

Response to reviewer's comments

Anonymous Referee #1:

1. This manuscript has been greatly improved. Most of the reviewers' comments have been properly addressed in the authors' responses. I have one more comment for the manuscript: The authors could add some recommendations to the last part of the manuscript based on their findings. For example, ship emissions might be an important source of Hg which has been neglected in previous emission inventory studies. Field measurements of Hg emissions from ships are needed to verify this point. Moreover, this was one of the very few studies that apply PMF to atmospheric Hg source apportionment. What were the limitations of this PMF application? What kind of special attention should be paid to in the PMF analysis for Hg in the future?

Overall, I think this manuscript is ready for publication on Atmospheric Chemistry and Physics after minor revision.

Response: Thanks for the reviewer's valuable suggestions. we added the sentences "It has to be noted that according to our results, ship emission was identified to be an important source of mercury which hasn't been included in previous emission inventory studies. Mercury emission factors from shipping are lacking and field measurements will be needed to verify it. Moreover, we realize that the application of PMF in the source apportionment of atmospheric mercury sources has certain limitations. Source-specific indicators are preferred, however, most indicators used for source identification have multiple sources, which have added uncertainties to our results. We suggest that in future research, the application of the PMF model is limited to the separation of the natural and total anthropogenic sources of GEM, which has been proved to be credible."

Response to reviewer's comments

Anonymous Referee #2:

1. Why do you only remove O₃? Do you ever test the impact of NH₃?

Response: Thanks for the comment. As a secondary pollutant, the formation processes of O₃ in the atmosphere are very complicated, which is controlled by the relative emissions of NO_x and VOCs in addition to solar radiation. In this regard, O₃ may not be a suitable input for PMF modeling and we removed it. In contrast, NH₃ mainly comes from primary emissions. One study at our sampling site have found the good correlation between NH₃ and temperature (Chang et al., 2019), and the soil emissions of GEM and NH₃ are treated in a similar way in air-quality modeling studies (Wright and Zhang, 2015; Zhang et al., 2010). Hence, we think that NH₃ can be regarded as an indirect tracer for the natural surface emissions of GEM.

2. The following, natural emissions, nature surface emissions, and surface emissions, seem refer to the same thing. Please be consistent throughout the whole text including in the figure. Moreover, re-emission is a significant source of atmospheric Hg, how do you consider its contribution?

Response: Thanks for the comment. We have carefully checked the full text and unified the term “natural surface emissions” to describe the natural sources of GEM in the revision. We agree with the reviewer that re-emission is a significant source of atmospheric mercury and its contribution has been included in the modeled GEM from natural surface emissions. However, it is difficult to separate the re-emission of deposited mercury and the emission of the original mercury in the natural surface by PMF only, which is also not the focus of this study.

3. Original comment 3: Ferrous metal smelting such as iron and steel smelting, instead of non-ferrous metal smelting, is one significant source of Ca emission. That is why I do not agree that The factor with high loading of Ca was assigned to cement production as the raw materials used in cement production contain a large amount of calcium compounds.

Response: We agree with the reviewer that ferrous metal smelting such as iron and steel smelting, cement production, and some other emission sectors all contribute to Ca emissions. The source profiles of those emission sectors can be similar at some extents. We did test to increase the number of PMF factors (e.g. 7, 8, and more), however, the separation of more detailed emission sources was not successful. Hence, the current PMF modeling framework may not well resolve more explicit emission source before introducing more specific tracers. This is the limitation of the PMF model if the selected indicator has multiple sources. We will try to improve it by introducing more unique tracers in the future works.

4. The authors should notice that it is just one case. Actually, the results of Figure 6 is still under doubt. For example, ship and vehicle emissions are two large anthropogenic emission sources in Shanghai. One of the problems to this result is that the indicators used in PMF

currently are not source-specific indicators and much depend on the subjective judgment of the authors. Under such situations, analyzing the uncertainty of the results is particularly important.

Response: We quite agree with the reviewer that most indicators used in PMF currently are not source-specific indicators and that contributed to the biggest uncertainties of the results. Currently, uncertainty analysis is not available via PMF. This is indeed the limitation of the PMF model.

In the conclusion section, we add the sentence “It has to be noted that according to our results, ship emission was identified to be an important source of mercury which hasn’t been included in previous emission inventory studies. Mercury emission factors from shipping are lacking and field measurements will be needed to verify it. Moreover, we realize that the application of PMF in the source apportionment of atmospheric mercury sources has certain limitations. Source-specific indicators are preferred, however, most indicators used for source identification have multiple sources, which have added uncertainties to our results. We suggest that in future research, the application of the PMF model is limited to the separation of the natural and total anthropogenic sources of GEM, which has been proved to be credible.”

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1 Assessing contributions of natural surface and anthropogenic emissions to
2 atmospheric mercury in a fast developing region of Eastern China from
3 2015 to 2018

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20
21 **Abstract**

22 Mercury (Hg) is a global toxic pollutant that can be released into the atmosphere through
23 anthropogenic and natural sources. The uncertainties in the estimated emission amounts are much
24 larger from natural than anthropogenic sources. A method was developed in the present study to
25 quantify the contributions of natural surface mercury emissions to ambient gaseous elemental
26 mercury (GEM) concentrations through application of positive matrix factorization (PMF) analysis
27 with temperature and NH₃ as indicators of GEM emissions from natural surfaces. GEM
28 concentrations were continuously monitored at a 2-hourly resolution at a regional background site
29 in the Yangtze River Delta in Eastern China during 2015-2018. Annual average GEM concentrations
30 were in the range of 2.03-3.01 ng/m³, with a strong decreasing trend at a rate of -0.32 ± 0.07 ng m⁻³
31 yr⁻¹ from 2015 to 2018, which was mostly caused by reduced anthropogenic emissions since 2013.
32 The estimated contributions from natural surface emissions of mercury to the ambient GEM
33 concentrations were in the range of 1.00-1.13 ng/m³ on annual average with insignificant interannual
34 changes, but the relative contribution increased significantly from 41% in 2015 to 57% in 2018,
35 gradually surpassing those from anthropogenic sources.

36

37 **1. Introduction**

38 Mercury has long been recognized as a toxic pollutant due to its bioaccumulation and health
39 effects (Driscoll et al., 2013b; Clarkson and Magos, 2006; Schroeder and Munthe, 1998; Horowitz et
40 al., 2017; Fu et al., 2012; Wright et al., 2018). Mercury in the atmosphere can be transported globally,
41 mostly in the form of gaseous elemental mercury (GEM) due to its long lifetime in air (Driscoll et
42 al., 2013a). Clarifying sources and quantifying emissions from the major sources of atmospheric
43 mercury are critical for understanding the biogeochemical cycle of mercury and developing mercury
44 reduction strategies. Mercury in the atmosphere is released from both natural and anthropogenic
45 sources. Natural sources include volcanoes, geological weathering, forest fires, re-emissions of pre-
46 deposited mercury from natural surfaces, etc (Gustin et al., 2008; Mason and Sheu, 2002). Among
47 these sources, emissions from natural surfaces are the major ones and a number of studies have been
48 devoted to understanding the processes of natural surface emissions (Xu et al., 1999; Lindberg et al.,
49 2002; Kocman et al., 2013). Anthropogenic sources mainly include coal-fired power plants, non-
50 ferrous metal smelters, and waste incineration (Friedli et al., 2009). Globally, natural sources
51 released about 5200 tons mercury into the atmosphere on an annual basis, which contributed up to
52 two-thirds of the global atmospheric mercury budget, while those by anthropogenic sources was
53 estimated to be around 2300 tons (Pirrone et al., 2010). In China, the total mercury emissions
54 released from natural and anthropogenic sources were estimated to be 574.5 ton yr⁻¹, and 571 ton
55 yr⁻¹, respectively (Wang et al., 2016; Zhang et al., 2015).

56 During the past decades, anthropogenic emissions of mercury in Europe and North America
57 have been reduced significantly through phasing out mercury from many commercial products as
58 well as benefiting from SO₂ and NO_x emission reduction from coal-fired utilities, resulting in
59 considerable decrease in atmospheric mercury concentrations in these regions (e.g., approximately
60 1-2% yr⁻¹ decrease from 1990 to 2013) (Streets et al., 2011; Zhang et al., 2016). In China,
61 anthropogenic mercury emissions decreased from 571 ton in 2013 to 444 ton in 2017 due to the co-
62 benefits of aggressive air pollutant control measures implemented in this period (Liu et al., 2019a).
63 GEM concentrations measured at a rural site north of Shanghai showed a substantially decreasing
64 trend from 2014 to 2016 (Tang et al., 2018).

65 With the decrease of anthropogenic mercury emissions in many parts of the world (Zhang et
66 al., 2016), the contributions of natural emissions to total mercury budget are expected to be more

67 important. However, the trends of natural emissions are still unclear due to the difficulties in directly
68 measuring GEM emissions from natural surfaces (Zhu et al., 2015). Existing estimates of GEM
69 emission from natural sources have large uncertainties (e.g., from 1500 to 5207 Mg yr⁻¹ on global
70 scale), limiting our understanding of the role of natural emissions in the global mercury cycle (Song
71 et al., 2015; Wang et al., 2014b). For example, a study at rural Beijing showed that modeled GEM
72 concentrations were underestimated by about 40% than measurements from April to September
73 2009 due to the absence of natural emission inventories (Wang et al., 2014a). Hence, it is meaningful
74 to develop a method to quantify the contributions of natural surface emissions to total mercury
75 budget in the atmosphere, especially in China where anthropogenic emissions have been fast
76 decreasing in recent years.

77 The purpose of the present study is to differentiate the contributions of natural surface
78 emissions and anthropogenic emissions to the measured ambient GEM concentrations collected
79 during a four-year period at a regional background site in the Yangtze River Delta (YRD) of Eastern
80 China. This was done by conducting positive matrix factorization (PMF) analysis with identified
81 variables as tracers of natural surface mercury emissions. Results presented in this study provide an
82 approach that can be potentially used for improving mercury emission databases for natural sources.

83

84 **2. Materials and methods**

85 **2.1 Site description**

86 Shanghai, situated in the YRD region, is one of the most developed cities in China. Like in
87 many other cities in China, severe air pollutions have occurred frequently in this city in the past
88 decades. A supersite has been set up next to the Dianshan Lake in Qingpu District of rural Shanghai
89 (Figure 1) as part of the framework of State Environmental Protection Scientific Observation and
90 Research Station. This supersite is designed to represent the regional scale air pollution
91 characteristics in the YRD region based on the following two considerations: (1) it is located in the
92 conjunction area of Shanghai, Jiangsu, and Zhejiang provinces; and (2) there are no large point
93 sources such as coal-fired power plants, nonferrous metal smelting, and cement production within
94 20km distance surrounding the site. This site was established in 2013 and its capacity has been
95 gradually built by measuring a set of atmospheric parameters, including meteorological factors,
96 trace gases, aerosol physical and chemical parameters, vertical profiles of ozone and particles, etc.

97 More detailed descriptions of the site can be found elsewhere (Qin et al., 2019;Duan et al., 2017).

98

99 **2.2 Measurements of gaseous elemental mercury**

100 An automated mercury vapor analyzer Tekran 2537B/1130/1135 was installed on the third floor
101 of a building for real time continuous GEM measurements since January 2015. GEM was measured
102 based on the principle of cold vapor atomic fluorescence spectroscopy (CVAFS) (Landis and Keeler,
103 2002). Briefly, ambient GEM was collected on gold traps and then thermally decomposed to GEM
104 before detection. The sampling interval of GEM was 5 minutes with a flow rate of 1L/min. More
105 details of this instrument can be found elsewhere (Mao et al., 2008).

106 Strict quality control procedures were followed during the sampling process. Denuders and
107 quartz filters were prepared and cleaned according to the instructions in Tekran technical notes
108 before sampling. Routine calibration with internal permeation source was performed every 47 hours
109 and manual injections of standard saturated mercury vapor were conducted to ensure the accuracy
110 of these automated calibrations. The KCl-coated denuder, Teflon-coated glass inlet, and impactor
111 plate were replaced weekly and quartz filters were replaced monthly. Individual extremely high
112 GEM concentrations that occasionally happened were regarded as outliers and were excluded from
113 the data analysis. In this study, the number of valid GEM data was 16266.

114

115 **2.3 Measurements of other air pollutants and meteorological parameters**

116 Water soluble ions in PM_{2.5} and soluble gases were continuously measured by Monitor for
117 Aerosols and Gases in ambient Air (MARGA) operated at a flow rate of 16.7 L/min with a time
118 resolution of one hour, as detailed in (Chang et al., 2016). Briefly, water-soluble gases in the airflow
119 were removed by an absorbing liquid, then the particles were induced by a supersaturation of water
120 vapor to grow into droplets before they were collected and transported into the analytical chamber.

121 Trace metals in PM_{2.5} were continuously measured by using the Xact 625 ambient metals
122 monitor (Cooper Environmental, Beaverton, OR, USA) operated at a flow rate of 16.7 L/min with
123 hourly resolution, as detailed in (Yu et al., 2019). Briefly, the particles in the airflow were deposited
124 onto a Teflon filter tape, and then transported into the spectrometer where the particles were
125 analyzed with an X-ray fluorescence. Black carbon in PM_{2.5} was measured by a multiwavelength
126 Aethalometer (AE-33, Magee Scientific). Ambient particles were collected on a paper tape at a flow

127 rate of 5 L/min. Aerosol light absorptions of BC were measured at seven wavelengths of 370, 470,
128 520, 590, 660, 880, and 950nm.

129 Sulfur dioxide, carbon monoxide, and PM_{2.5} were measured by Thermo Fisher 43i, Thermo
130 Fisher 48i-TLE, and Thermo Fisher 1405-F, respectively. Meteorological parameters including
131 ambient temperature, wind speed, and wind direction were obtained at the sampling site by using
132 the automatic weather station (AWS). Bivariate polar plots (BPP) were applied in this study to
133 explore how GEM concentrations change with different wind direction and wind speed, which has
134 proven to be a reliable method for identifying different source regions (Carslaw et al., 2006; Carslaw
135 and Ropkins, 2012; Chang et al., 2017). Here, the open-source software “openair” in R was used to
136 create BPPs (Carslaw and Ropkins, 2012).

137

138 **2.4 Positive matrix factorization (PMF)**

139 The PMF model has been proven to be a useful tool to provide quantitative source profiles and
140 source contributions (Xu et al., 2017; Gibson et al., 2015). The basic principle of PMF is that
141 concentrations of the samples were determined by the source profiles with different contributions,
142 which can be described as follows:

$$143 \quad X_{ij} = \sum_{k=1}^P g_{ik} f_{kj} + e_{ij} \quad (1)$$

144 where X_{ij} represents the concentration of the j th species in the i th sample, g_{ik} is the contribution
145 of the k th factor in the i th sample, f_{kj} provides the information of the mass fraction of the j th
146 species in the k th factor, e_{ij} is the residual for specific measurement, and P represents the number
147 of factors.

148 The objective function expressed in Eq. (2) below, which is the sum of the square of the
149 difference between the measured and modeled concentrations weighted by the concentration
150 uncertainties, needs to be minimized before the PMF model determines the optimal non-negative
151 factor profiles and contributions. (Cheng et al., 2015)

$$152 \quad Q = \sum_{i=1}^n \sum_{j=1}^m \left(\frac{X_{ij} - \sum_{k=1}^P A_{ik} F_{kj}}{S_{ij}} \right)^2 \quad (2)$$

153 where X_{ij} represents the concentration of the j th contamination in the i th sample, m is the total
154 number of pollutant, and n is the total number of sample. A_{ik} represents the contribution of the k th
155 factor on the i th sample and F_{kj} represents the mass fraction of the j th pollutant in the k th factor.
156 S_{ij} is the uncertainty of the j th pollutant on the i th factor and P is the number of factors. In this

157 study, we explored the number of factors from three to eight with the optimal solutions determined
158 by the slope of the Q value versus the number of factors. For each run, the stability and reliability
159 of the outputs were assessed by referring to the Q value, residual analysis, and correlation
160 coefficients between observed and predicted concentrations. Finally, we found that a six-factor
161 solution showed the most stable results and gave the most reasonable interpretation. A dataset
162 containing uncertainty values of each species was created and digested into the model, with the error
163 fraction being assumed to be 15% for GEM concentration and 10% for other compounds (Xu et al.,
164 2017;Polissar et al., 1998).

165 It should be noted that Fpeak model run at the strength of 0.5 was done by using the rotation
166 tools in PMF and the results were summarized in Table S1. For all seasons, the increase of the Q-
167 value due to the Fpeak rotation with a dQ was less than 1% of the Base Run Q (robust) value.
168 According to the User Guide of PMF5.0, it was acceptable when the %dQ was less than 5%. The
169 profiles and contributions of each source were examined and there were no significant differences
170 between the factor contributions of Base Run and rotation results. Hence, the Base Run results were
171 used in this study.

172

173 **2.5 Annual changes of anthropogenic mercury emission in China and YRD**

174 It was reported that the annual anthropogenic atmospheric mercury emission in China
175 significantly increased from 147 tons in 1978 to 549 tons in 2010 (Wu et al., 2016). In more recent
176 years, in order to cope with the severe air pollution situation, the Chinese government has taken
177 many rigorous and ambitious measures such as introduction of ultra-low emissions standards on
178 power plants and phasing out of small factories with high-emissions (Zheng et al., 2018). As a result,
179 mercury emissions from anthropogenic sources have since been declining in China. For the five-
180 year period of 2013-2017, annual total anthropogenic mercury emissions in China were estimated
181 to be 571, 547, 528, 486, and 444 tons, respectively, or a total decline of 127 tons. During the same
182 period, the reduction of anthropogenic mercury emissions reached 60 tons in eastern China (Liu et
183 al., 2019a).

184

185 **3. Results and Discussion**

186 **3.1 The measured gaseous elemental mercury**

187 **3.1.1 Decreasing trend of gaseous elemental mercury**

188 The measured annual mean GEM concentrations were 3.01 ± 1.03 , 2.58 ± 0.84 , 2.52 ± 0.84 ,
189 and 2.03 ± 0.69 ng/m³ from 2015 to 2018. By using the Theil-Sen function, monthly GEM exhibited
190 a significantly decreasing trend from 2015 to 2018 ($p < 0.05$) with a rate of -0.32 ± 0.07 ng m⁻³ yr⁻¹
191 (Figure 2a). This decreasing trend was consistent with the trends of mass concentrations of PM_{2.5}
192 and SO₂ (Figure 2b & 2c), which were attributed to the implementation of the Clean Air Action
193 since 2013 in China (Zheng et al., 2018). As mentioned earlier (Section 2.5), the nationwide
194 reduction of anthropogenic mercury emissions should be largely responsible for the significant
195 decrease in GEM concentration observed at the YRD regional background site.

196 Seasonal average GEM concentrations decreased from 3.62 ng/m³ to 2.17 ng/m³ with a rate of
197 -0.37 ng m⁻³ yr⁻¹ in spring, from 2.89 ng/m³ to 1.98 ng/m³ with a rate of -0.26 ng m⁻³ yr⁻¹ in summer,
198 from 2.62 ng/m³ to 1.94 ng/m³ with a rate of -0.22 ng m⁻³ yr⁻¹ in autumn, and from 2.91 ng/m³ to
199 1.82 ng/m³ with a rate of -0.35 ng m⁻³ yr⁻¹ in winter (Figure 3). The decreasing rates of GEM were
200 ~30% lower in the warm seasons than the cold seasons. Considering that seasonal variations of
201 anthropogenic emission were less temperature dependent, the different seasonal decreasing rates of
202 GEM between the warm and cold seasons should be mostly caused by the seasonal-dependent
203 emission amounts from natural sources, knowing that natural surface emissions are controlled by
204 solar radiation and temperature, among other factors (Howard and Edwards, 2018; Pannu et al.,
205 2014; Mason, 2009).

206

207 **3.1.2 Impact of temperature on ambient gaseous elemental mercury**

208 In a previous study we showed that GEM concentrations tended to rise with increasing
209 temperature in the YRD region, which was considered to be the effect of temperature-dependent
210 emission amounts from natural surfaces (Qin et al., 2019). Here, to qualitatively investigate the role
211 of natural surface emissions on ambient GEM concentration, diurnal profiles of the bi-hourly GEM
212 concentration and temperature are exhibited in Figure 4. If looking at the whole year data together,
213 moderate to high correlations were seen between the diurnal variations of GEM and temperature in
214 2016, 2017, and 2018 with R² being 0.30 to 0.86 ($p < 0.05$), except in 2015 with little correlation
215 with R² being only 0.03 ($p > 0.05$) (Figure 4a-4d). The maximum GEM concentrations generally
216 appeared around 10AM - 14PM, mostly coincided with daily peak temperature. These findings

217 provided strong evidence of temperature-dependent GEM sources.

218 Due to the large differences in ambient temperature between warm (from June to November)
219 and cold (from December to May) seasons in the YRD region, the effects of temperature-dependent
220 GEM sources on the ambient GEM concentrations should be different in different seasons. As
221 expected, high correlations between GEM concentrations and temperature were found in the warm
222 seasons with R^2 being in the range of 0.15 to 0.87 (Figures 4e-4h), while nearly no correlations in
223 the cold seasons (Figures 4i-4l). Thus, the influence of natural surface emissions on ambient GEM
224 concentration was important in the warm seasons, but may not be the case in the cold seasons. The
225 seasonal bivariate polar plots of GEM showed that high GEM concentrations were associated
226 frequently with air flows from the south and southwest and occasionally with those from the north,
227 particularly in summer (Figure S1). This was consistent with the findings in previous studies which
228 showed stronger natural surface emissions in South and Southwest China than North China (Wang
229 et al., 2016;Feng et al., 2005;Wang et al., 2006;Sommar et al., 2016). Hence, in the context of
230 significant reduction of anthropogenic mercury emission in China, especially in North China (Liu
231 et al., 2019b), natural surface emissions significantly impacted the ambient GEM concentrations at
232 this sampling site.

233

234 **3.2 Quantify the contributions from natural surface emissions to ambient gaseous elemental** 235 **mercury**

236 **3.2.1 Development of the approach**

237 A method is developed below for quantifying the contributions of GEM emissions from natural
238 surfaces to ambient GEM concentrations through application of the PMF model by introducing
239 specific variables related to natural surface emissions as traces. The first step is to identify what
240 variables are directly or indirectly related to the natural surface emissions of GEM. Temperature is
241 certainly a dominant one as has been demonstrated in existing soil-air fluxes studies of mercury
242 (Wang et al., 2014b;Zhu et al., 2016;Poissant and Casimir, 1998). The formation pathways of Hg^0
243 in soil are all related to temperature, an empirical rule suggests that a $10^\circ C$ temperature increase
244 doubles the rates for chemical reaction near room temperature, which has been proven to be
245 applicable to Hg^{II} reduction in boreal soil (Moore and Carpi, 2005;Quinones and Anthony,
246 2011;Wang et al., 2016;Pannu et al., 2014). Discussions in Section 3.1.2 also suggested temperature

247 as a potentially useful tracer for predicting natural surface emissions of GEM. A second candidate
248 of tracers could be ambient NH₃ concentration because soil emissions of GEM and NH₃, both of
249 which are temperature-dependent, are treated in a similar way in air-quality modeling studies
250 (Wright and Zhang, 2015;Zhang et al., 2010). As shown in Figure S2, the mean diurnal variations
251 of GEM concentrations highly correlated with ambient temperature as well as NH₃. From this
252 perspective, NH₃ can be regarded as an indirect proxy for the natural surface emissions of GEM. In
253 a previous study, we have applied principal component analysis for source apportionment of
254 mercury in this area, and the source factor with high loadings for temperature and NH₃ was
255 interpreted as natural surface emissions of GEM (Qin et al., 2019).

256 Hence, in this study, we included the data of temperature and NH₃ into the PMF model to
257 apportion the sources of GEM. As shown in Figures S3-S18, the source apportionment results for
258 all the seasons of 2015-2018 all resolved a similar factor with high loadings of temperature and
259 moderate loadings of NH₃ and GEM. This factor was thought to be the natural surface emission
260 sources of mercury. As for the other resolved factors, the factor with high loadings of V and Ni
261 evidently represented shipping emissions, because Ni and V have been considered as typical tracers
262 of heavy oil combustion which has been commonly used in marine vessels (Viana et al., 2009). The
263 factor with high loading of Ca was assigned to cement production as the raw materials used in
264 cement production contain a large amount of calcium compounds. Moderate loadings of multiple
265 species including Cr, Mn, and Fe were found in one factor which was identified as iron and steel
266 production. The factor with high loading of NO was identified as vehicle emissions, as the major
267 source of NO_x in the YRD region is mobile oil combustion (Tang et al., 2018). And the last factor
268 was identified as coal combustion due to the high loadings of As and Se, and moderate contributions
269 from Pb and SO₄²⁻. As, Se, and Pb were all typical tracers of coal combustion and the precursor of
270 SO₄²⁻ (i.e. SO₂) also mainly derived from coal combustion.

271 In order to verify the PMF modeling results, we first examined the PMF model performance.
272 Table S2 shows the coefficient of determination (R²) for GEM according to the observation-
273 prediction scatter plots (Figure S20-S23). The R² values ranged from 0.37 to 0.89, suggesting an
274 acceptable model performance. Figure S24-S27 display the time series of observed and predicted
275 GEM concentrations from 2015-2018, which revealed that, except for a few extremely high
276 observation values, the model can relatively well reproduce the observed GEM concentration on an

277 hourly basis.

278 To further verify the reliability of the resolved factors, the correlations between the mass
279 contributions of all factors to GEM and temperature were examined on the basis of diurnal profiles.
280 As shown in Figure S19, positive correlation was only found between the natural surface emissions
281 factor and temperature while the other resolved factors (i.e. vehicle emission, coal combustion,
282 shipping activities, cement production, and iron and steel production) did not show this relationship.
283 In addition, the relationship between particulate black carbon (BC) and GEM concentration was
284 investigated. On the one hand, BC mainly derived from various combustion processes, which were
285 also the main anthropogenic sources of atmospheric mercury. On the other hand, BC was never
286 introduced into the PMF modeling. As shown in Figure 5, the observed total GEM and BC
287 concentrations only showed weak correlations. This was mainly due to the fact that besides
288 anthropogenic sources, natural sources also contributed significantly to GEM. As a comparison,
289 anthropogenic GEM concentrations (extracted from PMF results) showed much better correlations
290 with BC from 2015 to 2018. In addition, the time-series of anthropogenic GEM concentrations
291 generally varied consistently with CO, which was also a tracer of fuel combustion (Figure S28). All
292 the evidences above corroborated that by using temperature and NH₃ as tracers for PMF modeling,
293 the separation of anthropogenic and natural GEM can be successfully achieved.

294 As for the specific anthropogenic mercury sources extracted from PMF results, Figure S29
295 shows that the time-series of coal combustion GEM also varied consistently with SO₂, indicating
296 that the coal combustion factor resolved by PMF was credible. As shown in Figure S30, the potential
297 source regions of shipping GEM were found mainly over coastal and oceanic areas, indicating the
298 shipping factor resolved in this study was also valid. Figure S31 and Figure S32 show that the PSCF
299 signals of cement production GEM were relatively weak in the YRD region, while there were
300 substantial high PSCF signals for iron and steel production GEM in Eastern China. All the results
301 above collectively confirmed that the PMF results were robust.

302 **3.2.2 Increasing contributions from natural surface emissions to ambient gaseous elemental** 303 **mercury**

304 Figure 6 summarizes the contributions of natural surface emissions and anthropogenic
305 emissions to GEM on seasonal basis from 2015 – 2018. The contributions of natural surface
306 emissions to GEM were ~40% higher in summer (1.15 ± 0.60 ng/m³) than winter (0.82 ± 0.57 ng/m³).

307 Besides, the contributions of natural surface emissions to GEM exhibited an upward trend, e.g.,
308 increased from 33% to 53% in spring, 47% to 62% in summer, 49% to 60% in autumn, and 34% to
309 52% in winter, from 2015-2018 (Figure 6). In contrast, the contributions from anthropogenic sources
310 to GEM showed a downward trend, of which the decreased contribution from coal combustion
311 accounted the most. Coal combustion has been widely regarded as the dominant anthropogenic
312 source of mercury emissions at the global scale, and China is known as the largest coal producer
313 and consumer in the world (Zhang et al., 2012; Wu et al., 2006). Since 2013, a series of key air
314 pollution control measures have been applied in China to reduce the emission of air pollutants
315 (Zheng et al., 2018). YRD regions also took actions by regulating on the amount of coal
316 consumption, promoting renewable energy development and so on (Zheng et al., 2016). Hence, the
317 decreased contribution of coal combustion was attributed to the implementation of aggressive air
318 pollutant control measures in China in recent years, which subsequently led to an increase in the
319 relative contribution of natural surface emissions to GEM.

320 The absolute GEM concentrations contributed by both natural surface emissions and
321 anthropogenic emissions can be extracted from the PMF modeling results. Figure 7 exhibits the
322 monthly and yearly profiles from 2015 to 2018. Strong seasonal cycles of GEM contributed by
323 natural surface emissions were seen, corresponding to the seasonal pattern of ambient temperature
324 (Figure 7g) and the simulated monthly Hg fluxes from natural surface emissions in China (Wang et
325 al., 2016). The annual GEM concentration contributed by natural surface emissions was estimated
326 to be 1.04 ± 0.55 ng/m³, 1.10 ± 0.56 ng/m³, 1.13 ± 0.56 ng/m³, and 1.00 ± 0.45 ng/m³ from 2015 to
327 2018, respectively (Figure 7a & 7b), which almost remained unchanged. This could be mainly
328 explained by the little variation of annual temperature (Fig. 7h) and wind pattern from 2015 to 2018
329 (Fig. S33). On the contrary, the annual GEM concentration contributed by anthropogenic emissions
330 was estimated to be 1.53 ± 1.04 ng/m³, 1.26 ± 0.78 ng/m³, 1.23 ± 0.95 ng/m³, and 0.82 ± 0.58 ng/m³
331 from 2015 to 2018, respectively, showing an obvious decreasing trend (Figure 7c & 7d). It was
332 noted that the GEM concentration contributed by anthropogenic emissions dropped the most from
333 2017 to 2018 with a rate of around 40%. By referring to the Table S3, SO₂ and CO also decreased
334 significantly of about 35% and 18%. As SO₂ and CO were the main primary gaseous pollutants
335 emitted from fuel combustions, their sharp decreases indicated the significant reduction of
336 anthropogenic emissions which was probably responsible for large drop of GEM from 2017 to 2018.

337 Overall, the relative contribution of natural surface emissions to ambient GEM was on the rise, e.g.,
338 from 41% in 2015 to 57% in 2018 on annual average (Figures 7e & 7f).

339

340 **4. Conclusions and Implications**

341 Through a four-year continuous measurement of GEM in the suburbs of Shanghai, a clear
342 decreasing trend was observed with the rate of $-0.32 \pm 0.07 \text{ ng m}^{-3} \text{ yr}^{-1}$, which was mainly due to the
343 reduction of anthropogenic mercury emissions. The lower decreasing rate in warm seasons than in
344 cold seasons and the high correlation between GEM concentrations and temperature suggested that
345 natural surface emissions significantly impacted the GEM concentrations. By demonstrating that
346 temperature and NH_3 can well serve as tracers of natural surface mercury emissions, distinguishing
347 natural vs. anthropogenic contributions to GEM was doable by introducing these tracers into the
348 PMF model. The results indicated that the contribution from anthropogenic mercury emissions was
349 declining, especially from coal combustion. The annual absolute contributions of natural surface
350 emissions were in the range of $1.00\text{-}1.13 \text{ ng/m}^3$, and the relative contribution of natural surface
351 emissions to GEM increasing form 41% in 2015 to 57% in 2018.

352 Measurements of GEM and other pollutants in a regional background area in Eastern China
353 demonstrated the effectiveness of emission control policies in this and surrounding regions in China
354 in recent years. The decreasing contributions from anthropogenic sources and the relatively stable
355 contributions from natural surface emissions to the ambient GEM have resulted in the relative
356 contributions of natural surface emissions surpassing those of anthropogenic emissions in more
357 recent years. This trend will likely continue for some years considering the current pollution levels
358 in China which needs further pollution abatement. This implies that even though the anthropogenic
359 emissions of mercury would continue to decrease, the legacy mercury in the natural surfaces will
360 continue to emit steadily for a long period of time. In addition, the natural release of mercury could
361 be enhanced under climate warming scenario. Hence, the atmospheric mercury concentration in
362 YRD or other parts of China will remain at relatively high levels in the near future, which brings
363 big challenges to China's policies on mercury emissions reduction. The methodology developed in
364 the present study could also shed some light on source apportionment of atmospheric mercury in
365 the other regions of the world, and has potential for improving emission databases from natural
366 surfaces where ambient GEM and auxiliary data are available.

367 It has to be noted that according to our results, ship emission was identified to be an important
368 source of mercury which hasn't been included in previous emission inventory studies. Mercury
369 emission factors from shipping are lacking and field measurements will be needed to verify it.
370 Moreover, we realize that the application of PMF in the source apportionment of atmospheric
371 mercury sources has certain limitations. Source-specific indicators are preferred, however, most
372 indicators used for source identification have multiple sources, which have added uncertainties to
373 our results. We suggest that in future research, the application of the PMF model is limited to the
374 separation of the natural and total anthropogenic sources of GEM, which has been proved to be
375 credible.

376

377 **Acknowledgments**

378 The authors acknowledge support of the National Key R&D Program of China (2018YFC0213105),
379 the National Natural Science Foundation of China (91644105, 21777029), and the Natural Science
380 Foundation of Shanghai (18230722600,19ZR1421100).

381

382 **Author contribution**

383 X.Q. and K. H. designed this study. X.Q. performed measurements and data analysis. X.W., Q.F.,
384 Q.Z., Y.L., and J.H. performed data collection. X.Q., L.Z., K.H., and C.D. wrote the paper. All have
385 commented and reviewed the paper.

386

387 **Competing interests**

388 The authors declare that they have no conflict of interest.

389

390 **Data availability**

391 All data used in this study can be requested from K.H. (huangkan@fudan.edu.cn).

392

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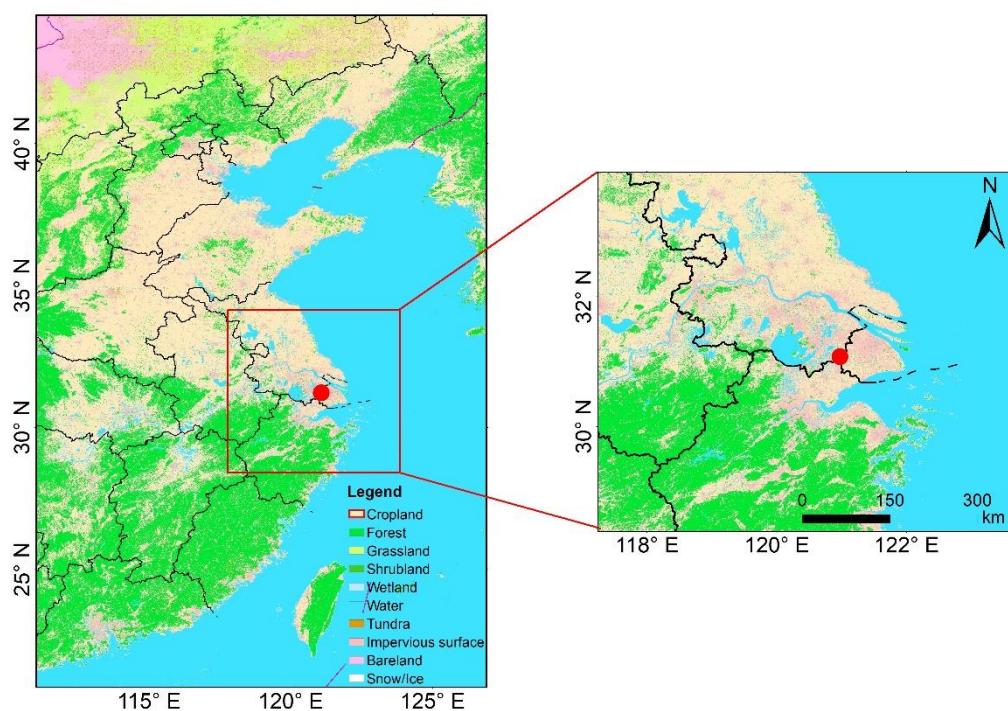
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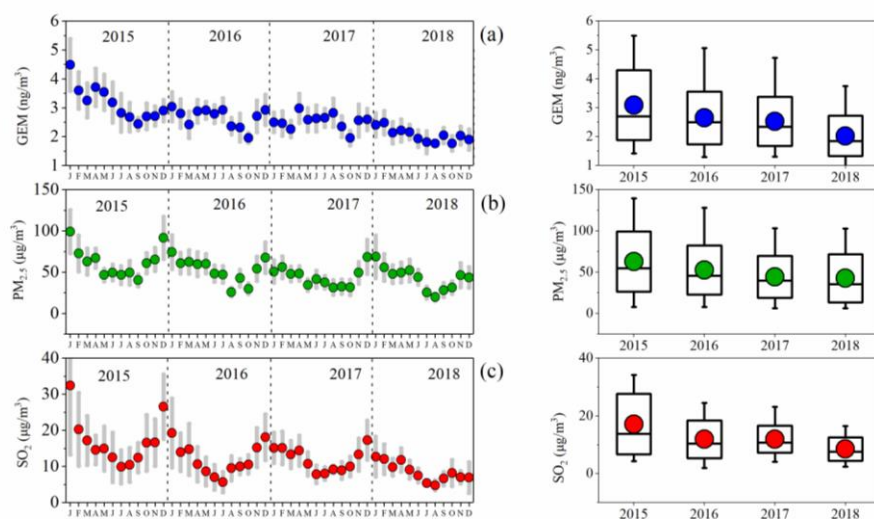
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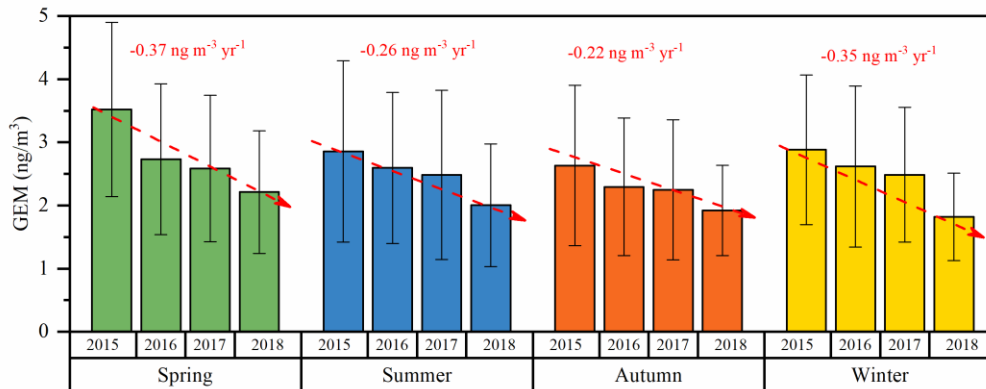
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567 Figure 1. The location of the Dianshan Lake (DSL) site in Shanghai, China. Different colors in the
 568 map represent different land cover types.
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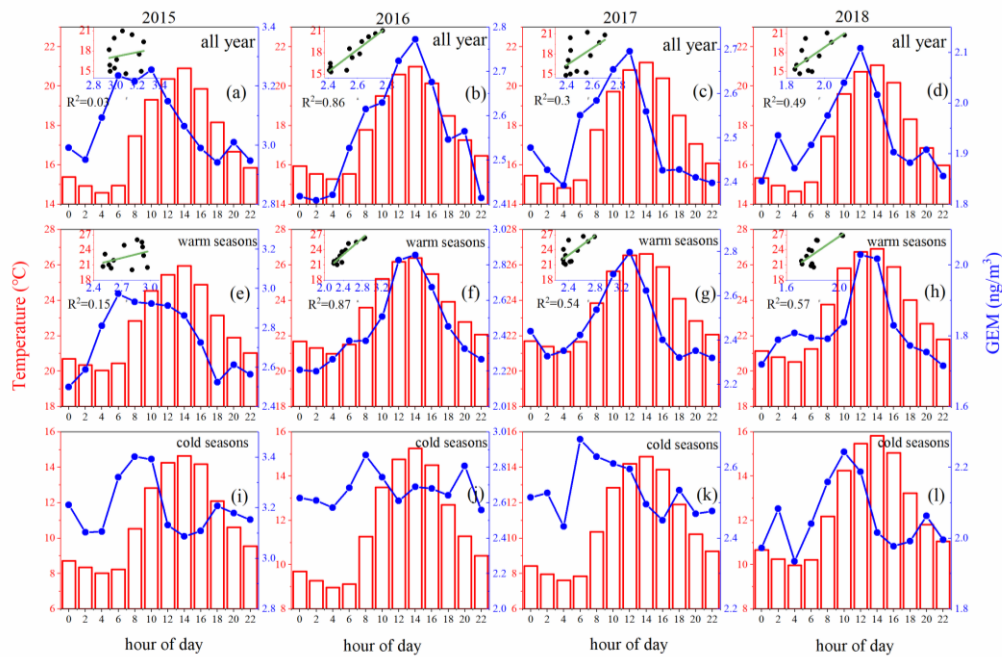
570
 571 Figure 2. Monthly and annual variations of (a) GEM, (b) PM_{2.5}, and (c) SO₂ concentrations from
 572 2015 to 2018.
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575 Figure 3. Seasonal variations of GEM concentrations from 2015 to 2018. The variation rates of
 576 GEM for each season are also shown in the figure.

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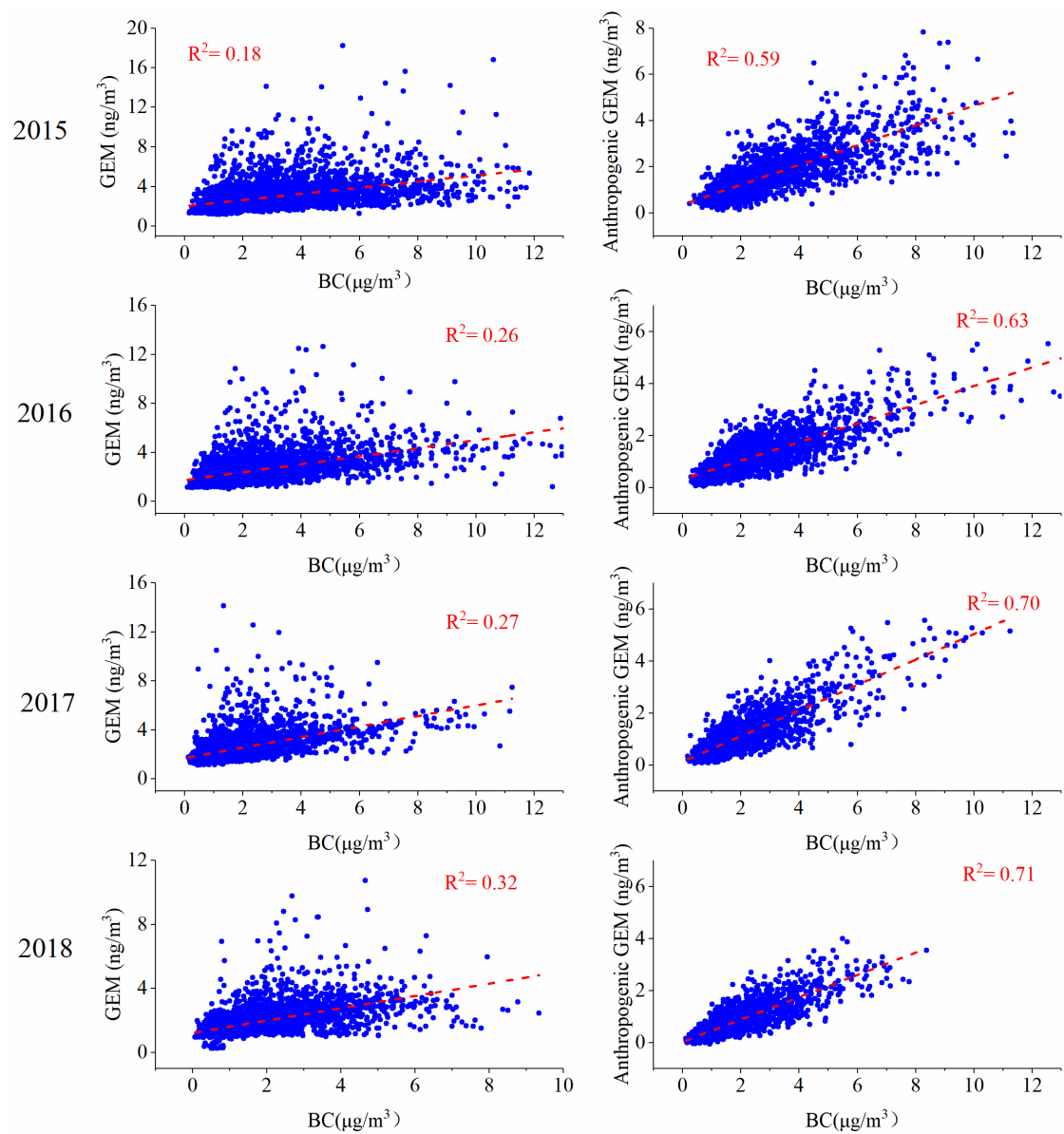


579 Figure 4. Diurnal patterns of bi-hourly GEM concentrations and temperature for the whole year (a-
 580 d), warm seasons (e-h), and cold seasons (i-l) during 2015 – 2018, respectively. The linear
 581 correlations between GEM and temperature are inserted as inner figures.

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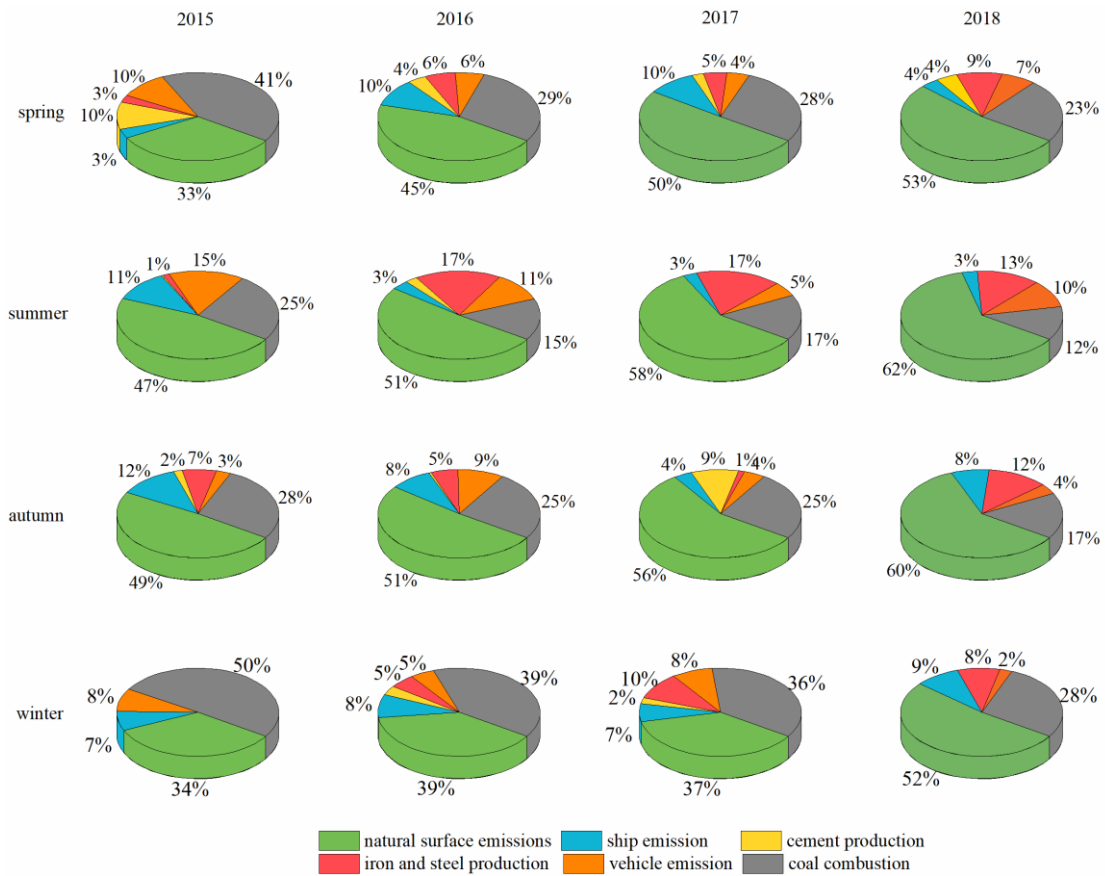
586 Figure 5. The relationship between observed GEM and BC, anthropogenic GEM (extracted from
 587 PMF results) and BC during 2015 – 2018

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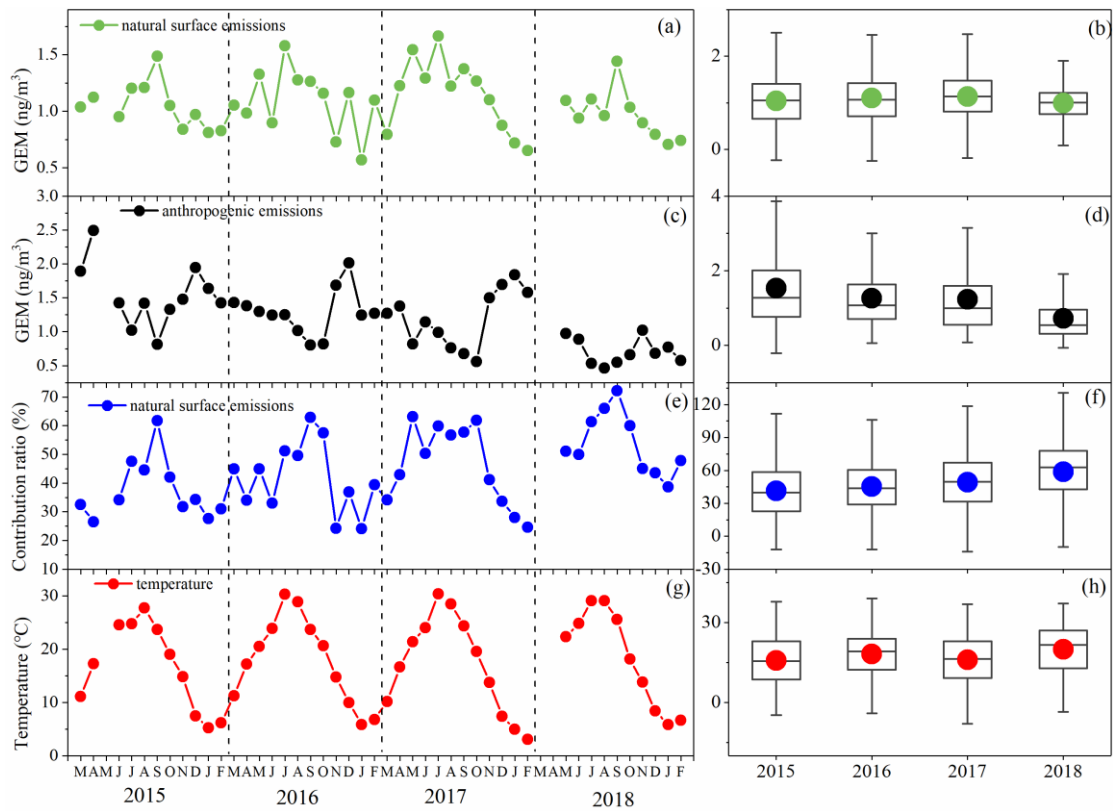
593 Figure 6. Contributions of natural surface emissions and anthropogenic sources to atmospheric

594 GEM in the four seasons during 2015 – 2018.

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599 Figure 7. The monthly and annual GEM concentrations contributed by natural surface emissions (a-
 600 b) and anthropogenic emissions (c-d) from 2015 to 2018. (e-f) The monthly and annual contribution
 601 of natural surface emissions to GEM concentrations from 2015 to 2018. (g-h) The corresponding
 602 ambient temperature from 2015 to 2018.