Diurnal and seasonal variation of Mercury species in the southeastern US

Yuling Wu and Udaysankar S. Nair, ESSC/ University of Alabama in Huntsville
Justin Walters and John Jansen, Southern Company
Eric Edgerton, Atmospheric Research & Analysis

1. Introduction

Health risks associated with mercury (Hg) exposure have generated a need to characterize the atmospheric input of Hg into ecosystems. While knowledge of spatial and temporal variations of atmospheric Hg species is needed for this purpose, long-term observations for such analysis are scant (Wiess-Penzias et al. 2009). This study utilizes co-incident observations of atmospheric Hg, other air pollutants and meteorological variables for the time period of 2005-2008 to characterize the spatio-temporal variation of Hg species at three different sites in the southeastern United States.

The three sites (Figure 1) considered in this study are: 1) The Outlying Landing Field (OLF), a coastal suburban location with only one known major anthropogenic source; 2) York, a rural site located ~50 km west of Atlanta, Georgia and; 3) Birmingham, Alabama an inland urban site surrounded by several, substantial anthropogenic sources.

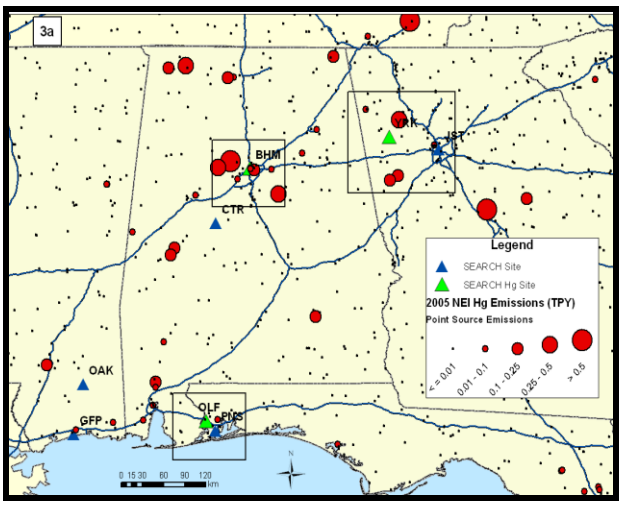

Figure 1. The locations of the three sites considered in this study are indicated by green triangles. Also shown are the major mercury emission sources identified in the 2005 National Emission Inventory (NEI) using red discs whose size is proportional to the emission strength.

2. Data and Methods

The Southeastern Aerosol Research and Characterization (SEARCH) facilities at the three study sites measure atmospheric concentrations of elemental mercury (Hg^0) and particulate mercury (HgP) every hour and reactive (oxidized) gaseous mercury (RGM) every two hours using a TEKRAN system (Landis et al. 2002, Weiss-Penzias et al. 2009). SEARCH facilities also measure concentrations of other atmospheric pollutants including O_3, NO, NO_2, HNO_3, NO_y, SO_2, CO, PM2.5, and PM10 at hourly intervals and meteorological variables including temperature, humidity, wind speed, wind direction, solar radiation, visibility, and precipitation at fifteen minute intervals. Continuous measurements of Hg species are available at OLF and BHM for the entire period of 2005 through 2008, while it is available for YRK only from 2007 onwards.

Annual and seasonal averages of diurnal patterns of Hg^0, HgP, and RGM are used to examine the overall and seasonal differences of these species at the three study sites. In order to analyze the diurnal cycle in exclusion of local emission effects, a procedure to identify the days during which plumes from local emissions impacted the measurements were developed. Examination of the measurements showed that the impact of emission sources in the vicinity are often characterized by sharp increase in concentrations of the Hg species and other co-emitted pollutants at the study sites. Days during which the measurements are impacted by the local emissions are identified using a threshold value of time rate of change of Hg concentration (6 pg m^{-3} h^{-1}). Multi-year and seasonal averages of diurnal cycles were constructed after filtering out measurements from days that were impacted by local emission events.

3. Results

3.1 Average Diurnal Variation of Hg Species

The diurnal pattern of the three Hg species averaged over the study period are similar for the OLF and YRK sites, but is substantially different at the BHM site (Figure 2a-c). The average Hg^0 concentrations exhibit a decreasing trend after midnight with minimum values being found early in the morning (~0600 LST) at both OLF and YRK, with the nocturnal minimum at OLF (1.28 ng m^{-3}) being less compared to YRK (1.32 ng m^{-3}). During daytime, the Hg^0 concentration initially increases at both sites and then remains relatively constant. However, at BHM, the decreasing trend at night and initial daytime increase of Hg^0 is followed by a steady decline that persists through the day reaching a minimum value at approximately 1700 LST. The Hg^0 concentration then increases rapidly and levels off before midnight. The annual average Hg^0 concentrations are of similar magnitude at OLF (1.35 ng m^{-3}) and YRK (1.35 ng m^{-3}) while it is substantially higher at BHM (2.12 ng m^{-3}).

The average diurnal pattern of RGM at all the sites shows the concentrations reaching a maximum around mid-day at the sites, but with substantial differences in the magnitude of the peak value. The maximum average concentration of RGM at YRK (18 pg m^{-3}) and BHM (150 pg m^{-3}) are approximately double and nineteen times the value found at the OLF site (8.5 pg m^{-3}), respectively.

The average diurnal pattern of HgP at OLF shows an increase in concentration during the daytime, followed by a decrease in the late afternoon and remains relatively constant during the night. There is very little diurnal variation of HgP at YRK. However, at BHM the HgP concentrations show a nocturnal increasing trend, reaching a maximum during the early morning hours and then decreases during the rest of the day. The annual average HgP concentration is lowest at OLF (2.5 pg m^{-3}) followed by YRK (4.4 pg m^{-3}) and is highest at BHM (~40 pg m^{-3}).

3.2 Seasonal Average Diurnal Variation of Hg Species

The seasonal average diurnal variation of Hg^0 (Figure 3a-c) at the three sites mirrors the annual average diurnal pattern. During all the seasons, a daytime increase in Hg^0 and nocturnal decreasing trend is observed at both the OLF and YRK sites. A daytime decrease of Hg^0 is also found at the BHM site during all the seasons. However, the average Hg^0 concentration at OLF and YRK is higher during spring (1.39 and 1.45 ng m^{-3}) and winter (1.41 and 1.39 ng m^{-3}) compared to summer (1.26 and 1.31 ng m^{-3}) and fall (1.30 and 1.25 ng m^{-3}). At BHM, the summer (2.22 ng m^{-3}) and spring (2.20 ng m^{-3}) average Hg^0 concentrations are similar and higher than that during fall (2.09 ng m^{-3}) and winter (1.97 ng m^{-3}).

The average RGM concentrations at all the sites are highest during the spring season and at a minimum in the summer. While the average diurnal patterns of RGM at OLF and YRK show a relatively smooth variation, the BHM site exhibits rapid variations (Figure 3d-3f), especially during fall and spring.

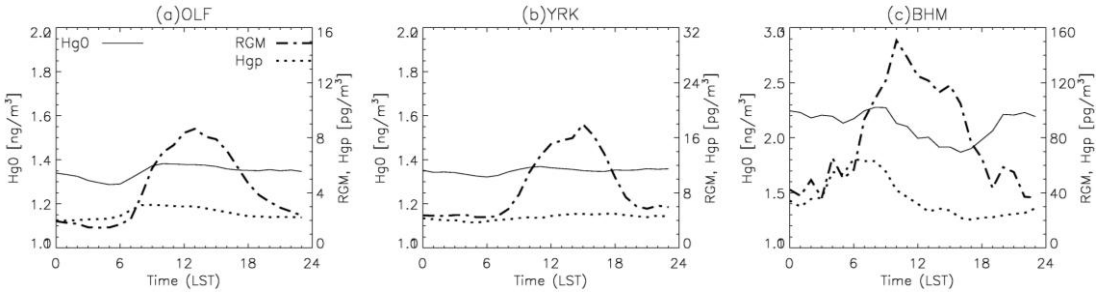

Figure 2. Average diurnal variation of mercury species at (a) OLF, (b) YRK, and (c) BHM.

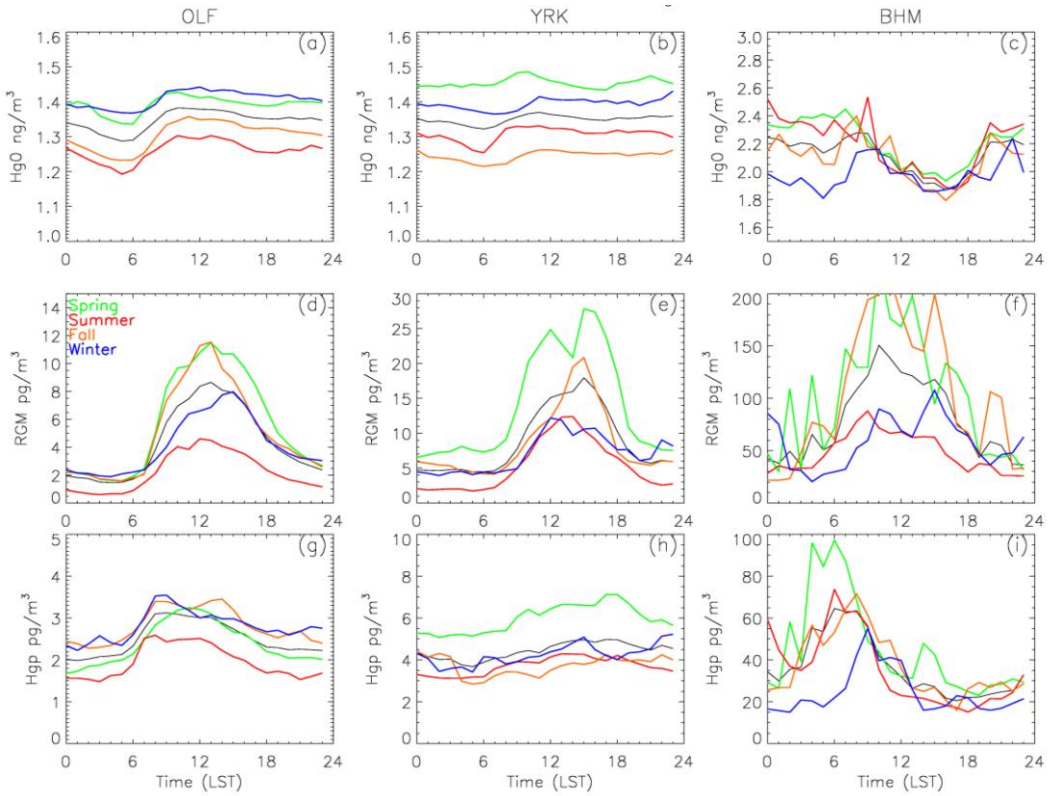

Figure 3. Seasonal variation of diurnal patterns of mercury species. Black line is for overall average.

During the daytime, the average diurnal pattern of HgP for all seasons shows an increasing tendency at OLF (Figure 3g). At YRK, substantial diurnal variation is found only during spring when a daytime increase of HgP is observed (Figure 3h). A steady decrease in daytime concentrations of HgP is observed at BHM during all seasons (Figure 3g-3i). Average HgP concentrations are maximum at YRK (5.95 pg m^{-3}) and BHM (45.8 pg m^{-3}) during the spring season, while at OLF (2.80 pg m^{-3}) the maximum is in the winter season. The minimum HgP concentrations occur during the summer at OLF (1.98 pg m^{-3}) and YRK (3.67 pg m^{-3}), and during the winter at BHM (24.0 pg m^{-3}).

4. Discussion

The diurnal pattern of Hg^0 and its seasonal variation at OLF and YRK (Figure 2, 3a-3b) are similar to that reported for other sites (e.g., Sigler et al. 2009). The decreasing trend at nighttime is a result of removal through dry deposition while the stable nocturnal boundary layer (NBL) prevents replenishment through mixing with the layer above the NBL. During the daytime, boundary layer mixing causes the Hg^0 to initially increase and become relatively constant, tending toward the concentrations at upper levels. This view is supported by observations of Sigler et al. (2009) that show the daytime concentrations at a lower elevation site (24 m) in New Hampshire approaching values similar to that measured at a higher elevation site (700 m) in the same region. However, vertical mixing at BHM would cause a decreasing trend of Hg^0 throughout the morning when the higher concentrations that have built up in the stable nocturnal boundary layer from local emissions sources mix progressively deeper into the residual boundary layer and, at times, into the free troposphere where there are lower Hg^0 concentrations. In order to examine the impact of local emissions, days during which the observational sites were influenced by local emissions were eliminated using the methodology described in section 2. When these days are excluded, the pattern of annual

average Hg^0 diurnal variation becomes more similar to those observed over OLF and YRK (Figure 4). However, the annual average value of Hg^0 is found to be still higher at BHM (2.12 ng m^{-3}) compared to OLF (1.35 ng m^{-3}) and YRK (1.35 ng m^{-3}), suggesting that there is a larger-scale urban contribution in addition to the local source contribution.

The seasonal variation of Hg^0 at YRK and OLF, where average values during winter and spring are higher than during fall and summer, is also consistent with observations at other sites in the United States (Sigler et al. 2009). These seasonal differences are also found to be true for BHM (not shown) when the local emission events are excluded.

The RGM concentrations at all the sites show maximum concentration around mid-day consistent with observations at other low elevation sites (Sigler et al. 2009). The maximum average concentrations in RGM at the YRK and OLF sites occurred during the spring season. At BHM, the spring and fall season exhibited average concentrations that are approximately equal, but higher than that for the other seasons. The lowest RGM concentration at all three sites was found to occur during summertime. This may be related to deeper boundary layer development in the summer for the cases of YRK and BHM, the two sites that see substantial RGM from local emissions. The differences in average magnitudes of RGM between the three sites become significantly less when the days impacted by local emissions are eliminated (Figure 4). The daytime-peak RGM concentrations after subtracting the local emissions at all three sites, indicates that there may be a common mechanism in the RGM pattern in the region.

The diurnal and seasonal variation of HgP does not show any consistent pattern between the three sites. However, there are some similarities in increasing HgP concentration trends during the early morning hours at OLF suggesting the presence of higher concentrations of HgP in the air aloft. Increasing trends of HgP concentrations at BHM, in the hours prior to sunrise, suggest the accumulation of HgP from anthropogenic emissions within the stable nocturnal boundary layer.

5. Summary

Long-term observations at the coastal suburban OLF site and rural YRK show that annual average Hg^0 concentrations are similar at the two sites. Seasonal averages at both the sites are higher during winter and spring compared to summer and fall. The pattern of Hg^0 diurnal variation at these sites shows boundary layer mixing causing the daytime surface concentrations to increase and reach values consistent with concentrations in air aloft. The annual average RGM concentrations at YRK are approximately twice that of OLF. The RGM concentrations at OLF and YRK reach a maximum around mid-day, with the maximum and minimum seasonal average concentration occurring during spring and summer. The annual average HgP concentration at YRK is approximately twice that of OLF. The HgP concentration at OLF increases during the daytime, suggesting mixing with air aloft with higher concentrations of HgP. At YRK, diurnal variation of HgP is less when compared to OLF.

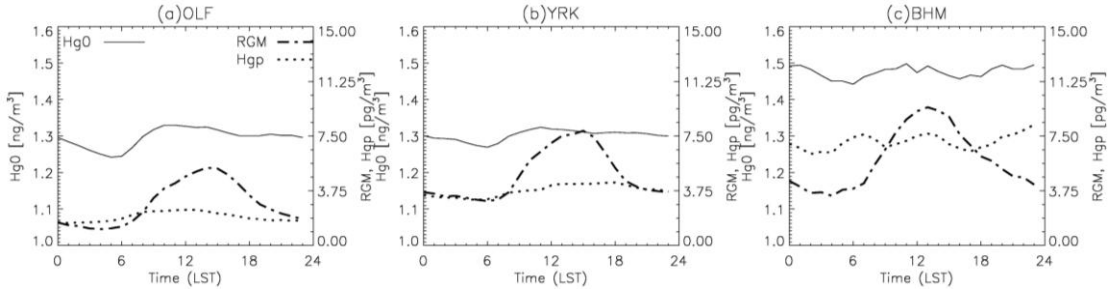

Figure 4. Same as Fig.1 but after local source contributions were removed.

Diurnal variation patterns of Hg species and average values at BHM are substantially different compared to the OLF and YRK sites. The average Hg^0 concentration at BHM is significantly higher compared to OLF and YRK and the diurnal patterns for all seasons show a steady decrease of Hg^0 during the day. Both the average RGM and the HgP concentrations at BHM are approximately nineteen times higher compared to OLF. The diurnal pattern of HgP shows a steady nocturnal increase, possibly due to emissions into the shallow nocturnal boundary layer and steady daytime decrease due to boundary layer mixing.

Interestingly, the diurnal patterns between the three sites become consistent and the average concentrations become comparable when the local emission events are excluded.

6. References

Landis, M.S., R. K. Stevens, F. Schaedlich, and E.M. Prestbo, 2002: Development and characterization of annular denuder methodology for the measurement of divalent inorganic reactive gaseous mercury in ambient air, Environ. Sci. Technol., 36, 3000-3009.

Sigler, J.M., H. Mao, and R. Talbot, 2009: Gaseous elemental and reactive mercury in Southern New Hampshire, Atmos. Chem. Phys., 9, 1929-1942.

Weiss-Penzias, P., M.S. Gustin, and S.N. Lyman, 2009: Observations of speciated atmospheric mercury at three sites in Nevada: Evidence for a free tropospheric source of reactive gaseous mercury, J. Geophys. Res., 114, D14302, doi:10.1029/2008JD011607.