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Emission and Long-Range Transport of Gaseous Mercury from a Large-Scale Canadian Boreal Forest Fire

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Field observations made at Harvard Forest [Petersham, MA, U.S.A. (42°54′ N, 72°18′ W)] during early July 2002 show clear evidence of long-range transport of gaseous mercury (Hg) in a smoke plume from a series of boreal forest fires in northern Quebec. These measurements indicated significant and highly correlated increases in Hg and CO during the plume event. The Hg:CO emissions ratio determined from the data (8.61×10^{-8} mol mol^{-1}) was combined with previously published information on CO emissions and biomass burned to determine a mean area-based Hg emission flux density for boreal forest fires (1.5 g Hg ha^{-1}), annual Hg emissions from Canadian forest fires (3.5 tonnes), and annual global Hg emissions from boreal forest fires (22.5 tonnes). Annual Hg emissions from boreal fires in Canada may equal 30% of annual Canadian anthropogenic emissions in an average fire year and could be as high as 100% during years of intense burning. The Hg:CO emissions ratio of this study was much lower than those reported for a temperate forest in Ontario and a pine/shrub vegetation in South Africa, suggesting that fire emission is dependent on biome/species and that any extrapolation from a single fire event to determine the global fire emission is speculative.

Introduction

Mercury (Hg) is an important trace element because of its potentially harmful impact on human health. Gaseous elemental mercury (Hg^0), which comprimises up >95% of the background global atmospheric concentration of Hg, is not readily absorbed by bare terrain, water, or vegetation, has a residence time in the atmosphere of 0.5−2 years (*1*), and can therefore be transported over long distances (*2*, *3*). Transported Hg^0 can be deposited to remote aquatic environments (*4*, *5*) where it may undergo methylation and subsequently bioaccumulate to dangerous levels in fish (*6*, *7*). Therefore, atmospheric emissions and transport are of particular importance to our interest in the global biogeochemical cycle of Hg.

Roughly half of the global atmospheric load of Hg is believed to be anthropogenic (*8*, *9*). Recent studies have suggested that large uncertainties are associated with present estimates of emission from natural sources and re-emission of previously deposited atmospheric Hg and better data are required in order to assess the magnitude, spatial distribution, and importance of these emissions relative to the direct anthropogenic emission (*10*, *11*).

Forest fires are an important pathway of material exchange between the biosphere and atmosphere. They result in the re-emission of previously deposited anthropogenic Hg along with some fraction of natural soil Hg (*12*). A recent study of a mixed-vegetation fire in the southern Cape Peninsula in Africa (*13*) suggests that Hg emissions from biomass burning in general may be a more significant pathway of Hg exchange between the biosphere and atmosphere than was previously believed, potentially accounting for 12−28% of annual global total gaseous mercury (TGM) emission. Laboratory experiments suggest that burning of litter and green vegetation results in nearly complete release, in mostly gaseous form, of Hg contained in the fuel, and that release of Hg from fires may be 104−526 t y^{-1} (1 *t* = 1000 kg) or 3.5−17.5% of natural Hg emissions and 1.6−8.0% of all emissions (*14*).

The magnitude of Hg emission from boreal forest fires is not well quantified. Direct measurements of Hg release from actual boreal fires would add confidence to our understanding of the contribution of this source to the global Hg budget. To this point, there is no published record of Hg emission from a large-scale natural fire in the Canadian boreal forests, much less subsequent long-range transport to the United States. However, large fires in this region have been linked to enhancements in carbon monoxide (CO) and volatile organic compounds (VOCs) in the mid-latitudes (*15*). These species as well as ozone (O_3) and aerosols may be transported in Canadian forest fire plumes as far as the southeastern United States, causing local enhancements in their concentrations (*16*). This raises questions regarding the role of fire in the annual Hg budget in North America, especially in Canada where anthropogenic emissions of Hg are significantly lower than in the United States (*17*, *18*).

We present evidence of long-range transport of Hg from a Canadian boreal fire by showing a clear relationship between enhancements in CO and Hg concentrations observed at a rural site in the northeastern United States and a large natural fire in northern Quebec. We use the relationship between Hg and CO emission from biomass combustion to estimate area-based and annual Hg emissions for Canadian fires and assess the potential contribution of natural boreal forest fire emissions to the regional and global atmospheric Hg budget.

Fire Event and Experimental Methods

This study focuses on a series of natural fires that occurred in the James Bay region of Quebec, approximately 500 km north of Montreal, during early July 2002. Approximately 250 fires burned more than 1 000 000 ha during July over an area of 20 000 000 ha bounded roughly by the James Bay coast on the west, the Manicouagan Reservoir in the east, Lake Mistassini in the south, and the Grande River in the north (*19*). The dominant species in this region are black spruce and jack pine, occurring primarily in monospecific stands (*20*, *21*).

NASA MODIS images clearly showed that northwesterly winds carried the fire plume as far south as southern New England and northern Pennsylvania/New Jersey on July 6, 2002, and as far south as northern Virginia, a distance of over 1300 km, on July 7 (Figure 1). By July 8, much of the plume

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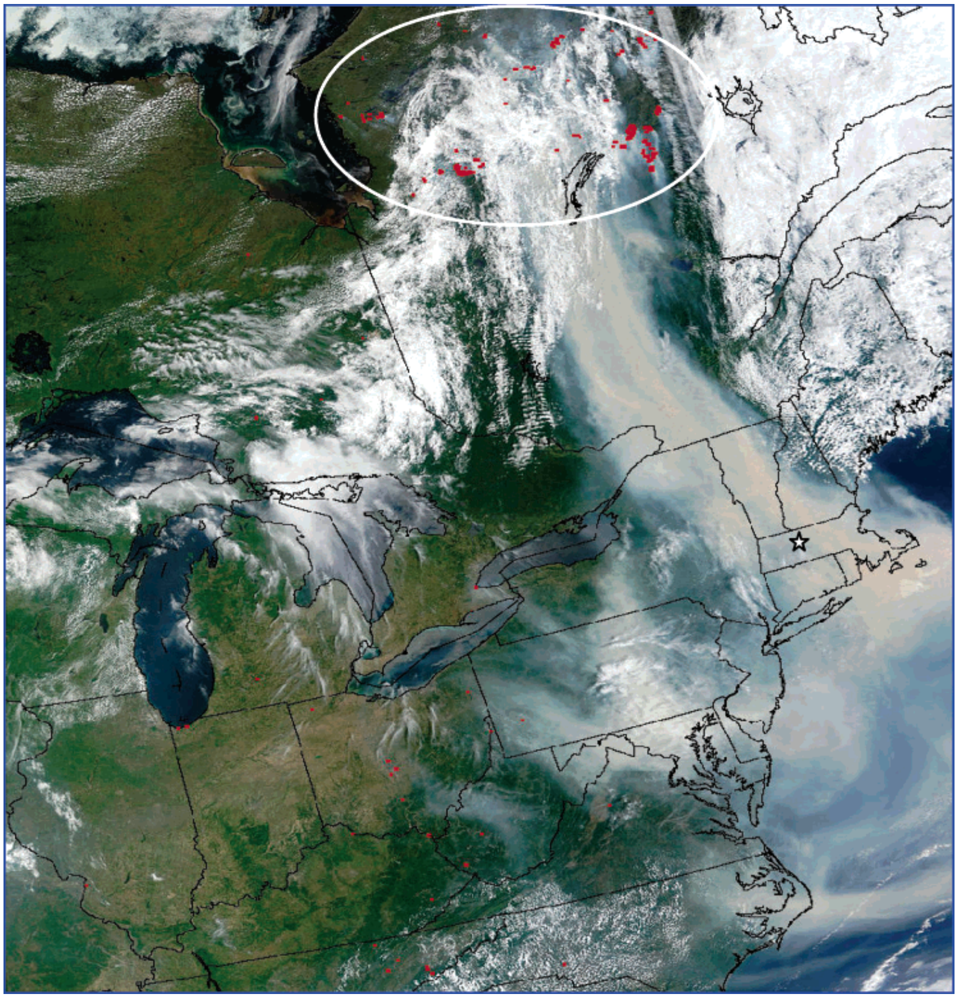

FIGURE 1. NASA Terra satellite image of Quebec fire plume extending along the East Coast of the United States (July 7, 2002, 16:35 UTC). The general burn area is enclosed in the white circle. The white star indicates measurement location (Harvard Forest). Photo courtesy NASA MODIS Image Gallery.

had moved off of the East Coast of the United States, no longer impacting southern New England. Backward air mass trajectories were computed from Harvard Forest using NOAA HYSPLIT-4 (*22*). Thirty-six h trajectories computed before, during, and after the event verify that the air masses impacting the site at the time of plume influence originated over the burn area (Figure 2). HYSPLIT trajectories show an increasingly westerly trend by 23:00 UTC (18:00 local time) on July 7 as the plume moved off of the East Coast.

The plume signal was monitored at Harvard Forest, a Long-Term Ecological Research (LTER) site located near Petersham, MA (42°54′ N, 72°18′ W). This is a rural site located >100 km from Boston, MA and Hartford, CT. A Teflon filter was mounted at the canopy height (24 m) on a 30-m walk-up tower. Air was drawn through the filter and into a mercury vapor analyzer (Model 2537A, Tekran, Inc.) that measured TGM at 5-minute intervals. The analyzer was calibrated daily against an internal permeation source and housed in a temperature-controlled trailer near the tower. The internal permeation source was verified to within 6% by laboratory manual injection tests. Continuous measurements of CO were made with a Dasibi absorbance analyzer on a 10-m tower located approximately 50 m from the walk-up tower (*23*).

The trajectory analysis was used to determine which TGM and CO data collected at Harvard Forest were from the Quebec smoke plume. The Hg:CO emission ratio was calculated using orthogonal or geometric mean regression slope as outlined in ref *24*. Only gaseous Hg was measured in this study, the vast majority of which was Hg^0 (*14*, *35*).

Results

The Quebec plume signal was clearly detected at Harvard Forest on July 7. CO concentrations reached a maximum of 950 ppb at 14:30 LST on July 7 (Figure 3), exceeding background levels by a factor of 4.5. CO concentration then steadily declined, returning to background levels by 06:00 LST on July 8 as wind direction and air mass trajectory shifted from northerly to northwesterly (Figure 2). Maximum TGM concentrations during the event approached 2.0 ng m^{-3}, an enhancement of approximately 40% above background (~1.4 ng m^{-3}). Degradation or enhancement of TGM or CO within the plume during transport was unlikely because of the lack of pollution sources along the flow path, the long lifetime of Hg^0, and the sufficiently long lifetime of CO (approximately 2 months in the summer), which makes it an excellent, regional-scale tracer of biomass burning (*25*).

Both CO (*13*) and CO_2 (*26*) have been used as tracer variables for determining Hg emission rates. In this case, a strong correlation between ambient Hg and CO was observed at Harvard Forest during the plume event. Orthogonal linear regression yields a Hg:CO emissions ratio of 8.61×10^{-8} mol mol^{-1} [6.15×10^{-7} g Hg (g CO)$^{-1}$, $R^2 = 0.89$, $n = 15$, Figure 4] during the event. When combined with the trajectory analysis (Figure 2), the highly significant correlation between CO and Hg provides credible evidence of long-range transport

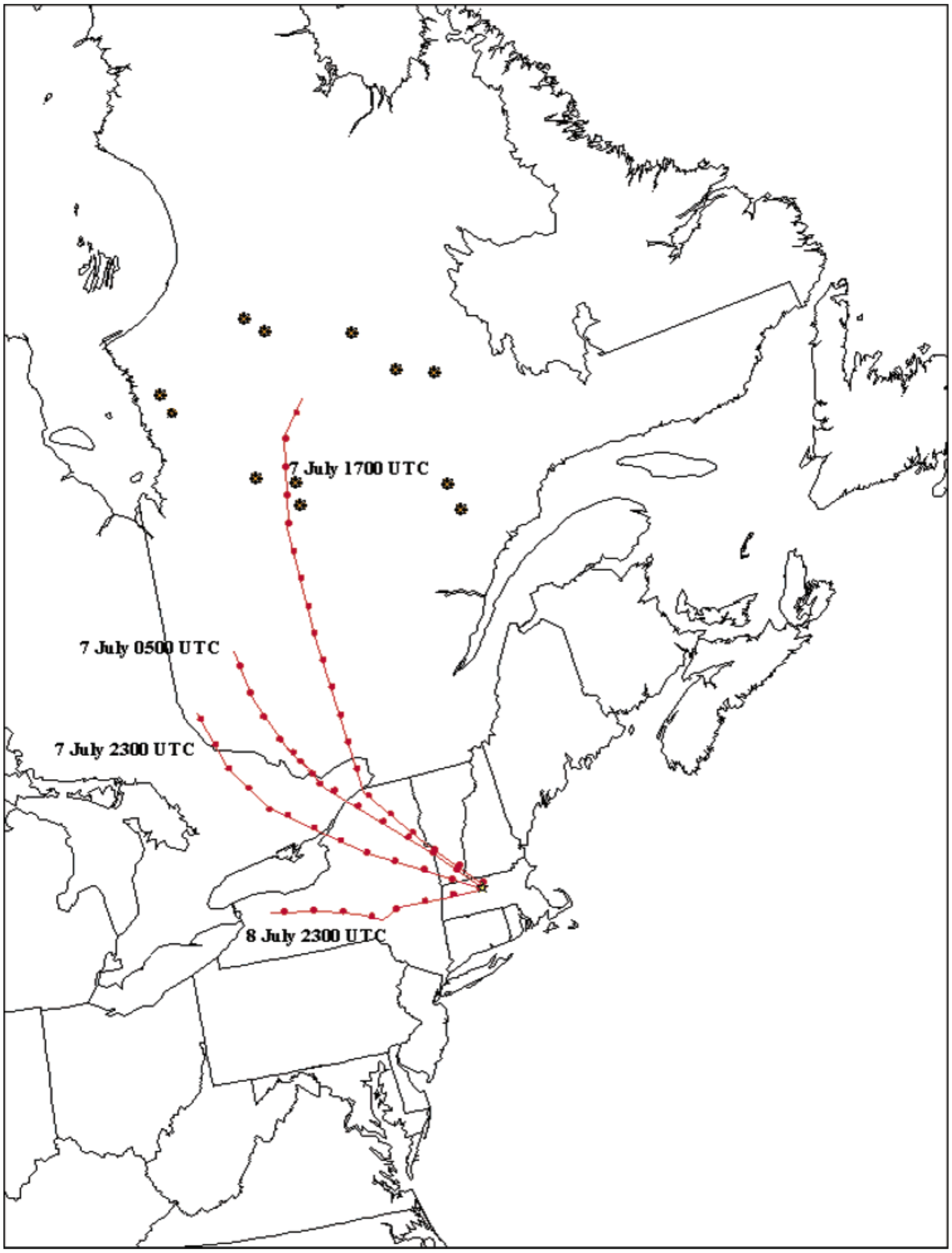

FIGURE 2. Ensemble of 36-h backward trajectories from Harvard Forest before, during, and after plume event. Asterisks represent major burn areas.

of Hg from a boreal forest fire. The data points for the plume event were isolated using the trajectory analysis, which is an effective means of determining plume influence at Harvard Forest based on changes in trajectory endpoint and direction (Figure 2). Also, a series of data points representing local and regional flow patterns preceding the plume event were selected and are displayed in Figure 4. The emissions ratio calculated for the plume event is considerably less than that for local and regional influences at Harvard Forest (2.80×10^{-7} mol mol^{-1}, $R^2 = 0.59$, $n = 92$), reflecting strong influences from local and regional pollution sources.

Discussion

In comparison with other similar studies, our data have unique advantages and weaknesses. Though remotely obtained, this is a direct measurement of Hg emission from a large-scale, naturally occurring boreal fire, which has advantages over previous studies of fire emissions which have focused on small-scale prescribed fires (e.g. ref *27*) or laboratory experiments (e.g. ref *14*). Prescribed fires are by nature small, spot measurements, burn fuels which are often slashed, trampled, or bulldozed and employ set moisture, weather, and fuel parameters intended to ensure a controlled and complete burn and therefore represent ideal and possibly unrealistic conditions. Though difficult to undertake, the importance of measuring emissions from large-scale wildfires is further underscored by the observation that they represent 90% of the total, global boreal forest area burned (*28*). In this particular case, since the observed smoke plume represented a conglomeration of emissions from many fires spread over a large area, these measurements are less subject to the potential bias due to site variability that may characterize spot measurements of emissions from individual, prescribed fires. However, a drawback of measurements of large fire events is that combustion stage and fuel types are not known precisely, making cross-validation against controlled experiments difficult.

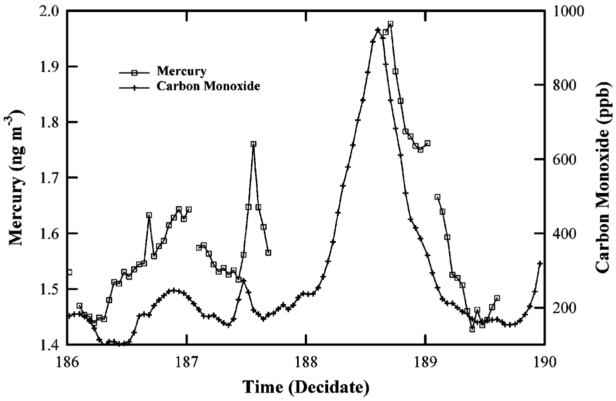

FIGURE 3. Temporal variation of mercury and carbon monoxide at Harvard Forest, MA, during local pollution and the fire plume event, July 5–8 (day of year 186–189), 2002. Data are hourly averages.

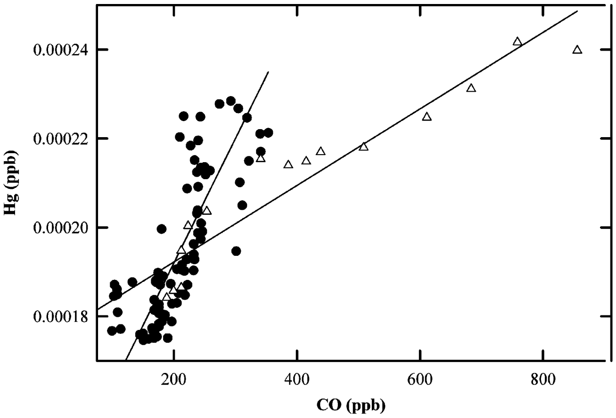

FIGURE 4. Orthogonal regression of Hg versus CO for local/regional pollution sources using data from a 4-day period before the fire plume (dots, $y = 1.36 \times 10^{-4} + 2.80 \times 10^{-7}x$; $R^2 = 0.59$, $n = 92$) and during the fire plume (triangles, $y = 1.75 \times 10^{-4} + 8.61 \times 10^{-8}x$; $R^2 = 0.89$, $n = 15$) at Harvard Forest, July 2002.

Application of the Hg:CO emission ratio reported here to approximate Hg release per unit area as well as extrapolation to large scales requires data on CO emission factor, species composition, and fuel consumption of the burn area. It is known that both CO and Hg emission factors depend on fire stage (*29, 14*). Since the ambient concentration measurement at Harvard Forest represents a mixture of fires in various stages of burn, it is appropriate to use a fire-averaged CO emission factor. The emission factors found in the literature for black spruce and jack pine for prescribed burns (*31–34*) and wildfires (*35*) are quite consistent, giving a mean value of 99.1 g CO (kg biomass)$^{-1}$ and a small standard deviation of 11.7 g CO (kg biomass)$^{-1}$ (number of observations = 7).

Based on data from an experimentally validated model, a mean fuel consumption of 2.40 (standard deviation 0.81) kg m^{-2} has been reported for Canadian boreal forests (*36*). Combining this mean fuel consumption, the fire-averaged CO emission factor and the Hg:CO emissions ratio given above, we estimate CO and Hg emission flux densities from Canadian boreal forest fires of 2400 kg CO ha^{-1} and 1.5 g Hg ha^{-1}. Combining the mean Hg flux density with an approximate area burned in the Quebec fires during July 2002 [1.1 million ha (ref 19)] results in a total release of 1.6 t Hg. We view this as an order of magnitude estimate only because the exact fuel consumption is not known.

Since spruce/jack pine-dominated fuel type represents a significant fraction of nearly every Canadian ecozone (*36*), it is appropriate to apply the above Hg emission flux density estimate to Canadian fires. Using a mean burn area of 2.3 million ha y^{-1} in the boreal zone (*44*), we determine an annual release of 3.5 t Hg from Canadian boreal forest fires. This is equal to roughly one-third of inventory estimates of annual anthropogenic Hg emission in Canada (~11 t in 1995 (*18*)). Boreal fires therefore play a highly significant role in the overall Canadian Hg budget. This role may be amplified during years of intense activity. Total forest area burned in Canada may be as high as 7.5 million ha in a particular year (*36*). Based on our measurements, such an intense fire year may result in a release of approximately 11 t of Hg. A single large fire such as the one studied by Wotawa and Trainer (*16*), which burned over more than 3 million ha over a 2-week period, could release 4.5 t of Hg.

Boreal forest fires are highly stochastic phenomena, determined largely by meteorological conditions and, to some extent, fuel availability and consumption. Total area burned throughout the biome often varies interannually by more than an order of magnitude (*37*). Such variability in area burned contrasts with African savannah fires, which typically account for the vast majority of global biomass burning emissions but tend to be relatively constant in interannual range and distribution (*38*). The total area burned by boreal fires worldwide is not known to any great degree of certainty. Estimates vary from 5 to 10 million ha y^{-1} (*39*) to more than 15 million ha y^{-1} (*40*). Satellite data suggest that the total area burned in a given year could vary between 3 million and at least 22 million ha (*41*). If 15 million ha y^{-1} is assumed to be the mean area burned globally, our measurements imply a mean annual global Hg emission from boreal fires of approximately 22.5 t. In a particularly intense year during which 22 million ha are burned, 33 t of Hg could be emitted globally from boreal fires.

This can only be considered an order of magnitude estimate since it assumes a uniform canopy composition, biomass consumption pattern, and Hg loading which may be disparate among Canadian and Russian boreal forests. For this same reason, extrapolation of our data to the entire globe is difficult. The Hg:CO emissions ratio reported here is approximately 40% and 55% of those reported for a wildfire in a pine/shrub landscape in South Africa (*13*) and a small-scale temperate/boreal wildfire in Ontario (*35*), respectively, reflecting the relatively low Hg concentration in live coniferous fuel (*14*) and relative absence of local pollution sources in northern Quebec. The variation in the emissions ratio suggests that fire emission is dependent on biome/species. Biomass burning is estimated to release 400–700 × 10^6 t CO y^{-1} to the atmosphere globally (*42, 43*). If this is combined with the Hg:CO emissions ratio found in ref *13*, the global fire emission of Hg would be 510–1140 t y^{-1}. This estimate would be lowered to only 250–430 t y^{-1} if the emissions ratio of this study is applied. Therefore, accurate determination of global Hg emissions from biomass burning using observations from one or a very few fire events, as existing studies have (*13, 14, 35*), is difficult. That the vast majority of global C emission from biomass burning occurs in tropical grasslands with a much different species composition for which no emissions data exist further implies that the total contribution of global biomass burning cannot be accurately determined without a better understanding of variation in Hg:CO emissions ratios across biomes.

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