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Identification of potential regional sources of atmospheric total gaseous mercury in Windsor, Ontario, Canada using hybrid receptor modeling

X. Xu[1] **and U. S. Akhtar**[1,*]

[1]Department of Civil and Environmental Engineering, University of Windsor, Windsor, Ontario, Canada, 401 Sunset Ave, Windsor, Windsor, N9B 3P4, Canada
[*]now at: Department of Chemical Engineering, University of Toronto, 200 College Street, Toronto, ON M5S 3E5, Canada

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Correspondence to: X. Xu (xxu@uwindsor.ca)

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Abstract

Windsor (Ontario) – the automotive capital of Canada does not have any significant mercury (Hg) sources. However, Windsor experiences trans-boundary air pollution as it is located immediately downwind of industrialized regions of the United States of America. A study was conducted in 2007 aimed to identify the potential regional sources of total gaseous mercury (TGM) and investigate the effects of regional sources and other factors on seasonal variability of TGM concentrations in Windsor.

TGM concentration was measured at the University of Windsor campus using a Tekran® 2537A Hg vapour analyzer. An annual mean of 2.02±1.63 ng/m^3 was observed in 2007. The average TGM concentration was high in the summer (2.48 ng/m^3) and winter (2.17 ng/m^3), compared to spring (1.88 ng/m^3) and fall (1.76 ng/m^3). Hybrid receptor modeling potential source contribution function (PSCF) was used by incorporating 72-h backward trajectories and measurements of TGM in Windsor. The results of PSCF were analyzed in conjunction with the Hg emissions inventory of North America (by state/province) to identify regions affecting Windsor. In addition to annual modeling, seasonal PSCF modeling was also conducted. The potential source region was identified between 24–61° N and 51–143° W. Annual PSCF modeling identified major sources southwest of Windsor, stretching from Ohio to Texas. The emissions inventory also supported the findings, as Hg emissions were high in those regions. Results of seasonal PSCF modeling were analyzed to find the combined effects of regional sources, meteorological conditions, and surface reemissions, on intra-annual variability of Hg concentrations. It was found that the summer and winter highs of atmospheric Hg can be attributed to areas where large numbers of coal fired power plants are located in the USA. Weak atmospheric dispersion due to low winds and high reemission from surfaces due to higher temperatures contributed to high concentrations in the summer. In the winter, the atmospheric removal of Hg was slow, but strong winds led to more dispersion, resulting in lower concentrations than the summer. Future studies could use smaller grid sizes and refined emission inventories, for more accurate analysis of source-receptor relationship of atmospheric Hg.

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Abbreviations of states/provinces: Alabama (AL), Arkansas (AR), British Columbia (BC), Georgia (GA), Iowa (IA), Illinois (IL), Indiana (IN), Kentucky (KY), Louisiana (LA), Manitoba (MB), Michigan (MI), Minnesota (MN), Mississippi (MS), Missouri (MO), Newfoundland and Labrador (NL), Ohio (OH), Ontario (ON), Oregon (OR), Pennsylvania (PA), Tennessee (TN), Texas (TX), West Virginia (WV), Wisconsin (WI).

1 Introduction

Mercury (Hg) is emitted into the atmosphere from both natural and anthropogenic sources. Gaseous elemental Hg (GEM, Hg^0) is chemically inert, exhibits high volatility and low solubility in water. These properties result in high atmospheric residence time, approximately 0.5–2 years, and thus, Hg^0 can be transported over long distances (Poissant et al., 2002). Monitoring of atmospheric elemental Hg has been conducted in urban, rural, and remote locations around the world (e.g. Sprovieri and Pirrone, 2008; Nguyen et al, 2008; Choi et al, 2009; Fu et al., 2009; Rutter et al., 2009). The majority of the monitoring studies employed Tekran® 2537A Hg vapour analyzer (Tekran Inc., Toronto, ON, Canada) which measures total gaseous Hg (TGM). Hg^0 constitutes 97–99% of the total atmospheric Hg with the remaining 1–3% encompassing other Hg species such as reactive Hg (Poissant, 2000; Lindberg et al., 2007). Elevated Hg concentrations were observed at remote lake regions far from the anthropogenic sources (Swain et al., 1992; Kellerhals et al., 2003). This indicates long range transportation and the consequent deposition is the major pathway of Hg contamination in remote locations. Thus, the emission of Hg from local sources affects not only the nearby areas; it also affects the global troposphere. Consequently, the observed Hg concentrations at a receptor site are affected by local, regional and global sources.

Hybrid receptor modeling has been used successfully for potential regional source identification of TGM, both for rural and urban areas (e.g. Poissant, 1999; Han et al., 2007, Choi et al., 2008). This method incorporates backward trajectories and observational Hg concentrations at the receptor site to obtain the potential source con-

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tribution function (PSCF). Results of PSCF provide potential regions that are related to high concentrations observed at the receptor site. This approach is advantageous since receptor concentrations are required, while emission data from individual sources are not essential (Lynam and Keeler, 2006). However, cross examination of potential source regions with emission inventory is desirable to prevent faulty identification. Techniques have also been developed to determine uncertain geographic regions of emission sources (e.g. Owega et al., 2006).

This research work was aimed at identifying the potential regional sources of TGM and also the effects of these regional sources on seasonal variability of TGM in Windsor, ON, Canada. Windsor is an industrialized urban city with a population of 200 000 (Statistics Canada, 2008). In addition to local sources associated primarily with the automobile industry, Windsor is situated along the Canada-USA border, downwind of several industrial states e.g. MI, OH and IN. As a result, Windsor also experiences trans-boundary air pollution. The combined effects of local anthropogenic sources and trans-boundary pollution have resulted with poor air quality in Windsor (Ontario Ministry of Environment, 2005, 2008). Investigation of contributing factors, such as regional transport and reemission of Hg, is paramount to understanding source and fate of Hg in an urban environment.

2 Methodology

2.1 Sampling site and instrumentation

The sampling site, shown in Fig. 1, was located on the campus of the University of Windsor (42°18.27′ N, 83°3.98′ W). The site was 27m north of Wyandotte St. West and opposite the Wyandotte St. entrance to the busiest border crossing between Canada and the USA – the Ambassador Bridge. The site was also in close proximity to Huron Church Road (approximately 200 m west); which is the main corridor leading to the bridge. Traffic is heavy in these areas due to the border crossing, local traffic and traffic associated with the University of Windsor.

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A Tekran® 2537A Hg vapour analyzer was used to measure TGM concentration in the ambient air at 5 min intervals. The sampling inlet height was 5 m above well kept grass. Particulate matter was removed from the sampling air by a 47 mm Teflon filter (Tekran Inc., 2006) which was replaced monthly. The Hg analyzer was calibrated automatically at 23 h intervals through the built-in permeation Hg source. Weekly routine maintenance was conducted to ensure proper operation of the equipment throughout the study period. Quality control was applied to exclude data from further analysis in the events of abnormal operation conditions.

Hourly meteorological data from 2007 were collected from the Environment Canada website (Environment Canada, 2008a). The parameters were measured at Windsor International Airport, located approximately 10 km southeast of the sampling site. Meteorological data considered in this study include: ambient air temperature, relative humidity, wind speed, and wind direction.

2.2 Annual and seasonal TGM concentrations

Five-minute TGM concentrations were averaged to hourly values. Then daily means were calculated. Eastern Standard Time (EST) was used for both the Hg concentrations and meteorological data. For seasonal analysis of TGM concentration, the study period of 2007 was divided into four seasons: winter, spring, summer and autumn. The winter months included: December, January and February; spring: March, April and May; summer: June, July and August; fall: September, October and November. The analysis of variance (ANOVA) was used to determine whether the difference in mean concentrations between the seasons is statistically significant. Tukey's test was also used for further comparison of seasonal means. All statistical analyses in this study were performed using MINITAB (Release 14, State College, Pennsylvania, USA) at 95% confidence interval.

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2.3 Identification of potential regional sources

A wind rose was generated to identify prevailing wind directions at Windsor for 2007 using WRPLOT View (Lakes Environmental, 2008). A pollution rose was also generated to identify the wind directions associated with high TGM concentrations in Windsor using Grapher (Version 7, Golden Software Inc., Colorado, USA). Although they do not describe the air mass path before reaching Windsor, the wind rose and pollution rose are simple techniques that facilitate visualization of the wind-concentration relation. The potential source regions were examined further using the hybrid modeling approach which was described previously (Hopke et al., 1995; Polisssar et al., 2001). Briefly, the backward trajectories of all days were modeled to identify the regions which the air mass traversed before arriving at the receptor site. Next, the receptor concentrations above a certain threshold were selected. Then the PSCF values of all grid cells in the domain of interest were calculated. A higher PSCF value indicates a higher probability that sources located in the corresponding regions are influencing the receptor site.

2.3.1 Backward trajectory

HYSPLIT (HYbrid Single-Particle Lagrangian Integrated Trajectory) Model 4 (Draxler and Rolph, 2003; Rolph, 2003) was used to construct the backward trajectories from the sampling site. Backward trajectories were modeled for 293 days in 2007; when daily TGM concentrations were available. The 72-h run time encompassed most of North America and therefore enabled identification of regional Hg sources that could affect Windsor TGM concentrations. The start time for trajectory models was zero hour EST (05:00 UTC). This time was chosen to minimize the effect of local sources and emphasize the effect of regional transport because it was expected that emissions from surfaces and local sources would be at a minimum at zero hour. The release height was chosen as 500 m above ground level for regional transport investigation (Gao et al., 1996; Hafner and Hites, 2003; Begum et al., 2005). The EDAS 40 km

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meteorological data were used since the dataset had the finest spatial resolution for North America that was available on the HYSPLIT website.

2.3.2 Potential source contribution function (PSCF)

The potential source region was identified by the geophysical region covered by the 72 h trajectories, which was 24° to 61° N and 51° to 143° W. For PSCF modeling, the region was divided into 1°×1° grid, resulting in 3404 grid cells. From 293 72-h simulations, there were six endpoints per cell on average. The number of back-trajectory endpoints in each cell was counted for all 293 days in 2007 and in all high concentration events. The high concentration events were considered as days when the receptor Hg concentrations were above a certain value. The probability of affecting the sampling site by each grid cell is related to the number of back-trajectory endpoints in that cell during high concentration events. Following Han et al. (2007), the PSCF is expressed as:

$$\mathrm{PSCF}(i,j) = (m_{ij}/n_{ij})W_{ij} \quad (1)$$

where n_{ij} and m_{ij} are the total number of back-trajectory segment endpoints that fall into the grid cell (i, j), during all days and in days when receptor concentrations were higher than the criteria value, respectively. A higher ratio of m_{ij}/n_{ij} indicates a higher probability of a particular grid through which a passing air mass would result in a higher receptor concentration. W_{ij} is an empirical weight function proposed by Zeng and Hopke (1989) to reduce the undue influence of small n_{ij} on the PSCF values:

$$W_{ij} = \begin{cases} 1.0 & n_{ij} > 2*\mathrm{Avg} \\ 0.75 & \mathrm{Ave} < n_{ij} \le 2*\mathrm{Avg} \\ 0.5 & 0.5*\mathrm{Ave} < n_{ij} \le \mathrm{Avg} \\ 0.15 & 0 < n_{ij} \le 0.5*\mathrm{Avg} \end{cases} \quad (2)$$

where Avg is the average number of trajectory segment endpoints in all cells.

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PSCF values were calculated for annual, as well as each season because the meteorological conditions and TGM concentrations are significantly different among the seasons. For annual potential source identification, the annual mean concentration was considered as the criteria value. For seasonal modeling, both the annual and individual seasonal means were used as the criteria values. The use of both values enables identification of the seasonal features of potential source regions as well as a comparison among the seasons.

The total number of endpoints for each grid cell was plotted on a map of North America to identify regions with frequent air mass passage to Windsor. The PSCF values for each cell were also plotted on the map to identify potential regional sources. However, the PSCF map alone is insufficient in establishing source-receptor relationships. In other words, regions having high PSCF values would be potential sources for Windsor only if there were significant Hg emissions. To identify areas with high rates of Hg air releases, annual Hg air emissions for states/provinces of USA and Canada were collected from the Toxic Release Inventory (USEPA, 2008) and National Pollutant Release Inventory (Environment Canada, 2008b), respectively. These data were also plotted on the map. All maps were created using ArcGIS Version 9.2 (Environmental Systems Research Institute Inc., Redlands, California, USA).

3 Results and discussions

3.1 Annual TGM concentration

A total number of 6659 hourly TGM concentrations were collected for 293 days in 2007. The concentrations were in the range of 0.83 to 40.9 ng/m^3. The overall average concentration was 2.02 ng/m^3 with a standard deviation of 1.63 ng/m^3. This annual concentration was higher than the reported Northern Hemisphere background concentration of 1.5–1.7 ng/m^3 for Hg^0 which constitutes almost 97% of TGM (Lindberg et al., 2007). The observed concentration was also higher than the average concentration of

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1.58 ng/m^3, which was observed at all rural sites of the Canadian Atmospheric Hg Measurement Network during 1995–2005 (Temme et al., 2007). However, it was slightly lower than 2.2–4.5 ng/m^3 observed in other urban sites in US and Canada, e.g., Toronto (2.48 ng/m^3, St. Denis at al., 2006; 4.5 ng/m^3, Song et al., 2009), Detroit (2.2 ng/m^3, Liu et al., 2007), Chicago (3.6 ng/m^3, Landis et al., 2002), Milwaukee, WI (2.48 ng/m^3, Rutter et al., 2008), New York (3.84 ng/m^3, Carpi and Chen, 2002), Broward County Florida (2.8–3.3 ng/m^3, Dvonch et al., 1995), and Connecticut (2.19–2.69 ng/m^3, Nadim et al., 2001). This places Windsor's ambient Hg concentrations in between rural and urban sites in US and Canada, indicating moderate contributions of local sources.

3.2 Seasonal variability of TGM and meteorological parameters

Statistical summary of seasonal TGM concentrations and meteorological parameters are presented in Table 1. In Windsor, summer conditions are characterized by high temperatures and low wind speeds, while winter conditions are characterized by low temperatures and frequent high wind speeds. The weather patterns are similar in spring and fall, with mild temperatures and medium wind speeds. Seasonal variability in Hg concentration was also observed. The highest seasonal TGM concentration of 2.48 ng/m^3 was seen in the summer, followed by a winter mean of 2.17 ng/m^3, whereas the means were lower in spring (1.88 ng/m^3) and fall (1.76 ng/m^3). The results of ANOVA indicate statistically significant ($p < 0.05$) differences in the mean concentrations among the four seasons. The results of Tukey's test indicate that the mean concentrations for winter and summer were statistically different, while the difference in the mean concentrations of spring and fall were statistically insignificant. Also, the summer and winter means were statistically higher than the means of spring and fall. Higher variability, indicated by the coefficient of variation, was observed in summer and winter, but low in spring and fall.

One possible reason for such higher TGM concentrations and higher variability in summer is elevated emissions from urban surfaces when temperature is high. Gabriel

et al. (2006) observed higher Hg fluxes during summer months, which stem from soil, grass, and pavement in an urban setting. A study conducted at several urban sites in New York (Capri and Chen, 2002) suggested that the emissions from urban surfaces could elevate ambient Hg concentrations. Another possible reason of high concentrations in summer is the increased electricity demand resulting in more coal combustion for power generation. There is no coal fired power plant in Windsor, however states to the south and southwest of Windsor (e.g., IL, IN, OH, and MI) are the largest source of mercury emission from coal fired power plants in North America (Keating, 2003). There were five coal fired power plants in ON which contributed one third of the provincial Hg emissions (Ontario Clean Air Alliance, 2007). Thus, transportation of airborne Hg from regional sources contributed to higher TGM concentrations. In addition, lower wind speeds during the summer (Table 1) decreased the dilution of atmospheric Hg. This resulted in an accumulation of Hg, in spite of the increased atmospheric reaction and removal. High concentrations in winter are attributable to increased energy demand for heating, resulting in increased coal combustion (St. Denis et al., 2006). The low atmospheric oxidant concentration (O_3) and low removal rate of atmospheric Hg in winter are other factors that elevated Hg concentrations (Stamenkovic et al., 2007). During the spring and fall, milder temperatures reduce the electricity demand for heating and cooling and consequently lead to lower concentrations and lesser variability. The above analysis suggests that transportation of airborne Hg from regional sources may significantly influence the overall TGM concentration as well as the seasonal variability in Windsor.

3.3 Potential regional sources

Figure 2a shows a wind rose using hourly wind directions for year 2007. The prevailing winds for the study period were between the south and the west. The pollution rose in Fig. 2b indicates that high TGM concentrations (i.e. the 75 and 95 percentiles) in Windsor were associated mostly with southwest and northeast winds.

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Figure 3 plots the total number of endpoints for each grid ($1^\circ \times 1^\circ$) from HYSPLIT simulation, demonstrating the geographical location of air masses arriving in Windsor. It shows air masses that traversed mostly over MI, WI, IL, IN, OH and ON before reaching Windsor. The prevailing air mass direction was between the northwest and the southwest, while fewer grid endpoints were found in the south, east, and northeast, which is consistent with the wind rose (Fig. 2a). However, the northwest direction was not prominent in the wind rose. In the 72-h simulation time, a few trajectories had travelled long distances: from OR and BC in the west and NL in the east.

3.3.1 Annual PSCF modeling

For annual PSCF modeling, there were 88 out of 293 available days in 2007 with the daily average concentration greater than the annual mean (i.e. the criteria value), thus were considered as high Hg concentration days. The PSCF modeling results are plotted in Fig. 4a. High PSCF values were observed in areas indicating OH, IN, IL, MO, KY, and TN in the southwest as the potential source regions, as well as IA in the west and MI, WI, MN up to MB in the west-north-west. Relatively high PSCF values were found in the northeast as well. The Gulf of Mexico in the south was also identified as a potential source area. Overall, the major source locations lie to the southwest of Windsor, stretching from OH to TX, consistent with the pollution rose (Fig. 2b). The potential regions identified from this study are similar to the potential regions, OH, IN, IL and WI, reported affecting New York (Han et al., 2007), and consistent with sources regions, within the Great Lakes watershed as well as the Ohio River Valley, reported in the Detroit MI study (Lynam and Keeler, 2005).

To verify the potentiality of these regions affecting Windsor TGM air quality, a Hg air emission rate (g/km^2) map for the USA and Canada is shown in Fig. 4b. The annual emission rate for each state/province was calculated by dividing the total air emission of all Hg compounds by the respective state/province area for the year 2006. The overall Hg emission rate was higher in the USA (6.18 g/km^2) compared to in Canada (0.76 g/km^2). The highest Hg emission rates of 33 to 51 g/km^2 were observed in IN,

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OH, PA, WV, and AL. Other high Hg emitting states were IL, KY, TN, LA, and GA. Thus, states that are southwest, south and southeast of Windsor were found to have high Hg releasing sources. In Fig. 4a, the Gulf of Mexico was identified as a source region of Hg. Annual atmospheric deposition, including both wet and dry, was 25 tons to the surface water of the Gulf of Mexico and an additional 22 tons of Hg discharged into the Gulf from the Mississippi River (Neff, 2008). Although air emissions from oceans were not included in Fig. 4b, reemission of Hg from Gulf of Mexico could be a potential source of Hg in Windsor. Results obtained from the emission inventory analysis supports the findings of the PSCF modeling (Fig. 4a): regions located in the southwest significantly affect Windsor TGM concentrations.

3.3.2 Seasonal PSCF modeling

For seasonal modeling, both annual mean and respective seasonal means (Table 1) were used for each season as the criteria value. The same weight function was used for all four seasons as in annual modeling. For comparison of potential regions among the seasons, the same color scheme for weighted PSCF values was used in the plots for all four seasons (Figs. 6 and 7).

Results of seasonal PSCF modeling using annual mean as the criteria value are presented in Fig. 5. In summer, significant source areas were identified southwest of Windsor, from OH to TX as shown in Fig. 5c, including MI, OH, IN, IL, MO, KS, OK, and TX. Presence of potential sources over a wide range of areas was observed in the winter, between the southwest and northwest regions, also in the north (ON) and in the south (Gulf of Mexico) (Fig. 5a). In spring, significant source areas were identified in the southwest (Fig. 5b) as in summer. The potential sources for these periods were located in OH, IN, IL, MO, and TN. Sources were also identified in the northeast, along the Ontario-Quebec corridor in spring. In fall (Fig. 5d), the southwest (OH, IN, IL and MO) were identified as source regions, although the PSCF values were lower compared with other seasons.

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The seasonal modeling depicts the seasonal distribution of potential source areas, which was marginalized by the annual modeling. Significant source areas were identified in specific directions for each season. More potential source regions were identified in summer and winter as the number of concentration exceedances above the annual mean were higher in these two seasons (30 and 25 days respectively), compared to in spring and fall (20 and 13 days respectively). Therefore, this method may not be well suited for comparison among the four seasons.

Figure 6 illustrates the seasonality in potential sources using respective seasonal means. The maximum number of exceedances over the criteria value was observed in fall with 36 days, followed by spring with 27 and lastly, both winter and summer with 15. As expected, more potential source areas were identified with the seasonal mean than with an annual mean (Fig. 5) in winter and summer, while less occurred in spring and fall. This is because less days were modeled in summer (Fig. 6c) using the seasonal mean (2.48 ng/m^3) as opposed to the annual mean (2.02 ng/m^3). MI, OH, IN, IL, AR, MS were identified as significant source regions in summer. Similarly, the potential sources in the south and in the west are responsible for high concentrations (>2.17 ng/m^3) in winter (Fig. 6a).

To further identify the regions responsible for high concentration days for each season, Table 2 lists all state/sprovinces in which there were at least two consecutive grids with weighted PSCF values >0.55, i.e. a high possibility of being a source region. Some regions such as MI, OH, IN, IL were identified in more than one season. Between the two modeling approaches, i.e. using seasonal and ammonal means, the consistency is more pronounced in the summer and winter. From the analysis it can be concluded that days with high Hg concentrations in the summer, spring and fall were affected mostly by the regions to the west and southwest of Windsor (MI, OH, IL and IN), with some influence of the east (ON) in the spring. High concentrations in the winter were affected by regions in the west and southwest (OH, IN, IL and IA) and some remote sources in the south (AL, Gulf of Mexico).

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The seasonal analysis also identified that in each season the regional influences, in terms of emissions and meteorology, affect Windsor's Hg concentration by slightly different mechanisms. Along with high surface emission, regional sources also contributed to the high concentrations observed in summer. High power consumption in summer results in more Hg emissions from the coal fired power plants. A number of coal fired power plants are located in the southwest region of Windsor. This region was also identified as potential source region in seasonal PSCF modeling. Thus air masses carrying Hg from southwest of Windsor at low wind speed (less dilution of Hg) lead to elevated concentrations in Windsor. For the other three seasons, the picture was more complex. In winter, anthropogenic emissions are also high due to high energy consumption for heating. The southwest contributions were not as strong as in summer (Figs. 6 and 7), however there was long range transport from the south, i.e. AL and Gulf of Mexico. On the other hand, higher wind speeds (Table 2) led to more dispersion. Also, there are less chemical transformation and deposition due to low temperatures. The net effect of these major factors led to elevated TGM concentrations in winter. In spring and fall, though the air mass came mostly from the southwest regions, Hg emissions from surfaces and anthropogenic sources were both low compared to summer and winter, resulting in lower TGM concentrations in Windsor.

The seasonal PSCF modeling reveals seasonal features which cannot be ascertained from annual modeling alone. Between the two schemes, maps created using the annual mean identify the distribution of potential sources among the four seasons since the same criteria value was applied. However, seasons with means above the annual average will have fewer high concentration days modeled in comparison with other seasons. The use of respective seasonal means enables the identification of potential sources responsible for high concentration days in each season, thus a comparison among the four seasons is possible. The similarity between Figs. 6 and 7 is apparent, indicating that the modeling results are not very sensitive to a few high concentration days. These events were present in modeling using either seasonal or annual mean, but not part of the counter approach. For example, there were 15 and

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25 days in winter for modeling with seasonal and annual means, respectively. Thus, there were 10 more events modeled with annual mean than with seasonal. The difference in the days had generally not affected the outcome. However, this may not be the case for other datasets. For identification of potential sources, the application of both annual and seasonal means was useful for seasonal PSCF modeling. It was recommended using both methods in the seasonal modeling. When the resources are limited, however, the use of seasonal means is preferred.

A major shortcoming of the hybrid receptor modeling method is that the uncertainty of potential source regions could be large due to the exclusion of emissions in the analysis. As a result, faulty identification of source regions is not unlikely. The use of by state/province emission inventories in this study provides a mechanism to screen potential source regions qualitatively. Nonetheless, smaller grid sizes and better refined emission inventories would allow for more detailed and more accurate analysis of source-receptor relationship of atmospheric Hg. This kind of inventory should include seasonal emissions of individual point sources, such as: coal fired power plant, metal processing, and waste incineration, as well as county wide emissions of area sources.

4 Conclusions

Hybrid receptor modeling using HYSPLIT and PSCF was analyzed in conjunction with the Hg emission inventory of North America, to identify the potential source regions affecting Windsor's TGM concentrations. From the annual PSCF modeling, the major sources were identified southwest of Windsor stretching from OH to TX. Potential sources in the northwest (MI to MB), the west (IA), the northeast (ON) and the south (the Gulf of Mexico) were also identified.

Seasonal modeling identified potential source regions in specific directions for each season. High Hg concentration days in summer, fall and spring were affected mostly by the regions west/southwest of Windsor, where there are a large number of coal fire power plants. In winter, high concentrations were affected by regions in the

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west/southwest and some remote sources in the south including the Gulf of Mexico. Weather related processes, i.e., reemission, chemical reactions and sequential atmospheric removal by dry/wet deposition, atmospheric mixing and dispersion also play import roles in modulating seasonal Hg concentrations. The seasonal modeling was found beneficial for analysis of major factors affecting intra-annual variability of Hg concentrations in an urban setting.

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Table 1. Statistical summary of seasonal TGM concentrations and meteorological parameters in Windsor in 2007.

	Winter	Spring	Summer	Fall
Concentration (ng/m^3)				
N	1962	1478	1062	2157
Min	1.19	0.85	0.92	0.83
Median	1.81	1.71	1.85	1.63
Max	40.9	14.3	27.9	13.6
Mean	2.17	1.88	2.48	1.76
SD	2.01	0.78	2.68	0.58
Coefficient of variation (%)	93	41	108	33
Meteorological Parameters				
Temperature, $^\circ$C, mean (SD)	−2.9 (5.6)	9.8 (8.8)	22.8 (4.5)	13.3 (8.2)
Relative humidity, %, mean (SD)	75.3 (12.6)	63.1 (16.7)	64.4 (15.5)	70.6 (16.4)
Wind speed, km/h, mean (SD)	18.1 (9.5)	17.6 (9.7)	12.0 (7.3)	13.9 (8.5)

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Table 2. Source regions responsible for high TGM concentrations in Windsor.

Season	Using annual mean	Using seasonal mean
Summer	MI, OH, IN, IL, IA, MO, AR, MS, KS, TX	MI, IN, IL, AR, MS
Winter	OH, IN, IL, IA, MB, SK, AL, Gulf of Mexico, ON	IA, AL, Gulf of Mexico
Spring	IN, IL, MO, KY, TN, TX	MI, OH, IN, IL, IA, TN, AL, MO, AR, TX, QC, ON, AB
Fall	IL, MO	OH, IN, IL, MO, KY, AL, TX, WI, MN, ND, VA, ON, MB

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Fig. 1. Map of sampling location at the University of Windsor, Windsor, Ontario, Canada (Letter A indicates the sampling site. Base maps adapted from Google Maps Canada, 2009).

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Potential regional sources of atmospheric total gaseous mercury

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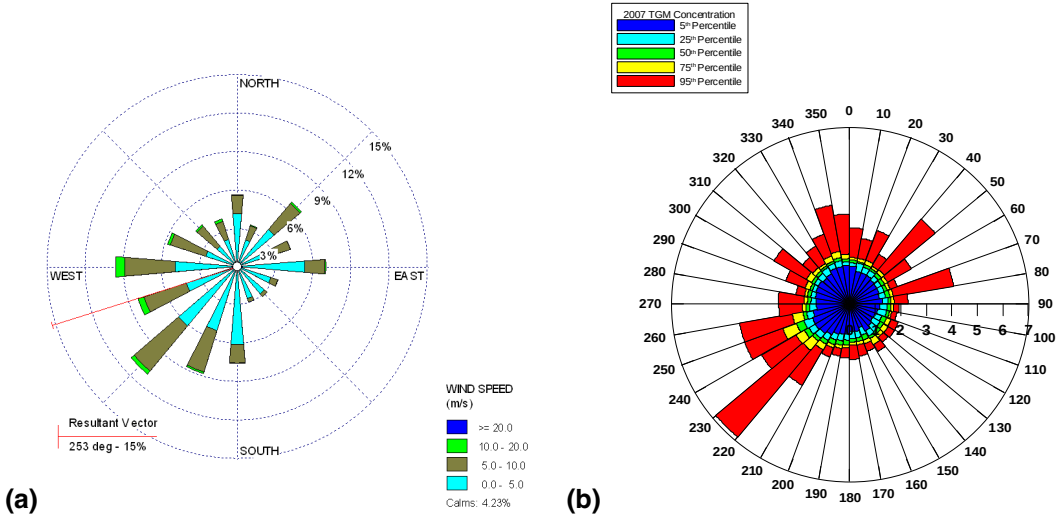

Fig. 2. (a) Wind rose, and **(b)** Hg pollution rose (ng/m^3) for Windsor, 2007.

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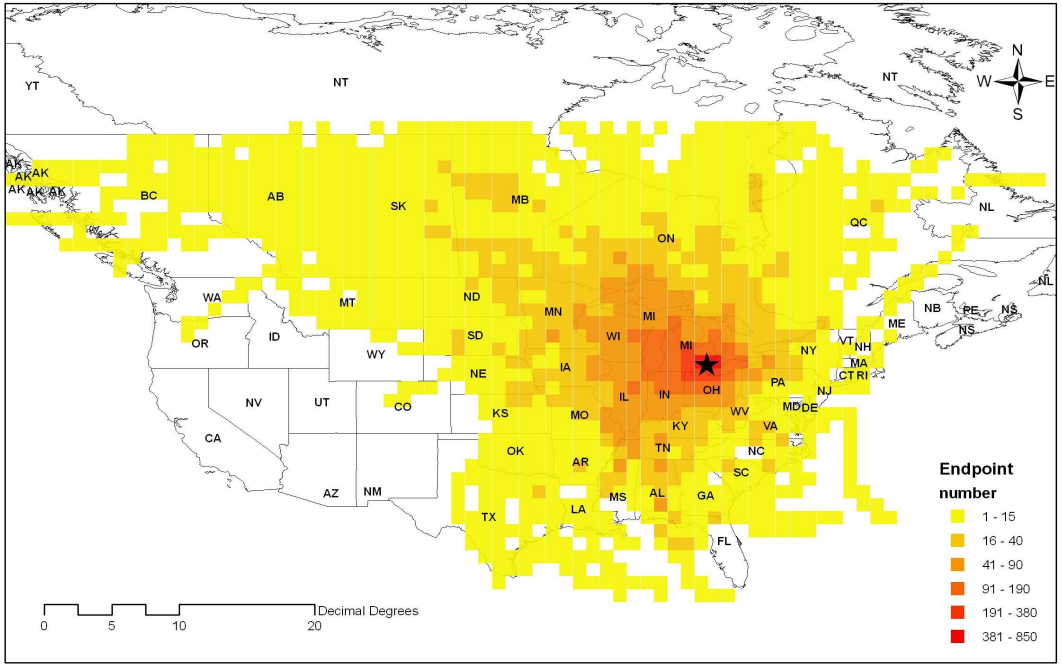

Fig. 3. Map of total number of end points in each grid cell (Star indicates Windsor).

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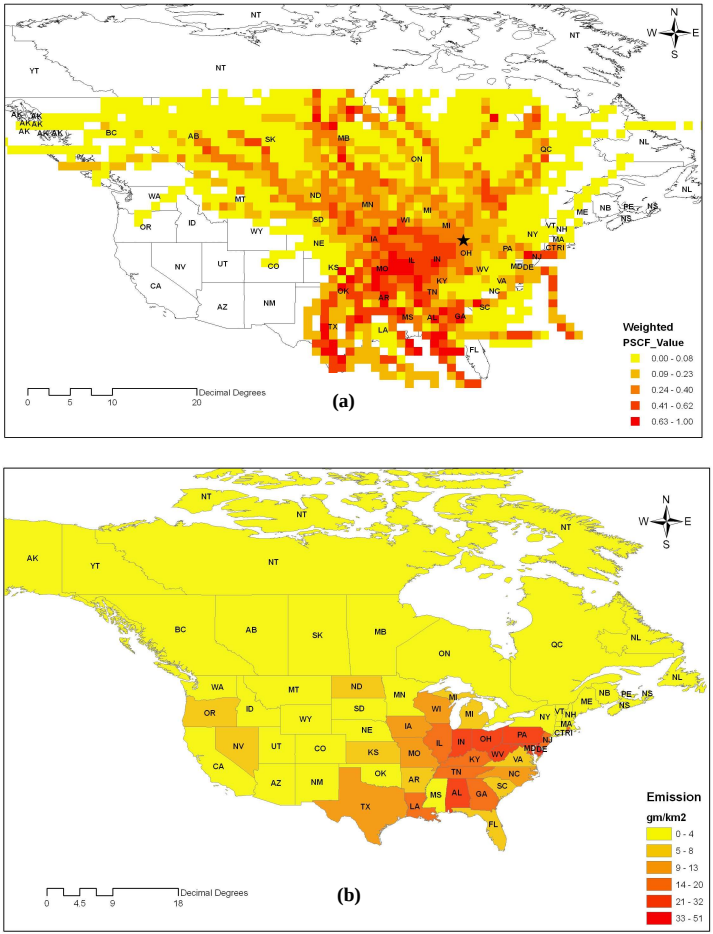

Fig. 4. (a) Map of weighted PSCF Value for Windsor (Star indicates Windsor), and **(b)** annual (2006) air emission rate (g/km^2) of all mercury compounds in US and Canada.

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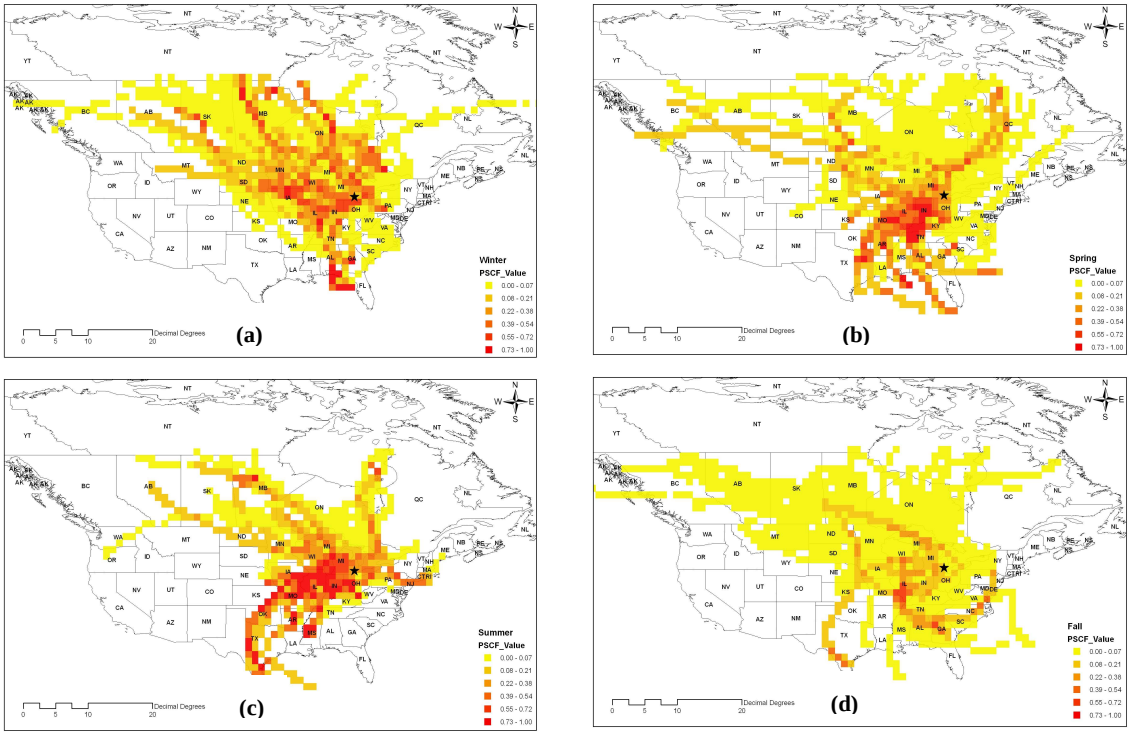

Fig. 5. Weighted PSCF for Windsor in **(a)** winter, **(b)** spring, **(c)** summer and **(d)** fall, using the annual mean of 2.02 ng/m^3.

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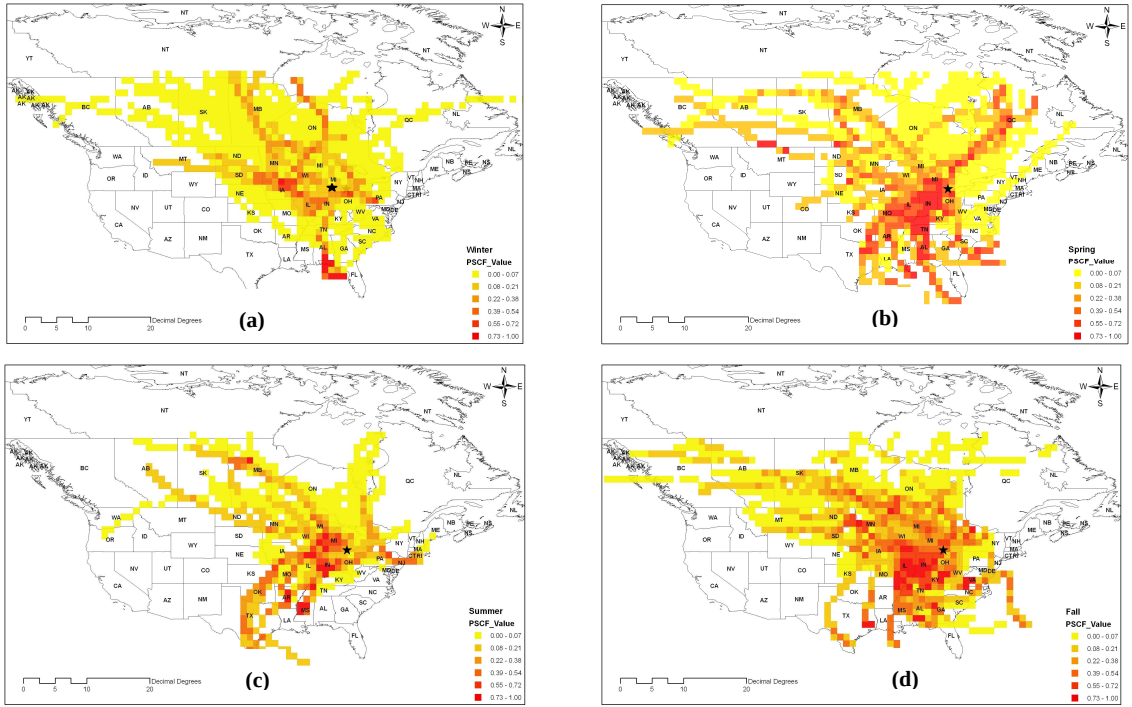

Fig. 6. Weighted PSCF for Windsor in **(a)** winter, **(b)** spring, **(c)** summer, and **(d)** fall, using seasonal means.

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