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Anthropogenic emission of mercury to the atmosphere in the northeast United States

Xuhui Lee
School of Forestry and Environmental Studies, Yale University, New Haven, Connecticut

O. Russell Bullock Jr
NOAA, Research Triangle Park, North Carolina

Robert J. Andres[1]
University of Alaska, Fairbanks, Alaska

Abstract. The severity and spatial extent of the health impact of anthropogenic mercury (Hg) emission to the atmosphere depend on the emission rate and chemical form of the emitted species. The few measurements of combustion flue gas give highly variable results about how the emission is divided between the elemental (Hg°) and reactive forms and are difficult to extrapolate to a regional scale. Here we combine measurement of total gaseous mercury (TGM) and carbon dioxide (CO_2) concentrations at a background site in the winter with carbon (C) emission inventory to show that at a regional (500 km) scale, the effective anthropogenic Hg° flux is $41(\pm 2)$ $\mathrm{g\,km^{-2}\,yr^{-1}}$ in the north-east United States. This regional-scale flux was higher under clear skies than under cloudy skies, suggesting some removal of Hg° by cloud water, but the physical mechanisms of the removal are yet to be identified.

Introduction

Hg in emission plumes is divided between reactive form consisting mainly of divalent species in gaseous and particulate phases and gaseous Hg°. The relatively inert Hg° can undergo long-range transport whereas the reactive species are thought to be subject to rapid deposition near their emission sources [*Mason et al.*, 1994; *Bullock et al.*, 1998]. Model assessment of Hg fate is very sensitive to the rate and speciation of Hg emission [*Bullock et al.*, 1998]. Analytical methods for Hg speciation of exit gases and emission plumes are still controversial [*US EPA*, 1997]. The few measurements available for combustion flue gases give results that vary greatly depending on feed material, operating temperature and pollution control technology [*Carpi*, 1997; *Galbreath and Zygarlicke*, 1996; *Lindqvist and Rodhe*, 1985] and are difficult to extrapolate to a regional scale. Furthermore, because of the small temporal scales of these analytical methods, little is known about how the emission plumes interact with the ambient atmospheric variables.

In this study we combine measurement of ambient CO_2 and TGM concentration with C and Hg inventory data to estimate the Hg emission rate and speciation at a regional scale in the northeast United States. This region has the highest Hg emission of the country [*US EPA*, 1997] and thus a precise of knowledge of the emission rate is important for assessing its environmental impact. The novel method used here should be also applicable in other parts of the world.

Data and Method

We monitor TGM and CO_2 concentrations on a continuous basis at a mixed forest of coniferous and deciduous trees in Connecticut (73°14'W, 41°58'N), 50 km away from the nearest point combustion sources. TGM was measured with a Tekran analyzer and was corrected for water vapor density effect [*Lee*, 2000]. The analyzer was calibrated against an internal permeation source certified to an accuracy of 5%. Of all the 30-min TGM observations, 99% lie below 2.43 $\mathrm{ng\,m^{-3}}$ STP (standard temperature and pressure, 0°C, 101.3 kPa), with an annual (June 1999 – May 2000) mean of 1.64 $\mathrm{ng\,m^{-3}}$ (Figure 1), which is typical of mid-latitude, background sites in the Northern Hemisphere [*Slemr et al.*, 1985]. Our instrument did not speciate Hg; previous observation showed that >95% of TGM is in elemental form [*Lindberg and Stratton*, 1998; *Fitzgerald et al.*, 1991]. Particulate Hg concentration in this area is low (20 $\mathrm{pg\,m^{-3}}$, *Olmez et al.* [1998]).

CO_2 was measured with a Licor infrared gas analyzer whose calibration standard is accurate to within 1%. Wintertime CO_2 is an excellent tracer for Hg at mid- to high latitudes for three reasons. First, previous studies show that wintertime CO_2 is an accurate tracer that captures the influence of combustion sources in the northeast United States [*Bakwin et al.*, 1994; *Potosnak et al.*, 1999]. Second, combustion sources are the major sources category comprising >90% of total Hg emission in this region. The remaining Hg sources (area, manufacturing) are also situated at locations of significant C emission by fossil fuel consumption [*US EPA*, 1997]. Third, anthropogenic C source strength is well understood and quantified to high accuracy [*Andres et al.*, 1996].

In the following, we will limit our analysis to data collected in the winter when the biological CO_2 flux was low (Figure 1). The excellent correlation between TGM and CO_2 during this period supports our use of CO_2 as a tracer

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[1] Now at University of North Dekota.

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for Hg (Figure 2). To further reduce the biological influence on the CO_2 measurement, we only use observations made in the daytime, convective conditions when the surface values are representative of the full mixed layer. With such data schemes, the linear correlation between CO_2 and TGM is typically >0.85 on weekly intervals and is 0.73 over the whole period.

The Hg inventory data we use is for period 1994-1995 [*US EPA*, 1997]. The C inventory data for the same period was obtained using the method described in *Andres et al.* [1996]. The Hg and C emission rates, averaged over an area within a 500-km radius of the monitoring site, were 75 g of total Hg and 432 t of C per km^2 per year.

Results and Discussion

Figure 3 shows the scatter plot of all valid 30-min observations of TGM and C concentrations referenced to STP. Since both TGM and CO_2 are subject to measurement errors, an orthogonal X-squares regression is chosen over the ordinary least squares method [*Press et al.*, 1977; *Bakwin et al.*, 1994] to establish the linear fit shown in Figure 3. The regression slope is 0.094 (±0.004) (g TGM)/(t C), which is equivalent to the ratio of the emission rates of the two species at a regional scale [*Bakwin et al.*, 1994; *Stehr et al.*, 2000]. Multiplying the regression slope by the inventory C flux of 432 t of C per km^2, we obtain a regional Hg° flux of 41 (±2) $g\,km^{-2}\,yr^{-1}$. The regional Hg° flux is 54% of the total anthropogenic Hg emission (75 $g\,km^{-2}\,yr^{-1}$), thus implying that the remaining 46% must have been reactive species deposited rapidly near the source. In making this estimate, we assume that Hg° is the only form of the gaseous Hg at our site. We also note that the Hg° flux is an effective one that reflects the actual emission less the removal mechanisms between the source and the monitoring site.

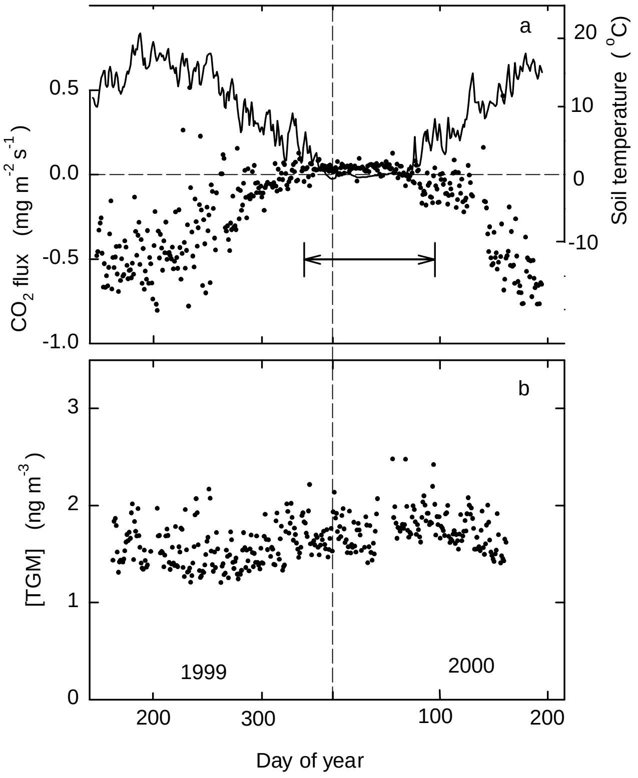

Figure 1. Seasonal variations of three variables: a, midday CO_2 flux (dots), measured with eddy covariance over the forest, is low in the winter when soil temperature at 5-cm depth (line) is near the freezing point. A negative (positive) flux denotes CO_2 uptake (release) by the forest. Arrow indicates period used for the TGM versus CO_2 correlation analysis; b, daily mean TGM concentration at STP.

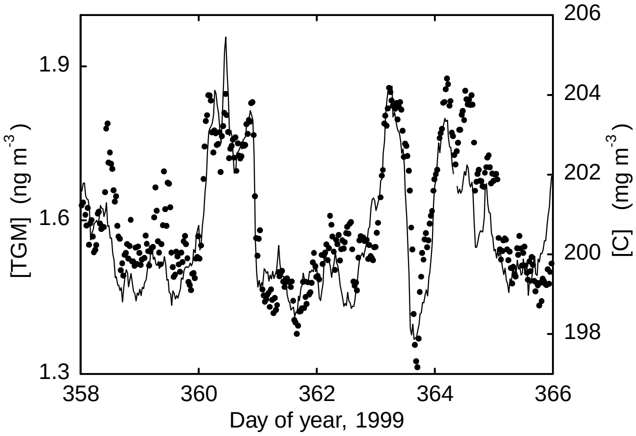

Figure 2. A 1-week time series showing the correlation between C (line) and TGM (dots) concentrations typical of the winter months.

In a modeling study, *Shia et al.* [1999] assume a Hg° emission rate of 40 $g\,km^{-2}\,yr^{-1}$ for the northeast United States. Of this, 2/3 is natural emission and 1/3 is anthropogenic, the latter of which is much lower than our estimate. Our regional-scale speciation is in close agreement with the suggestion that global anthropogenic Hg emission be equally divided between the elemental and reactive forms [*Mason et al.*, 1994], but differ from measurements of combustion flue gas which suggest that 60–80% of the emission be in the divalent form [*Carpi*, 1997].

To investigate how environmental factors interact with the fate of Hg emission, we sort the data by air temperature,

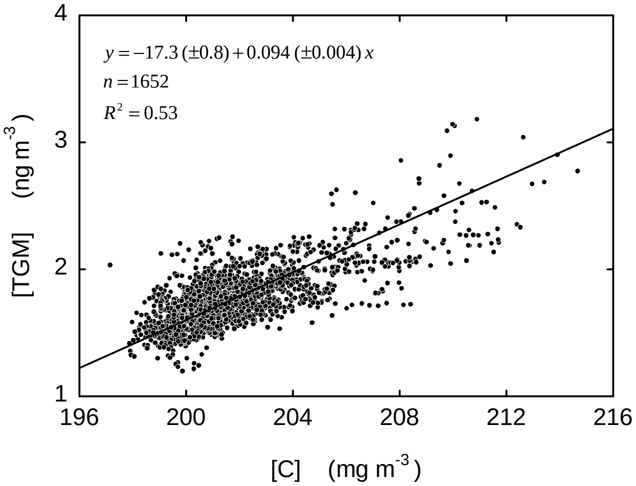

Figure 3. Scatter plot of daytime TGM and C concentrations referenced to STP. Also shown are regression line and equation, ±1 standard error of estimate (numbers in parentheses), number of observations (n) and coefficient of determination (R^2).

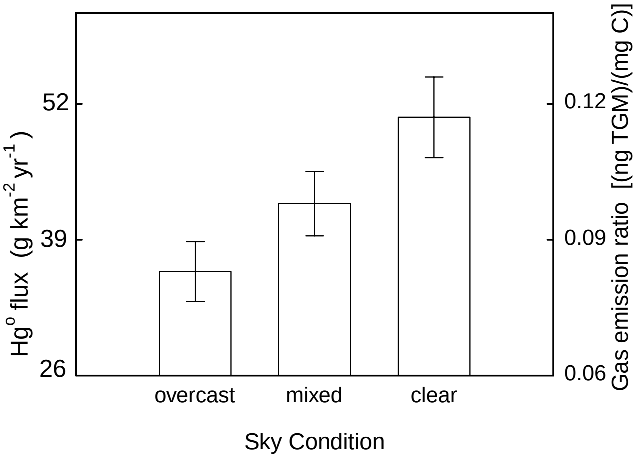

Figure 4. Hg° flux and gas emission ratio under three sky conditions. The emission ratio is taken as the slope of the regression of the concentration data for each sky class. Error bars are ±1 standard error of estimate. Hg° flux is computed by multiplying the emission ratio by the inventory C flux of 432 $\mathrm{t\,km^{-2}\,yr^{-1}}$.

absolute humidity, sky condition, wind direction, and source region defined by air mass backward trajectory [*NOAA*, 2000], and apply the above orthogonal X-squares regression to the subsets of the concentration data. Of these factors, only cloudiness exerts a statistically significant influence on the effective flux (Figure 4). We find a clear trend with cloudiness. The effective Hg° flux is 41% higher under clear skies than under overcast skies (with a 95% confidence level for the difference) while the value under mixed skies falls between the two. The cloud ceiling was generally less than 1 km on the overcast days. Air turnover time below this altitude is on the order of minutes [*Stull*, 1988], so it is reasonable to expect Hg° emitted near the ground to interact with cloud water at a local scale (<5 km, given a mixed-layer wind speed of 5 $\mathrm{m\,s^{-1}}$) around the emission sources. If we omit photolysis and other possible effects, the flux difference between clear and overcast skies suggests a rate of cloud removal up to 15 $\mathrm{g\,km^{-2}\,yr^{-1}}$. The exact chemical transformations, however, can not be determined by the tracer correlation analysis.

The above standard errors are those of the orthogonal regression only. The overall accuracy of our results will depend on the extent to which $\mathrm{CO_2}$ and TGM concentrations are interfered by natural emission and the radius of influence represented by the tracer correlation technique. Biological C flux (Figure 1; 0.03 $\mathrm{mg\,CO_2\,m^{-2}\,s^{-1}}$ or 260 $\mathrm{t\,C\,km^{-2}\,yr^{-1}}$) was comparable in magnitude to the anthropogenic C flux. No data was available for natural Hg° flux at the site; wintertime data from mid-latitude sites suggests that this is on the order of 1 $\mathrm{ng\,m^{-2}\,hr^{-1}}$ (9 $\mathrm{g\,km^{-2}\,yr^{-1}}$) [*Lee et al.*, 2000; *Kim et al.*, 1995; *Xiao et al.*, 1991 ; *Schroeder et al.*, 1989], which is an order of magnitude smaller than the anthropogenic Hg flux. The terrestrial C sources are a major factor contributing to the random noise in Figure 3, but because they are extremely diffuse in space, they should not affect the slope of the regression.

The above regional inventory fluxes are for an area of 500 km radius around the site, a size thought to be represented by the tracer technique [*Potosnak et al.*, 1999]. Expansion of the radius of influence to 1000 km reduces the area-averaged C inventory flux by 8% and Hg flux by 18%. Our estimates of the Hg° flux and speciation should therefore be viewed with this in mind. The relative trend with cloudiness (Figure 4) is however less subject to this uncertainty.

A third uncertainty is related to the EPA Hg inventory data. It is possible that the inventory does not account for all emission sources. This may affect our estimate of the regional-scale speciation but should not affect the Hg° flux because the latter is determined from the ambient measurement and C inventory.

Our "top-down" approach is an effective and low-cost way of determining Hg emission at a regional scale. If operated over multiple years and combined with observations of other well-studied atmospheric tracers [*Stehr et al.*, 2000; *Parrish et al.*, 1998], it will enable us to track changes of fuel mix and control technology and to separate contributions by source category. We argue that data of this kind should lead to improved estimates of the global Hg budget.

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Xuhui Lee, School of Forestry and Environmental Studies, Yale University, 370 Prospect Street, New Haven, CT 06511, USA. (e-mail: xuhui.lee@yale.edu)

O. R. Bullock Jr, Air Resources Laboratory, NOAA, Research Triangle Park, North Carolina, USA

R. J. Andres, University of Alaska, Fairbanks, Alaska, USA

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