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Canadian and U.S. Sources Impacting the Mercury Levels in Fine Atmospheric Particulate Material across New York State

ILHAN OLMEZ,*,†
MICHAEL R. AMES, AND GULEN GULLU‡
Massachusetts Institute of Technology, Nuclear Reactor Laboratory, 138 Albany Street, Cambridge, Massachusetts 02139

An extensive atmospheric sampling and analysis program has been completed in order to identify and apportion the sources of mercury associated with fine atmospheric particulate material ($d_a < 2.5\ \mu m$). Samples of fine atmospheric particulate material were collected daily, at five remote sites in New York State, over a period of 2 years. The trace element composition of 1200 of these samples was determined by Instrumental Neutron Activation Analysis. Results of both meteorological and statistical analyses of the data indicate that approximately 55% of the fine particulate mercury originated from smelters in Ontario and Quebec, and 25% originated from a mixture of regional sources in the Midwestern United States. A decline in the average measured particulate Hg concentration, beginning in February 1993, has been attributed to reduced emissions from one or more of the major Canadian smelters.

Introduction

Mercury has been known as a potent environmental hazard in aquatic ecosystems since 1960 when the consumption of Hg-contaminated fish was identified as the cause of Minamata disease (*1*). Although the concentration of Hg in natural waters is typically on the order of 1 pg/g or ppt, the conversion of inorganic forms of Hg to an organic form (e.g., methylmercury) by aquatic microorganisms and the subsequent bioaccumulation of this organic form in fish tissues can result in concentrations in fish of 1 μg/g or ppm (*2*). Although the direct discharging of Hg compounds to waterways has been prohibited in the United States for more than 2 decades (*3*), Hg continues to be released to the atmosphere at an estimated rate of 4000 t per year globally (*4*). Due to long-range atmospheric transport, elevated Hg levels have been found in natural waters and fish in many regions that are far from major sources (*5*−*8*).

Although only a few percent of atmospheric Hg is associated with particulate matter and it is not the major form of anthropogenic Hg emitted to the atmosphere (*4*, *9*), it may often be the major form of the mercury deposited from the atmosphere because of its short atmospheric lifetime (*10*−*12*). The predominant form of atmospheric mercury (>95%) is the elemental vapor Hg^0, which is found in remote areas at concentrations ranging from about 1 to 5 ng/m^3 (*13*, *14*). In this form, Hg has an atmospheric lifetime of about 1 year (*12*), becomes well-mixed hemispherically, and can be considered a global pollutant. Mercury associated with fine aerosols ($<2.5\ \mu m$) however has an atmospheric lifetime on the order of 1 week and thus constitutes a regional scale pollutant (*14*). Mercury associated with coarse aerosols ($d_a > 2.5\ \mu m$) and as soluble species is generally deposited from the atmosphere within a few days, so Hg in these forms impacts the area local to its source (*15*). The importance of accounting for Hg in the particulate phase in the prediction of the overall depositional flux of Hg from the atmosphere has been demonstrated both in field studies (*12*) and through physical/chemical modeling analyses (*16*).

By collecting daily, 24-h aerosol samples across New York State over a period of 2 years, analyzing these samples for a large number of trace elements, and applying receptor modeling techniques to the resulting data set, it has been possible to identify and apportion the sources of Hg and other measured trace elements in the aerosols. The 24-h sampling time was long enough that sufficient material was collected for reliable elemental analyses, but was generally short enough that each sample represented a single atmospheric trajectory and, hence, a single source or source group. The 2 year duration of the program ensured that all of the seasonally dependent prevailing wind patterns would be represented among the samples.

The coupled application of compositional and meteorological receptor modeling techniques has previously been applied as a means of source identification for atmospheric pollutants on both local and regional scales (*17*−*21*). The sources of collected particulates can often be identified through the observation of known or inferred elemental markers or ratios. This is because the elemental composition patterns of the atmospheric particulates are conserved during transport (*22*−*24*). Mercury may be emitted as primary particulates, or Hg may be adsorbed from the vapor phase onto particles such as carbon soot; once in this form, it is basically unreactive (*16*, *25*). The large number of elements that were measured in each sample made it possible to use a wide variety of marker elements and ratios for source identification.

The use of receptor modeling proved to be essential for the identification of the relevant sources because, in contrast to dispersion or mass balance models, the types of receptor models employed here do not require the sources to be well characterized—or even identified—prior to the analysis. Although the emission of vapor phase Hg has been measured or estimated for many anthropogenic sources, there are significantly less data for the emission of Hg (or other trace elements) in the particulate phase. By using receptor modeling, it was possible to identify sources that had either been previously uncharacterized in terms of their particulate phase Hg emissions or for which emissions data would have been difficult to obtain. These included small local sources, area sources, and transboundary (i.e., Canadian) sources.

Experimental Section

Particulate Sampling and Analysis. In 1991 five sampling sites in remote locations across New York State were selected to be used in an extensive study of atmospheric trace metals (Figure 1). The program included the collection and analysis

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* Corresponding author tel: (617)253-2995; fax: (617)253-7300; e-mail: mrames@mit.edu.

† Present address: Fatih University, Buyuk Cekmece, Istanbul, Turkey.

‡ Present address: Middle East Technical University, Ankara, Turkey.

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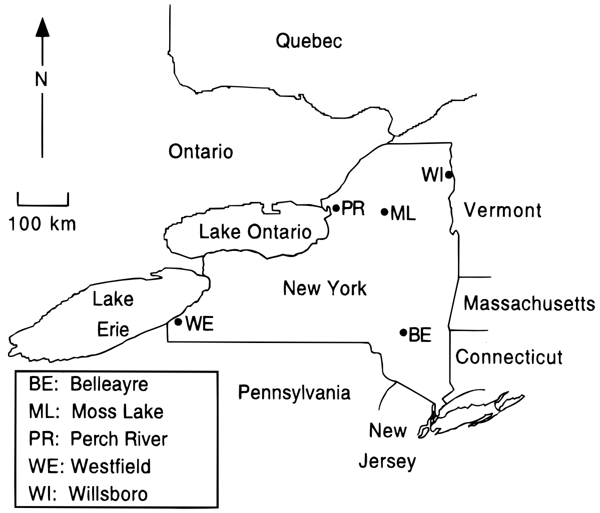

FIGURE 1. Sampling sites for the collection of atmospheric particulates in New York State. These five sites were also used for the collection of vapor phase mercury, and two sites, Moss Lake and Willsboro, were used for weekly integrated wet deposition sampling.

of fine and coarse particulate material, vapor phase mercury, and wet deposition. Particulate samples were collected daily for 24-h periods, from December 1991 through September 1993. The material was collected on 37-mm Teflon membrane filters using automatic dichotomous samplers (sampler model 245, Graseby/Andersen Samplers Inc., Smyrna, GA). The samplers have PM-10 inlet assemblies that exclude particles larger than 10 μm, followed by a virtual impactor which then separates the aerosols into fine (<2.5 μm) and coarse ($2.5-10$ μm) fractions based on their aerodynamic diameters. The sampler design is based on a U.S. Environmental Protection Agency (U.S. EPA) development and testing program for size-fractionated aerosol collection (*26, 27*). Flow rates through the fine and coarse filters were 0.9 and 0.1 m^3/h respectively, and were calibrated on a quarterly basis using either a dry gas flow meter or an electronically timed bubble chamber. Weekly sample changes were performed by personnel from either the New York State Department of Environmental Conservation (NYSDEC) Division of Air Resources or the Adirondack Lakes Survey Corporation (ALSC).

Of the roughly 6000 collected samples, about 1200 fine fraction samples (typically two or three samples from each site, for each week) were analyzed for Hg and 38 other trace elements by Instrumental Neutron Activation Analysis (INAA) using a procedure similar to that described by Olmez (*28*). Mercury concentrations were determined using an improved methodology that is both free from previously encountered spectral interferences due to selenium activation and is also more sensitive than past techniques (*29*). The INAA is a nondestructive analytical tool that requires no sample preparation and yields concentrations of up to 45 elements in a single sample with extremely low detection limits (typically $0.01-0.2$ ng). Reference materials used in the analyses were from the National Institute of Standards and Technology: Mercury in Sediment (RM8408), Coal Fly Ash (SRM1633), and Orchard Leaves (SRM1571).

Receptor Modeling. The basic goal of receptor modeling, as applied to the understanding of chemicals in the environment, is to identify and apportion sources of these chemicals based on measurements of their behavior at an ambient receptor site. A significant feature of many types of receptor modeling is that they do not require detailed source emission profiles or the estimation of the species' atmospheric transport, transformation, and deposition properties. Two types of receptor models were employed in this study: a simple meteorological analysis using back-projected air mass trajectories and a statistical multivariate model, Factor Analysis (FA).

Three-day, mixed-layer, back-projected air mass trajectories terminating at each of the five sampling sites were calculated for most of the sampling days by Gerald Keeler at The University of Michigan using the Branching Atmospheric Trajectory model (*30, 31*). The air mass trajectories were employed to determine the average concentrations and the overall contributions of observed Hg levels originating from various compass directions and also to confirm the source identification by FA.

Factor analysis is a particular formulation of a class of multivariate receptor models that are based on the reconstruction of a measured variable by a linear combination of source terms. Mathematically, the goal of FA is to reduce the dimensionality of a data set of interrelated variables so that a small number of derived variables, or factors, can explain the maximum amount of variance in the original data set. The advantage of FA over the more commonly used approach of Chemical Mass Balance (CMB), is that CMB requires that the emissions of most of the contributing sources be fairly well characterized. This information is often not available, particularly in the case of trace elements, for several reasons: the emissions have not been measured; the source type consists of a mixture of many sources; or the relevant sources have not been identified. The FA overcomes these difficulties by using the information contained in the correlations between the observed species to determine the number of significant sources, their compositions, and the source contributions (*32*).

The numerical outcome of applying FA to a data set of environmental measurements is the generation of two matrixes: the factor loading matrix and the factor score matrix. The factor loading matrix contains the normalized source composition information for each of the measured species or parameters and has dimensions of n by p, where n is the number of measured variables and p is the number of factors or sources. The identification of a specific source type or region with a factor is accomplished using known marker species or ratios. The factor score matrix is made up of the normalized source contributions to each sample; it has dimensions of p by m, where m is the number of samples. In general terms, the product of these two matrixes should reproduce the original data set, which has dimensions of n by m.

Because FA requires an initial normalization of the data, the factor score matrix has an average value of zero for each source; therefore, it cannot be used to estimate the sources' contributions to the measured concentrations. To perform this estimate, the factor score matrix must be partially unnormalized so that the average contributions from each source group may be accounted for. A method for performing the conversion from the initial, normalized factor scores into absolute factor scores (AFS) was developed by Thurston and Spengler (*33*). A multiple linear regression (MLR) can then be performed using the AFS matrix as the independent variables and the measured concentration matrix as the dependent variables. This process results in an estimate of the daily contribution from each source to the measured concentration of each species.

The major limitation in the use of FA as a means of identifying individual sources of a measured species is the fact that observed correlations between species may be due to conditions other than their common origin. The combining of two or more sources into a single factor may be due to spatial effects such as the mixing together of two sources that are collinear with the receptor site (referred to as smearing) or to temporal effects such as common weekly or

TABLE 1. Summary Statistics for Fine particulare Mercury Measurements at the Five Sampling Sites[a]

site	no. of measurements	arithmetic mean concn (all samples)	arithmetic mean concn (minus outliers)	median concn	site background concn
Belleayre	253	37	36	20	9
Moss Lake	229	41	34	20	7
Perch River	242	64	57	31	12
Westfield	219	54	42	25	11
Willsboro	261	47	40	21	8

[a] All concentrations are in (pg/m^3). Due to limitations in the statistical receptor modeling, several outliers (concentrations greater than about 5σ from the mean for one or more of the elements) needed to be excluded from the FA at each site.

seasonal variations in emissions (*34*). The former condition can result in regional factors, which are made up of a mixture of independent sources that are both close enough to each other and far enough from the receptor site that they cannot be individually identified by the model. A second limitation of FA is that the model is not mathematically constrained to produce physically meaningful results, and so it occasionally produces negative estimated contributions from minor sources (*35*).

Results and Discussion

Summary statistics for fine particulate Hg levels at the five sampling sites are provided in Table 1. Because the frequency distribution of the data follows a log-normal distribution, the arithmetic mean is greatly influenced by a small number of very high concentration measurements; therefore, the median concentration is also given. The particulate Hg levels found in this study are comparable to those found previously at similar sites in Vermont and Michigan (*12*), in Wisconsin (*36*), and in the Nordic countries (*37*). The receptor site background was been operationally defined as the most frequently occurring concentration of the log-normal fitting of data. Site background concentrations were used to substitute for missing data points and measurements below detection limits for all of the elements in the FA. This method for completing the data matrix does not significantly impact the FA results when compared directly with other methods.

Overall Directional Patterns. Back-projected air mass trajectories terminating at each of the sampling sites were used to plot the average concentrations and percent contributions of fine particulate Hg arising from each of eight directional sectors (Figure 2, panels a and b, respectively). The values in the first of these figures are the mean measured Hg concentrations averaged over only those sampling periods when the air mass trajectories were contained within a single sector. The effect of specific sources being relatively close to one of the sampling sites can be seen in three cases: in the northern sector at Westfield, which is influenced by the Toronto area 130 km away; in the northeastern sector at Willsboro, which is influenced by Burlington, VT, 15 km away; and in the northeastern sector at Perch River, where an aluminum production facility is about 120 km away. Figure 2b shows the overall, relative impact on the Hg levels from sources in the various sectors. The values in this figure are the total of the measured Hg concentrations associated with trajectories from each sector divided by the total of all the measured concentrations. Therefore, this figure includes the effects of the dominant meteorological patterns in the region: the prevalence of westerly winds and the rarity of easterly winds. Even though there are significant Hg sources to the east or northeast of some of the sites (e.g., Willsboro), these have only a minor influence on the overall Hg levels. The most influential sources of Hg impacting the region are within the northwest, west, and southwest sectors, all of which are directed away from most of New York State itself.

Source Identification. The FA was applied to the measured data from each of the sites in order to identify the types of sources impacting the Hg levels of fine aerosols in the region. Table 2 shows the factor loadings for sources with positive Hg loadings and for those elements or ratios that were used as markers for source identification. Individual loadings are a measure of the correlation between the variance of the original variables and the variance of the derived factors. The identification of a source type with each of the factors and observed differences among the sites are discussed below.

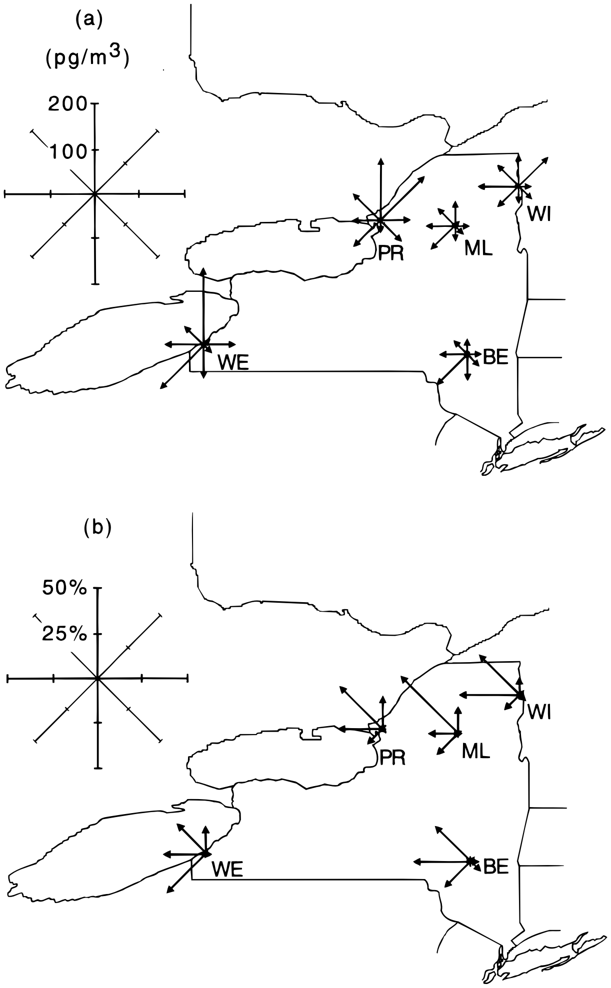

FIGURE 2. Average fine particulate mercury concentrations (a) and overall percent fine particulate mercury contributions (b) originating from eight directional wind sectors.

The strongest Hg loadings were observed for factors that are associated with copper smelting. This identification was principally made by means of their high loadings of As and the ratio of As:Se. Arsenic and Se are emitted from various anthropogenic sources, and their presence is generally used as a marker for coal-burning activities. Although the ratio of As:Se in most atmospheric particulate material and in

TABLE 2. Factor Loadings for Source Types and Source Regions (Shown with Corresponding Wind Directions) of Fine Particulate Mercury[a]

	source																						
	copper smelters					U.S. regional (SW, W)					crustal material				oil refining & combustion			Canadian regional (N, NW)		other smelters		local sources	
site	**BE**	**ML**	**PR**	**WE**	**WI**	**BE**	**ML**	**PR**	**WE**	**WI**	**ML**	**PR**	**WE**	**WI**	**BE**	**ML**	**WI**	**PR**	**WI**	**WE**	**WI**	**PR**	**WE**
Na			0.51						0.39									**0.39**	**0.84**				0.32
Mg											0.41	0.42	0.32	0.37			0.38		0.65			**0.37**	0.62
Al											0.61		0.73	0.71								**0.69**	0.40
Cl			0.71		0.38	0.40			0.34										0.61	0.29			
Sc									0.25		**0.87**	**0.88**	**0.82**	**0.83**									
Ti									0.45														**0.42**
V					0.44	0.37	0.45			0.50		0.33	0.30		**0.41**			**0.62**	**0.45**				
As	**0.31**	**0.63**	**0.50**	**0.25**	**0.35**	0.60	0.52	0.59	0.68	0.25		0.35							0.30	0.36	0.63		
Se						**0.88**	**0.88**	**0.88**	**0.81**	**0.81**											0.34		
Cd							0.57	0.43	0.62										0.58	**0.25**	**0.34**		
In								0.31	0.48											**0.50**	**0.77**		
Sb	0.29					**0.72**	**0.80**	**0.72**	**0.78**	**0.58**													
Ba												0.47						0.25					0.74
La						0.34	0.33	0.39		0.41	**0.64**	**0.64**	**0.78**	**0.61**	**0.62**	**0.51**	**0.48**	0.45					
Hg	**0.75**	**0.65**	**0.55**	**0.79**	**0.81**	**0.22**	**0.17**	**0.40**	**0.25**	**0.05**	**0.03**	**0.04**	**0.09**	**0.05**	**0.10**	**0.25**	**0.07**	**0.13**	**0.17**	**0.14**	**0.03**	**0.12**	**0.10**
As/Se	**0.37**	**0.73**	**0.65**		**0.22**														0.28	**0.86**	**0.55**		
La/Sm						0.28	0.32			0.25					**0.81**	**0.78**	**0.89**	0.61				0.30	

[a] Only those elements used for source identification are shown, and loadings less than 0.25 have been omitted (except for Hg). Factor loadings for source markers and Hg are in boldface.

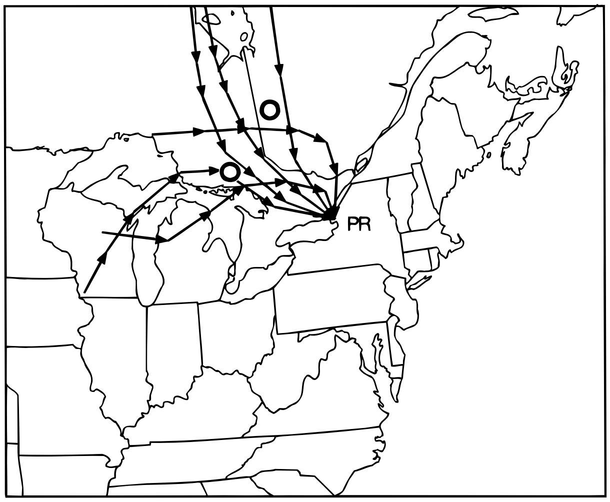

FIGURE 3. Back-projected air mass trajectories terminating at the Perch River site for the samples with the six highest factor scores for the copper smelter factor. The circles show the locations of the two largest copper smelting facilities in the region. Each segment of the trajectory represents a 6-h interval.

aged coal combustion aerosols is approximately 1, in this study, the ratio of As:Se was often found to be significantly greater, reaching as high as 8 or 9. Ratios in this range indicate an additional arsenic source or a source with a substantially different emission pattern. Elevated ratios of As:Se were previously observed by Small et al. (*38*) at five different copper smelter locations and by Rahn and Lowenthal (*22*) for atmospheric particulate material originating from Canadian smelters. Therefore, the ratio of As:Se was used to distinguish between the influences of smelters and coal combustion. The ratio of As:Se was found to be highest when the air mass trajectories passed through eastern Ontario and western Quebec where several large smelters are located. Representative air mass trajectories that were associated with the greatest factor scores for copper smelting at Perch River site are shown in Figure 3. Copper smelter emissions were differentiated from those of other smelters (cadmium, zinc, etc.) by higher Hg factor loadings and the absence of high loadings of the elements In and Cd. A non-copper smelter factor was identified at all of the sites, but very small positive Hg loadings were observed only for Willsboro and Westfield possibly due to the slight smearing into this factor of emissions from urban areas near the sites and collinear with the smelters.

The U.S. regional source, which represents mixed, aged, high-temperature combustion emissions, is characterized by elements such as Se, Sb, and As. This factor has previously been defined as a “regional sulfate component” because it accounts for substantial amounts of the sulfate observed in the eastern United States (*17*). Significant U.S. regional factor loadings for Hg were observed at all of the sampling sites. This factor is consistently associated with southwesterly and westerly winds for all of the sites in this study, indicating the midwestern United States as the relevant source region. Representative trajectories that were associated with the greatest factor scores for the U.S. regional source at Perch River are shown in Figure 4.

High factor loadings of Al, Sc, and the rare earth elements indicate contributions from crustal material or more simply, natural, windblown dust. Factor analysis indicates a small positive Hg loading from crustal material at all of sites except Belleayre.

Oil-related sources such as refining and combustion are indicated by high loadings of the ratio of La:Sm. Concentration patterns of rare earth elements in fine aerosols originating from oil-related sources are different than the natural, crustal rare earth abundance pattern due to high concentrations of La in the zeolites used for catalytic petroleum cracking (*39*). Emissions from oil combustion may be differentiated from those of refineries by the presence of V in the former, although it is often difficult to distinguish clearly between these two related and sometimes co-located source types. Oil-related emissions are correlated with Hg in a single factor at the three easternmost sites. The influence of oil-related sources is also evident in the U.S. regional factor at these sites and in the Canadian regional and local factors at Perch River. An oil-related factor was also identified at Westfield, but there was no Hg associated with it there.

Results of this study include the identification of a factor with a specific Canadian regional signature representing a mixture of various industrial emissions along with marine

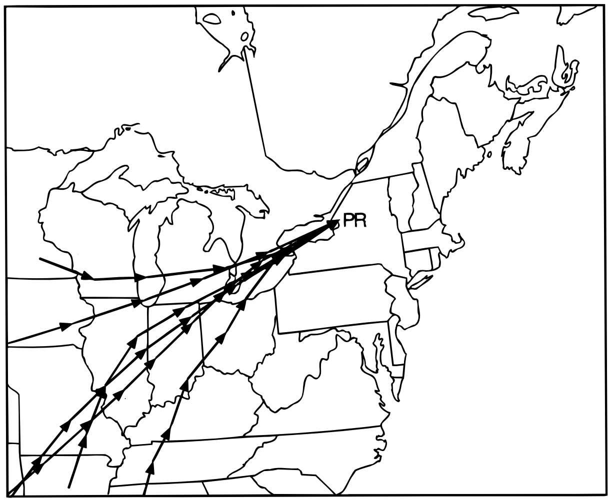

FIGURE 4. Back-projected air mass trajectories terminating at the Perch River site for the samples with the six highest factor scores for the U.S. regional factor. Each segment of the trajectory represents a 6-h interval.

aerosols that most likely originate from the Hudson Bay. Characteristic elements for this Canadian regional factor (and their sources) include V (oil combustion); Na, Cl, and Br (marine); and Cd (smelting). Wind patterns associated with the highest factor scores for this regional source at all of the sampling sites are from the north and northwest, indicating that the sources are located in Ontario and Quebec. Although the Canadian regional source group is observed at every site, positive loadings for Hg were observed only at Willsboro and Perch River. This is likely due to the inclusion in this factor of smelter emissions mentioned above.

Local industrial sources were identified at two of the sampling sites. Aluminum processing emissions were evident at Perch River as indicated by the presence of very high Al and moderate Mg loadings. The strength of the Al loading in this factor was such that the Al loading in the crustal factor, where Al is usually found, was only 0.16. This factor also contained elements such as Au and Cr, which indicates that emissions from precious metals works to the north became mixed with the Al facility emissions. A separate precious metals factor was identified for the other sampling sites but was not associated with Al or Hg at those sites. Because this factor was not seen at any of the other sites and because it was also identified in the coarse fraction samples that were collected at Perch River during the same period, the source must be fairly local to Perch River. Aluminum processing facilities at Massena, NY, about 120 km to the northeast of Perch River, were identified as the probable source for this factor.

An unusual variety of elements appeared in a single factor at Westfield. Paint-related emissions were indicated by high loadings of Ti and Ba, which are used in paints as a pigment (TiO_2) and an extender ($BaSO_4$), respectively. A paint incinerator, in Erie County near the Westfield site, was identified as the probable source related to this factor.

Source Apportionment. To estimate the particulate Hg contributions from each of the identified sources, a multiple linear regression was performed using the daily absolute factor scores as the independent variables and the daily measured Hg concentrations as the dependent variables. The average Hg contributions from each source type to the ambient fine particulate Hg concentrations are shown in Figure 5. Overall, the model attributes about 55% (from 30% to 80%) of the measured fine particulate Hg in the region to smelters and 25% (from 5% to 45%) to U.S. regional sources. The other sources account for only a few percent of the Hg on average, although at a few sites they contribute up to 20%. The unexplained contributions are the constant offsets from the MLR; at four of the sites they can be compared with the site background concentrations, which average 9.4 pg/m^3 (Table 1). The negative unexplained value at Willsboro indicates that the model has overestimated the source contributions there.

Differences among the sites are due to differences in the proximity of the sources to the individual sites and the mixing in of emissions from additional sources at certain sites under particular meteorological patterns. Back-projected air masses associated with the greatest impact from the U.S. regional factor at Perch River and the non-copper smelter factor at Westfield may be influenced by emissions from Buffalo, NY, and Toronto, Ontario. Similarly, trajectories for the non-copper smelter factor at Willsboro may be influenced by emissions from Burlington, VT. Mercury from these urban and/or industrialized areas therefore has been attributed to the major source associated with these factors.

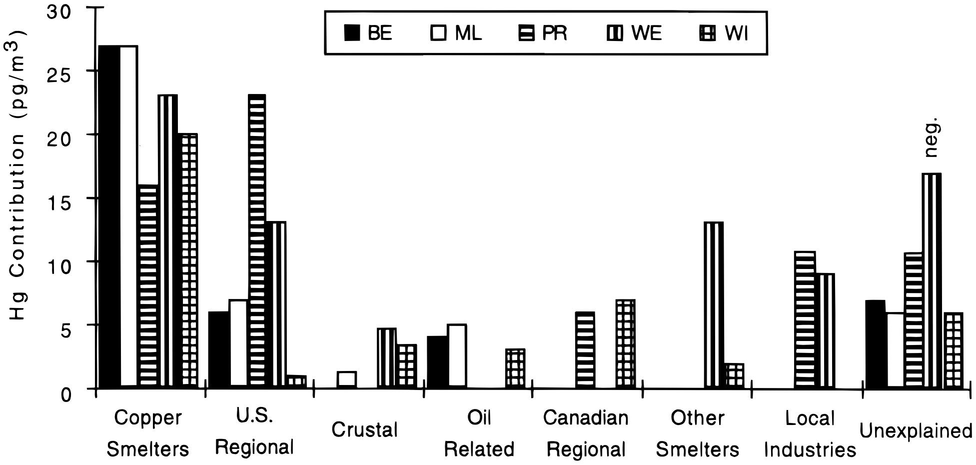

FIGURE 5. Calculated contributions to the fine particulate mercury concentrations from each of the source groups identified by the receptor modeling. Oil-related contributions are a combination of oil combustion impacts at Belleayre and oil refining impacts at Moss Lake and Willsboro. The values shown as unexplained are the differences between the total calculated contributions and the average measured concentrations at each site; this is negative at Willsboro due to the total of the model's estimates being greater than the average measured concnertation. The total of the contributions shown here do not equal the measured average values because of small negative calculated contributions for some of the sources.

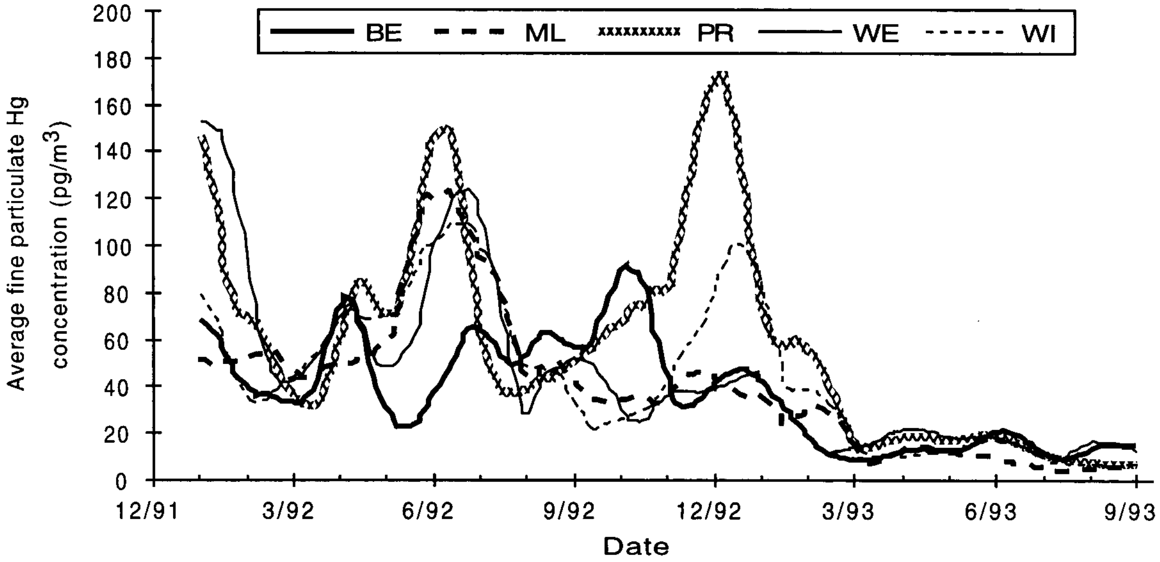

FIGURE 6. Smoothed, monthly average fine particulate mercury concentrations at the five receptor sites showing common overall influences among the sites and the decline in concentrations beginning in early 1993.

Unfortunately, a mathematical error analysis for multivariate receptor models has not been developed (*32*), and therefore a quantitative measurement of the accuracy of the calculated source contributions cannot be derived. Also, because of the lack of mathematical constraints in the model, some of the calculated contributions from minor sources are negative, and the sum of the calculated contributions at Westfield are greater than the average measured Hg concentration by about 30%. Nevertheless, because data from the sites were treated completely independently, the general agreement among the results from the five sites may be taken as a validation of the model's source contribution estimates.

As an independent confirmation of the these results, the measured directional contributions shown in Figure 2b agree fairly well with the corresponding calculated contributions shown in Figure 5. Averaging over all of the sampling sites, the total of the calculated contributions from the Canadian regional and smelting related sources accounts for 58% of the measured Hg. These sources are all in an area to the north, northwest, and to a degree, west of the sampling sites. On the basis of the air mass trajectory data, 44% of the average measured Hg contributions originate from north and northwest. Furthermore, excluding the areas around Toronto and Montreal, the smelting facilities in eastern Ontario and western Quebec are the only major industries within these sectors. The U.S. regional sources that contributed an average of 25% of the measured Hg are all found within the southwestern and portions of the western trajectory sectors; air mass trajectories from the southwest contributed an average of 18% of the measured Hg. Western sector contributions, which average 28% of the measured Hg and which include both of the above source groups (as well as a few others), can make up the differences between the contributions based on the AFS−MLR calculations and those based on the trajectory sector analysis. On a site by site basis, the calculated source group contributions and the measured trajectory sector contributions typically agree within about 10%.

Overall Temporal Patterns. Over the entire sampling period, the Hg concentrations at the five sites follow somewhat similar trends (Figure 6). Three periods of elevated concentrations were observed at two or more of the sites. High Hg levels observed in the winter months were matched by northerly and northwesterly winds and also with the seasonal concentration patterns for other elements originating primarily from Canada such as Na, Cl, and V. The period around June 1992 was also influenced by occasional northerly winds. Differences among the sites are due to the relationships among the source regions, the site locations, and the prevailing winds. The southernmost site, Belleayre, was the least affected by these seasonal meteorological patterns.

The most obvious feature of Figure 6, however, is the drop in Hg concentrations at all of the sites from February 1993 until the end of the sampling in September 1993. When these consistently low Hg levels were first observed, several possibilities for the decline were investigated and ruled out. These included equipment malfunctions, analytical problems, and changes in the filter collection efficiency. The drop was observed only for particulate phase Hg concentrations, not for any other element, nor for vapor phase Hg that was also being measured at the same sites in a separate part of this study. It was concluded that the lower concentrations were due to a reduction in Hg emissions at one or more major sources. The calculated daily contributions from each of the source groups were examined, and it was found that only contributions from the copper smelter sources displayed a decline similar to the measure Hg decline. It was subsequently determined that process technology changes were undertaken and additional emission controls were installed at some of the Canadian smelting facilities at about the time the decline in Hg concentrations was observed (*40*). If these controls were the cause for the measured decrease in particulate Hg, then a clear relationship between source controls and distant environmental impact has been demonstrated. It would also further validate the source identification and apportionment discussed above. However, due to a lack of information about the past or present particulate emissions profiles of these facilities, it is not possible to determine which of the facilities, modifications, or emission controls may be responsible for the measured reduction in Hg levels (*41*).

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Literature Cited

(1) Kurland, L. T.; Faro, S. N.; Seidler, H. *World Neurol.* **1960**, *1*, 370−391.

(2) Porcella, D. B. In *Mercury Pollution: Integration and Synthesis*; Watras, C. J., Huckabee, J. W., Eds.; Lewis Publishers: Boca Raton, FL, 1994; pp 3−20.

(3) Douglas, J. *EPRI J.* **1994**, *April/May*, 14−21.

(4) Mason, R. P.; Fitzgerald, W. F.; Morel, F. M. M. *Geochim. Cosmochim. Acta* **1994**, *58*, 3191−3198.

(5) Sorensen, J. A.; Glass, G. E.; Schmidt, K. W.; Huber, J. K.; Rapp, G. R., Jr. *Environ. Sci. Technol.* **1990**, *24*, 1716−1727.

(6) Slemr, F.; Langer, E. *Nature* **1992**, *255*, 433.

(7) Nater, E. A.; Grigal, D. F. *Nature* **1992**, *358*, 139.

(8) Fitzgerald, W. F.; Vandal, G. V.; Mason, R. P. *Water, Air Soil Pollut.* **1991**, *56*, 745−767.

(9) Lindberg, S. E. *Atmos. Environ.* **1980**, *14*, 227−231.

(10) Mason, R. P.; Fitzgerald, W. F.; Vandal, G. M. *J. Atmos. Chem.* **1992**, *14*, 489−500.

(11) Watras, C. J.; Bloom, N. S.; Hudson, R. J. M.; Gherini, S.; Munson, R.; Claas, S. A.; Morrison, K. A.; Hurley, J.; Wiener, J. G.; Fitzgerald, W. F.; Mason, R.; Vandal, G.; Powell, D.; Rada, R.; Rislov, L.; Winfrey, M.; Elder, J.; Krabbenhoft, D.; Andren, A. W.; Babiarz, C.; Porcella, D. B.; Huckabee, J. W. In *Mercury Pollution: Integration and Synthesis*; Watras, C. J., Huckabee, J. W., Eds.; Lewis Publishers: Boca Raton, FL, 1994; pp 153−177.

(12) Keeler, G.; Glinsorn, G.; Pirrone, N. *Water, Air Soil Pollut.* **1995**, *80*, 159−168.

(13) Lindqvist, O.; Rodhe, H. *Tellus* **1985**, *37B*, 136−159.

(14) Ames, M.; Gullu, G.; Olmez, I. *Atmos. Environ.* **1998**, *32*, 865−872.

(15) *Regional Acid Deposition: Models and Physical Processes*; National Center for Atmospheric Research: Boulder, CO, 1982).

(16) Petersen, G.; Munthe, J.; Pleijel, K.; Bloxam, R.; Kumar, A. V. *Atmos. Environ.* **1998**, *32*, 829−843.

(17) Hopke, P. K.; Gladney, E. S.; Gordon, G. E.; Zoller, W. H.; Jones, A. G. *Atmos. Environ.* **1976**, *10*, 1015−1025.

(18) Tuncel, S. G.; Olmez, I.; Parrington, J. R.; Gordon, G. E.; Stevens, R. K. *Environ. Sci. Technol.* **1985**, *19*, 529−537.

(19) Dzubay, T. G.; Stevens, R. K.; Gordon, G. E.; Olmez, I.; Sheffield, A. E.; Courtney, W. J. *Environ. Sci. Technol.* **1988**, *22*, 46−52.

(20) Keeler, G. J.; Spengler, J. D.; Koutrakis, P.; Allen, G. A.; Raizenne, M.; Stern, B. *Atmos. Environ.* **1990**, *24A*, 2935−2950.

(21) Keeler, G. J.; Pierson, W. R. *Atmos. Environ.* **1994**, *28*, 1535−1548.

(22) Rahn, K. A.; Lowenthal, D. H. *Science* **1984**, *223*, 132−139.

(23) Gordon, G. E. *Environ. Sci. Technol.* **1988**, *22*, 1132−1142.

(24) Keeler, G. J.; Samson, P. J. *Environ. Sci. Technol.* **1989**, *23*, 1358−1364.

(25) Seigner, C.; Wrobel, J.; Constantinou, E. *Environ. Sci. Technol.* **1994**, *28*, 1589−1597.

(26) Stevens, R. K.; Dzubay, T. G. U.S. Environmental Protection Agency, ESRL, Report EPA-600/2-78-112, 1978.

(27) Camp, D. C.; VanLehn, A. L.; Loo, B. W. U.S. Environmental Protection Agency, ESRL, Report EPA-600/2-78-118, 1978.

(28) Olmez, I. In *Methods of Air Sampling and Analysis*, 3rd ed.; Lodge, J. P., Jr., Ed.; Lewis: Boca Raton, 1989; pp 143−150.

(29) Olmez, I.; Ames, M. R.; Aras, N. K. *Proceedings of the 1993 U.S. EPA/A&WMA International Symposium: Measurements of Toxic and Related Air Pollutants*, Durham, NC, May 3−7, 1993; Air & Waste Management Association: Pittsburgh, PA, 1993.

(30) Keeler, G. J. In *Interim Data Interpretation Report of MIT/ALSC Data Set*; Massachusetts Institute of Technology, Nuclear Reactor Laboratory Report MITNRL-060; Massachusetts Institute of Technology: Cambridge, MA, 1994.

(31) Heffter, J. L. Air Resources Laboratories−Atmospheric and Dispersion Model (ARL-ATAD) Technical Memo ERL, ARL-81; National Oceanographic and Atmospheric Administration: Rockville, MD, 1980.

(32) Henry, R. C. In *Receptor Modeling for Air Quality Management*; Hopke, P. K., Ed.; Elsevier Science Publishers: Amsterdam, 1991; pp 117−144.

(33) Thurston, G. D.; Spengler, J. D. *Atmos. Environ.* **1985**, *19*, 9−25.

(34) Keeler, G. J.; Japar, S. M.; Brachaczek, W. W.; Gorse, R. A., Jr.; Norbeck, J. M.; Pierson, W. R. *Atmos. Environ.* **1990**, *24A*, 2795−2805.

(35) Henry, R. C. *Atmos. Environ.* **1987**, *21*, 1815−1820.

(36) Fitzgerald, W. F.; Watras, C. J. *Sci. Total Environ.* **1989**, *87/88*, 223−232.

(37) Iverfeldt, Å. *Water Air Soil Pollut.* **1991**, *56*, 251−266.

(38) Small, M.; Germani, M. S.; Small, A. M.; Zoller, W. H.; Moyers, J. L. *Environ. Sci. Technol.* **1981**, *15*, 293−299.

(39) Olmez, I.; Gordon, G. E. *Science* **1985**, *229*, 966−968.

(40) Trip, L. Personal communication, Environment Canada, Environmental Protection Service, Air Pollution Prevention Directorate, Transboundary Air Issues Branch, Hull, Quebec, November 7, 1996.

(41) A more detailed account of this study may be found in *Upstate New York Trace Metals Program, Vol. 1: Mercury* Olmez, I., Ames, M., Gullu, G., Che, J. Gone, J. K., Eds.; MIT Report MITNRL-064; Massachusetts Institute of Technology, Nuclear Reactor Laboratory: Cambridge, MA, 1996.

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