



- 1 Recent decrease trend of atmospheric mercury concentrations in East China: the
- 2 influence of anthropogenic emissions
- 3 Yi Tang^{1, 2}, Shuxiao Wang^{1, 2*}, Qingru Wu^{1, 2*}, Kaiyun Liu^{1, 2}, Long Wang³, Shu Li¹, Wei Gao⁴, Lei
- 4 Zhang⁵, Haotian Zheng^{1, 2}, Zhijian Li¹, Jiming Hao^{1, 2}
- 5
- 6 ¹ State Key Joint Laboratory of Environmental Simulation and Pollution Control, School of
- 7 Environment, Tsinghua University, Beijing 100084, China
- 8 2 State Environmental Protection Key Laboratory of Sources and Control of Air Pollution Complex,
- 9 Beijing 100084, China
- 10 3 School of Environment and Energy, South China University of Technology, Guangzhou, 510006,
- 11 China
- 12 4 Yangtze River Delta Center for Environmental Meteorology Prediction and Warning, Shanghai,
- 13 20030, China
- 14 5 State Key Laboratory of Pollution Control & Resource Reuse, School of the Environment, Nanjing
- 15 University, Nanjing, 210023, China
- 16
- 17
- 18 * Correspondence to: Shuxiao Wang (shxwang@tsinghua.edu.cn)
- 19 Qingru Wu (wuqingru06@163.com)
- 20

21 Abstract

- Measurements of gaseous elemental Hg (GEM), other air pollutants including SO₂, NO_X, O₃, PM_{2.5}, CO, and meteorological conditions were carried out at Chongming Island in East China from March 1 in 2014 to December 31 in 2016. During the sampling period, GEM concentrations significantly decreased from 2.68±1.07 ng m⁻³ in 2014 to 1.60±0.56 ng m⁻³ in 2016. Monthly mean
- 26 GEM concentrations showed a significant decrease with a rate of -0.60 ng m⁻³ yr⁻¹ (R^2 =0.6389,
- 27 p<0.01 significance level). Combining the analysis of potential source contribution function (PSCF),
- 28 principle component analysis (PCA), and emission inventory, we found that Yangtze River Delta
- 29 (YRD) region was the dominant source region of atmospheric mercury in Chongming Island and





- 30 the main source industries included coal-fired power plants, coal-fired industrial boilers, and cement
- 31 clinker production. We further quantified the effect of emission change on the air Hg concentration
- 32 variations at Chongming Island through a coupled method of trajectory clusters and air Hg
- 33 concentrations. It was find that the reduction of domestic emissions was the main driver of GEM
- 34 decline in Chongming Island, accounting for 66% of the total decline. The results indicated that air
- 35 pollution control policies targeting SO₂, NO_x and particulate matter reductions had significant co-
- 36 benefits on atmospheric mercury.





37 **1 Introduction**

Mercury (Hg) is of crucial concern to public health and the global environment for its neurotoxicity, long-distance transport, and bioaccumulation. The atmosphere is an important channel for global mercury transport. Once atmospheric Hg deposits to the aquatic system, it can be transformed into methylmercury (MeHg) which bio-accumulates through the food web and affects the central nervous system of human beings (Mason et al., 1995). Hg is therefore on the priority list of several international agreements and conventions dealing with environmental protection, including the *Minamata Convention on Mercury*.

45 Atmospheric Hg exists in three operationally defined forms: gaseous elemental mercury (GEM), gaseous oxidized mercury (GOM), and particulate-bound mercury (PBM). And the sum of GEM 46 47 and GOM is known as total gaseous mercury (TGM). In the atmosphere, Hg mainly presents as 48 GEM, accounting for over 95% of the total. GEM is stable in the troposphere with a long residence 49 time (0.5 - 2 years) and can be transported at regional and global scale (Lindberg et al., 2007). GEM 50 can be oxidized through photochemical reaction to GOM, which can be converted to PBM upon 51 adsorption/absorption on aerosol surfaces. Both GOM and PBM are more soluble and quickly 52 scavenged through dry and wet deposition (Schroeder and Munthe, 1998).

53 The atmospheric Hg observation results are important evidences to assess the effect of Hg 54 emission control. During the past decades, significant decreases of GEM concentrations in Europe 55 and North America have been observed (Cole et al., 2013; Weigelt et al., 2015). Air Hg 56 concentrations in the northern hemisphere are reported to decline by 30-40% between 1990 and 57 2010 (Zhang Y et al., 2016). Such a decrease is consistent with the decrease in anthropogenic Hg 58 emissions inventory in Europe and North America (Streets et al., 2011). So far, most of the longterm observations on the ground sites have been carried out in the developed countries. For the 59 developing countries such as China, limited atmospheric Hg observations have been carried out (Fu 60 et al., 2008b; Zhang H et al., 2016; Hong et al., 2016) and there is no official national monitoring 61 62 network of atmospheric Hg. Therefore, there are few continuous multi-year observation records of 63 China's air Hg published (Fu et al., 2015).

64 China is the largest emitter of atmospheric Hg in the world. Atmospheric Hg emissions in China





65 accounted for 27% of the global total in 2010 (UNEP, 2013), which led to high air Hg concentrations 66 in China. Therefore, atmospheric Hg observations in China are critical to understand the Hg cycling at both regional and global scale. China's Mercury emissions had increased from 147 t yr⁻¹ in 1978 67 to around 538 t yr⁻¹ in 2010 due to the dramatic economic development (Zhang L et al., 2015; Wu 68 69 et al., 2016; Hui et al., 2017). Atmospheric mercury monitoring that spanned the longest periods 70 (from 2002 to 2010) in Guiyang, southwestern China witnessed the increase of mercury emissions 71 in China (Fu et al., 2011). However, recently atmospheric Hg emissions in China have been 72 estimated decreasing since 2012 (Wu et al., 2016). This decreasing trend needs to be confirmed by 73 atmospheric Hg observations. 74 In this study, we measured GEM, other air pollutants (eg., PM2.5 and NOx), and meteorological 75 parameters (eg., temperature and wind speed) at a remote marine site of Chongming Island in East 76 China during 2014-2016. We analyzed annual and seasonal variation of GEM and the potential

impact factors. Combining the analysis of potential source contribution function (PSCF), principle component analysis (PCA), and emission inventory, the potential source regions and source industries of atmospheric Hg pollution at the monitoring site are identified. In addition, a coupled trajectories and air Hg concentration method is developed to assess the effect of Hg emission change from different regions on air GEM concentration variation at the monitoring site.

82 2 Materials and methods

83 2.1 Site descriptions

84 The monitoring remote site (31°32'13"N, 121°58'04"E, about 10 m above sea level) locates at the 85 top of weather station in Dongtan Birds National Natural Reserve, Chongming Island, China (Figure 1). As China's third largest island, Chongming Island locates in the east of Yangtze River Delta 86 87 region with a typical subtropical monsoon climate. It is rainy, hot, with southern and southeastern 88 winds in summer and is dry, cold, and with northwestern wind in winter. The dominant surface types 89 are farmland and wetland. There are no large anthropogenic emission sources in the island and no 90 habitants within 5 km distance from the site. The downtown Shanghai area is 50 km to the southwest 91 of the site.





92 **2.2 Sampling methods and analysis**

During the monitoring period, we used TekranTM 2537X/1130/1135 instruments to monitor 93 speciated Hg in the atmosphere, which was widely used for air Hg observation in the world. 94 Continuous 5-minute of GEM was measured by TekranTM 2537X Hg vapor analyzer with the 95 detection limit of 0.1 ng m⁻³ at a sampling flow rate of 1.0 L min⁻¹ during two campaigns: March 96 1, 2014 to December 31, 2015 and March 26 to December 31, 2016. The sampling inlet was 1.5 m 97 98 above the instrument platform. 99 The 2537X analyzer was calibrated automatically every 25 h using the internal Hg permeation 100 source inside the instrument, and the internal permeation source was calibrated every 12 months 101 with manual injection of Hg by a syringe from an external Hg source (module 2505). Two zero and 102 two span calibrations were performed for each calibration of gold trap A and B, respectively. The 103 error between gold trap A and gold trap B was limited to ± 10 %. The impactor plates and quartz 104 filter were changed in every two weeks. The quartz filter was changed once a month. The denuders 105 were recoated once every two weeks following the procedure developed by Landis et al. (2002). 106 During the sampling campaigns, PM_{2.5}, O₃, NO_x, CO and SO₂ were also monitored by Thermo 107 Scientific TEOM 1405D, Model 49i O3 Analyzer, Model 48i CO Analyzer, Model 42i-TL NOx 108 Analyzer and Model 43i SO₂ Analyzer, respectively. The detection limits of O₃, SO₂, NO_x, CO and 109 $PM_{2.5}$ are 1.0, 0.5, 0.4, 0.04 and 0.1 μ g m⁻³, respectively. The meteorological parameters including 110 air temperature, wind speed, and wind direction are measured by Vantage Pro2 weather station 111 (Davis Instruments). The instruments are tested and calibrated periodically. All data are hourly 112 averaged in this study. 113 2.3 Sources apportionment of atmospheric mercury pollution

114 2.3.1 PSCF model

To identify the source areas for pollutants with a relatively long lifetime such as GEM (Xu and Akhtar, 2010), the PSCF values for mean GEM concentrations in grid cells in a study domain are calculated by counting the trajectory segment endpoints that terminate within each cell. The number of endpoints that fall in the *ij*-th cell are designated n_{ij} . The number of endpoints for the same cell having arrival times at the monitoring site corresponding to GEM concentrations higher than a specific criterion is defined to be m_{ij} . The criterion in this study is set as the average Hg concentration





121 during our study period. The PSCF value for the *ij*-th cell is then defined as:

122
$$PSCF_{ij} = \frac{m_{ij}}{n_{ii}} W_{ij} \tag{1}$$

123 where W_{ij} is an empirical weight to reduce the effects of grid cells with small n_{ij} values. In this

study, W_{ij} is defined as in the following formula, in which Avg is the mean n_{ij} of all grid cells with

125 n_{ij} greater than zero:

126
$$W_{ij} = \begin{cases} 1.0 & n_{ij} > 2 * Avg \\ 0.7 & Avg < n_{ij} \le 2 * Avg \\ 0.42 & 0.5 * Avg < n_{ij} \le Avg \\ 0.17 & n_{ij} \le 0.5 * Avg \end{cases}$$
(2)

127 The PSCF value indicates the probability of a grid cell through which polluted events occurs. 128 More method details can be found in the study of Polissar et al. (Polissar et al., 1999). In this study, 129 the domain that covered the potential contribution source region (105 °-135 °E, 15 °-45 °N) was 130 divided into 22500 grid cells with 0.2 ° ×0.2 ° resolution. 72-hour back trajectories were generated 131 hourly from 1 March, 2014 to 31 December, 2015 and from March 26 to December 31 in 2016 by 132 TrajStat, a software including HYSPLIT for trajectory calculation with trajectory statistics modules 133 (Wang et al., 2009). PSCF map was plotted using ArcGIS version 10.1. 134 2.3.2 Principal component analysis (PCA) 135 Correlation between Hg and other pollutant concentrations are used to identify source industries. 136 Strong positive loadings (loading>0.40) with SO₂ and PM_{2.5} typically indicate the impact of coal 137 combustion, and strong positive loadings with GEM and CO have often been used as an indicator 138 for regional transport because both pollutants have similar source and stable chemical properties 139 (Lin et al., 2006; Pirrone et al., 1996). In this study, PCA was applied to infer the possible influencing 140 factors of GEM in 2014 and 2016. Prior to analysis, each variable was normalized by dividing its 141 mean, and pollutant concentrations (SO₂, CO, NO_x, PM_{2.5}) were averaged to 1-h sampling intervals 142 to match the hourly mercury monitoring during sampling period. The results in 2016 had no CO

143 data due to instrument broken. Statistics analyses were carried out by using SPSS 19.0 software.

144 **2.4 Quantification method of source contribution**

145 To further quantitatively assess the effect of change in emissions from different regions on air 146 concentrations variation at a certain monitoring site, a quantitative estimation method which coupled 147 trajectories with air Hg concentrations was developed. We firstly identified the trajectories by using





148 the National Oceanic and Atmospheric Administration (NOAA) Hybrid Single-Particle Lagrangian 149 Integrated Trajectory (HYSPLIT) model. The gridded meteorological data at a horizontal resolution 150 of 1 °×1 ° were obtained from the Global Data Assimilation System (GDAS) (Draxler and Hess, 151 1998). The starting heights were set to be 500 m above ground level to represent the center height 152 of boundary layer where pollutants are usually well mixed in boundary layer. Secondly, each 153 trajectory was assigned with GEM concentration by matching the arriving time in Chongming site. 154 Third, the backward trajectories which coupled with Hg concentrations were clustered into groups 155 according to transport patterns by using NOAA HYSPLIT 4.7. Thus, the grouped clusters were applied to identify the Hg source regions. The Hg average concentration of the cluster *j* was then 156 157 calculated as equation (3). And, the trajectory weighted concentration in the cluster j as equation 158 (4). At last, the contribution of reduction at a certain region on Hg concentration at monitoring sites 159 in a certain period can be calculated as equation (5).

161

$$C_{j,t} = \frac{\sum_{i=1}^{n} C_{i,j,t}}{\sum_{i=1}^{n} N_{i,j,t}}$$

(3)

162
$$TWC_{j,t} = \frac{\sum_{i=1}^{n} N_{i,j,t}}{\sum_{j=1}^{m} \sum_{i=1}^{n} N_{i,j,t}} \times C_{j,t}$$
(4)

163

164 where *N* refers to a certain trajectory. *j* refers to a certain cluster. *t* is the studied period, and *n* is 165 the number of trajectory. *m* is the number of cluster. *C* is the GEM concentration, ng m⁻³. *TWC* refers 166 to the trajectory weighted concentration, ng m⁻³

167
$$CR_{j} = \frac{TWC_{j,t_{2}} - TWC_{j,t_{1}}}{\sum_{j=1}^{m} TWC_{j,t_{2}} - \sum_{j=1}^{m} TWC_{j,t_{1}}}$$
(5)

where *CR* refers to the contribution of GEM reduction. t_1 and t_2 refers to the two period participating to comparison, namely year 2014 and 2016 in this study, respectively.

170 This approach is a simple method to quantify the influence of anthropogenic emissions on GEM





- 171 concentration variation. It should be noted that errors always exist in calculating trajectories, causing
- 172 uncertainties in all trajectory-based approaches. Trajectory errors vary considerably in different
- 173 situation. Draxler (1996) suggested uncertainties might be 10% of the travel distance. Besides, this
- 174 method required similar meteorological conditions of the periods participated in comparison so as
- 175 to reduce the interference from meteorology.

176 2.5 Regional atmospheric Hg emissions

177 Regional atmospheric Hg emissions by month are calculated by using both the technology-based 178 emission factor methods and transformed normal distribution function method. Detailed 179 introduction of these two methods are described in our previous study (Wu et al., 2016). 180 Conventional air pollutant (SO2, PM2.5, and NOx) emissions were calculated following the study of 181 Zhao et al. (2013). The source regions included in the emission inventory consisted of Shanghai, 182 Jiangsu, Zhejiang, and Anhui provinces according to the PSCF results (See section 3.3). The studied 183 emission sectors included coal-fired power plants, coal-fired industrial boilers, residential coal-184 combustion, cement clinker production, iron and steel production, zinc smelting, lead smelting and 185 other small emission sectors (eg., municipal solid incineration, biomass incineration, copper 186 smelting, aluminum production, gold production, other coal combustion, oil combustion, and 187 cremation). The monthly Hg emissions were mainly distributed according to fuel combustions or 188 products productions by month (Table S1). For small emission sectors, the annual emissions were 189 equally distributed into monthly emissions. The GEM emissions from natural sources followed the 190 study of Wang et al. (2016).

191 **3 Results and discussions**

192 **3.1 Decreasing trends of atmospheric Hg during 2014-2016**

The average concentrations of GEM in 2014 and 2016 were 2.68 ± 1.07 ng m⁻³ and 1.60 ± 0.56 ng m⁻³, respectively. The GEM concentrations in 2014 were significantly higher than the Northern Hemisphere back-ground concentration (about 1.5 ng m⁻³) (Sprovieri et al., 2010) and those measured in other remote and rural locations in China (Zhang H et al., 2015; Fu et al., 2008a; Fu et al., 2009). However, in 2016, the GEM concentration (1.60 ± 0.56 ng m⁻³) was similar to the background concentrations in the Northern Hemisphere. During this period, monthly GEM





199

200 significance level) (Figure 2). 201 Table 1 showed the Hg variation trends in different regions. Significant decreases of GEM 202 concentrations in North hemisphere over the past two decades have been well documented (Weigelt 203 et al., 2015; Cole et al., 2013; Kim et al., 2016). Weigelt et al. (2015) showed that GEM concentrations decreased from 1.75 ng m⁻³ in 1996 to 1.4 ng m⁻³ in 2009 at Mace Head, Europe. 204 205 Ten-year trends of GEM concentrations at six ground-based sites in the Arctic and Canada also showed a decreasing trend at a rate of 13-35 pg m^{-3} y⁻¹ (Cole et al., 2013). In South Korea, the 206 207 observed GEM concentration also had significant decrease in recent years (Kim et al., 2016). In south hemisphere, at the Cape Point of South Africa, GEM concentrations decreased from 1.35 ng 208 209 m⁻³ in 1996 to 0.9 ng m⁻³ in 2008 and rose after then (Martin et al., 2017). However, limited GEM 210 monitoring sites and relative short-time spans in China restricted the views of long-term trends in 211 atmospheric Hg concentration in this region. A preliminary assessment indicated that atmospheric 212 Hg concentrations in China kept increasing before 2012 (Fu et al., 2015). The decreasing trend 213 observed in our study was accordant with the unpublished data in Mt. Changbai during 2014-2015 214 cited in the review of Fu et al. (2015). But much sharper decrease of Hg concentrations was observed 215 in our study. The specific reasons for the Hg concentration decrease in our study will be discussed 216 in section 3.4. One potential worry is that the calculated trend will be sensitive to seasonal variation 217 and the missing data in January and February of both 2014 and 2016 may impact the downward 218 trend. To evaluate the impact of the missing data, we estimate the Hg concentrations in the missing 219 months based on the least squares method from the data of the same months during 2011-2017 220 (Figure S1). Combining the estimated data, we re-fit the Hg concentrations and downward trend

concentrations showed a significant decrease with a rate of -0.60 ng m⁻³ yr⁻¹ (R^2 =0.6389, p<0.01

still maintained robust and similar to the downward trend in manuscript (Figure 2 and Figure S2).

222 Thus, we assume that the missing data is not very important and will not impact our main conclusion.

223 **3.2 Seasonal variation of GEM concentrations**

Figure 3 showed the monthly variation of GEM concentrations in Chongming Island during the monitoring period. Observed GEM concentrations showed an obvious seasonal cycle. The mean GEM concentration in warm season (from April to September) is 0.29 ng m⁻³ higher than that in cold season. Such seasonal variation trend is also observed at Nanjing, Miyun, Mt. Ailao, Mt.





228 Waliguan, and Shangri-La (Zhang et al., 2013; Zhang et al., 2016; Fu et al., 2015; Zhu et al., 2012). 229 On the other hand, the means of GEM at Mt. Gongga, Mt. Daimei, Mt.Leigong, and Mt. Changbai 230 in China are relatively higher in cold seasons. The average of atmospheric Hg concentrations in the 231 north hemisphere also have a trough value in summer (Sprovieri et al., 2016). 232 Seasonal variations of GEM concentration are generally attributed to the following factors, 233 including natural and anthropogenic emissions, atmospheric chemical reaction, and air mass 234 transportation. The higher Hg concentrations in cold seasons in Mt. Ailao and Mt. Waliguan were 235 mainly explained by coal-combustion for urban and residential heating during cold seasons. 236 Whereas, increasing solar radiation and soil/air temperature dominate the higher Hg concentrations 237 in Mt. Gongga and Mt. Leigong. In addition, sites in southern, eastern, and northeastern China also

238 impacted from anthropogenic emissions of GEM from the north and west by the northerly winter 239 monsoon while the sites located in western, southwestern, and northern China were impacted in 240 the warm season (Fu et al., 2015). As to most sites in the northern hemisphere, high wet Hg 241 precipitation induced probably by faster GEM oxidation led to lower Hg concentrations in summer. 242 As to the observation site in Chonming island, we observed almost synchronized trends 243 between emissions and air Hg concentrations in Figure 4. The annual emissions from both natural 244 source and anthropogenic source in YRD region (Anhui, Zhejiang, Jiangsu, and Shanghai) was -245 0.75 and 10.3 t, respectively. It should be pointed that the natural emissions here is a net natural 246 emissions, which is the byproducts of a bi-directional Hg flux, time, and area. When the data is 247 negative, it means GEM dry deposition to the calculated surfaces. Otherwise, it means GEM 248 emissions to air. The natural emissions varied from -5.4 t to 8.4 t with the highest value in summer 249 and the lowest value in winter. The anthropogenic emissions were in the range of 2.5-2.7 t, which 250 is almost unchanged compared to the natural emissions. Therefore, we supposed that the seasonal 251 cycle of GEM concentrations was dominated by natural emissions (Figure 4). The seasonal trend 252 of natural emissions is closely related with the canopy types in YRD areas, where widely 253 subtropical forests, paddy field, and dry farming were observed (Figure S3). The high temperature 254 will speed up decomposition of organic compound in soil, which lead to Hg emissions from 255 farmland and forest in YRD region (Luo et al., 2016; Yu et al., 2017). In autumn and winter, with 256 the decrease of temperature (Table S2), the role of soil changed from Hg source to sink, which





257 reduces the Hg concentrations in the air (Wang et al., 2016). At the same time, the growing 258 vegetation in autumn also absorbs air Hg, resulting lower Hg concentrations compared to that in 259 winter. Besides, more air mass transportation from North China and YRD was another reason of 260 higher Hg concentration in winter than that in autumn. According to the statistics of backward 261 trajectories in section 3.4, the air mass from North China and YRD region (NW and SW in Table 262 S3) in autumn and winter accounted for 73% and 95% of the total trajectory in autumn and winter, 263 respectively. We also noted that the seasonal variation of emissions is more significant than that of Hg concentrations. Higher wet Hg deposition in summer is a potential impact factor, which reached 264 265 about 6.6 times of that in winter (Zhang et al., 2010). On one aspect, abundant Br at the coastal 266 site of Chongming and higher O₃ concentrations and solar radiation will lead to faster GEM 267 oxidation in summer.

268 **3.3 Source apportionment of atmospheric Hg pollutions**

269 According to the PSCF result, YRD region, including Shanghai, Jiangsu, Anhui, and Zhejiang 270 provinces, was the dominant source region in both 2014 and 2016 (Figure 5). Therefore, Hg 271 emissions from these areas would contribute to high proportion of Hg pollution in Chongming 272 Island. The offshore area mainly around Jiangsu province also has a high PSCF value because some 273 trajectories from North China, especially Shandong province, transport to Chongming Island 274 through this area. Compared to the result in 2014, the PSCF value had an obvious decline in East 275 China Sea in 2016. This decline may be contributed by the downward trend of GEM concentrations 276 in north hemisphere (Zhang et al., 2016).

277 PCA method was applied to preliminarily identify the source industries. In the studied period, 278 totally 2 factors were identified in 2014 and 2016, respectively. The factor 1 had strong factor 279 loadings of GEM, SO₂, NO_x, CO, and PM_{2.5} in both 2014 and 2016 (No CO data in 2016 due to 280 equipment problems). The factor 1 accounted for 49% variance in 2014 and 50% variance in 2016 281 (Table 2). The results indicated common significant source sectors of the above five air pollutants, 282 which can also be proven from emission inventories (Table 3). The dominant source industries 283 included coal-fired power plants, coal-fired industrial boilers, and cement clinker production. The 284 PCA results showed that anthropogenic emissions were the main sources of GEM during the 285 sampling period.





The factor 2 in 2014 and 2016 both had a strong positive loading on O_3 and negative loading on NO_x. The anti-correlation between O_3 and its precursor NO_x could be an indication of air exchange between planet boundary layer (PBL) and troposphere. However, the low loading on GEM of factor 2 indicated that Factor 2 had no relationship with GEM concentrations at Chongming from the aspect of whole year data.

291 **3.4 The influence of anthropogenic emissions**

292 To further understand the reason of the downward trend, we firstly compared the meteorological 293 conditions in both 2014 and 2016. We noted that the difference of annual temperature, solar radiation, and relative humidity were constrained in the range of 17.13±7.48 °C, 165.55±45.87 W m⁻² and 294 295 75.38±5.82%, respectively (Table S2). The coefficient of variation for annual mean of these 296 meteorological conditions in 2014 and 2016 was 2.6%, 6.7% and 0.2%, respectively. In addition, 297 the wind rose was similar, and the dominating wind was from SE in both 2014 and 2016 (Figure S4). The HYSPLIT results also provided similar trajectories in 2014 and 2016 (Figure 6). Therefore, 298 299 we assumed that the meteorological condition was not the dominant reason of GEM decline at 300 Chongming site.

301 To further quantify the driver of GEM decline, a trajectory-based analysis method was used in 302 this study. The 72-h air mass back trajectories were calculated using HYSPLIT for every 8 hours 303 starting at the observation site. Approximately 918 and 832 trajectories were calculated in sampling 304 period in 2014 (Mar 1 to Dec 31, 2014) and 2016 (Mar 26 to Dec 31, 2016), respectively. The 305 trajectories were grouped into 3 clusters in each year according to geographical regions (Figure 6). 306 The first cluster of trajectories mainly passed through the regions (eg., North China) north and 307 northwest to Chongming Island before arriving to our monitoring site, which was denoted as cluster 308 NW. The second cluster mainly passed through the regions west and southwest to Chongming, 309 which was signed as cluster SW. The third type mainly originated from the East China Seas, South 310 Korea, Japan and Northeast Asia continent, and then arrived to our monitoring sites directly without 311 passing the mainland China. This type of trajectories was named as cluster EAST. Some trajectories 312 originated from the East China Sea and crossed the mainland China before arriving Chongming 313 were grouped into cluster NW or SW depending on the regions it crossed. The trajectories for each 314 of the three clusters in 2014 and 2016 were shown in Table 4.





315 Table 4 showed the detail statistics data of the three classifications. From 2014 to 2016, the whole 316 China region (NW, SW) contributed to 66% of GEM decline at Chongming Island. These results 317 reflected the effectiveness of existing air pollution control measures in China (SC, 2013; MEP, 2014). 318 Meanwhile, the NW region, SW region, and EAST region causes 47%, 19%, and 34% for GEM 319 decline, respectively (Table 4). The largest contribution of reduction was observed in the cluster 320 NW, suggesting that air pollution controls on anthropogenic emissions in NW region dominated the 321 recent decrease of GEM concentrations at Chongming site. We also noted that the largest decline of 322 Hg concentrations was observed in the cluster SW (1.51 ng m⁻³), which indicated more effective air 323 pollution control in the regions where the air mass of the cluster SW passed. However, since the 324 proportion of the trajectories in the cluster SW was much less than that in the cluster NW, the 325 contribution of cluster SW to GEM decline in our observation site was lower.

326 **4 Conclusion**

327 Atmospheric Hg was continuously measured for three years at a regional background site in the 328 YRD region. During the sampling period, a downward trend for GEM concentrations (-0.60 ng m⁻³ y-1) at Chongming Island was observed. The seasonal GEM cycle was dominated by the natural 329 330 emissions while the annual GEM concentration trend was mainly impacted by anthropogenic 331 emissions. By using a new approach that considers both cluster frequency and the Hg concentration 332 associated with each cluster, we quantified that atmospheric Hg from NW region, SW region, and EAST region have caused 47%, 19%, and 35% decline of GEM concentrations at Chongming 333 334 monitoring site, respectively. The result suggested that reduction of anthropogenic emissions in 335 mainland China was the main cause of the recent decreasing trend of GEM concentration at 336 Chongming site. The air pollution control policies in China, especially the pollution control in the 337 coal-fired power plants, coal-fired industrial boilers, and cement clinker production in YRD region 338 and Shandong province, have received significant co-benefit of atmospheric mercury emission 339 reductions. On the other hand, emission reduction from the EAST region, where clusters arrived to 340 Chongming monitoring site directly without passing the mainland China, implies global effort on 341 atmospheric Hg emission control under the guidance of Minamata Convention on Mercury. 342 Considering that the Minamata Convention on Mercury had come into force in 2017, continuous





343	long-term observation of atmospheric Hg in China will be required for the assessment of policy
344	effectiveness.
345	
346	Data availability. All data are available from the authors upon request.
347	
348	Competing interests. The authors declare that they have no conflict of interest.
349	
350	Acknowledge. This work is sponsored by the Natural Science Foundation of China (No. 21607090),
351	Major State Basic Research Development Program of China (973 Program) (No. 2013CB430000),
352	National Key R&D Program of China (No. 2016YFC0201900)
353	
354	
355	
356	
357	





358 **References**

- 359 Cole, A. S., Steffen, A., Pfaffhuber, K. A., Berg, T., Pilote, M., Poissant, L., Tordon, R., and Hung,
- 360 H.: Ten-year trends of atmospheric mercury in the high Arctic compared to Canadian sub-Arctic
- and mid-latitude sites, Atmospheric Chemistry and Physics, 13, 1535-1545, 2013.
- 362 Draxler, R. R.: Trajectory Optimization for Balloon Flight Planning, International Journal for
- 363 Numerical Methods in Fluids, 5, 13-23, 1996.
- 364 Draxler, R. R., and Hess, G. D.: An overview of the hysplit-4 modeling system for trajectories,
- 365 Australian Meteorological Magazine, 47, 295-308, 1998.
- 366 Fu, X. W., Feng, X. B, Zhu, W. Z., Wang, S. F.*, and Lu, J. L.*: Total gaseous mercury
- 367 concentrations in ambient air in the eastern slope of Mt. Gongga, South-Eastern fringe of the Tibetan
- 368 plateau, China, Atmospheric Environment, 42, 970-979, 2008a.
- 369 Fu, X. W., Feng, X. B., Zhu, W. Z., Zheng, W., Wang, S. F., and Lu, J. Y.: Total particulate and
- 370 reactive gaseous mercury in ambient air on the eastern slope of the Mt. Gongga area, China, Applied
- 371 Geochemistry, 23, 408-418, 2008b.
- 372 Fu, X. W., Feng, X. B., Wang, S., Rothenberg, S., Shang, L., Li, Z., and Qiu, G.: Temporal and
- 373 spatial distributions of total gaseous mercury concentrations in ambient air in a mountainous area
- 374 in southwestern China: implications for industrial and domestic mercury emissions in remote areas
- in China, Science of the Total Environment, 407, 2306-2314, 2009.
- 376 Fu, X. W., Feng, X. B., Qiu, G. L., Shang, L. H., and Zhang, H.: Speciated atmospheric mercury
- and its potential source in Guiyang, China, Atmospheric Environment, 45, 4205-4212, 2011.
- 378 Fu, X. W., Zhang, H., Yu, B., Wang, X., Lin, C. J., and Feng, X. B.: Observations of atmospheric
- 379 mercury in China: a critical review, Atmospheric Chemistry and Physics, 15, 9455-9476, 2015.
- 380 Hong, Q. Q., Xie, Z. Q., Liu, C., Wang, F. Y., Xie, P. H., Kang, H., Xu, J., Wang, J. C., Wu, F. C.,
- 381 He, P. Z., Mou, F. S., Fan, S. D., Dong, Y. S., Zhan, H. C., Yu, X. W., Chi, X. Y., and Liu, J. G.:
- 382 Speciated atmospheric mercury on haze and non-haze days in an inland city in China, Atmospheric
- 383 Chemistry and Physics, 16, 13807-13821, 2016.
- 384 Hui, M. L., Wu, Q. R., Wang, S. X., Liang, S., Zhang, L., Wang, F. Y., Lenzen, M., Wang, Y. F., Xu,
- 385 L. X., Lin, Z. T., Yang, H., Lin, Y., Larssen, T., Xu, M., and Hao, J. M.: Mercury flows in China and





- 386 global drivers, Environmental Science & Technology, 51, 222-231, 2017.
- 387 Kim, K. H., Brown, R. J. C., Kwon, E., Kim, I. S., and Sohn, J. R.: Atmospheric mercury at an urban
- 388 station in Korea across three decades, Atmospheric Environment, 131, 124-132, 2016.
- 389 Landis, M. S., Stevens, R. K., Schaedlich, F., and Prestbo, E. M.: Development and characterization
- 390 of an annular denuder methodology for the measurement of divalent inorganic reactive gaseous
- 391 mercury in ambient air, Environmental Science & Technology, 36, 3000-3009, 2002.
- 392 Lindberg, S., Bullock, R., Ebinghaus, R., Engstrom, D., Feng, X. B., Fitzgerald, W., Pirrone, N.,
- 393 Prestbo, E., and Seigneur, C.: A synthesis of progress and uncertainties in attributing the sources of
- 394 mercury in deposition, Ambio, 36, 19, 2007.
- 395 Luo, Y., Duan, L., Driscoll, C. T., Xu, G., Shao, M., Taylor, M., Wang, S. X, and Hao, J. M.:
- 396 Foliage/atmosphere exchange of mercury in a subtropical coniferous forest in south China, Journal
- 397 of Geophysical Research Biogeosciences, 121, 2016.
- 398 Martin, L. G., Labuschagne, C., Brunke, E. G., Weigelt, A., Ebinghaus, R., and Slemr, F.: Trend of
- atmospheric mercury concentrations at Cape Point for 1995–2004 and since 2007, Atmospheric
- 400 Chemistry and Physics, 17, 2393-2399, 2017.
- 401 Mason, R. P., Reinfelder, J. R., and Morel, F. M. M.: Bioaccumulation of mercury and
- 402 methylmercury, Springer Netherlands, 915-921 pp., 1995.
- 403 Ministry of Environmental Protection (MEP) and State Administration for Quality Supervision and
- 404 Inspection and Quarantine (AQSIQ): Emission standard of air pollutants for boilers, MEP, Beijing,
- 405 China, 2014.
- 406 Pirrone, N., Keeler, G. J., and Nriagu, J. O.: Regional differences in worldwide emissions of mercury
- 407 to the atmosphere, Atmospheric Environment, 30, 2981-2987, 1996.
- 408 Polissar, A. V., Hopke, P. K., Paatero, P., Kaufmann, Y. J., Hall, D. K., Bodhaine, B. A., Dutton, E.
- 409 G., and Harris, J. M.: The aerosol at Barrow, Alaska: long-term trends and source locations,
- 410 Atmospheric Environment, 33, 2441-2458, 1999.
- 411 State Council of the People's Republic of China (SC): Action plan of national air pollution
- 412 prevention and control, SC, Beijing, China, 2013.
- 413 Schroeder, W. H., and Munthe, J.: Atmospheric mercury-An overview, Atmospheric Environment,
- 414 32, 809-822, 1998.





- 415 Sprovieri, F., Pirrone, N., Ebinghaus, R., Kock, H., and Dommergue, A.: A review of worldwide
- 416 atmospheric mercury measurements, Atmospheric Chemistry and Physics, 10, 8245-8265, 2010.
- 417 Streets, D. G., Devane, M. K., Lu, Z., Bond, T. C., Sunderland, E. M., and Jacob, D. J.: All-Time
- 418 releases of mercury to the atmosphere from human activities, Environmental Science & Technology,
- 419 45, 10485-10491, 2011.
- 420 Sprovieri, F., Pirrone, N., Bencardino, M., amp, apos, Amore, F., Carbone, F., Cinnirella, S.,
- 421 Mannarino, V., Landis, M., Ebinghaus, R., Weigelt, A., Brunke, E.-G., Labuschagne, C., Martin, L.,
- 422 Munthe, J., Wängberg, I., Artaxo, P., Morais, F., Barbosa, H. d. M. J., Brito, J., Cairns, W., Barbante,
- 423 C., Di éguez, M. d. C., Garcia, P. E., Dommergue, A., Angot, H., Magand, O., Skov, H., Horvat, M.,
- 424 Kotnik, J., Read, K. A., Neves, L. M., Gawlik, B. M., Sena, F., Mashyanov, N., Obolkin, V., Wip,
- 425 D., Feng, X. B., Zhang, H., Fu, X., Ramachandran, R., Cossa, D., Knoery, J., Marusczak, N.,
- 426 Nerentorp, M., and Norstrom, C.: Atmospheric mercury concentrations observed at ground-based
- 427 monitoring sites globally distributed in the framework of the GMOS network, Atmospheric
- 428 Chemistry and Physics, 16, 11915-11935, 10.5194/acp-16-11915-2016, 2016.
- 429 Arctic Monitoring and Assessment Programme and United Nations Environment Programme
- 430 (AMAP/UNEP). Global Hg Assessment 2013: Sources, missions, Releases and Environmental
- 431 Transport, AMAP/UNEP, Geneva, Switzerland, 2013.
- 432 Wang, Y. Q., Zhang, X. Y., and Draxler, R. R.: TrajStat: GIS-based software that uses various
- 433 trajectory statistical analysis methods to identify potential sources from long-term air pollution
- 434 measurement data, Elsevier Science Publishers B. V., 938-939 pp., 2009.
- 435 Weigelt, A., Ebinghaus, R., Manning, A. J., Derwent, R. G., Simmonds, P. G., Spain, T. G., Jennings,
- 436 S. G., and Slemr, F.: Analysis and interpretation of 18 years of mercury observations since 1996 at
- 437 Mace Head, Ireland, Atmospheric Environment, 100, 85-93, 2015.
- 438 Wu, Q., Wang, S., Li, G., Liang, S., Lin, C. J., Wang, Y., Cai, S., Liu, K., and Hao, J.: Temporal
- 439 Trend and Spatial Distribution of Speciated Atmospheric Mercury Emissions in China During 1978-
- 440 2014, Environmental Science & Technology, 50, 13428-13435, 2016.
- 441 Xu, X., and Akhtar, U. S.: Identification of potential regional sources of atmospheric total gaseous
- 442 mercury in Windsor, Ontario, Canada using hybrid receptor modeling, Atmospheric Chemistry and
- 443 Physics, 10, 7073-7083, 2010.





- 444 Yu, Q., Luo, Y., Wang, S., Wang, Z., Hao, J., and Duan, L.: Gaseous elemental mercury (GEM)
- 445 fluxes over canopy of two typical subtropical forests in south China, Atmospheric Chemistry and
- 446 Physics Discussions, 1-27, 10.5194/acp-2017-349, 2017.
- 447 Zhang, G. y., Zhou, L. m., Zheng, X. m., and Huang, W. d.: Temporal Distribution and Potential Hazards
- 448 of Wet Depositon Mercury in Yangtze River Estuary, Urban Environmental & Urban Ecology, 1-4, 2010.
- 449 Zhang, H., Fu, X. W., Lin, C. J., Wang, X., and Feng, X. B.: Observation and analysis of speciated
- 450 atmospheric mercury in Shangri-La, Tibetan Plateau, China, Atmospheric Chemistry and Physics,
- 451 15, 653-665, 2015.
- 452 Zhang, H., Fu, X. W., Lin, C.-J., Shang, L. H., Zhang, Y. P., Feng, X. B., and Lin, C.: Monsoon-
- 453 facilitated characteristics and transport of atmospheric mercury at a high-altitude background site
- 454 in southwestern China, Atmospheric Chemistry and Physics, 16, 13131-13148, 2016.
- 455 Zhang, L., Wang, S. X., Wang, L., Wu, Y., Duan, L., Wu, Q. R., Wang, F. Y., Yang, M., Yang, H.,
- 456 Hao, J. M., and Liu, X.: Updated emission inventories for speciated atmospheric mercury from
- 457 anthropogenic sources in China, Environmental Science & Technology, 49, 3185-3194, 2015.
- 458 Zhang, Y. X., Jacob, D. J., Horowitz, H. M., Chen, L., Amos, H. M., Krabbenhoft, D. P., Slemr, F.,
- 459 St Louis, V. L., and Sunderland, E. M.: Observed decrease in atmospheric mercury explained by
- 460 global decline in anthropogenic emissions, Proceedings of the National Academy of Sciences of the
- 461 United States of America, 113, 526, 2016.
- 462 Zhao, B., Wang, S. X., Liu, H., Xu, J. Y., Fu, K., Klimont, Z., Hao, J. M., He, K. B., Cofala, J., and
- 463 Amann, M.: NOx emissions in China: historical trends and future perspectives, Atmospheric
- 464 Chemistry and Physics, 13, 9869-9897, 2013.
- 465 Zhu, J., Wang, T., Talbot, R., Mao, H., Hall, C. B., Yang, X., Fu, C., Zhuang, B., Li, S., Han, Y., and
- 466 Huang, X.: Characteristics of atmospheric Total Gaseous Mercury (TGM) observed in urban
- 467 Nanjing, China, Atmospheric Chemistry and Physics, 12, 12103-12118, 2012.
- 468





469 Figure citation

- 470 Figure 1. The location of the Chongming monitoring site in Shanghai, China
- 471 Figure 2. Trends of monthly average GEM concentrations and their least squares fit
- 472 Figure 3. Monthly variations of GEM concentration at remote sites in China (Fu et al.,
- 473 2015;Sprovieri et al., 2016)
- 474 Figure 4. Seasonal cycle of GEM concentrations and emissions during 2014-2016. The bars
- 475 represent the standard deviation of seasonal average.
- 476 Figure 5. Source regions of GEM at monitoring site from PSCF model in 2014(a) and 2016(b)
- 477 Figure 6. The back trajectories map for cluster NW, SW and EAST in 2014(a) and 2016(b)
- 478 (NW Northwest; SW Southwest; EAST East).

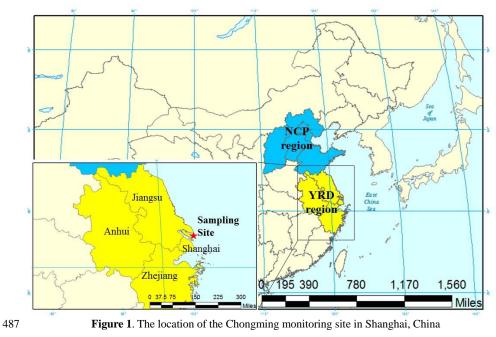




480	Table citation
481	Table 1. Historical variation trends of atmospheric Hg in previous studies
482	Table 2. PCA component loading of GEM and the co-pollutants
483	Table 3. Main air pollutant emitted by the different sector in YRD region
484	Table 4. The statistics of cluster and estimated contribution of GEM reduction in 2014 and 2016
485	

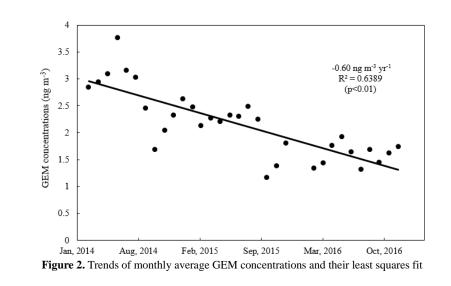








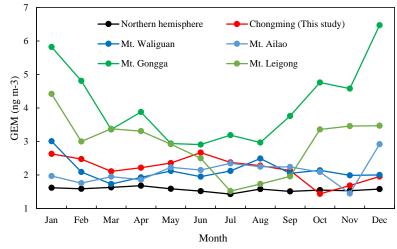








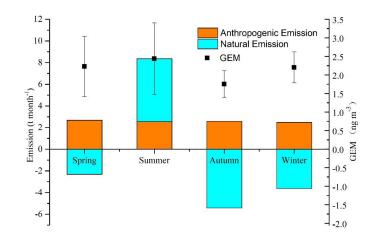




491 Figure 3. Monthly variations of GEM concentration at remote sites in China (Fu et al.,
492 2015;Sprovieri et al., 2016)







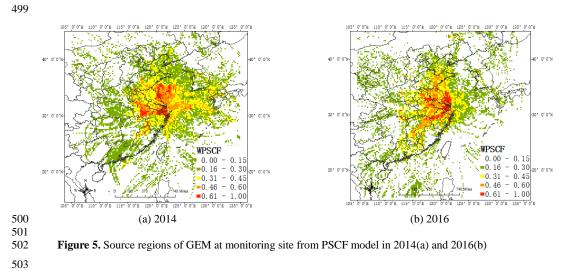
495

496 Figure 4. Seasonal cycle of GEM concentrations and emissions during 2014-2016. The bars

497 represent the standard deviation of seasonal average.

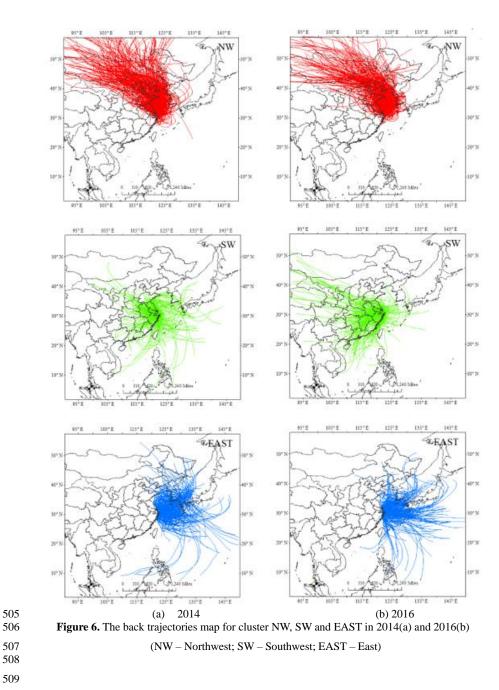














507



511



Monitoring site	Durat ion	TGM trend (pg m ⁻³ yr ⁻¹)	Variation trend	Site description	Reference
Alert, Canada	2000- 2009	-13(-21,0)	-0.9%/y	remote arctic, tundra	Cole et al 2013
Kuujjuarapik, Canada	2000- 2009	-33(-50,-18)	-2.1%/y	forest/tundra, sub-arctic	Cole et al 2013
Egbert, Canada	2000- 2009	-35(-44,-27)	-2.2%/y	forest/agricultural, urban within 100km	Cole et al 2013
Zeppelin Stn, Norway	2000- 2009	+2(-7,+12)	no trend	remote arctic mountain ridge, tundra	Cole et al 2013
St.Anicet, Canada	2000- 2009	-29(-31,-27)	-1.9%/y	flat, grassy, rural, urban/industrial within 100 km	Cole et al 2013
Kejimkujik, Canada	2000- 2009	-23(-33,-13)	-1.6%/y	Forested rural	Cole et a 2013
Head, Ireland	1996- 2009		-1.3±0.2%/y	located on the western coast of Ireland, the nearest city is 55km to the east	Weigelt et al. 2015
Hannam dong, South Korea	2004- 2011	no trend (3.54±1.46 ng/m3) decrease to 2.34±0.73 ng/m3		In the center of Seoul	Kim et al 2016
Hannam dong, South Korea	2013- 2014			metropolitan city	Kim et al 2016
Chongming Island, China	2014- 2016	-520	-29.4%/y	remote, wet land and farmland with 20km	This stud

512

513





515

516

Table 2. PCA component loading of GEM and the co-pollutants

2014				2016		
	Factor 1	Factor 2		Factor 1	Factor 2	
SO_2	0.763	0.142	SO_2	0.821	-0.088	
NO _X	0.766	-0.201	NO _X	0.699	-0.522	
O_3	-0.113	0.977	O ₃	-0.41	0.968	
PM _{2.5}	0.853	0.052	PM _{2.5}	0.875	0.053	
GEM	0.664	0.024	GEM	0.775	-0.19	
CO	0.793	0.12				
Component	Combustion	Exchange of PBL and troposphere	Component	Combustion	Exchange of PBL and troposphere	
Variance explain	49.359	17.525	Variance explain	50.625	75.735	

517 Note: Text in bold phase were regarded as high loading (factor loading>0.40)





Table 3. Main air pollutant emitted from the different sectors in YRD region

	SO_2 (kt)	NO _x (kt)	PM _{2.5} (kt)	GEM(t)
Coal-fired power plants	1823.76	1638.31	171.31	18.52
Coal-fired industrial boilers	1526.73	649.94	198.11	17.02
Residential coal combustion	344.57	77.34	95.21	1.04
Cement clinker production	421.17	622.33	362.27	11.56
Iron and steel production	505.03	156.16	240.6	3.99
Biomass incineration	13.99	92.25	556.18	0.61
Other sectors	7225.32	2872.43	832.05	5.39





Year	Cluster	Trajectories		GEM	Trajectory	Contribution
		Numbers	Ratio	concentration, C _j (ng m ⁻³)	weighted concentration, TWC _j , (ng m ⁻³)	to GEM reduction , CR _i
2014	NW	414	45%	2.46	1.11	
	SW	215	23%	3.37	0.79	
	EAST	289	31%	2.58	0.81	
2016	NW	322	39%	1.56	0.49	47%
	SW	258	31%	1.86	0.62	19%
	EAST	252	30%	1.44	0.35	35%

Table 4. The statistics of cluster and estimated contribution of GEM reduction in 2014 and 2016