Observatory (Supplementary Figure S3). For the remaining 8 high PBM events  
309 (supplementary Table S1), no significant correlations were observed between PBM concentrations  
310 and GEM. However, these events were generally accompanied by typical GEM (mean =  $1.76 \pm$   
311  $0.20 \text{ ng m}^{-3}$ ) and CO (mean =  $110 \pm 11$  ppb) concentrations, low relative humidity (mean =  $33.0 \pm$   
312  $24.1\%$ ), and elevated GOM concentrations (mean =  $52 \pm 29 \text{ pg m}^{-3}$ ). Also, a significant positive  
313 correlation between PBM and GOM concentrations was observed for some of these events  
314 (supplementary Table S1). Therefore, these events were not likely related to direct anthropogenic  
315 pollution. The air masses related to these 8 PBM events mainly originated from the middle free  
316 troposphere over the North Atlantic Ocean (Supplementary Figure S4). We therefore suggest that  
317 gas-particle partitioning of GOM in the middle free troposphere over the North Atlantic Ocean and  
318 during long-range transport followed by mixing with European boundary layer air prior to ending  
319 at PDM Observatory were the major cause for these 8 high PBM events.

320 Figure 3 shows two typical PBM events (PBM events #12 and #19 in supplementary Table  
321 S1) with PBM and GEM anti-correlated. During the PBM event #12 (from 19 to 21 February 2012,  
322 Figure 3A), the maximum PBM concentration reached up to  $85 \text{ pg m}^{-3}$ , which was accompanied



323 by low GEM ( $1.47 \text{ ng m}^{-3}$ ), low GOM ( $25 \text{ pg m}^{-3}$ ), low atmospheric aerosol number  
324 concentrations ( $150 \text{ nbp cm}^{-3}$ , Supplementary Table S1), and low relative humidity (6%) but  
325 elevated CO concentration (128 ppb). The maximum PBM concentration during PBM event #19  
326 was  $40 \text{ pg m}^{-3}$  (Figure 3B), which is lower than that of PBM event #12. PBM event #19 showed  
327 elevated GOM concentrations (up to  $131 \text{ pg m}^{-3}$ ), higher atmospheric aerosol number  
328 concentration (up to  $1609 \text{ nbp cm}^{-3}$ , Supplementary Table S1) but relatively lower CO  
329 concentrations (111 ppb) (Supplementary Table S1). Hysplit and Flexpart back trajectory analysis  
330 shows that the air masses related to the PBM event #12 mainly originated from North America and  
331 passed over high-latitude areas in the upper free troposphere prior to ending at the PDM  
332 Observatory (Figure 4). PBM event #19 originated mostly from middle and upper free troposphere  
333 over the Eastern North Atlantic Ocean and passed over West Europe in the middle and lower free  
334 troposphere before ending at PDM Observatory (Figure 4). We find good agreement between  
335 Hysplit and Flexpart in terms of air mass geographical origin and altitude over 10 days.

336 Gas-particle partitioning of GOM and heterogeneous oxidation of GEM at aerosols surfaces  
337 were suggested to be two important pathways for the formation of PBM in the atmosphere  
338 (Lindberg et al., 2002; Amos et al., 2012; Subir et al., 2012). For PBM event #12, direct intrusion  
339 of PBM-enriched air from the upper free troposphere likely played a dominant role. PBM event  
340 #19 was likely related to gas-particle partitioning of GOM generated in the middle and upper free  
341 troposphere over the North Atlantic Ocean during the transport over Western Europe. The  
342 mechanisms and kinetics related to production of PBM are currently not well known. In the  
343 present study, we find that PBM concentrations and PBM/GOM ratios during all the events were  
344 both significantly anti-correlated with the atmospheric aerosol number concentrations ( $p < 0.05$ ,  
345 Supplementary Table S2). This result indicates that concentrations of atmospheric aerosols may  
346 not play a dominant role in the formation of PBM in the middle and upper free troposphere and/or  
347 during the transport to the PDM Observatory, although atmospheric aerosol number  
348 concentrations observed at PDM Observatory might be partially related to anthropogenic sources  
349 in the boundary layer and not representative of that in the middle and upper free troposphere. On  
350 the other hand, both PBM concentrations and PBM/GOM ratios during the high PBM events were  
351 significantly anti-correlated with simulated mean temperature of air masses ending at the PDM  
352 Observatory ( $p < 0.05$  for both, Supplementary Table S2). Also, PBM/GOM ratios were found to be  
353 significantly anti-correlated with simulated mean solar radiation flux ( $p < 0.05$ , Supplementary  
354 Table S2). These results agree with previous studies which suggested that cold temperature and  
355 lower winter time solar radiation enhance gas-particle partitioning of GOM and minimize the  
356 decomposition of PBM by photoreduction, respectively, which in turn facilitates the accumulation  
357 of PBM in the middle and upper free troposphere (Lindberg et al., 2002; Sprovieri et al.,



2005;Rutter and Schauer, 2007;Amos et al., 2012). Previous studies also suggested that aerosol uptake of atmospheric oxidants and atmospheric GEM oxidation rates may be enhanced at cold temperature(Carlaw et al., 1997;Michelsen et al., 1999;Lindberg et al., 2007), which in turn facilitates the production of PBM via heterogeneous GEM oxidation and gas-particle partitioning of GOM.

### 3.3 High GOM events

High GOM events were identified as the concentrations higher the 95<sup>th</sup> percentile GOM level (93 pg m<sup>-3</sup>) (Supplementary Table S3). For the 61 high GOM events observed, 50 events were observed with a significant anti-correlation between GOM and GEM concentrations. Also, the remaining 11 high GOM events were not likely related to direct anthropogenic pollution because GEM, CO, and atmospheric aerosol number concentrations were not elevated and no positive correlations are observed between these parameters and GOM concentrations. We therefore conclude that the high GOM events at PDM Observatory were primarily related to in situ oxidation of GEM, which is consistent with previous studies at high-altitude sites (Sheu et al., 2010;Swartzendruber et al., 2006;Fain et al., 2009).

In general, ozone, hydroxyl radical (OH·), nitrate radical (e.g. NO, NO<sub>y</sub>), and reactive halogens (e.g. Br·, BrO, IO) are considered as potential oxidants involved in the conversion of GEM to GOM in the atmosphere (Lin and Pehkonen, 1999;Goodsite et al., 2004). However, the kinetics and relative contributions of these oxidants in the production of atmospheric GOM are not well understood. In the present study, we observed that GOM and ozone concentrations were positively correlated during 24 high GOM events (Supplementary Table S3). Meanwhile, hourly mean ozone concentrations associated with GOM peaks during the 24 high GOM events ranged from 41.4 to 98.5 ppb with an average value of 62.5 ppb, and were relatively higher than the annual mean of 49.4 ppb. The most pronounced example was observed in 16 May, 2012 (GOM Event #7, Figure 5). Clear positive correlations between GOM and ozone concentrations were also reported at MBO station, USA (Swartzendruber et al., 2006;Timonen et al., 2013), but elevated ozone concentrations as high as 105 ppb (5-min mean) during high GOM events #7 were not observed in any previous observations at high-altitude sites. The highly elevated ozone concentrations as well as low CO concentrations and relatively humidity demonstrate that event #7 was mainly related to intrusions from the upper free troposphere. This assessment was further supported by the backward trajectory analysis which shows the major origins of air masses from the upper free troposphere over the Arctic region and North America (Figure 6). At the night during event #7 when an upper tropospheric intrusion dominated, ozone concentrations were significantly anti-correlated with GEM ( $GEM = -9.3 \text{ pg m}^{-3}/\text{ppb} \times O_3 \text{ ppb} + 2190 \text{ pg m}^{-3}$ ,  $R^2 =$



393 0.72  $p < 0.01$ ) and positively correlated with GOM concentrations ( $\text{GOM} = 2.69 \text{ pg m}^{-3}/\text{ppb} \times \text{O}_3$   
394  $\text{ppb} - 113 \text{ pg m}^{-3}$ ,  $R^2 = 0.96$ ,  $p < 0.01$ ). The correlations indicated a total depletion of GEM in the  
395 upper free troposphere when ozone exceeds 235 ppb, and corresponding GOM concentrations up  
396 to approximately  $520 \text{ pg m}^{-3}$ . This finding is in agreement with aircraft observations of GEM and  
397 GOM+PBM fractions in the upper free troposphere and tropopause (Talbot et al., 2007; Lyman and  
398 Jaffe, 2012).

399 For the 24 high GOM events positively correlated with ozone, many air masses (10 out of the  
400 24 high GOM events) originated from the upper troposphere over the Arctic region and the  
401 remainder from the middle troposphere over the North Atlantic Ocean (Supplementary Figure S5).  
402 This implies that the frequent southward intrusion of upper tropospheric air from the Arctic region  
403 may be an important source of high GOM levels at PDM Observatory and mid-latitudes. In  
404 general, atmospheric ozone levels exhibit a clear vertical profile with concentrations increasing  
405 with altitude (Browell et al., 2003; Chevalier et al., 2007), and this may explain well the observed  
406 positive correlation between GOM and ozone concentrations. However, this by no means  
407 demonstrates that ozone is the exclusive oxidant during these events. In fact, nitrate radical (e.g.  
408  $\text{NO}$ ,  $\text{NO}_y$ ) levels were found to be tightly correlated with ozone in the upper free troposphere (Gao  
409 et al., 2014; Kohler et al., 2013; Slemr et al., 2009). The vertical profiles of hydroxyl radical and  
410 reactive halogens are not well established (Brune et al., 1998). However, elevated  $\text{BrO}$  and  
411  $\text{OH}$  levels were reported in the middle and upper free troposphere by previous studies (Brune et  
412 al., 1998; Fittenberger et al., 2000). Therefore, these oxidants could also contribute to the  
413 oxidation of GEM in the middle and upper free troposphere.

414 Nine of the high GOM events showed anti-correlations between GOM and ozone  
415 concentrations (Supplementary Table S3), which are in contrast with GOM events influenced by  
416 the middle and upper tropospheric air. Back trajectory analysis suggests that these events were  
417 influenced by air masses originated from and/or passed over the North Atlantic in the lower free  
418 troposphere (Supplementary Figure S6). This type of events was similar as that observed in the  
419 Pacific Ocean MBL (Timonen et al., 2013; Laurier et al., 2003), indicating a decrease in ozone  
420 concentration is a general feature of GOM production in lower free troposphere over oceans and  
421 MBL. It is possible that reactive halogen and hydroxyl radicals were involved in this type of GOM  
422 events, the formation of which in the MBL over oceans were thought to deplete atmospheric  
423 ozone (Bloss et al., 2003; Obrist et al., 2011; Read et al., 2008).

424 High GOM events were also reported to be related to oxidation of GEM in MBL over the  
425 Arctic region during Polar spring and Pacific Ocean during warm seasons (Steffen et al.,  
426 2008; Timonen et al., 2013). For the high GOM events in the present study, we did not observe  
427 clear evidence for the sources of GOM from the MBL over the Arctic region or the North Atlantic



428 Ocean. Therefore, the oxidation of GEM in the free troposphere was likely the predominant source  
429 of high GOM at PDM Observatory. The remaining 28 high GOM events (Supplementary Table  
430 S3), with GOM poorly correlated with ozone and GEM concentrations, probably reflect the  
431 combined effect of intrusions of GOM-enriched air from middle and upper free troposphere, lower  
432 free troposphere over the Atlantic Ocean and mixing of boundary layer air over Europe during  
433 long-range transport.

434

### 435 **3.4 Seasonal trends of high PBM and GOM events**

436 The high PBM events were predominantly observed in winter and spring (from November to  
437 April, Figure 7), which accounted for approximately 80% of the total high PBM events. In  
438 contrast, high GOM events were predominantly (~69%) observed in the summer and autumn  
439 (from May to October). The monthly variations in the frequencies of high PBM and GOM events  
440 were consistent with the monthly means of PBM and GOM concentrations, respectively. This is  
441 the first observation suggesting that high PBM and GOM events in the free troposphere in the  
442 middle latitude display distinct seasonal patterns (t test:  $p < 0.05$ ).

443 ARTs related to the high PBM events in spring and winter showed maximum values in the  
444 upper free troposphere over North America (accounting for 35% of total high PBM ARTs),  
445 followed by the middle free troposphere over the North Atlantic Ocean (29%), the upper free  
446 troposphere over the Arctic region (22%) and the middle free troposphere over the Europe (13%)  
447 (Figure 8). The maximum high PBM ARTs over North America in spring and winter were partly  
448 attributed to increasing origins of air masses from this region under the influence of westerlies in  
449 the mid-latitude (Figure 9). Additionally, the ratios of high PBM ARTs to total ARTs over North  
450 America were also elevated in winter and spring compared to summer and spring. It is noteworthy  
451 that the ratios of high PBM ARTs to total ARTs in winter and spring were significantly higher (t  
452 test,  $p < 0.05$ ) than that in summer and autumn over all the studied regions (Figure 9). This result  
453 may imply that the middle and upper free troposphere of the Northern Hemisphere may be more  
454 enriched in PBM in spring and winter than in summer and autumn. This conclusion is consistent  
455 with the modeling result at low-altitude sites in North America which was likely due to cold  
456 season subsidence of PBM enriched air from the upper troposphere and lower stratosphere (Amos  
457 et al., 2012). There are currently no observations regarding the seasonal trends of atmospheric  
458 PBM in the middle and upper free troposphere of the Northern Hemisphere. In spring and winter  
459 increasing PBM concentrations the middle and upper free troposphere of the Northern Hemisphere  
460 are apparently in contrast with the lower atmospheric aerosol concentrations observed at PDM  
461 Observatory as well as other high altitudes in Europe and North America (Browell et al.,  
462 2003; Asmi et al., 2011). We therefore proposed that other factors other than atmospheric aerosols



463 played a more important role in the seasonal variations of high PBM events at PDM. As we  
464 discussed earlier, cold temperature and lower solar radiation may favor the production and  
465 accumulation of PBM in the free troposphere. Northern Hemisphere high-latitudes are  
466 characterized by relatively lower air temperature and solar radiation during the cold season, which  
467 may facilitate the production and accumulation of PBM in the middle and upper troposphere in  
468 cold season and explain our seasonal variations in atmospheric PBM concentrations. In summer  
469 the highest residence times were observed in the lower and middle free troposphere over the North  
470 Atlantic Ocean (accounting for 72% of total residence times). The lower and middle free  
471 troposphere over the North Atlantic Ocean in summer produced many high GOM events (more  
472 details below), which are responsible for the highest ARTs associated with high PBM events in  
473 this region via gas-particle partitioning of atmospheric GOM.

474 ARTs related to the high GOM events showed maximum values over the North Atlantic  
475 Ocean regardless of seasons (accounting for 62-84% of total residence times). High GOM ARTs  
476 over the North Atlantic Ocean mainly correspond to the lower and middle free troposphere (Figure  
477 10). In summer when most of high GOM events were observed, high GOM ARTs showed  
478 maximum values in the lower free troposphere over the subtropical North Atlantic Ocean.  
479 Maximum high GOM ARTs were mainly observed in the middle free troposphere over the  
480 temperate and sub-arctic North Atlantic Ocean in spring and autumn (Figure 10 and 11). The  
481 maximum high GOM ARTs over the subtropical North Atlantic Ocean in summer were partially  
482 attributed to frequent origins of air masses from this region (Figure 11). Also, it is found that the  
483 ratios of high GOM ARTs to total ARTs over the subtropical North Atlantic Ocean in summer  
484 were up to an order of magnitude higher than that in other seasons over the temperate and  
485 sub-arctic North Atlantic Ocean in summer. These results imply that the lower free troposphere  
486 over the subtropical North Atlantic Ocean may be of specific significance for the production of  
487 GOM in summer. For other seasons, the maximum high GOM ARTs over the temperate and  
488 sub-arctic North Atlantic Ocean were related to frequent intrusions of air masses from the middle  
489 and upper free troposphere (Figure 10 and 11).

490 The summer maximum high GOM events are also similar to observations at the Dead Sea,  
491 Israel (Moore et al., 2013), which were associated with elevated BrO concentrations in the MBL.  
492 Many recent studies also suggested that other oxidants such as hydroxyl radical ( $\text{OH}\cdot$ ), iodine  
493 oxides (IO), chlorine atoms (Cl $\cdot$ ), ozone, nitrogen oxides (e.g.  $\text{NO}_2$ ) should be also involved in the  
494 production of GOM in the atmosphere (Dibble et al., 2012; Wang et al., 2014; Weiss-Penzias et al.,  
495 2015). Previous studies observed that  $\text{OH}\cdot$ , IO and  $\text{NO}_2$  concentrations in the MBL and lower free  
496 troposphere over the subtropical and tropical North Atlantic Ocean are highest in summer  
497 (Spivakovsky et al., 2000; Savage et al., 2004; Wang et al., 2014; Martin et al., 2008), which may





498 explain the maximum summer high GOM ARTs in the lower free troposphere over the subtropical  
499 North Atlantic Ocean. On the other hand, atmospheric oxidants in the middle and upper free  
500 troposphere also display clear seasonal cycles. For instance, Fitzenberger et al.(2000) observed  
501 that BrO concentrations in the middle and upper free troposphere over the Arctic region were  
502 relatively higher in summer than in winter. Additionally, previous studies also suggested that  
503 tropospheric column ozone and OH· concentrations in the Northern Hemisphere are highest in  
504 summer (Spivakovsky et al., 2000;Liu et al., 2006).These oxidants may favor the in situ  
505 production of GOM in the middle and upper free troposphere in summer.  
506

### 507 **3.5 Potential source regions of PBM and GOM in different layers of troposphere**

508 The major potential source regions of PBM at PDM Observatory were located over the  
509 temperate and sub-arctic North Atlantic Ocean and over Northwest Europe, whereas the major  
510 potential source regions of GOM at PDM Observatory were located in the subtropical North  
511 Atlantic Ocean (Figure 12). The PSCF analysis regarding the different atmospheric layers suggests  
512 that major source regions of PBM and GOM were both from the middle and upper free  
513 troposphere over the temperate and sub-arctic North Atlantic Ocean, Arctic region, North America,  
514 and Northwest Europe, which were followed by the lower free troposphere over the subtropical  
515 North Atlantic Ocean. On the other hand, the boundary layer over the Atlantic Ocean, Europe, and  
516 North America played a minimal role in the sources of PBM and GOM at PDM Observatory. It  
517 should be pointed out that, owing to the trailing effect (areas upwind and downwind of actual  
518 source regions are likely identified as possible source regions), some of the identified source  
519 regions of PBM and GOM might be overestimated. As we discussed earlier, many high PBM and  
520 GOM events were related to air masses that originated from or traveled in the upper free  
521 troposphere over the Arctic region and sub-arctic North America. The transport of these air masses  
522 frequently took a southward route (Stohl et al., 2000), which may overestimate the contributions  
523 of source regions over the temperate and sub-arctic North Atlantic Ocean and Northwest Europe.  
524

## 525 **4 Conclusions**

526 In the present study, we consider one full year of atmospheric Hg speciation observations at  
527 the high-altitude Pic du Midi (PDM) Observatory, located in the middle latitudes. Unlike previous  
528 studies at other high-altitude sites (mainly conducted in warm seasons or in the tropics), we  
529 observed multiple high PBM events (up to 98 pg m<sup>-3</sup>) in addition to multiple high GOM events  
530 (up to 295 pg m<sup>-3</sup>), which were mainly related to in situ atmospheric transformations. The seasonal  
531 variations in the occurrence of high PBM and GOM events were significantly different with most  
532 of the high PBM and GOM events occurring in cold seasons (winter and spring) and warm



533 seasons (summer and autumn), respectively. Our study suggests that an important fraction of  
534 depleted GEM is in the form of PBM in the middle and upper troposphere in cold seasons. These  
535 findings should be taken into account by modeling approaches to better understand the fate of Hg  
536 in the global atmosphere. Furthermore, our results suggest that the sources of high PBM and GOM  
537 events were also different. High PBM events in cold seasons were mainly related to intrusions  
538 from the upper troposphere over temperate and sub-arctic North American and Arctic regions as  
539 well as the middle troposphere over the temperate North Atlantic Ocean and Europe. On the other  
540 hand, high GOM events were attributed to in situ production in the middle and lower free  
541 troposphere over the subtropical North Atlantic Ocean. These seasonal and regional patterns may  
542 be caused by a combination of factors including variations of atmospheric oxidants and  
543 meteorological parameters (e.g. temperature and solar radiation). As GOM and PBM are readily  
544 deposited to Earth's surfaces, the frequent export of PBM- and GOM-enriched air from North  
545 America, the Arctic region and the North Atlantic Ocean are expected to enhance wet and dry  
546 deposition and cause environmental risk of mercury in European ecosystems. This should be  
547 further evaluated using modeling approaches.

548

#### 549 **Supplementary material:**

550 Tables of the identified 44 high PBM events, 61 high GOM events and Pearson's correlation  
551 analysis between PBM and meteorological parameters and atmospheric pollutants are shown in  
552 Tables S1-S3.

553 Time series of atmospheric Hg speciation, backward trajectories of the 30 high PBM events  
554 related to upper tropospheric intrusions, backward trajectories of the 6 anthropogenic impacted  
555 high PBM events, backward trajectories of the 8 mixed high PBM events, backward trajectories of  
556 the 24 high GOM events related to intrusions from middle and upper troposphere, backward  
557 trajectories of the 9 high GOM events related to marine free tropospheric air are shown in Figure  
558 S1-S6.

559

560

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566

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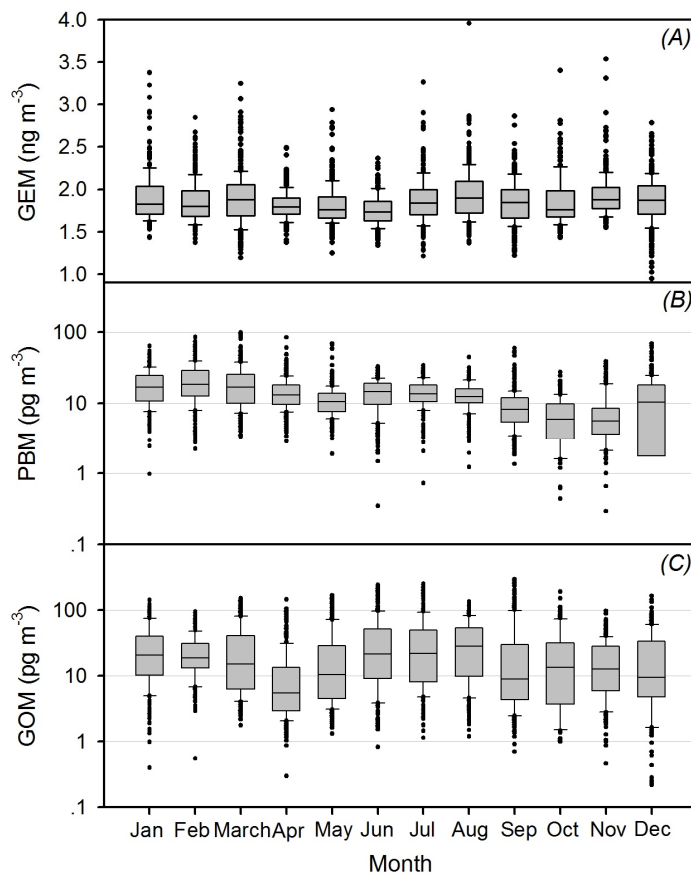
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822 Figure 1. Monthly variation of atmospheric GEM (A), PBM (B), and GOM (C) at PDM  
823 Observatory. Box lines indicate the 10<sup>th</sup>, 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup>, 90<sup>th</sup> percentiles, and data points  
824 indicate concentrations below 10<sup>th</sup> and above 90<sup>th</sup> percentiles.

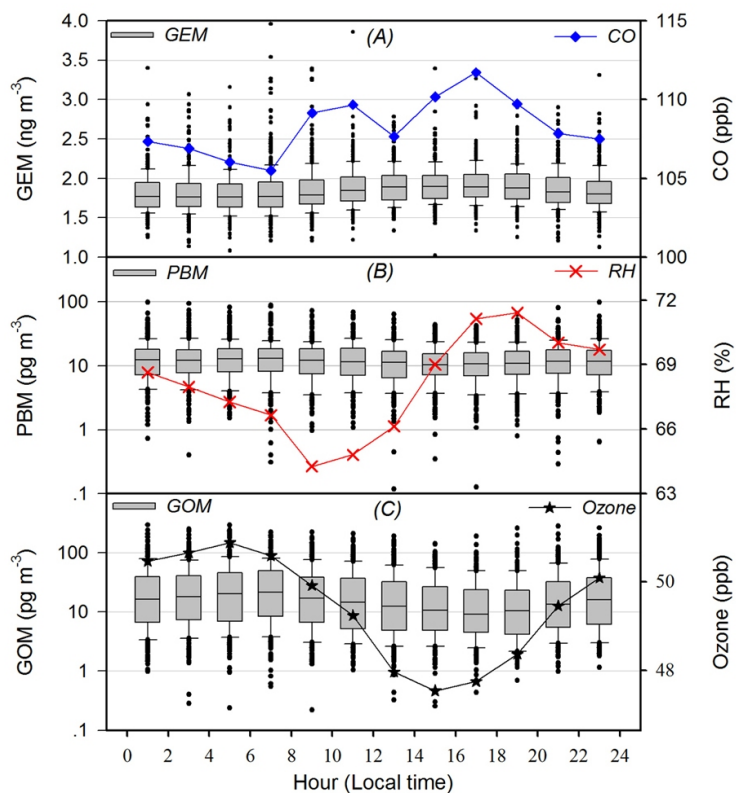


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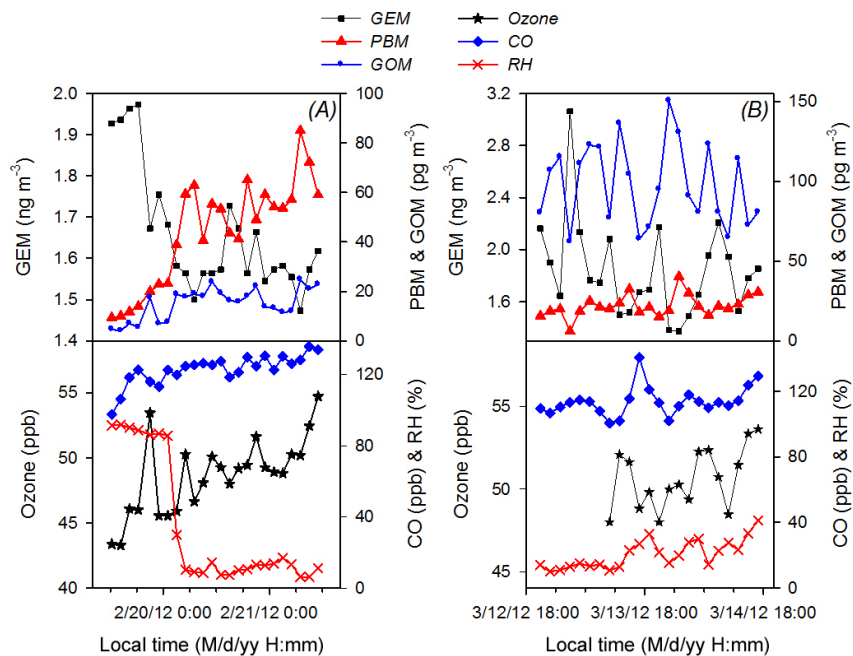
827 Figure 2. Diel, two-hour averaged, variations of atmospheric GEM and CO (A); PBM and relative  
828 humidity (RH) (B); and GOM and ozone (C) at PDM Observatory. Box lines indicate the 10<sup>th</sup>,  
829 25<sup>th</sup>, 50<sup>th</sup>, 75<sup>th</sup>, 90<sup>th</sup> percentiles, and data points indicate concentrations below 10<sup>th</sup> and above  
830 90<sup>th</sup> percentiles.



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833 Figure 3. Time series of GEM, PBM, GOM, ozone, CO, and relative humidity (RH) during high  
834 PBM event #12 (A) and #19 (B).  
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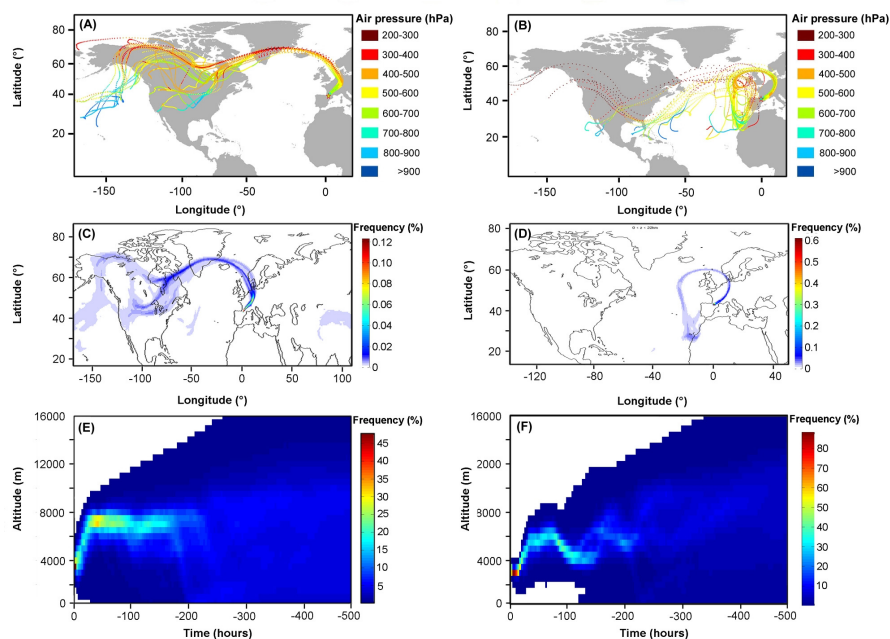


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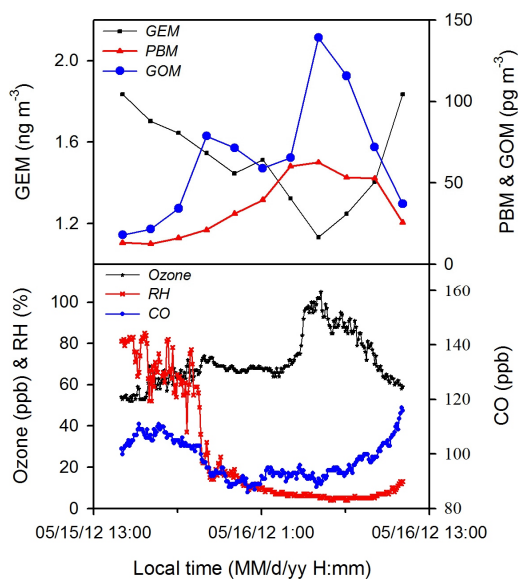
838 Figure 4. 240-h Hysplit air mass backward trajectories for the typical high PBM events #12 (A)  
839 and #19 (B), Flexpart simulated air mass source regions of high PBM events #12 (C) and #19  
840 (D) and Flexpart simulated air mass travelling heights of PBM events #12 (E) and #19 (F). To  
841 reduce the uncertainty related to Hysplit trajectory simulations (Gustin et al., 2012), Hysplit  
842 trajectories were calculated for each of the events ended at 27 locations evenly-distributed in  
843 a  $0.5^{\circ} \times 0.5^{\circ}$  grid cell and at a height of -500 m, 0 m, and 500 m around the PDM Observatory.



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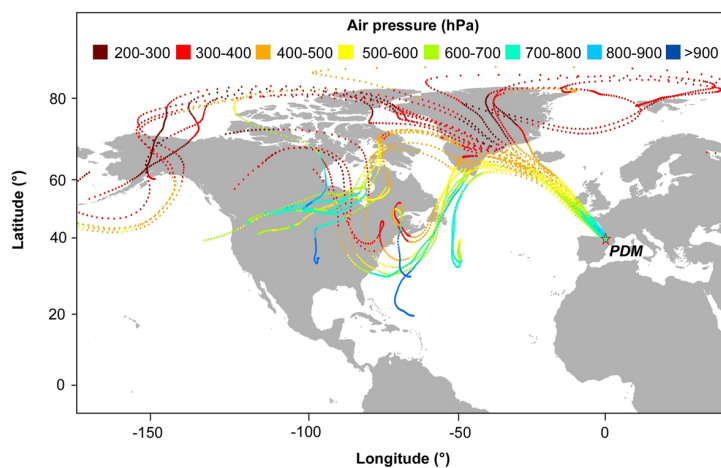
846 Figure 5. Time series of GEM, PBM, GOM, ozone, CO, and relative humidity (RH) during high  
847 GOM event #7.



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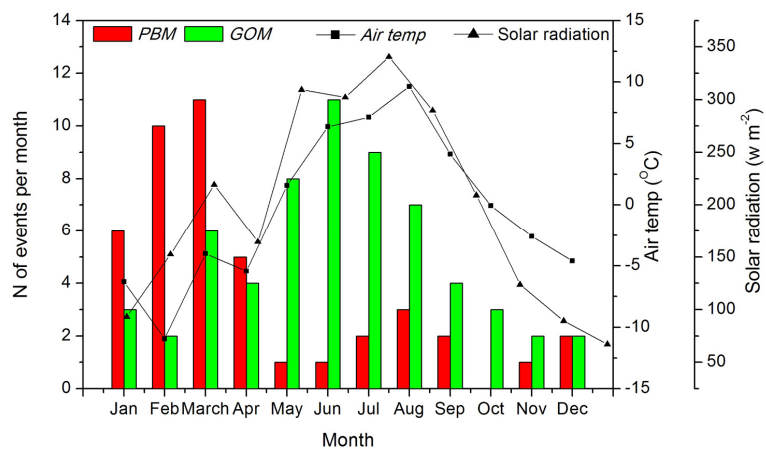
852 Figure 6. 168-h Hysplit air mass backward trajectories for the typical high GOM event #7. To  
853 reduce the uncertainty related to trajectory simulations (Gustin et al., 2012), trajectories were  
854 calculated for 27 locations evenly-distributed in a  $0.5^\circ \times 0.5^\circ$  grid cell and at a height of -500  
855 m, 0 m, and 500 m around the PDM Observatory.



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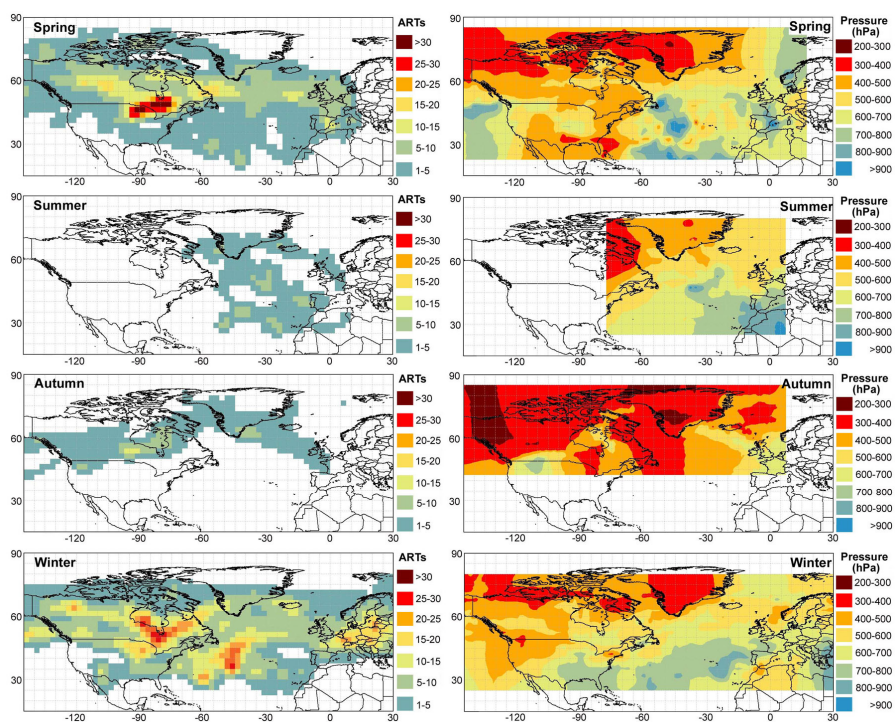
860 Figure 7. Monthly variations in the frequency of high PBM and GOM events at PDM  
861 Observatory.



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867 Figure 8. Air mass residence times (ARTs) and averaged pressure of air masses associated with  
868 high PBM events for each season during the study period.

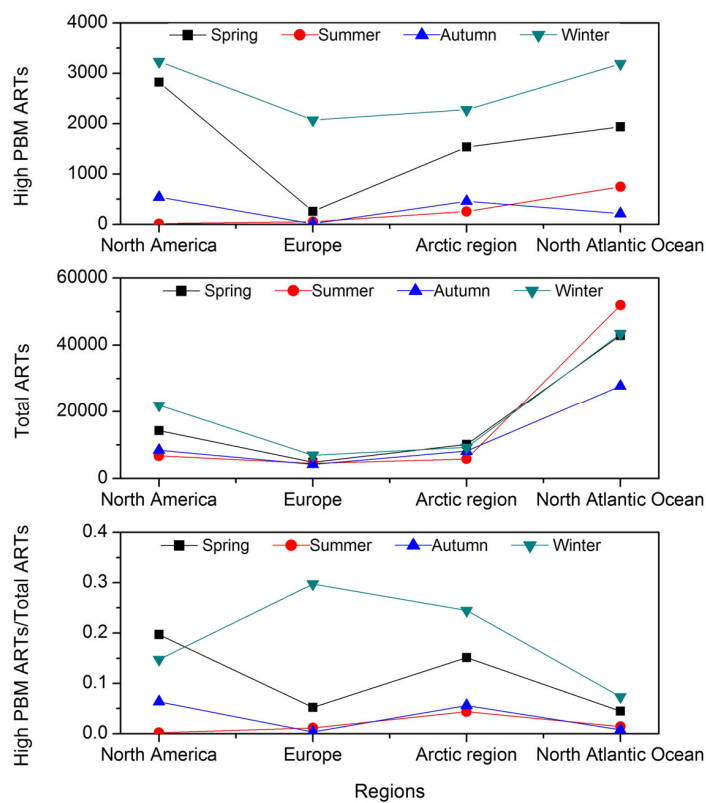


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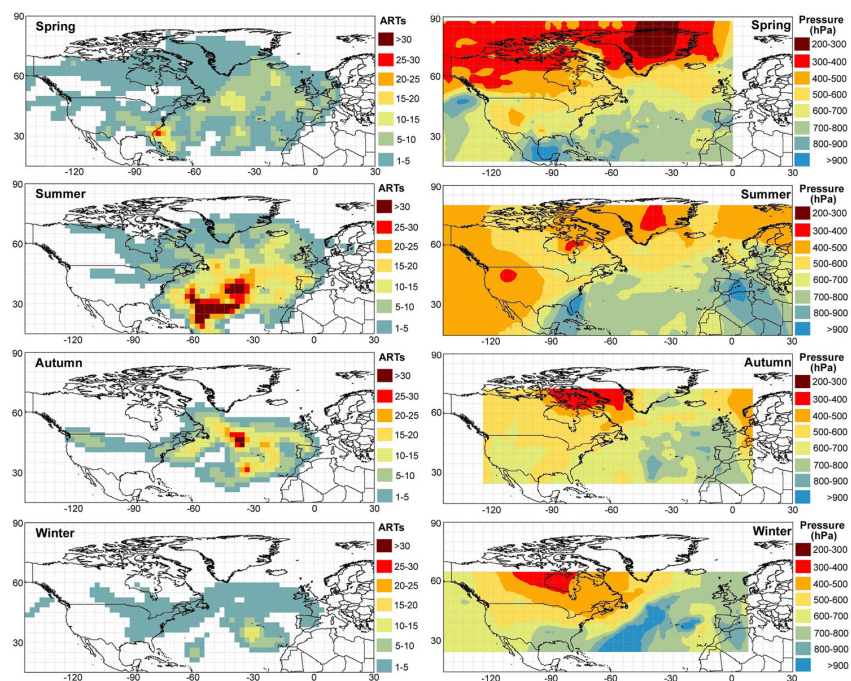
872 Figure 9. Seasonal variations in air masses residence times associated with high PBM events (high  
 873 PBM ARTs, top), total residence times of all the air masses (Total ARTs, middle) and high  
 874 PBM ARTs/Total ARTs ratios (bottom) in the North America, Europe, Arctic region and  
 875 North Atlantic Ocean.



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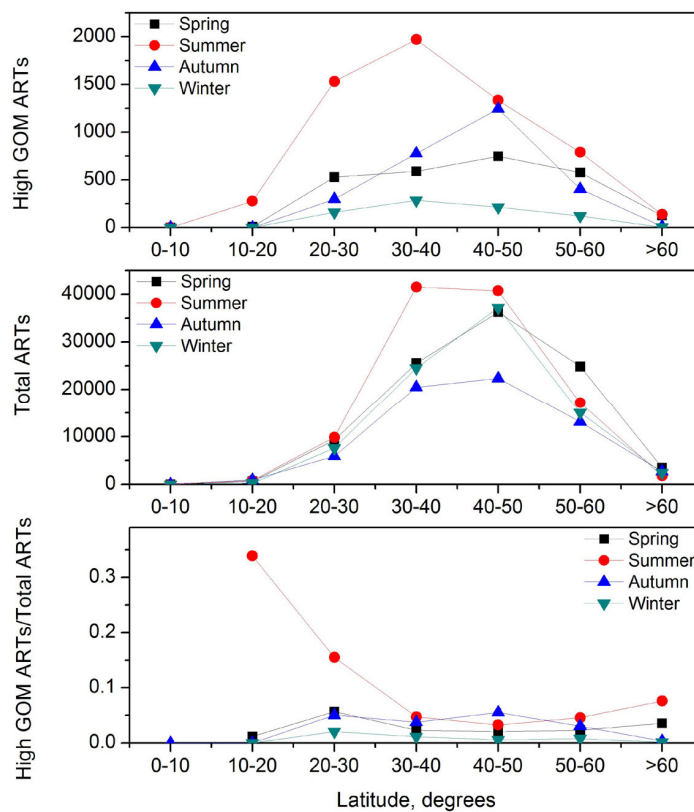
892 Figure 10. Air mass residence times (ARTs) and averaged pressure of air masses associated with  
893 high GOM events for each season during the study period.



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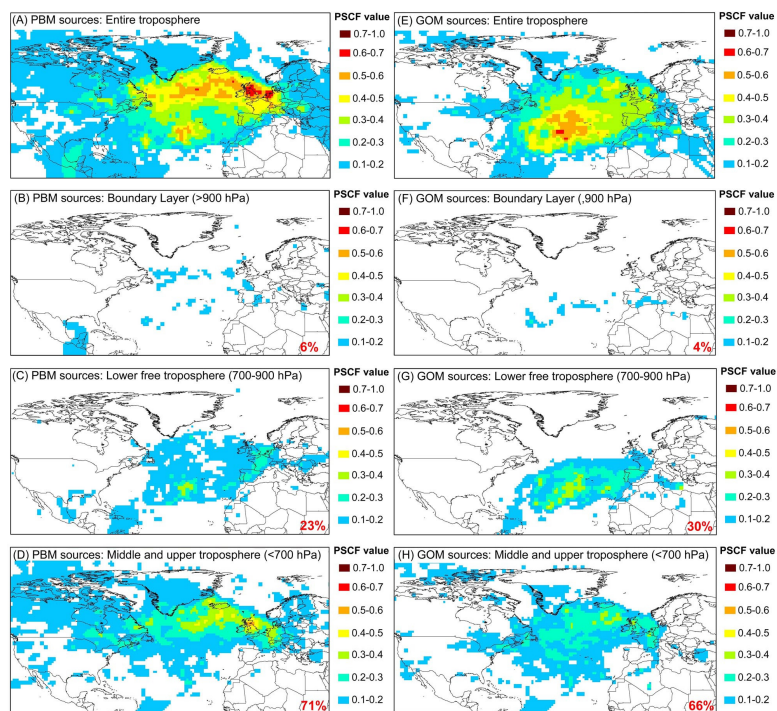
898 Figure 11. Latitude dependence of Air masses residence times (ARTs, top) associated with high  
899 GOM events, total residence times of all the air masses (Total ARTs, middle) and high GOM  
900 ARTs/Total ARTs ratios (bottom) over the North Atlantic Ocean for each season.



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905 Figure 12. Map showing the identified potential source regions of PBM during the whole study  
906 period for (A) entire troposphere, (B) boundary layer, (C) lower free troposphere, and (D)  
907 middle and upper troposphere and potential source regions of GOM for (E) entire troposphere,  
908 (F) boundary layer, (G) lower free troposphere, and (G) middle and upper  
909 troposphere.



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