1　**Impacts of Large-Scale Circulation on Urban Ambient Concentrations**
2　**of Gaseous Elemental Mercury in New York, USA**

3　Huiting Mao[1][†], Dolly Hall[2], Zhuyun Ye[1], Ying Zhou[1], Dirk Felton[3], and Leiming Zhang[4]

4　[1]Department of Chemistry, State University of New York College of Environmental Science and
5　 Forestry, Syracuse, NY 13210
6　[2]Department of Atmospheric and Oceanic Science, University of Maryland, College Park, MD
7　 20742
8　[3]Bureau of Air Quality Surveillance, Division of Air Resources, New York State Department of
9　 Environmental Conservation, Albany, NY 12233
10　[4]Air Quality Research Division, Science and Technology Branch, Environment and Climate
11　 Change Canada, Toronto, M3H 5T4, Canada

12　[†]Correspondence to: hmao@esf.edu

13

14

15   **Abstract**

16   The impact of large-scale circulation on urban gaseous elemental mercury (GEM) was

17   investigated through analysis of 2008 – 2015 measurement data from an urban site in New York

18   City (NYC), New York, USA. Distinct annual cycles were observed in 2009-2010 with mixing

19   ratios in warm seasons (i.e. spring-summer) 10-20 ppqv (~10%-25%) higher than in cool seasons

20   (i.e. fall-winter). This annual cycle was disrupted in 2011 by an anomalously strong influence of

21   the North American trough in that warm season and was reproduced in 2014 with annual

22   amplitude enhanced up to ~70 ppqv associated with a particularly strong Bermuda High. North

23   American trough axis index (TAI) and intensity index (TII) were used to characterize the effect

24   of the North American trough on NYC GEM especially in winter and summer. The intensity and

25   position of the Bermuda High had a significant impact on GEM in warm seasons supported by a

26   strong correlation (r reaching 0.96, $p<0.05$) of GEM with Bermuda High intensity indices in

27   summer. Regional influence on NYC GEM was supported by the GEM-carbon monoxide (CO)

28   correlation with r of 0.24-0.66 ($p \sim 0$) in most seasons and larger r in summers. Interannual

29   variations were found in simulated regional and local anthropogenic contributions, averaged at

30   ~75% (67%-83%) and 25% (17%-33%), respectively, to wintertime NYC anthropogenically

31   induced GEM concentrations. Results from this study suggest the possibility that the

32   increasingly strong Bermuda High over the past decades could dominate over anthropogenic

33   mercury emission control in affecting ambient concentrations of mercury via regional build-up

34   and possibly enhancing natural and legacy emissions.

35

36

37

Atmospheric
Chemistry
and Physics
Discussions

1. Introduction

Atmospheric mercury (Hg) is a prevailing pollutant that has global consequences for both human and ecosystem health, and hence Hg emission control is imperative. Mercury in the atmosphere is operationally defined in three forms, gaseous elemental mercury (GEM), gaseous oxidized mercury (GOM), and particulate-bound mercury (PBM). Total gaseous mercury (TGM) is the sum of GEM and GOM. The most abundant of these three forms is GEM with a lifetime of 0.5 - 1 year (Driscoll et al., 2013) and mixing ratios on the order of hundreds of parts per quadrillion (ppqv) (~ a few ng m^{-3} at 1 ng m^{-3} = 112 ppqv in a standard atmosphere; unit conversion was done in a standard atmosphere hereafter) compared to GOM and PBM with lifetimes of hours to weeks and mixing ratios often on the order of single ppqv (~ a few pg m^{-3}).

The median concentration of TGM/GEM in global continental remote areas was 1.6 ng m^{-3} (180 ppqv) estimated from a large body of measurement studies (Mao et al., 2016), and the background concentration of GEM in the Northern Hemisphere was 1.5 – 1.7 ng m^{-3} (168 – 190 ppqv) (Lindberg et al., 2007). Urban concentrations of GEM/TGM in the U.S. varied over 0.05 – 324 ng m^{-3} (5.6 – 36288 ppqv) (Mao et al., 2016). In comparison, urban concentrations and their temporal variability were larger than rural, remote, and high elevation concentrations in the Northern Hemisphere (e.g., Kim and Kim, 2001; Feng et al., 2003; Denis et al., 2006; Liu et al., 2007; Peterson et al., 2009; Sprovieri et al., 2010; Zhu et al., 2012; Lan et al., 2012, 2014; Chen et al., 2013; Civerolo et al., 2014; Fu et al., 2015; Brown et al., 2015; Mao et al., 2016 and references therein) owing to numerous controlling factors including anthropogenic and legacy emissions, deposition, meteorology, transport, and atmospheric chemistry (Mao et al., 2016).

Over the United States measurements from the Atmospheric Mercury Network (AMNet) sites, located in urban, suburban, rural, and remote areas, suggested that monthly median GEM

Atmospheric
Chemistry
and Physics
Discussions
Open Access
EGU

61   mixing ratios varied from 148 to 226 ppqv (~1.32 to 2.02 ng m^{-3}) with urban values at the higher

62   end of the range (Lan et al., 2012). Urban ambient atmospheric TGM/GEM concentrations in

63   Canada on average ranged over 1.7 – 4.5 ng m^{-3} (190 – 504 ng m^{-3}) (Mao et al., 2016; reference

64   therein). Urban GEM/TGM concentrations in Asia could be an order of magnitude larger than

65   those in the U.S., Canada, and Europe (Mao et al., 2016; references therein). Many studies

66   identified local sources as a predominant factor controlling urban ambient concentrations

67   (Gabriel et al., 2005; Lyman and Gustin, 2009; Wang et al., 2013; Feng et al., 2003; Fang et al.,

68   2004; Zhu et al., 2012; Hall et al., 2014; Seo et al., 2016; Kim et al., 2016). In some urban

69   locations nighttime daily maximums and spring-summer annual peaks were attributed to local

70   and regional sources followed by boundary layer dynamics and meteorological conditions (Liu et

71   al., 2007; Cheng et al., 2009; Liu et al., 2010; Nair et al., 2012; Zhu et al., 2012). Surface

72   emissions were also suggested to play a major role in warm season annual maximums (Denis et

73   al., 2006; Zhu et al., 2012). Some sites experienced early morning daily maximums with the

74   strongest diurnal variation in summer, due possibly to local anthropogenic sources and surface

75   emissions (Stamenkovic et al., 2007; Peterson et al., 2009). Wintertime annual maximums were

76   attributed to less oxidation of GEM (Stamenkovic et al., 2007) and periods of cold and stagnant

77   air probably leading to build-up of pollution and more Hg evasion prompted by wet conditions

78   (Peterson et al., 2009). Temporal variations of GEM concentrations could be attributed to the

79   combined influence of environmental variables, anthropogenic sources, photochemistry, and

80   regional transport (Xu et al., 2014).

81   Some studies suggested that regional sources dominated over local ones in contributing to

82   urban ambient Hg concentrations (e.g., Liu et al., 2007; Kim et al., 2013; Engle et al.; 2010; Xu

83   et al., 2014; Hall et al., 2014). On interannual time scales, the impact of regional transport, in

84   comparison to local sources, could vary greatly due to large variability in atmospheric circulation

85   and subsequently affect urban ambient concentrations very differently. Additional emission

86   control is anticipated in the future associated with the Mercury and Air Toxics Standards

87   (MATS) rule and the United Nations Environment Program (UNEP) international Minamata

88   Treaty (Selin, 2014). To regulate future emissions, it is important to understand and quantify

89   contributions of local versus regional sources to urban ambient concentrations. The objective of

90   this paper is to examine the seasonal, annual, and interannual variability of GEM in the Bronx

91   Borough of New York City (NYC) and its relation with large-scale circulation, and the

92   contributions of local and regional sources to NYC ambient GEM concentrations.

93   **2. Site Description, Measurement Data, and Analysis Methods**

94   The site discussed herein is maintained by the New York State Department of

95   Environmental Conservation (NYSDEC) as a part of AMNet under the National Atmospheric

96   Deposition Program (NADP). The site is located in a densely populated area of NYC, in the

97   borough of Bronx at the Pfizer Plant Research Laboratory within the New York Botanical

98   Garden (40.8679°N, 73.8781°W). The Bronx site is in close proximity to densely populated

99   local anthropogenic sources as well as downwind of many regional sources (Fig. 1).

100   GEM was measured every 5 minutes using a Tekran (Toronto, ON) model 2537B cold

101   vapor atomic fluorescence (CVAF) analyzer with a nominal detection limit of <0.1 ng m^{-3} (~11.2

102   ppqv). The instrument was calibrated daily with an internal permeation source. The Tekran

103   system was operated according to standard operating procedures from the NADP's AMNet. The

104   AMNet site liaison performs annual site visits, which include manual injections to verify the

105   internal permeation source, and is responsible for quality assurance of the data (Civerolo et al.,

106   2014). Additional details can be found in Landis et al. (2002) and Gay et al. (2013).

Atmospheric
Chemistry
and Physics
Discussions

107   Measurement data of sulfur dioxide (SO_2), nitrogen dioxide (NO_2), carbon monoxide

108   (CO), temperature, wind direction, and wind speed were averaged hourly. The SO_2

109   measurements were taken using a TEI 43C and a 43i TLE instrument using equivalent method

110   060 and pulsed fluorescence. The NO_2 measurements were taken using a TEI 42C instrument

111   using reference method 074 and chemiluminescence and catalytic conversion. CO was measured

112   by a TEI 48C and an API 300EU instrument using reference method 054 with non-dispersive

113   infrared absorption. The technical details of the deployment of these instruments are given by

114   the NYSDEC at www.dec.ny.gov/chemical/8541.html and in the 2016 Annual Monitoring

115   Network Plan (www.dec.ny.gov/docs/air_pdf/2016plan.pdf).

116   The impact of regional and local anthropogenic sources was simulated using the NOAA

117   Hybrid Single Particle Lagrangian Integrated Trajectory model (HYSPLIT) dispersion version

118   (Draxler and Hess, 1997, 1998; Draxler, 1999; Stein et al., 2015) for the winters and summers of

119   2009 – 2015. HYSPLIT was driven by the EDAS 40 km model output over a domain extending

120   westward to OH, southward to northern VA, and northward to include New England (Fig. 10a),

121   with a total of 522 counties reporting Hg emissions that were extracted from the Environmental

122   Protection Agency's National Emission Inventory 2011 (https://www.epa.gov/air-emissions-

123   inventories/2011-national-emissions-inventory-nei-data). Two emission scenarios of 120-hour

124   forward dispersion simulations were conducted for each day of a season. One included

125   emissions from all the 522 countries, and another excluded emissions from the five boroughs in

126   NYC. The difference in NYC GEM concentrations between the two scenarios was used to

127   approximate the effect of anthropogenic emissions in NYC (denoted as local sources) versus

128   outside of NYC (denoted as regional sources) on NYC ambient Hg concentrations, not

129   considering loss in transit.

Atmospheric
Chemistry
and Physics
Discussions

130   In the analysis of the North American trough, the trough axis index (TAI) and trough

131   intensity index (TII) defined by Bradbury et al. (2002) were used to quantify the position and

132   intensity of the North American trough. The seasonal TAI quantifies the mean longitudinal

133   position of the quasi-stationary midtropospheric East Coast trough. The TAI domain extends

134   from 120°W to 30°W and the southern to northern boundaries ranged from 40°N to 50°N. The

135   TAI index was calculated by averaging the longitudinal positions (Lon) of the minimum 500-hPa

136   heights (H_{min}) observed at each of the four latitudinal steps (j=40°, 42.5°, 45°, and 47.5°N)

137   within the index range, to produce a practical index in longitudinal units (relative to the prime

138   meridian):

139                          $TAI = average\ [Lon(H_{min})_j]$

140   The TII is an estimate of wave amplitude at 42.5°N and is the mean height change at the 500-hPa

141   surface from equal distances east and west of the East Coast trough axis. It was calculated:

142                          $TII = \{[(H_{min})_i - H_{i+30°}] + [(H_{min})_i - H_{i-30°}]\}/2$

143   The more negative TII is, the stronger the influence of the North American Trough would be.

144   The 2.5° x 2.5° reanalysis data from the National Center of Environmental Protection/National

145   Center of Atmospheric Research were used to calculated seasonal average TAI and TII.

146   Additional details about TAI and TII can be found in Bradbury et al. (2002).

147   **3. Results and Discussion**

148   **3.1 General Characteristics of Diurnal, Seasonal, and Interannual Variation**

149   Five-minute average GEM mixing ratios were more often larger during the warm seasons

150   (summer-spring) than the cool seasons (fall-winter) (Fig. 2), in agreement with previous urban

151   site studies (Denis et al., 2006; Liu et al., 2007; Zhu et al., 2012; Zhang et al., 2013; Civerolo et

152   al., 2014). The annual cycles were not as distinct and reproducible as those in rural

153   environments such as southern New England, where annual maximums were found in winter and

154   minimums in fall (Mao et al., 2008; Sigler et al., 2009; Mao and Talbot, 2012).

155   Three salient features were evident in the interannual variation of a range of percentile

156   mixing ratios of GEM (Fig. 3; Table 1). First, the 2009 – 2010 cool season percentile values of

157   GEM were the lowest of all cool seasons. Second, the 2011 warm season percentile values were

158   the lowest of all warm seasons, even lower than in the cool season of the same year, not

159   reproducing the 2009 and 2010 annual cycles. Third, the 2014 and 2015 seasonal percentile

160   values were mostly the highest of the study period and for the first time since 2011, warm season

161   values exceeded the cool season ones reproducing the 2009 and 2010 annual cycles.

162   The most pronounced diurnal cycles occurred in summer, as shown in seasonal average

163   diurnal cycles in Figure 4, with a peak between 02:00 and 06:00 UTC and a minimum between

164   10:00 and 16:00 UTC, which is consistent with previous studies for urban locations (e.g. Denis et

165   al., 2006; Liu et al., 2007; Zhu et al., 2012; Lan et al., 2012). In summers of 2009 – 2012, the

166   daily maximum was ~170-190 ppqv and the daily minimum ~140-160 ppqv. In summers of

167   2014 and 2015 mixing ratios were elevated greatly throughout the day with daily peaks reaching

168   ~200 and 290 ppqv and minimums ~180 and 225 ppqv, respectively. The diurnal amplitude,

169   defined as the difference between the daily maximum and minimum, was up to ~50 ppqv in

170   summer, ~20 ppqv in fall and spring, and <10 ppqv in winter.

171   During 2008 – 2013, the cool seasons experienced much larger interannual variability of

172   GEM than the warm seasons did, whereas in 2014 and 2015 GEM concentrations were elevated

173   significantly above other years in all seasons (Fig. 4). Over 2008 - 2013, the largest interannual

174   variability up to ~40 ppqv difference was observed between the lowest GEM mixing ratios in fall

175   2009 and largest in falls 2011 and 2012, whereas springs and summers experienced much less

Atmospheric
Chemistry
and Physics
Discussions

176   interannual variability except spring and summer 2011, as aforementioned, that saw the lowest

177   GEM mixing ratios, ~ 20 ppqv lower than all other warm seasons.

178   **3.2. Interannual Variation of Cool Season GEM**

179   The 2009 – 2010 cool season exhibited the lowest percentile values whereas most of

180   winter 2014 and cool season 2014-2015 percentile values were the highest of the study period

181   (Table 1; Fig. 3). The difference in percentile values between the two cool seasons ranged from

182   33-34 ppqv in the 25th and median values to 112 ppqv in the 90th percentile value. The possible

183   effect of anthropogenic emission changes on those interannual variations in GEM concentrations

184   was the very first to be examined. EPA national emission inventories showed a 13% decrease

185   from 2008 (31810 kg) to 2011 (27695 kg), and then an increase of 2% to 2014 (28270 kg) in

186   total emissions from the Eastern US, including states east of the Mississippi River, of which

187   NYC emissions increased from 125 kg in 2008 to 145 kg in 2011 and to 199 kg in 2014

188   (https://www.epa.gov/air-emissions-inventories/2014-national-emissions-inventory-nei-data).

189   Using an average PBL height of 1000 m over the Eastern US (the surface area for the Eastern US

190   is 2.483×10^{12} m^2), a decrease of 4115 kg from 2008 to 2011 emissions was converted to ~200

191   ppqv and averaged at ~0.2 ppqv d^{-1} over all days of the three years, and an increase of 575 kg

192   from 2011 to 2014 emissions was converted to ~0.03 ppqv d^{-1}. The potential change in NYC

193   atmospheric concentrations were estimated to be ~3 ppqv d^{-1} from the 2008 – 2011 NYC

194   emission increases alone and ~6 ppqv d^{-1} from the 2011 – 2014 increase. The potential changes

195   in ambient concentrations caused by the regional emission decrease/increase were negligible

196   compared to the observed interannual difference. Those caused possibly by NYC emission

197   increases could be significant but appeared to be inconsistent with the changes in ambient

198   concentrations in two ways. First, from 2010 to 2011 NYC emissions increased and yet

Atmospheric
Chemistry
and Physics
Discussions

Open Access

EGU

199   summertime ambient concentrations decreased by 10 ppqv throughout the seasonal averaged

200   diurnal cycle (Fig. 4). Second, the observed increase from summer 2012 to summer 2014 was

201   nearly 90 ppqv throughout the seasonal averaged diurnal cycle, a factor of 15 larger than the

202   effect of the local emission rise as estimated above.

203   Legacy and natural emissions could be another driver for the observed interannual

204   variations in GEM. However, seasonal mean temperature and GEM from the Bronx location

205   were not found to be correlated, which suggested that the effect of changes in legacy and natural

206   emissions on ambient GEM might not be dominant. In addition, using Zhang et al. (2016)'s

207   estimated annual natural and reemissions 9.4 to 13.0 $\mu g\ m^{-2}$ for the Bronx site during 2009-2014,

208   the maximum year-to-year change was calculated to be ~1 ppqv d^{-1} assuming an average

209   planetary boundary layer (PBL) height of 1000 m. This change alone could not explain the

210   observed interannual variations. It alludes to the potential effect of *regional* legacy and natural

211   emissions as well as chemistry, which needs to employ modeling tools and is beyond the scope

212   of this study. Here, it was hypothesized that atmospheric circulation was the predominant factor

213   causing interannual variation in Bronx ambient GEM concentrations.

214   To validate this hypothesis, circulation patterns were examined first using the Bronx site

215   wind data. In falls 2008, 2009, 2011, and 2013, wind came from all four quadrants with

216   comparable frequency ranging over 15% - 30% of the season, whereas in fall 2010 the

217   northwesterly (270°-360°) was more frequent (37%), and the northeasterly (0°-90°) became

218   predominant (~50 – 74%) in falls 2012 and 2014 (Fig. 5a). The winters experienced

219   northwesterly winds (270°-360°) more often ranging from ~40% to 65% of the season with the

220   exception of winter 2015 when a little below 40% of the season on par with southwesterly wind

221   (180°-270°) (Fig. 5a). Wind speed was averaged seasonally for the four wind quadrants (Fig.

Atmospheric
Chemistry
and Physics
Discussions

Open Access

EGU

222   5b). The strongest wind, reaching over 3 m s^{-1}, appeared in the northwesterly (270°-360°) in

223   winter and spring from 2009 to 2013. Over 2014 and 2015 the most distinct change was

224   northwesterly wind speed being significantly reduced to a little over 2 m s^{-1}. The next in line was

225   southwesterly (180°-270°) wind hovering around 2 m s^{-1} in the cool seasons except 2009-2010

226   when it was lowered to 1 m s^{-1}, nearly halved compared to other years. Wind speed in the two

227   easterly quadrants (0°-180°) was comparable varying over 1 – 2 m s^{-1} except that in spring 2013

228   it reached 2.5 m s^{-1} and was particularly low (0.5 m s^{-1}) in the 2014 cool season.

229   Since Hg sources are mostly concentrated to the west, southwest, south, and northeast of

230   the Bronx site with much fewer sources to the northwest (Fig. 1), GEM mixing ratios would vary

231   expectedly corresponding to air masses arriving from different directions. This was clearly

232   suggested by mixing ratios of GEM averaged seasonally for the four wind quadrants (Fig. 5c).

233   Generally, seasonally averaged GEM mixing ratios were larger by ~20-50 ppqv in the two

234   southerly than those in the northerly quadrants. One exception was summer 2014 when the

235   average concentration in the northeasterly quadrant reached up to 275 ppqv, and the frequency of

236   the northeasterly was the highest at 70% with average speed less than 1 m s^{-1}. Such weak wind

237   indicated fairly calm conditions in the region and the wind direction data were not meaningful.

238   Overall, in addition to local emissions, interannual variability in the origin of the air masses

239   reaching Bronx appeared to cast significant influence on the ambient concentrations of GEM in

240   the city.

241   Two cases, the lowest percentile values in the 2009–2010 cool season and the highest in

242   2014-2015, were used to elaborate on this point. What stood out in the 2009 – 2010 cool season

243   was very low frequency (14%) of wind from the southwesterly quadrant (180°-270°) in fall 2009

244   and the largest frequency of wind from the northwesterly quadrant (67%, 270°-360°) in winter

245   2010 combined with nearly the lowest wind speed (≤ 1 m s^{-1}) in the three quadrants (0°-270°)

246   (Figs. 5a-c). This indicated that the particularly low mixing ratios in the cool season of 2009 –

247   2010 were likely caused by over 4 times more frequent influx of relatively cleaner Canadian air

248   masses and slowest southerly flow of more polluted air.

249   The second case is winter 2014 when GEM averaged in the four wind quadrants reached

250   the maximums of all time respectively (Fig. 5c). Coincidently the frequency of wind from the

251   northwesterly quadrant (270°-360°) was nearly the lowest of all cool seasons barely reaching

252   40% of the season compared to up to 67% in winter 2010 (Fig. 5a). Meanwhile, the frequency of

253   wind from the southwesterly quadrant (180°-270°) reached a high of 34% of all cool seasons,

254   and the wind speed of ~2 m s^{-1} was comparable to the northwesterly. This is a strong indication

255   of arrival of air masses rich in GEM originating from the heavy emitters in the Northeastern U.S.

256   Urban Corridor via flow nearly as frequent and as fast as the relatively clean northwesterly.

257   Winter 2015 showed similar wind patterns, also coincided with high GEM concentrations.

258   Such variations in wind direction and speed at the Bronx site can be better understood in

259   the context of large-scale circulation. The climatological 500 hPa geopotential height (GPH)

260   (1980-2010) for cool seasons during 1980-2010 exhibited the North American trough centered

261   over coastal southeastern Canada extending southwestward over the Eastern US (Fig. 6a). All

262   cool seasons experienced variations of this pattern except cool seasons 2009-2010 and 2013-

263   2014 that appeared to be anomalous (Figs. 6b and 6c). Specifically the trough in winter 2010

264   shifted eastward farthest out over the ocean and was the weakest, evidenced in the maximum

265   TAI (62°W) and nearly the least negative TII value (-80 m) (Fig. 6d). In contrast, the trough in

266   winter 2014 was situated the farthest over land and the strongest of all winters, backed by the

267   most negative TAI (85°W) and nearly the most negative TII value (-201 m) (Fig. 6d) . This

268   suggested that in winter 2010 the Northeast US was most frequently under the influence of air

269   masses from higher latitudes via flow on the backside of the North American trough whereas

270   much less so due to the East U.S. positioned near the axis to the front of the trough in winter

271   2014. This was further clearly reflected in the maps of sea level pressure (SLP) for the two

272   winters. The unusual winter 2010 circulation was signified by northerly gradient flow (Fig. 6f)

273   from the backside of the Icelandic Low, which shifted toward the south and west near

274   Newfoundland compared to its 1980-2010 climatological position right between and below

275   Greenland and Iceland (Fig. 6e). This indicated predominant transport of relatively clean air

276   from Canada combined with strong ventilation of continental pollution, likely leading to the least

277   polluted air in winter 2010 of all 7 winters. In contrast, in winter 2014 NYC appeared to be on

278   the periphery of high pressure systems in predominantly slow northwesterly and southwesterly

279   flow regimes (Fig. 6g). This explains the least frequent, lowest wind speed in the easterly wind

280   quadrants during winter 2014 (Fig. 5b), which is conducive to regional build-up of air pollution,

281   resulting in the highest mixing ratios of GEM of all winters. More evidence was shown in

282   Section 6 using modeled contributions to NYC ambient concentrations from local versus

283   regional anthropogenic sources.

284   **3.3 Interannaul Variation of Warm Season GEM**

285   **3.3.1 Annual maximums in warm seasons of 2009 and 2010**

286   The annual cycles of GEM at the Bronx site in 2009 and 2010, with larger values in

287   spring and summer (Table 1; Figs. 2 and 3), is consistent with measurements from some urban

288   and industrial locations in the literature (Lindberg and Stratton, 1998; Liu et al., 2007; Zhu et al.,

289   2012; Xu et al., 2014). Lindberg and Stratton (1998) and Liu et al. (2007) attributed such annual

290   cycles to local anthropogenic sources, while Zhu et al. (2012) and Xu et al. (2014) speculated

Atmospheric
Chemistry
and Physics
Discussions

Open Access
EGU

291   reemission from soils to be a potential dominant factor. In NYC, impervious surfaces comprise

292   95% of the total land surface (Adler and Tanner, 2013), which, considering local sources alone,

293   makes reemission of Hg from soils much less significant than anthropogenic emissions from the

294   area. Indeed no correlation between seasonal temperature and GEM was found for the Bronx

295   site as mentioned in Section 3.2. It thus seemed unlikely that NYC legacy emissions contributed

296   to the 2009 and 2010 annual cycles. The impact of regional vs. local anthropogenic sources on

297   NYC GEM concentrations was studied in Section 6, and quantifying the impact of *regional*

298   natural and legacy emissions calls for a regional modeling approach, which is beyond the scope

299   of this study. Here we focused on the potential impact of circulation on NYC GEM

300   concentrations.

301   In the warm seasons, Bronx was on the periphery of the Bermuda High in transition to

302   under the influence of the North American trough, and consequently Bronx was, as most of the

303   eastern US was, more frequently under the high pressure system influence (Figs. 7c,f), which is

304   usually lower wind speed. This is consistent with the annual cycle of wind speed shown in

305   Figure 5b, with wind mostly lower in spring-summer and higher in fall-winter conducive to

306   regional pollution build-up, which could explain why Bronx saw larger peaks of GEM in the

307   warm season than in the cool season.

3.3.2 Lowest GEM in warm season 2011 and highest in 2014

309   In examining wind in the warm season 2011, what stood out was that Bronx experienced

310   significantly increased frequency (37%) of northeasterly wind at wind speed nearly 2 m s^{-1} in

311   spring and decreased frequency of (20%) of northwesterly wind in summer compared to the

312   spring and summer in 2009 and 2010 (Fig. 5a). In summer 2014 nearly 80% of the season had

313   northeasterly wind (0°-90°) and there was unusually weak wind (~1 m s^{-1}) in all four wind

Atmospheric
Chemistry
and Physics
Discussions

314   quadrants (Figs. 5a,b), which suggested calm conditions. In summer 2011GEM concentrations

315   in the northeasterly wind quadrant were averaged ~145 ppqv, ~ 30 ppqv lower than that in the

316   most polluted southerly quadrants (Fig. 5c). In contrast, summer 2014 GEM in the northeasterly

317   quadrant was averaged 275 ppqv compared to ~160 – 200 ppqv in the other three quadrants (Fig.

318   5c). The unusually high concentration was an indication of build-up under calm conditions.

319   The anomalously increased occurrence of northeasterly wind in summer 2011 indicated

320   unusual circulation. Compared to the 1980-2010 climatology, the 500 hPa GPH in spring 2011

321   showed the weakest North American trough of all springs (Fig. S1), evidenced in the

322   westernmost trough axis position (TAI = 108°W) and the smallest intensity (TII = -27 m) of all

323   springs (Fig. 7a). The 500 hPa GPH in summer 2011 suggested the strongest North American

324   trough (TII = -87 m) and the second easternmost trough axis position (TAI = 66°W) of all

325   summers (Fig. 7b; Fig. S2). This suggested that the Northeast U.S. in summer 2011 was

326   frequently under significant influence of the backside of the trough, i.e. sweeping air flow from

327   higher latitudes subsiding to the surface in midlatitudes.

328   Near the surface, the 1980-2010 SLP climatology suggested that in spring NYC was

329   situated in the gradient flow of the Bermuda High and a trough from the Icelandic Low (Fig. 7c),

330   conducive to transport of emissions from upstream source regions such as upstate New York,

331   Ohio (OH) and Pennsylvania (PA), while in summer under the influence of the Bermuda High

332   favorable to regional build-up (Fig. 7f). However, in spring 2011, the trough of the Icelandic

333   Low gave way to the Canadian High leaving NYC locked in a zone between the Canadian High

334   and subtropical high (Fig. 7d), possibly cutting regional transport short in addition to strong

335   subsidence of cleaner higher latitudinal air leading to the lowest concentrations of GEM of all

336   springs. Similarly unusual was summer 2011 when NYC was under less influence of the

337   Bermuda High than that of the North American Trough unfavorable to regional build-up (Figs.

338   7g). These speculations appeared to be consistent with the fact that both seasons saw unusual

339   equal chances of winds from the four quadrants (Fig. 5a) over Bronx and its surrounding areas.

340   The 500 hPa TAI and TII values (Figs. 7b) and the 500 hPa GPH map in summer 2014

341   (Fig. S2) suggested the weakest North American trough (TII = -44 m) of all summers, with its

342   axis on average at 72°W, near the East Coast. This indicates that summer 2014 experienced the

343   strongest influence of the Bermuda High on the East Coast (Figs. 7e,h) of all summers during the

344   study period, the polar extreme of the 2011 warm season. Corresponding to that, the summer

345   2014 SLP map (Fig. S4) exhibited the Bermuda High ridge over the Eastern U.S. more north-

346   extending than in other years, which is consistent with weak winds in all directions as shown in

347   Fig. 5b. This dynamic situation led to regional build-up conducive to the highest GEM mixing

348   ratios in all wind quadrants.

349   To be quantitative, domain (25°N-50°N, 95°W-70°W) average SLP was used as an

350   indicator to gauge the influence of the Bermuda High, and the number of grids with SLP

351   exceeding 1014 hPa over the domain, the northernmost latitude, and westernmost longitude of

352   the 1014 hPa isobar were used to gauge the horizontal spatial extent of the influence of the

353   Bermuda High. These four indices for the summers of 2009 – 2015 were plotted together with

354   summertime median mixing ratios of GEM in Figure 8. The summertime median mixing ratio of

355   GEM was correlated with the four indices at r ranging over $0.84 – 0.96$ ($p = 0.06 – 0.009$), best

356   correlated with the northernmost latitude that the 1014 hPa isobar reached at $r=0.96$ ($p=0.009$).

357   The lowest GEM in summer 2011 was associated with the weakest influence of the Bermuda

358   High indicated by its smallest spatial extent, reflected in the lowest domain averaged SLP (1013

359   hpa), the fewest grids with SLP > 1014 hPa (44), and the southernmost latitude (37°N) the 1014

16

Atmospheric
Chemistry
and Physics
Discussions

360   hPa isobar reached. The trough over the East Coast reached its southernmost point down to

361   North Carolina compared to other summers (Fig. S4), indicating more widespread influence of

362   relatively clean Canadian air on the Eastern US sweeping out the heavily polluted air in the

363   region. One may argue that the positive correlations shown above appeared to be driven by one

364   point in summer 2014, due to missing/unavailable data in summers 2013 and 2015. It should be

365   noted that the dramatic increase in GEM in summer 2014 needs to be put in the perspective of

366   the seasons proceeding and following summer 2014, when GEM was increased consistently in

367   seasons from winter 2014 through spring 2015 compared to all previous years. Therefore, the

368   large increase in summer 2014 was most likely not fortuitous, and more importantly such

369   increases were consistent with the driving physical mechanisms as suggested in the large scale-

370   circulation.

371   It should be noted that the seasonal median GEM values in the four wind quadrants

372   exhibited trends largely consistent with those in the overall seasonal values (r=0.71 – 0.93, $p \sim 0$),

373   and the ones in the more polluted southerly quadrants were slightly more so (r=0.93, $p \sim 0$) (Fig.

374   5c). This suggests that changes in ambient mixing ratios occurred in air masses coming from all

375   directions, whether they were from the relatively clean northwest and northeast, or the heavily

376   polluted regions southeast and southwest of Bronx. This was perhaps because the lifetime of

377   GEM is long enough for air from all wind directions to be regionally mixed. Overall, the fact

378   that the GEM values in the two relatively more polluted quadrants were correlated with the

379   overall values suggested that the trend in the ambient GEM mixing ratio was possibly associated

380   in large part with changes in anthropogenic emissions.

381   **4. Relationships Between GEM and Anthropogenic Tracers**

382   Correlations between Hg and several tracers (e.g., CO, SO_2, and NO_2) have been

383   commonly used to identify Hg anthropogenic sources, source-receptor relationships, and/or

384   emission ratios. The linear correlation between CO and GEM, especially in winter, in rural

385   locations despite their different sources, reflects their emission ratios in regionally well-mixed air

386   masses (e.g., Mao et al., 2008). At the Bronx site, seasonal GEM and CO were found to be

387   correlated with r up to 0.66 ($p{\sim}0$) in all seasons over 2008 -2013, indicating significant, year-

388   round *regional* influence, and the two were notably not correlated in all the seasons from winter

389   2014 through spring 2015. Over 2008 – 2013 r^2 values of GEM-CO were larger in warm than in

390   cold seasons with the maximums exceeding 0.40 in spring 2010 and winter – summer 2011(Fig.

391   9). The slope value varied from the smallest (${\sim}0.14$ ppqv ppbv^{-1}) in spring-summer 2010 to the

392   largest (0.21 ppqv ppbv^{-1}) in summer 2012 (Fig. 9), close to and higher than the upper end of the

393   range, 0.06 – 0.14 ppqv ppbv^{-1}, from rural southern New Hampshire (NH) during winters 2004 –

394   2007 (Mao et al., 2008). This was greatly different from the GEM-CO correlation in rural

395   southern NH in winter only due to confounding factors such as legacy emissions and wet

396   deposition in summer (Mao et al., 2008; Lombard et al., 2011). Bronx experiencing more

397   significant GEM-CO correlation in warm seasons indicated better regionally mixed air masses,

398   influenced predominantly by anthropogenic emissions, than in cool seasons. This is consistent

399   with the cool and warm seasonal circulation patterns as discussed in Sections 3.2 and 3.3, which

400   is that in warm seasons NYC was predominantly under the influence of the subtropical high

401   conducive to regional mixing and build-up of pollutants.

402   No correlation between GEM and CO over 2014 – 2015 could be due in part to the more

403   dramatic emission reductions in CO than changes in GEM in the Eastern U.S. The high

404   percentile values of CO at the Bronx site had been affected by anthropogenic emission

405   reductions over the years, while the 10th and 25th percentile values remained fairly constant in all

Atmospheric
Chemistry
and Physics
Discussions
Open Access
EGU

406   seasons (Fig. S5). Zhou et al. (2015) suggested that baseline CO in Northeastern US rural areas

407   was controlled by a multitude of factors including global biomass emissions, large-scale

408   circulation, and cyclone activity. At the Bronx site, the low percentile value, close to regional

409   baseline levels, was possibly determined by a range of factors, whose importance could have

410   varied from year to year.

411   Unlike previous studies (e.g., Jen et al., 2013; Choi et al., 2013), GEM at the Bronx site

412   was found hardly correlated with SO_2 while somewhat to moderately correlated with NO_2 ($r =$

413   $0.22 - 0.64$, $p<0.0001$) (Table 2), despite abundant sources co-emitting GEM, SO_2, and NO_2

414   locally and upwind. In addition to different lifetimes, different magnitude and timing of

415   emission reduction implementations and source types of the three compounds could have

416   affected their relation. Total Hg anthropogenic emissions in NYC were increased by 16% from

417   2008 to 2011, mainly in miscellaneous non-industrial NEC and waste disposal emissions, and

418   further increased by 37% from 2011 to 2014 primarily in fuel combustion. As aforementioned,

419   emissions of Hg in the Eastern U.S. decreased by 13% from 2008 to 2011 and increased by 2%

420   from 2011 to 2014.   In contrast, total SO_2 emissions in NYC decreased steadily by 30% from

421   2008 to 2011 followed by a further decrease of 43% to 2014, while over the Eastern U.S

422   decreased by 48% from 2008 to 2011 and furthered by another 29% decrease in 2014. The effect

423   of these decreases in SO_2 emissions was reflected in the Bronx data, with a 58% decrease in the

424   seasonal median mixing ratio of SO_2 from 9.2 ppbv in winter 2009 to 2.8 ppbv in winter 2015

425   (Fig. S6). As for NO_2, fuel and mobile combustion emissions comprised >99.5% of the total

426   NO_x emissions in NYC and ~90% over the Eastern US. NYC NO_x emissions changed

427   insignificantly (1%) from 2008 to 2011 and by 15% from 2011 to 2014, while Eastern US

428   mobile and fuel combustion emissions were decreased by 16% and 33%, respectively, from 2008

Atmospheric
Chemistry
and Physics
Discussions

Open Access

EGU

429   to 2011, and further decreased by 13% and 9%, respectively, to 2014. These varying changes

430   possibly contributed to confounding the emission signature of GEM vs. NO_x and altered that of

431   GEM vs SO_2.

432   The effect of local emissions can be accentuated by the correlation between GEM and

433   SO_2 and between GEM and NO_2 for the SO_2 and NO_2 mixing ratios exceeding their respective

434   seasonal 95th percentile concentrations. However, nearly no correlation between GEM and SO_2

435   as well as between GEM and NO_2 was found in this subset of data (Table 2). It should therefore

436   be cautioned that tracer correlation could not be used to identify source types of GEM or

437   estimate emission ratios of GEM to SO_2 or NO_2 in NYC.

438   **5. Regional vs. Local Contributions to NYC Ambient GEM Concentrations**

439   HYSPLIT dispersion simulations were used to obtain a quantitative comparison of the

440   effects of sources outside and inside NYC on NYC ambient concentrations of GEM.   As stated

441   in Section 2, the modeling domain extended westward to OH and southward to northern VA, and

442   northward to include New England (Fig. 10a), with a total of 522 counties reporting Hg

443   emissions. Shown in Figure 10b is the contribution, in percentage of the total contribution from

444   all anthropogenic emissions in the domain, to NYC ambient concentrations of GEM from

445   anthropogenic emissions alone from local sources, and in Figure 10c is the contribution of

446   emissions from regional anthropogenic sources. There was clearly interannual variability in the

447   contribution of local versus regional anthropogenic sources. Local emissions averaged a

448   contribution of 25% in all winters of 2009 – 2015 with the period minimum of 17% in winter

449   2011 and the maximum of 33% in winter 2013 (Fig. 10b).   Conversely, the contribution of

450   regional sources averaged a contribution of 75% in all winters with the largest 83% in winter

451   2011 and the lowest 67% in winter 2013 (Fig. 10c). Compared to that in the winter of the same

452   year, contributions from local sources were larger (by up to 12% in 2009) in summer 2009, 2011,

453   2012, and 2014, close in summer 2010, and 10% smaller in summer 2013 (Fig. 10b).

454   A close examination revealed largely consistent relation between NYC GEM mixing

455   ratios and source contributions. As suggested in Section 3.2, Bronx in winter 2010 experienced

456   the lowest concentrations of GEM in all percentile values, and yet, interestingly the simulated

457   local contribution in winter 2010 was in the mid-range of the 7 winters. This indicates that the

458   particularly low background concentration in the sweeping northerly flow led to less regional

459   contribution to NYC Hg concentrations than regional sources would in other years. In contrast,

460   winter 2014 saw the highest 25th, 50th, 75th, and 90th percentile concentrations of GEM, and yet

461   the contribution of local sources (~22%) was not even higher than average (25%). As

462   aforementioned, in winter 2014 the Eastern U.S. was most likely under the least dynamic

463   conditions conducive to regional build-up of air pollution, which resulted in a higher than

464   average contribution from regional sources and conversely lower than average contribution from

465   local sources (Fig. 10c). Consistent with GEM, the lower percentile mixing ratios of CO, SO_2,

466   and NO_2 appeared to be elevated or stopped decreasing compared to those in the previous year

467   (Figs. S5,S6).

468   The HYSPLIT dispersion model simulations suggested that close to three quarters of the

469   anthropogenically induced concentration of GEM in NYC was from regional sources. It should

470   be noted that to save computational time, the simulation domain used in this study was smaller

471   than ideal. With a larger regional domain, the significance of regional anthropogenic sources

472   could be enhanced. In addition, other factors/processes might have competed with the effect of

473   anthropogenic emission reductions, such as legacy and natural emissions, deposition,

474   meteorology, and/or large-scale circulation. Nearly 90% of the model simulation domain is

Atmospheric
Chemistry
and Physics
Discussions

Open Access

EGU

475   covered by vegetation. SMOKE model output in Ye et al. (2017) suggested that the ratio of

476   anthropogenic to legacy and natural emissions was 0.3 over the domain. Legacy and natural

477   emissions could become dominant under warmer and wetter conditions in summer. Moreover,

478   Hg deposition could be impacted by changes in physical parameters such as light, temperature,

479   and plant species (Rutter et al., 2011). Indeed changes of -30% to 50% in Hg deposition were

480   simulated for the Eastern US from the 2000s to the 2050s due to changes in precipitation

481   (Megaritis et al., 2014). Net GEM surface emissions were estimated to be dominant in summer

482   and net dry deposition in other seasons at majority of AMNet monitoring sites in eastern North

483   America (Zhang et al., 2016). Since Hg deposition and legacy emissions are closely linked,

484   these studies indicate potential changes in legacy emissions in response to variable

485   meteorological conditions and changing climate with subsequent effects on atmospheric Hg

486   concentrations.   Therefore, with legacy and natural emissions accounted for, regional

487   contributions to NYC ambient Hg concentrations would be even more dominant.

488   **6. Summary**

489   For the Bronx site in NYC, distinct annual cycles of GEM were found in 2009 and 2010

490   with higher concentrations in warm than in cool seasons by 10 – 20 ppqv (~10% – 25%),

491   consistent with urban annual cycles reported in the literature. This annual cycle was not

492   reproduced in 2011 with anomalously low concentrations in the warm season and occurred again

493   in 2014 with significantly enhanced annual amplitude up to ~70 ppqv. Such temporal variability

494   in the urban GEM concentration was found to be driven by that in large-scale circulation.

495   Seasonal median mixing ratios of GEM was found to be correlated with both the North

496   American TAI and TII in winter and with TII in summer. Further, the intensity and position of

497   the Bermuda High pressure system had a significant impact on Bronx GEM concentrations in

Atmospheric
Chemistry
and Physics
Discussions

498   warm seasons. This was evidenced in the strong correlation ($r = 0.84 - 0.96$, $p = 0.06 - 0.009$) of

499   seasonal median mixing ratios of GEM with four Bermuda High intensity indices, best correlated

500   at $r=0.96$ ($p=0.009$) with the northernmost latitude that the 1014 hPa isobar reached. The year of

501   2014 experienced anomalously strong influence of the Bermuda High resulting in the largest

502   GEM mixing ratios of the entire study period in all percentile values throughout the year. The

503   regional influence on GEM concentrations in Bronx was corroborated by significant, year-round

504   GEM-CO correlation (r up to 0.66, $p \sim 0$) over 2008 - 2013. This correlation disappeared

505   completely from winter 2014 through spring 2015 possibly resulting from their very different

506   emission changes in the Eastern U.S.

507   HYSPLIT dispersion model simulations suggested that regional sources outside of NYC

508   contributed to ~75% (67% - 83%) of the anthropogenic portion of the ambient GEM

509   concentration and NYC emissions the remaining ~25% (17% - 33%). Significant interannual

510   variation in the regional and local contributions was found to be consistent with that in large-

511   scale circulation. The fact that there was no clearly defined trend in GEM concentrations at the

512   Bronx site during the study period, despite decreases anthropogenic emission reductions in the

513   Eastern U.S. from 2008 to 2014, suggested that other factors/processes, such as large-scale

514   circulation and legacy/natural emissions, might have dominated over anthropogenic emission

515   reductions.

516   The North Atlantic Subtropical High over $1978 - 2007$ had reportedly become more

517   intense, and its western ridge had displaced westward with an enhanced meridional movement

518   (Li et al., 2011). The increasing intensity and spatial extent of the high pressure system could

519   cast a strong influence on the Northeastern US with subsequent effect on ambient concentrations

520   of Hg via regional build-up and changing legacy emissions. This could dominate over the effect

Atmospheric
Chemistry
and Physics
Discussions

521   of anthropogenic emission reductions, as suggested by this study. Indeed Zhu and Liang (2013)

522   recommended that strong decadal variations in the Bermuda High should be considered in the

523   U.S. air quality dynamic management. Therefore controlling urban ambient concentrations of

524   Hg needs to account for the overall impact of multiple factors, which may not be dominated by

525   emission reductions.

526   **Acknowledgments**

534   **References**

535   Adler, F. R., and Tanner, C. J.: Urban Ecosystems: Ecological Principles for the Built

536   Environment, 353 pages, Cambridge University Press; 1st edition, 2013.

537   Bradbury, J. A., Keim, B. D., and Wake, C. P.: U.S. East Coast Trough Indices at 500 hPa and

538   New England Winter Climate Variability, J. Clim., 15, 3509-3517, 2002.

539   Brown, R. J. C., Goddard, S. L., Butterfield, D. M., Brown, A. S., Robins, C., Mustoe, C. L., and

540   McGhee, E. A.: Ten years of mercury measurement at urban and industrial air

541   quality monitoring stations in the UK, Atmos. Environ., 109, 1-8, 2015.

542   Chen, L., M. Liu, Z. Xu, R. Fan, J. Tao, D. Chen, D. Zhang, D. Xie, and J. Sun: Variation trends

543   and influencing factors of total gaseous mercury in the Pearl River Delta - A highly

Atmospheric
Chemistry
and Physics

Discussions

Open Access

EGU

544   industrialized region in South China influenced by seasonal monsoons, Atmos. Environ., 77,

545   757-766, 2013.

546   Cheng, I., Lu, J., and Song, X.: Studies of potential sources that contributed to atmospheric

547   mercury in Toronto, Canada, Atmos. Environ., 43, 6145–6158, 2009.

548   Choi, H., Huang, J., Mondal, S., and Holsen, T. M.: Variation in concentrations of three mercury

549   (Hg) forms at a rural and a suburban site in New York State, Sci. Total Environ., 448, 96-

550   106. doi:10.1016/j.scitotend.2012.08.052, 2013.

551   Civerolo, K. L., Rattigan, O. V., Felton, D. H., Hirsch, M. J., and DeSantis, S.: Mercury wet

552   deposition and speciated air concentrations from two urban sites in New York State;

553   temporal patterns and regional context, Aeros. Air Qual. Res.,

554   doi:10.4209/aaqr.2014.03.0052, 2014.

555   Denis, M. S., Song, X., Lu, J. Y., and Feng, X.: Atmospheric gaseous elemental mercury in

556   downtown   Toronto,   Atmos.   Environ.,   40(21),   4016-4024,

557   doi:10.1016/j.atmosenv.2005.07.078, 2006.

558   Draxler, R. R. (1999), HYSPLIT4 user's guide, NOAA Tech. Memo. ERL ARL-230, NOAA Air

559   Resources Laboratory, Silver Spring, MD.

560   Draxler, R. R., and Hess, G. D.: An overview of the HYSPLIT_4 modeling system of

561   trajectories, dispersion, and deposition, Aust. Meteor. Mag., 47, 295-308, 1998.

562   Draxler, R. R., and Hess, G. D.: Description of the HYSPLIT_4 modeling system, NOAA Tech.

563   Memo. ERL ARL-224, NOAA Air Resources Laboratory, Silver Spring, MD, 24 pp, 1997.

564   Driscoll, C. T., Mason, R. P., Chan, H. M., Jacob, D. J., and Pirrone, N.: Mercury as a global

565   pollutant: sources, pathways, and effect, Environ. Sci. Technol., 47, 4967–4983, 2013.

Atmospheric
Chemistry
and Physics
Discussions

566   Engle, M. A., Tate, M. T., Krabbenhoft, D. P., Schauer, J. J., Kolker, A., Shanley, J. B., and

567   Bothner, M. H.: Comparison of atmospheric mercury speciation and deposition at nine sites

568   across central and eastern North America, J. Geophys. Res.-Atmos., 115,

569   doi:10.1029/2010JD014064, 2010.

570   Fang, F., Wang, Q., and Li, J.: Urban environmental mercury in Changchun, a metropolitan city

571   in Northeastern China: source, cycle, and fate, Sci. Total Environ., 330, 159 – 170, 2004.

572   Feng, X., Tang, S., Shang, L., Yan, H., Sommar, J., and Lindqvist, O.: Total gaseous mercury in

573   the atmosphere of Guiyang, P. R. China, Sci. Total Environ., 304, 61 – 72, 2003.

574   Fu, X. W., Zhang, H., Yu, B.,Wang, X., Lin, C.-J., and Feng, X. B.: Observations of atmospheric

575   mercury in China: a critical review, Atmos. Chem. Phys., 15, 9455–9476, doi:10.5194/acp-

576   15-9455-2015, 2015.

577   Gabriel, M. C., Williamson, D. G., Brooks, S., and Lindberg, S.: Atmospheric speciation of

578   mercury in two contrasting Southeastern US airsheds, Atmos. Environ., 39, 4947–4958,

579   2005.

580   Gay, D. A., Schmeltz, D., Prestbo, E., Olson, M., Sharac, T. and Tordon, R.: The Atmospheric

581   Mercury Network: Measurement and Initial Examination of an Ongoing Atmospheric

582   Mercury Record across North America, Atmos. Chem. Phys., 13, 11339–11349, 2013.

583   Hall, C. B., Mao, H., Ye, Z., Talbot, R., Ding, A., Zhang, Y., Zhu, J., Wang, T., Lin, C. J., Fu,

584   C., and Yang, X.: Sources and dynamic processes controlling background and peak

585   concentrations of TGM in Nanjing, China, Atmosphere, 5(1), 124-155, 2014.

586   Jen, Y.-H., Yuan, C.-S., Hung, C.-H., Ie, I.-R., and Tsai, C.-M.: Tempospatial Variation and

587   Partition of Atmospheric Mercury during Wet and Dry Seasons at Sensitivity Sites within a

588   Heavily Polluted Industrial City, Aeros. Air Quality Res., 13, 13-23, 2013

Atmospheric
Chemistry
and Physics
Discussions

589   Kim, K. H., and Kim, M. Y.: The temporal distribution characteristics of total gaseous mercury

590   at an urban monitoring site in Seoul during 1999–2000, Atmos. Environ., 35, 4253–4263,

591   2001.

592   Kim, K. H., Yoon, H. O., Brown, R. J., Jeon, E. C., Sohn, J. R., Jung, K., Park, C. G., and Kim,

593   I. S.: Simultaneous monitoring of total gaseous mercury at four urban monitoring stations in

594   Seoul, Korea, Atmos. Res., 132, 199-208, 2013.

595   Kim, K.-H., Brown, R. J., Kwon, E., Kim, I.-S., and Sohn, J.-R.: Atmospheric mercury at an

596   urban station in Korea across three decades, Atmos. Environ., 131, 124-132, 2016.

597   Landis, M. S., Stevens, R. K., Schaedlich, F. and Prestbo, E. M.: Development and

598   Characterization of an Annular Denuder Methodology for the Measurement of Divalent

599   Inorganic Reactive Gaseous Mercury in Ambient Air. Environ. Sci. Technol., 36, 3000–

600   3009, 2002.

601   Lan, X., Talbot, R., Castro, M., Perry, K., and Luke, W.: Seasonal and diurnal variations of

602   atmospheric mercury across the US determined from AMNet monitoring data, Atmos. Chem.

603   Phy., 12(4), 10569-10582. doi:10.5194/acp-12-10569-2012, 2012.

604   Lan, X., Talbot, R., Laine, P., Lefer, B., Flynn, J., and Torres, A.: Seasonal and diurnal

605   variations of total gaseous mercury in urban Houston, TX, USA, Atmosphere, 5, 399–419,

606   2014.

607   Li, W., Li, L., Fu, R., Deng, Y., and Wang, H.: Changes to the North Atlantic Subtropical High

608   and Its Role in the Intensification of Summer Rainfall Variability in the Southeastern United

609   States, J. Clim., 24(5), 1499-1506, 2011.

610   Lindberg, S., Bullock, R., Ebinghaus, R., Engstrom, D., Feng, X., Fitzgerald, W., Pirrone, N.,

611   Prestbo, E., and Seigneur, C.: A synthesis of progress and uncertainties in attributing the

612   sources of mercury in deposition, *Ambio, 36*(1), 19-32, 2007.

613   Lindberg, S. E., and Stratton, W. J.: Atmospheric mercury speciation: concentrations and

614   behavior of reactive gaseous mercury in ambient air, Environ. Sci. Technol., 32, 49–57,

615   1998.

616   Liu, B., Keeler, G. J., Dvonch, J. T., Barres, J. A., Lynam, M. M., Marsik, F. J., and Morgan, J.

617   T.: Temporal variability of mercury speciation in urban air, Atmos. Environ., 41(9), 1911-

618   1923. doi:10.1016/j.atmosenv.2006.10.063, 2007.

619   Liu, B., Keeler, G. J., Dvonch, J. T., Barres, J. A., Lynam, M. M., Marsik, F. J., and Morgan, J.

620   T.: Urban-rural differences in atmospheric mercury speciation, Atmos., Environ., 44, 2013-

621   2023, 2010.

622   Lyman, S. N., and Gustin, M. S.: Determinants of atmospheric mercury concentrations in Reno,

623   Nevada, USA, Sci. Total Environ., 408(2), 431-438, 2009.

624   Lombard, M. A. S., Bryce, J., Mao, H., and Talbot, R.: Mercury deposition in southern New

625   Hampshire, 2006 - 2009, Atmos. Chem. Phys., 11, 7657–7668, www.atmos-chem-

626   phys.net/11/7657/2011/doi:10.5194/acp-11-7657-2011, 2011.

627   Mao, H., Talbot, R., Sigler, J. M., Sive, B. C., and Hegarty, J. D.: Seasonal and diurnal variation

628   in Hg° over New England, Atmos. Chem. Phys., 8, 1403-1421, 2008.

629   Mao, H., and Talbot, R.: Long-term variation in speciated mercury at marine, coastal and inland

630   sites in New England: Part I Temporal Variability, Atmos. Chem. Phys.,12, 5099-5112,

631   doi:10.5194/acp-12-5099-2012, 2012.

632   Mao, H., Cheng, I., and Zhang, L.: Current understanding of the driving mechanisms for

633   spatiotemporal variations of atmospheric speciated mercury: a review, Atmos. Chem. Phy.,

634   16, 1–28, 2016, www.atmos-chem-phys.net/16/1/2016/, doi:10.5194/acp-16-1-2016, 2016.

Atmospheric
Chemistry
and Physics
Discussions

635   Megaritis, A. G., Murphy, B. N., Racherla, P. N., Adams, P. J., Pandis, S. N., Impact of climate

636   change on mercury concentrations and deposition in the eastern United States, Sci. Total

637   Environ. , 487, 299-312, doi: 10.1016/j.scitotenv.2014.03.084, 2014.

638   Nair, U. S., Wu, Y., Walters, J., Jansen, J., Edgerton, E. S.: Diurnal and seasonal variation of

639   mercury species at coastal-suburban, urban, and rural sites in the southeastern United States,

640   Atmos. Environ., 47, 499-508, 2012.

641   Peterson, C., Gustin, M., and Lyman, S.: Atmospheric mercury concentrations and speciation

642   measures from 2004 to 2007 in Reno, Nevada, USA, Atmos. Environ., 43(30), 4646-4654.

643   doi:10.1016/j.atmosenv.2009.04.053, 2009.

644   Rutter, A. P., Schauer, J. J., Shafer, M. M., Creswell, J., Olson, M. R., Clary, A., Robinson, M.,

645   Parman, A. M., and Katzman, T. L.: Climate Sensitivity of Gaseous Elemental Mercury Dry

646   Deposition to Plants: Impacts of Temperature, Light Intensity, and Plant Species, Environ.

647   Sci. Technol., 45(2), 569-575, 2011.

648   Selin, N. E.: Global change and mercury cycling: Challenges for implementing a global mercury

649   treaty, Environ. Toxicol. Chem., 33, 6, 1202–1210, 2014.

650   Seo, Y.-S., et al.: Characteristics of total gaseous mercury (TGM) concentrations in an industrial

651   complex in South Korea: impacts from local sources, Atmos. Chem. Phys., 16, 10215–

652   10228, 2016.

653   Sigler, J. M., Mao, H., and Talbot, R.: Gaseous elemental and reactive mercury in southern New

654   Hampshire, Atmos. Chem. Phys., 9, 1929-1942, 2009.

655   Sprovieri, F., Pirrone, N., Ebinghaus, R., Kock, H., and Dommergue, A.: A review of worldwide

656   atmospheric mercury measurements, Atmos. Chem. Phys., 10(17), 8245-8265.

657   doi:10.5194/acp-10-8245-2010, 2010.

Atmospheric
Chemistry
and Physics
Discussions

658   Stamenkovic, J., Lyman, S., and Gustin, M. S.: Seasonal and diel variation of atmospheric

659   mercury concentrations in the Reno (Nevada, USA) airshed, Atmos. Environ., 41, 6662–

660   6672, 2007.

661   Stein, A. F., Draxler, R. R., Rolph, G. D., Stunder, B. J. B., Cohen, M. D., and Ngan, F.:

662   NOAA's HYSPLIT atmospheric transport and dispersion modeling system, Bull. Amer.

663   Meteor. Soc., 96, 2059-2077, http://dx.doi.org/10.1175/BAMS-D-14-00110.1, 2015.

664   Wang, Y., Huang, J., Hopke, P. K., Holsen, T. M., Rattigan, O. V., Chalupa, D. C., and Utell, M.

665   J.: Effect of the shutdown of a large coal-fired power plant on ambient mercury species,

666   Chemosphere, 92, 360–367, 2013.

667   Xu, X., Akhtar, U., Clark, K., and Wang, X.: Temporal Variability of Atmospheric Total

668   Gaseous Mercury in Windsor, ON, Canada, Atmosphere, 5, 536-556,

669   doi:10.3390/atmos5030536, 2014.

670   Ye, Z., Mao, H., Hogrefe, C., Zhang, Y., and Jaegle, L.: Regional photochemical model

671   evaluation of speciated ambient mercury and mercury wet and dry deposition, to be

672   submitted to J. Adv. Model. Earth Sys. , 2017.

673   Zhang, L., Wang, S., Wang, L. and Hao, J. M.: Atmospheric mercury concentration and

674   chemical speciation at a rural site in Beijing, China: Implications of mercury emission

675   sources., *Atmos. Chem. Phys., 13*(20), 10505-10516. doi:10.5194/acp-13-10505-2013, 2013.

676   Zhang, L., et al.: The estimated six-year mercury dry deposition across North America, Environ.

677   Sci. Technol., doi: 10.1021/acs.est.6b04276, 50, 12864-12873, 2016.

678   Zhou, Y., Mao, H., Demerjian, K., Hogrefe, C., and Liu, J.: Baseline carbon monoxide and

679   ozone in the northeast US over 2001–2010, Atmos. Chem. Phys. Discuss., 15, 27253–27309,

680   2015.

Atmospheric
Chemistry
and Physics
Discussions

681   Zhu, J., Wang, T., Talbot, R., Mao, H., Hall, C. B., Yang, X., and Huang, X.: Characteristics of

682   atmospheric total gaseous mercury (TGM) observed in urban Nanjing, China, Atmos. Chem.

683   Phy., 12(24), 12103, doi:10.5194/acp-12-12103-2012, 2012.

684   Zhu, J., and Liang, X.-Z.: Impacts of the Bermuda High on Regional Climate and Ozone over the

685   United States, J. Clim., 26, 1018-1026, 2013.

686

Atmospheric
Chemistry
and Physics
Discussions

687
688
689
690
691
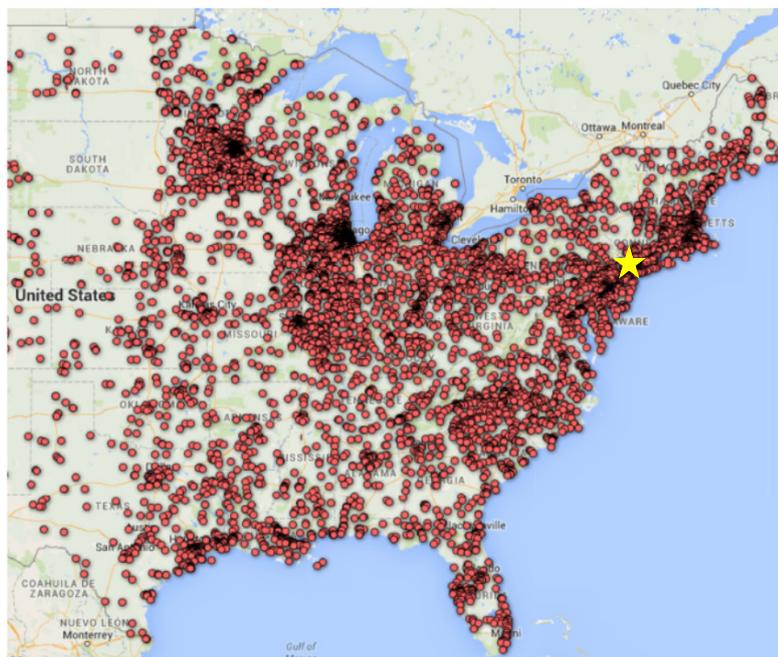
Figure 1. Map of mercury emission sources in the Eastern US.
The yellow asterisk marks the location of the Bronx site.

692

693

694

695

696
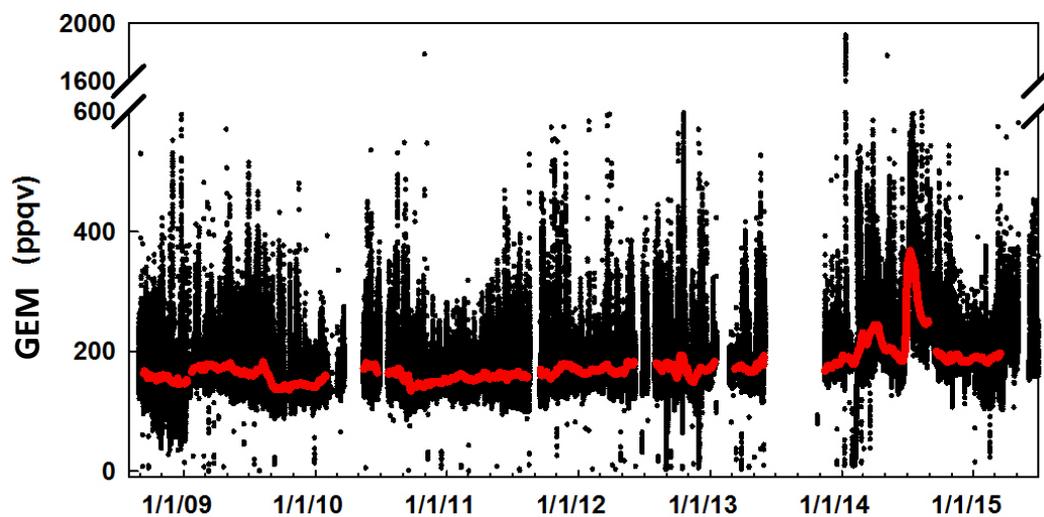
Figure 2. Time series of 5-min average GEM mixing ratios (black dots) with 30-day running average (red line) during the study period.

697   202

698

699

700

701

702

703

704

705

706

707

708

709

710

711

Figure 3. Seasonal 10th, 25th, 50th, 75th, and 90th GEM percentile values. The blue shaded
areas are the cool seasons.

712

713

714

715

716

717

718

719

Atmospheric
Chemistry
and Physics
Discussions

Figure 4. Seasonal averaged diurnal cycles of GEM for spring, summer, fall, and winter.

Atmospheric
Chemistry
and Physics
Discussions

Open Access

EGU
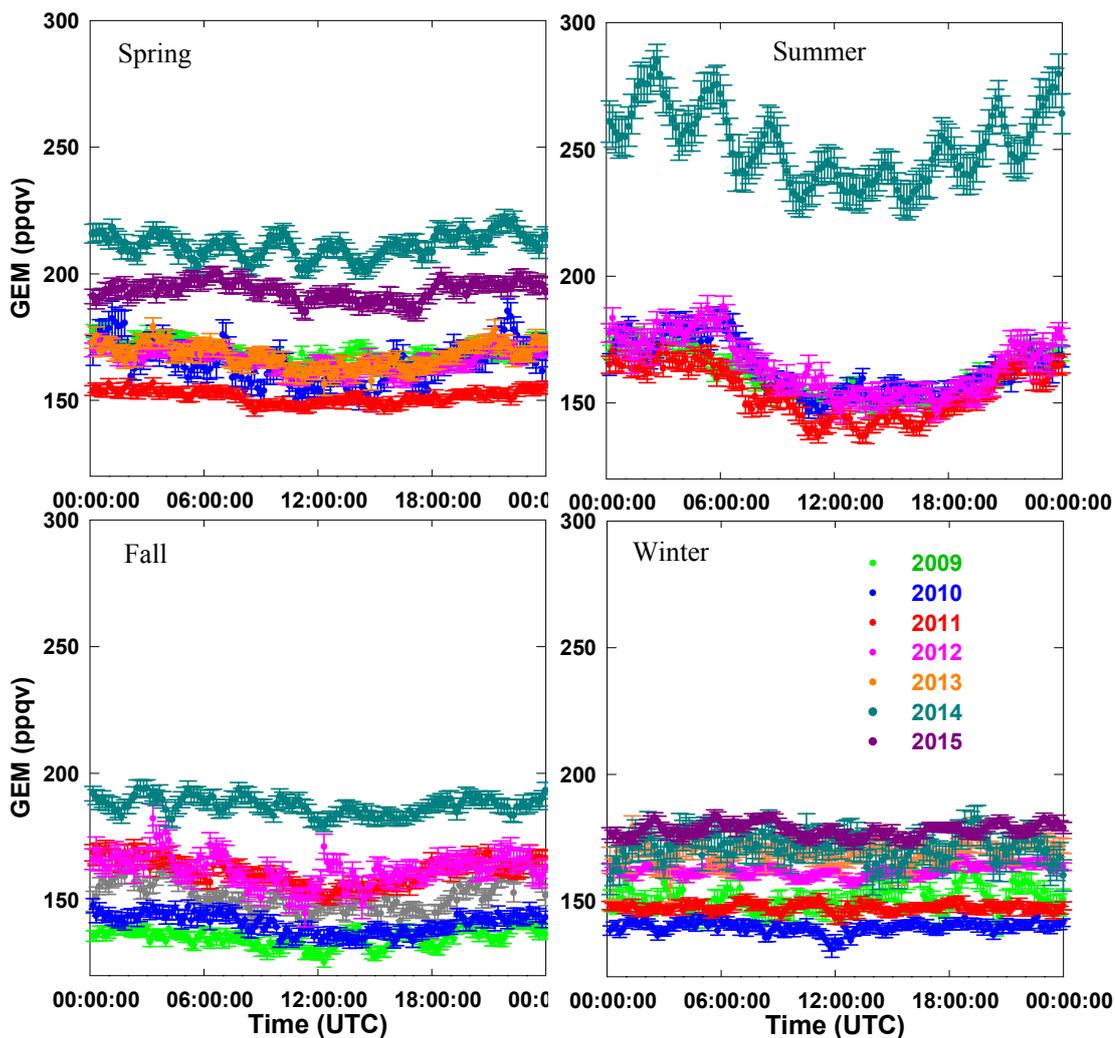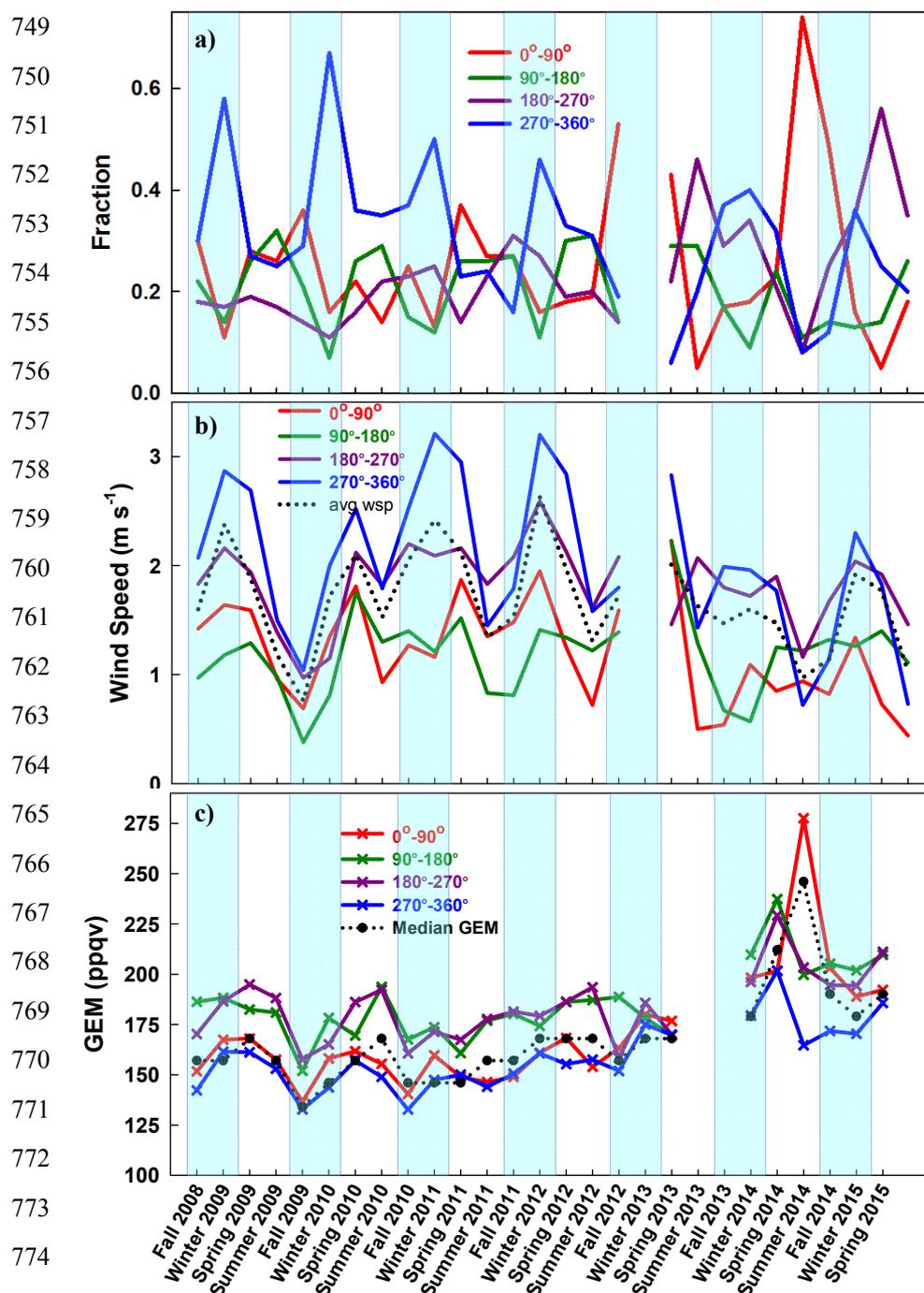
Figure 5. a) Fraction of wind coming from, b) wind speed, and c) TGM averaged
in the four wind quadrants in each season. The shaded areas indicate the cool
seasons. In b) the black dotted line indicates the wind speed averaged in all
directions. In c) the black dotted line and black solid dots represent the overall
median values of GEM.

777

778

779

780

781

782
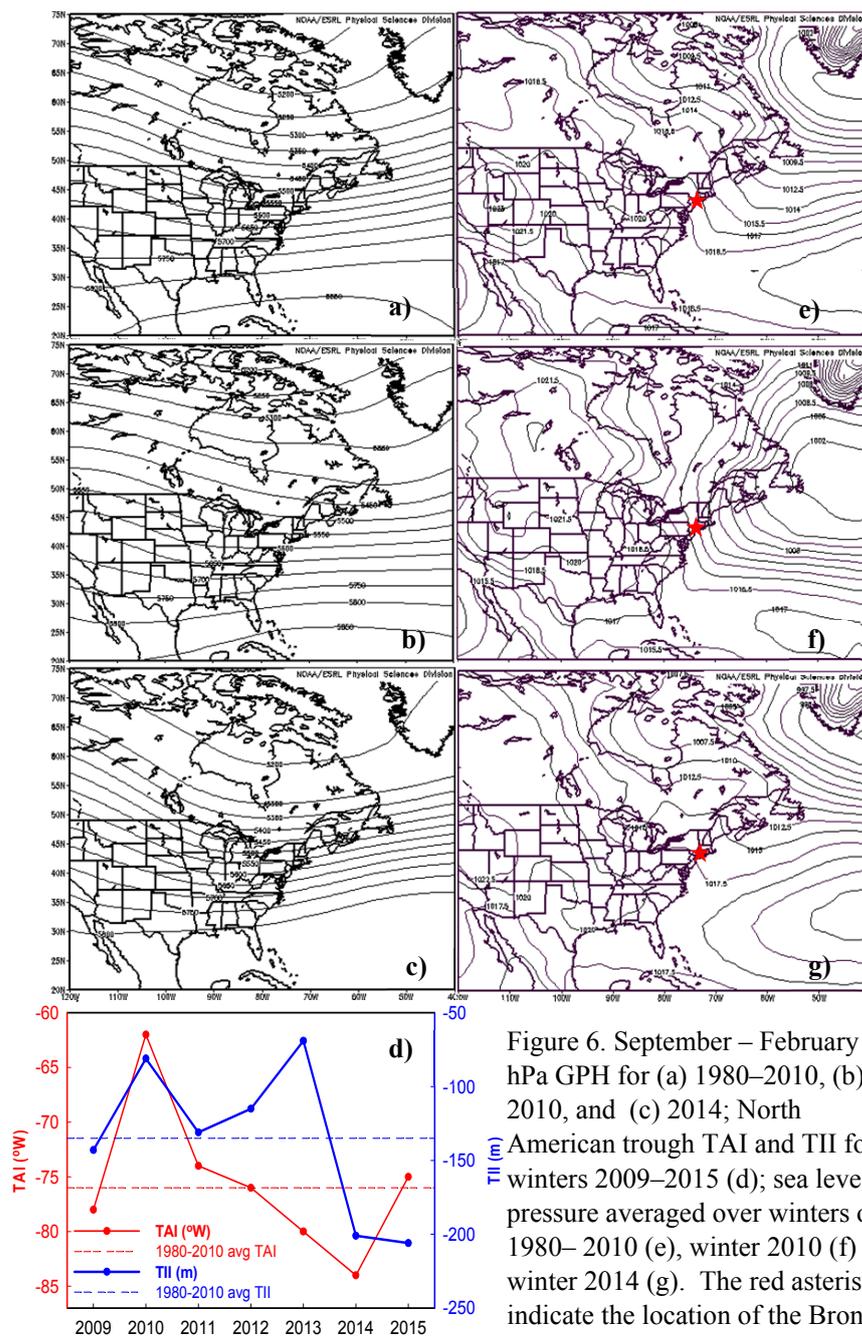
Figure 6. September – February 500 hPa GPH for (a) 1980–2010, (b) 2010, and (c) 2014; North American trough TAI and TII for winters 2009–2015 (d); sea level pressure averaged over winters of 1980– 2010 (e), winter 2010 (f) and winter 2014 (g). The red asterisks indicate the location of the Bronx site. (Courtesy: NOAA ESRL PSD Interactive Climate Analysis).

783

784

785

786

787

788

789

790

79

79

79

79

79

79

79

79

79

80

80

80

803
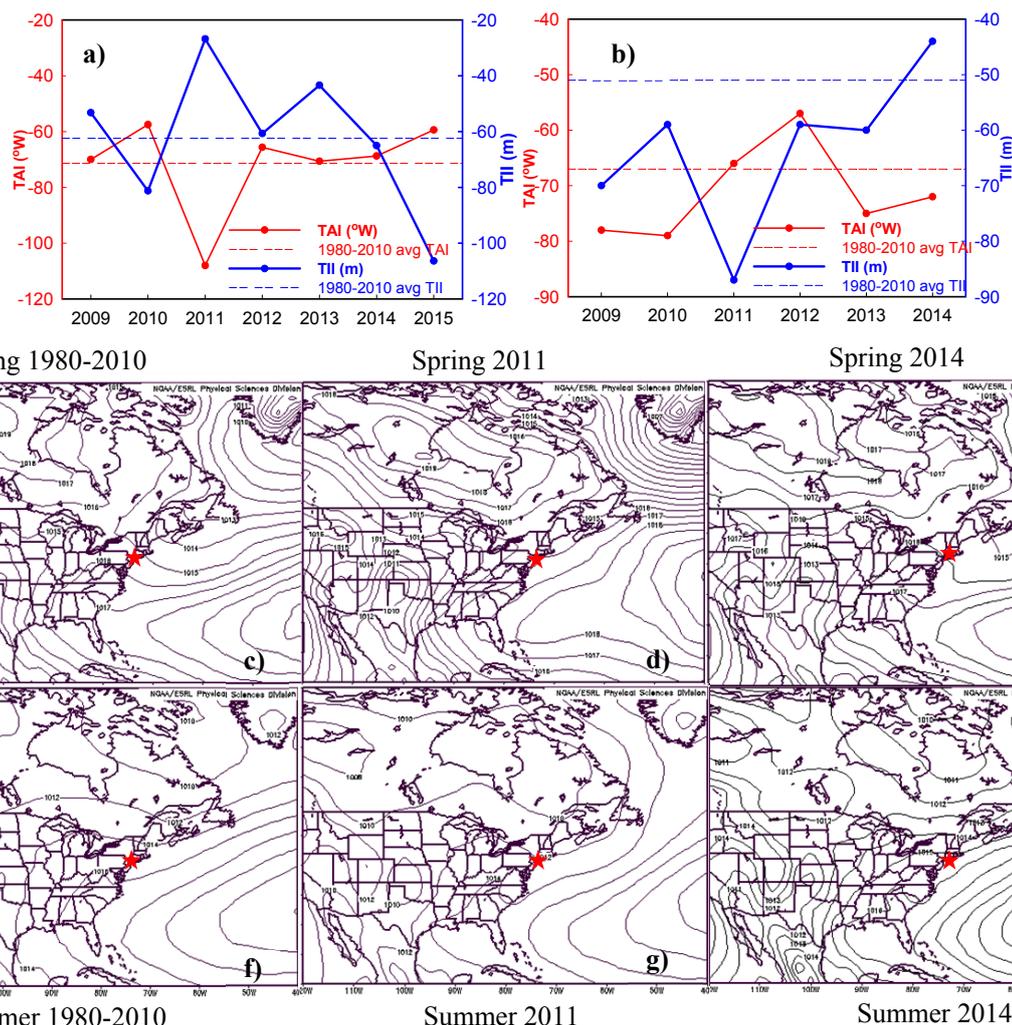
Figure 7. The axis position (TAI) and intensity (TII) of the 500 hPa North American Trough in spring (a) and summer (b). Sea level pressure (SLP) in spring (c) 1980-2010, (d) 2011, and (e) 2014. SLP in summer (f) 1980 – 2010, (g) 2011, and (h) 2014. The red asterisks indicate the Bronx site location. (Courtesy: NOAA ESRL PSD Interactive Climate Analysis)

807

808

809

810

811

812

813

814

815

816

817

818 Figure 8. Average sea level pressure (SLP) over the domain of 25°N-50°N, 95°W-
819 70°W (black), number of grids with SLP > 1014 hPa (red), the northernmost
     latitude (blue) and the westernmost longitude (magenta) the 1014 hPa SLP contour
820 reached, and seasonal median GEM mixing ratios (green) in the summer.

821

822

823

824

825

826

827

828

829

830

831
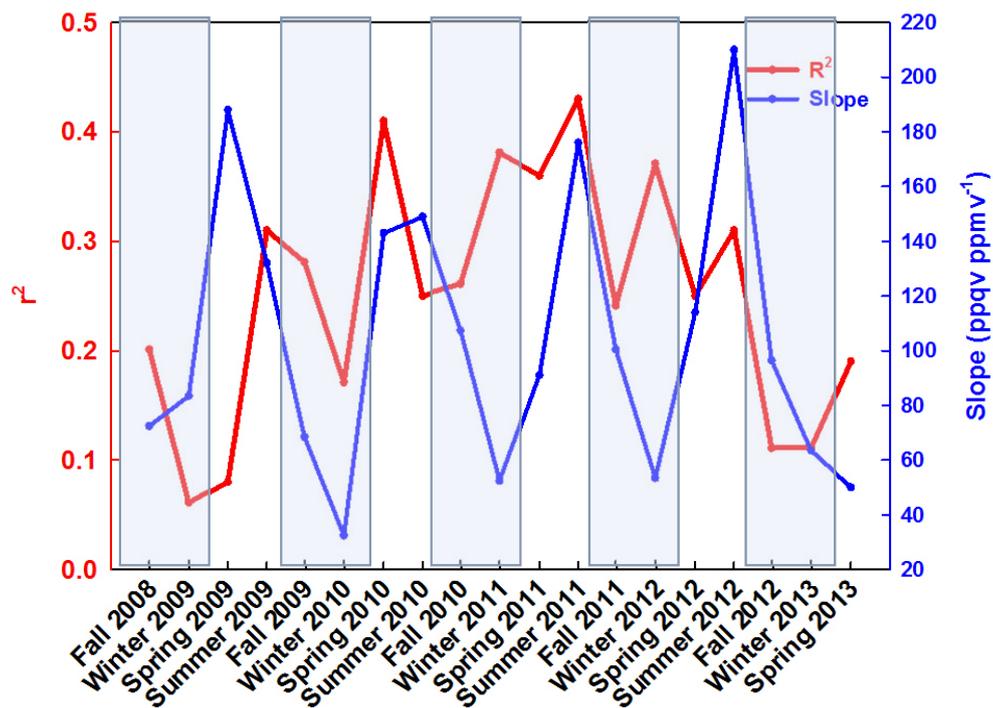
Figure 9. Values of r^2 (red) and slope (blue) of GEM-CO correlation during each season from 2008 to 2013. All r^2 values were statistically significant with p approaching 0.

832

833

834

835
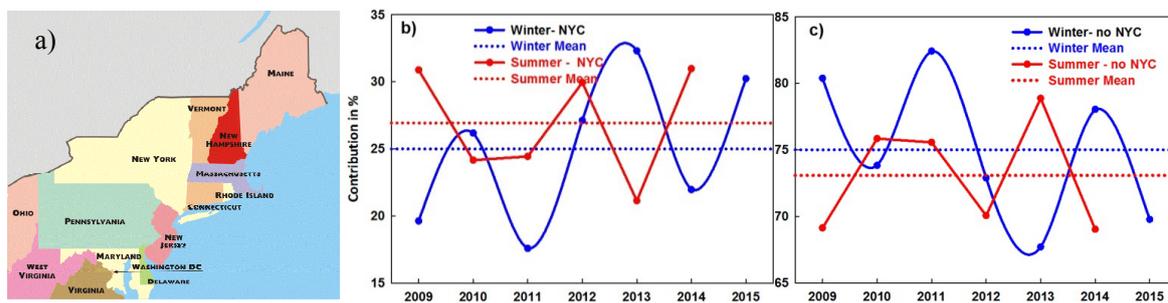
Figure 10. a) Counties and states that contributed to Hg in NYC; b) Contributions (in %) of NYC sources to NYC Hg concentrations; c) Contributions (in %) of sources outside of NYC to NYC Hg concentrations in winter (blue) and summer (red).

836 Table 1. Seasonal statistic metrics of GEM mixing ratios from the Bronx site.

		10th	25th	Median	75th	90th	Range	Sample #
2008	Fall	123	134	157	179	213	22-963	14900
2009	Winter	112	134	157	179	202	11-7302	9861
	Spring	146	157	168	190	224	11-15310	15129
	Summer	123	146	157	190	224	11-515	15577
	Fall	112	123	134	157	179	11-470	13291
2010	Winter	123	134	146	157	168	11-392	10414
	Spring	134	146	157	190	224	56-448	4383
	Summer	123	134	168	201	224	78-526	9303
	Fall	112	123	146	168	190	11-1781	12245
2011	Winter	134	134	146	168	179	11-314	15364
	Spring	134	134	146	168	190	34-784	15653
	Summer	123	134	157	179	224	22-526	12548
	Fall	134	146	157	190	224	22-3886	12949
2012	Winter	146	157	168	190	224	11-1064	15264
	Spring	134	146	168	190	224	11-1546	13888
	Summer	134	146	168	190	235	11-2766	8406
	Fall	134	142	157	190	246	11-896	13210
2013	Winter	146	157	168	190	224	11-1064	7905
	Spring	146	157	168	190	224	11-526	12124
	Summer	-	-	-	-	-	-	-
	Fall	-	-	-	-	-	-	-
2014	Winter	134	168	179	202	280	11-1915	14709
	Spring	168	190	212	246	291	34-1770	15317
	Summer	168	202	246	325	392	123-1064	13161
	Fall	157	168	190	213	246	101-538	12847
2015	Winter	157	168	179	190	213	11-381	15250
	Spring	157	179	190	224	246	101-795	11124

837

Atmospheric
Chemistry
and Physics
Discussions

838 Table 2. Pearson correlation coefficients (r) between GEM and SO$_2$ and between GEM and NO$_2$
839 with *p* values in parenthesis, for seasons during fall 2008 - spring 2015.

	All data		SO$_2$ & NO$_2$ > 95th percentile	
	SO$_2$	NO$_2$	SO$_2$	NO$_2$
Fall 2008	-0.04 (=0.0675)	0.28 (<0.0001)	0.08 (=0.471)	-0.03 (=0.810)
Winter 2009	0.14 (<0.0001)	0.29 (<0.0001)	-0.21 (=0.0877)	-0.05 (=0.687)
Spring 2009	0.08 (=0.0006)	0.22 (<0.0001)	-0.02 (=0.832)	0.09 (=0.41)
Summer 2009	0.15 (<0.0001)	0.43 (<0.0001)	0.50 (<0.0001)	0.25 (=0.0152)
Fall 2009	0.22 (<0.0001)	0.50 (<0.0001)	-0.29 (=0.0067)	-0.03 (=0.776)
Winter 2010	0.36 (<0.0001)	0.49 (<0.0001)	0.06 (=0.592)	0.07 (=0.569)
Spring 2010	0.03 (=0.549)	0.34 (<0.0001)	-0.13 (=0.507)	0.13 (=0.505)
Summer 2010	0.10 (<0.0001)	0.45 (<0.0001)	-0.07 (=0.605)	0.22 (=0.105)
Fall 2010	0.09 (=0.0005)	0.35 (<0.0001)	-0.01 (=0.929)	-0.06 (=0.567)
Winter 2011	0.44 (<0.0001)	0.64 (<0.0001)	-0.23 (=0.0267)	-0.04 (=0.670)
Spring 2011	0.01 (=0.706)	0.36 (<0.0001)	0.01 (=0.901)	0.24 (=0.0156)
Summer 2011	0.15 (<0.0001)	0.48 (<0.0001)	-0.12 (=0.285)	0.11 (=0.296)
Fall 2011	0.20 (<0.0001)	0.48 (<0.0001)	0.19 (=0.0839)	0.20 (=0.0685)
Winter 2012	0.18 (<0.0001)	0.51 (<0.0001)	0.11 (=0.285)	0.11 (=0.278)
Spring 2012	0.10 (<0.0001)	0.40 (<0.0001)	-0.12 (=0.268)	-0.16 (=0.125)
Summer 2012	0.13 (<0.0001)	0.24 (<0.0001)	-0.10 (=0.475)	0.02 (=0.903)
Fall 2012	-0.18 (<0.0001)	0.08 (=0.0005)	-0.34 (=0.0011)	-0.37 (=0.0004)
Winter 2013	0.09 (=0.0021)	0.37 (<0.0001)	-0.22 (=0.102)	-0.29 (=0.0282)
Spring 2013	-0.02 (=0.478)	0.43 (<0.0001)	0.03 (=0.786)	0.38 (=0.0004)
Summer 2013	N/A	N/A	N/A	N/A
Fall 2013	N/A	N/A	N/A	N/A
Winter 2014	-0.15 (<0.0001)	0.01 (=0.638)	-0.25 (=0.0154)	0.05 (=0.638)
Spring 2014	0.05 (=0.0167)	0.35 (<0.0001)	0.05 (=0.608)	0.05 (=0.654)
Summer 2014	0.12 (<0.0001)	0.26 (<0.0001)	-0.15 (=0.167)	0.08 (=0.449)
Fall 2014	-0.12 (=0.0001)	0.33 (<0.0001)	0.05 (=0.612)	0.05 (=0.608)
Winter 2015	0.26 (<0.0001)	0.57 (<0.0001)	0.02 (=0.835)	0.03 (=0.816)
Spring 2015	0.12 (<0.0001)	0.48 (<0.0001)	0.05 (=0.656)	0.07 (=0.557)

840
841
842
843
844
845
846