Atmos. Chem. Phys. Discuss., 13, C2571–C2591, 2013
www.atmos-chem-phys-discuss.net/13/C2571/2013/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Concentration-weighted trajectory approach to identifying sources of Speciated Atmospheric Mercury at an Urban Coastal Site in Nova Scotia, Canada" *by* I. Cheng et al.

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Received and published: 21 May 2013

We greatly appreciate the reviewer for providing valuable comments which have helped us to improve the paper. Our point-by-point responses are detailed below.

Original comment: Summary: In general the topic of this paper is of high scientific interest and worth publishing in ACP. However, in its current state the paper fails to give answers on the questions raised in title, abstract, and introduction. This is mainly due to some significant weaknesses in the applied methodology.

Atmospheric mercury can be considered a 'hot topic'. The problem of global mercury pollution is a focus of several international conventions such as the UNEP mercury program and the UN-ECE Long-Range Transport of Atmospheric Pollution Convention Task Force on Hemispheric Transport of Air pollution (HTAP). Major scientific questions are the oxidization processes of elemental mercury, global and regional transport patterns, and a better understanding of mercury emissions.

This discussion paper is dedicated to the source apportionment of speciated mercury measured at an urban site at the Canadian east coast by means of backward trajectory modelling. Thus, it approaches several of the above mentioned scientific questions. First of all, long time measurements of speciated mercury are still relatively rare. As such these measurements are worth being published and will improve the current state of knowledge about atmospheric mercury pollution. Secondly, linking elevated concentrations of GEM, GOM, and PBM to different sources can help to improve the understanding of emission processes.

Title, Abstract, and Introduction: The aim of the paper is presented concisely and especially the introduction is well written and gives a good overview about different trajectory modelling approaches. There is a good argument why to use a CWT based approach instead of a PSCF approach.

Response: Thank you for your feedback on the strengths of the paper. We hope we have addressed the following weaker points in the revised paper.

Original comment: Methods: 2.1 Site description: It would be important to know which other parameters besides mercury are measured at the described location. Secondary parameters like CO, NOx, SO2 could be key to determine the sources of elevated mercury concentrations. For example a trajectory from the open ocean with increased concentrations of SO2 or sulphate would point towards an influence of emissions from ships.

Response: No other pollutants were measured at the Dartmouth site (men-

tioned in section 2.3 in the revised paper). We previously conducted a study for a different coastal site with speciated atmospheric mercury and secondary parameters (e.g., particulate ions, ozone) and examined them with trajectories from the open ocean and other trajectory origins. Here is a link to the study: http://onlinelibrary.wiley.com/doi/10.1002/jgrd.50169/abstract

Original comment: 2.2 Speciated atmospheric Hg measurements: The measurements are well described. The Tekran instruments are currently the standard devices for measuring elemental and speciated mercury and QA/QC procedures seem to be in accordance with best practise.

2.3 Additional data: it is unclear why the authors use only emissions from industrial sources. This decision seems not to be in line with the aim of the paper. There are also emission data available for non-point sources for the US and Canada in the US EPA 2005 NEI v4 inventory (see ftp://ftp.epa.gov/EmisInventory/). Further, there are estimates about the air-sea flux of mercury in the atlantic ocean (e.g. Soerenson et al, 2010; Sunderland and Mason, 2007) which could be used to approximate the release of GEM from the Ocean. Finally there are gridded global mercury emissions available from AMAP, which also include the residential combustion sector (see http://amap.no/Resources/HgEmissions/).

Soerensen, A. L. et al., An Improved Global Model for Air-Sea Exchange of Mercury: High Concentrations over the North Atlantic, Environ. Sci. Technol. 44, 8574–8580, 2010.

Sunderland, E. M. and R. P. Mason, Human impacts on open ocean mercury concentrations, Global Biogeochemical Cycles, 21(4), 2007.

Response: The two references suggested in this comment were used to interpret the CWT results over the ocean in section 3.6 in the revised paper. The emphasis was on industrial Hg point source emissions in section 3.3 and 3.4 of the ACPD paper because Hg emissions data from 2010-2011 were available which corresponded with the sam-

pling period of the Hg measurements and precise locations of these Hg point sources were available allowing us to sum up the Hg emissions for each grid cell. These can be compared directly with the CWTs for each grid cell using statistical analysis (section 3.4 ACPD paper). Source areas were also compared with non-point sources reported in previous literature and 2008 National Emissions Inventory (section 3.5 ACPD paper).

The most recent gridded global mercury emissions that we found on the AMAP website were from 2000. Given the uncertainties with Hg emissions inventory, it would be more ideal to use more recent data to match the 2010-2011 sampling period of the speciated atmospheric Hg measurements.

Original comment: 2.4 Determination of CWTs: This section misses a thorough discussion of trajectory model uncertainties. (e.g. Scheele, 1996; Stohl, 1997). First of all, because of the inherent uncertainty of trajectory models in general a single trajectory is not enough to determine the source of an air parcel. This is the reason why HYSPLIT allows the use of ensemble and matrix trajectory runs, as well as different reanalysis data sets as meteorological basis for the model calculations. It is common practise to use ensemble runs to reduce the model uncertainty. Uncertainties tend to be especially high near the planet surface, thus it is questionable why 100m is used to characterize air masses at the sampling location. Furthermore, a single starting time cannot represent the source for an aggregated air sample taken over the course of 2 hours. As an example I attached a pdf of a HYSPLIT run using trajectory ensembles with starting time 12h, 13h, and 14h. When using only a single trajectory the identified source could be either the Atlantic Ocean or an industrial area in the east US (see Fig. 1). The resolution chosen for the calculation of CWTs seems fair. Although it might be even indicated to use a lower resolution such as 1o x 1o to account for the uncertainty of the trajectories. In general the resolution should be chosen in a way that the majority of trajectory end points from an ensemble are aggregated to the same grid cells. Moreover, the altitude of the trajectories is not incorporated into the method at all. It is of course a huge difference whether the air parcel travels through a grid cell at 1000m

or at 100m. Finally, a duration of 48 hours could be too short for long lived species like GEM or low wind speed episodes. For PBM it could be important to use the first precipitation event (also available in HYSPLIT) to determine the length of the trajectory because PBM is effectively scavenged by precipitation.

Scheele, M.P., et al., Sensitivity of trajectoried to data resolution and its dependence on the starting point: in or outside a tropopause fold. Meteorol. Appl.3, 267-273 (1996).

Stohl, A., Computation, Accuracy and applications of trajectories – a review and bibliography, Atmos. Environ. 32, (6), 947-966, (1998).

Response: In the revised paper (section 3.7), a more detailed discussion on the model uncertainties and limitations have been added and includes the findings from the Scheele et al. (1996) and Stohl (1998) references. It is also discusses how these trajectory uncertainties are related to the model parameters selected. A detailed response is provided below as well:

The study did not perform sensitivity analyses on the back trajectory simulations using ensemble and matrix trajectories and varying the starting height and trajectory duration. The example of trajectory ensemble in the reviewer comment Fig. 1 shows there are uncertainties with the distances travelled by the back trajectories due to small offsets in the meteorological data in the HYSPLIT ensemble model. According to HYSPLIT (http://ready.arl.noaa.gov/hysplit-bin/trajtype.pl), the starting height ideally needs to be > 250 m for running trajectory ensembles because of the offsets. A starting height of 100 m was chosen because it is more representative of the height of the Hg measurements, which was nearly at sea-level (coastal site). Different starting positions and heights will affect the back trajectories and does not lead to more accurate trajectories (Stohl, 1998); therefore, it's best to choose one that is representative of the Hg measurement location. In the CWT model equation, the Hg concentration should correspond with the arrival of the back trajectory at the site. In future work, speciated atmospheric Hg measurements need to be taken at a higher elevation so that

a higher starting height and ensemble trajectories can be applied. Similarly, increasing the number of start times (currently every 3 hours to hourly start times) requires continuous hourly speciated atmospheric Hg concentrations in the CWT model. But the sampling and analysis cycle for GOM and PBM species at Dartmouth and other mercury monitoring networks is 3 hours.

A lower grid resolution could reduce uncertainties with the trajectory distance, but a potential drawback is the less precise identification of potential source areas. The CWT results were not examined at different altitudes; the results included all trajectory segment endpoints passing through the grid cell from any height. We verified that all the trajectory segment endpoints were at an altitude below the model ground level of 1.6 km. It might not be very useful for examining the trajectory segment endpoints in each grid cell at different altitudes because there are uncertainties with vertical mixing and turbulence; thus it would be difficult to differentiate between surface emissions and stack emissions from a grid cell. The main reasons for using 48 hour trajectory duration was because of the potential dry and wet deposition of shorter-lived Hg species (GOM and PBM with atmospheric residence times of only days to weeks) and there are less uncertainties (due to interpolation and wind field errors) in the trajectory position using a shorter duration as oppose to a longer one (Stohl, 1998). The 48 hour trajectories did extend to the U.S. east coast, where most of the regional Hg emission sources are located.

Original comment: p4189:11: "It is a rigorous approach because for every concentration one back trajectory needs to be generated, which added up to 5178 back trajectories from 2010–2011." Of course the number of trajectories is not necessarily correlated to the quality of the results.

Response: We deleted the first part of the sentence. This sentence describes how many back trajectories were generated and why. Readers could potentially use it for reference if they are applying the CWT model. The number of trajectories affects the number of trajectory segment endpoints in the grid cells. It was mentioned in the ACPD

paper on p. 4191 in lines 8-13 that too few endpoints would lead to the false identification of source areas and that grid cells with < 2 were considered highly uncertain.

Original comment: p4190:20 'Since counting the endpoints in the 2400 grid cells can be a time-consuming task, a more automated process was created using typical data spreadsheet functions, e.g. database count function with the latitude/longitude boundaries for each grid cell as the counting criteria' Do not dwell on the obvious.

Response: This sentence was deleted in the revised paper.

Original comment: 2.5 CPF: Why not also use the previously calculated trajectories for this purpose? Or are these measured wind directions? These could of course be useful to determine local sources like onroad traffic, harbor and ship emissions, residential heating emissions, industrial area emissions.

Response: Yes, the CPF is based on measured wind directions (emphasized in section 2.4 in the revised paper). They were used to identify local sources, since the 40 km resolution of the back trajectories would be too coarse. Section 3.6 in the ACPD paper previously discussed about the local sources mentioned in the comment and also potential new sources of Hg emission.

Original comment: 3. Results: In general the results part contains many questions but only very few answers. Basically, it shows that the chosen methodology is not appropriate to answer those questions.

Response: CWT model illustrated the locations of source areas and comparison with Hg emissions inventory allowed us to identify potential types of industrial Hg sources affecting Dartmouth and conduct statistical analysis between the modeled source areas and industrial Hg emissions from each grid cell (ACPD paper section 3.3 and 3.4). Source areas were also compared with non-point sources (local and regional) reported in previous literature findings and 2008 National Emissions Inventory (ACPD paper section 3.5 and 3.6). In the revised paper (section 3.6), we compared CWT results over the

ocean with those from a recent modeling study and there were consistencies between the results. Some of the questions raised in the results are due to model uncertainties and limitations, which have been added to the revised paper in section 3.7.

Original comment: 3.1 Overall concentrations: It would be good to also give median concentrations and a plot of the actual measurements. (If there are certain extreme mercury events that are limited in time it would be interesting to do a detailled analysis of these events)

Response: The median concentrations of GEM, GOM, and PBM were added to revised paper in section 3.1 and the time-series measurements were plotted in Figure 2. They are also included here: Median: 1.62 ng/m3, 1.1 pg/m3, and 1.6 pg/m3; Mean: 1.67 ng/m3, 2.1 pg/m3, and 2.3 pg/m3 for GEM, GOM, and PBM respectively

The Condition Probability Function in section 3.6 in the ACPD paper had previously examined wind directions associated with elevated Hg events (defined as $\geq$ 75th percentile in each season) and this analysis was focused on identifying potential local Hg sources contributing to elevated atmospheric Hg.

Original comment: 3.2 Seasonal concentrations: This paragraph is fine. I would suggest a different order for the results part. Being an urban station, it is important to first determine the influence of local sources before looking at regional transport patterns. The relatively low GEM, GOM, and PBM measurements indicate that the site could be appropriate to determine long range transport and thus regional sources of mercury. However, episodes which are dominated by local sources should not be used for this analysis.

Response: In the revised paper, the analysis of local Hg sources contributing to elevated Hg events using conditional probability function was moved to section 3.3, where we originally had the seasonally CWT model results and analysis of regional sources of Hg.

Original comment: 3.3 Seasonal CWTs for GEM, GOM, and PBM: It is very interesting to see the results of the CWT calculations. Especially for meteorological conditions where air masses come from the south-west it seems obvious to determine the large industrial area there as a source for mercury. (At least if local sources have been filtered out as suggested above). Moreover, figures 2-4 show some distinct trajectories from the north and the west that seem to be influenced by major point sources. It would be interesting to go more into detail here and describe these sources. (e.g. Indicate in the plot which are the >5kg/a sources) On the other hand, it is risky to determine the Atlantic as a source only because trajectories have passed over it (see the attached figure). It could easily be polluted air transported from the land over the ocean. Especially for GEM 48hour trajectories seem too short for this conclusion since the species is extremely stable. On page 4196 line 21-25 you state that the Atlantic is a source for mercury in summer because of shorter trajectories. So it should be clear that this result is an artefact and you need to calculate longer trajectories and only count those that do not pass over land. On page 4196 line 19,20 you identify the water bodie between Maine and Nova Scotia as a source. How important are ship emissions in this area? Can you be sure it is not another artefact of the CWT methodology?

Response: The local urban Hg sources cannot be filtered out using the conditional probability function analysis (i.e. sources in the wind direction associated with elevated Hg concentrations) because this method does not entirely rule out the impacts from regional Hg sources due to potential mixing between regionally transported air and local air. Figures 2 to 4 in the ACPD paper had shown higher CWTs from the north and west directions and the types of Hg point sources in those areas were previously discussed in section 3.3 in the ACPD paper. For example, p.4194-lines 19-23 discussed about Hg sources in Quebec and Ontario and Quebec; p.4195-lines 1-4 discussed about Quebec and central Ontario; p.4195-lines 25-29, and many other examples in section 3.3. The red circles in figures 2 to 4 are the locations of industrial Hg point sources emitting > 5 kg/year and this information included in the figure captions of the revised paper.

In the revised paper, we included an explanation that larger CWTs in the Atlantic Ocean do not always suggest that the ocean was the source of GEM, especially when the large CWTs are located over the ocean but near the coastline (last paragraph of section 3.4). If this was the case, large CWTs for PBM would also be observed over the ocean. It was previously shown that back trajectories originating from land and coastal areas was associated with PBM and other pollutants (e.g., O3, PM2.5, SO2) at a coastal site (Cheng et al., 2013). Based on comparison of Fig. 2 (CWT for GEM) and Fig. 4 (CWT for PBM) in the ACPD paper, there generally were more source areas in the CWT GEM plots (more orange areas) than the CWT PBM plots (more yellow areas); thus we can infer that the ocean was the main GEM source.

Regarding page 4196 lines 21-25, the sentence stated, “As a result of the shorter back trajectories in the summer, GEM, GOM, and PBM concentrations at Dartmouth were predominately affected by sources in Quebec and experienced minimal influence from regions with a high density of industrial Hg sources (southwestern Ontario and northeastern US).” This is not related to the Atlantic Ocean being a source of GEM because of shorter trajectories. The summer plots in the ACPD paper in Fig. 2 illustrated large CWTs located over the open ocean (orange colour near the bottom right of the plot), which indicates the trajectories travelled long distances as well. We also included a plot of the locations of all the trajectory segment endpoints in Fig. 7 in the revised paper, illustrating that similar to other seasons, the trajectories in the summer travelled as far as eastern Canada and the Mid-Atlantic Ocean (sentence also included in section 3.4 in the revised paper where we discussed summer CWT results). Therefore, longer trajectory duration is not necessary.

Regarding page 4196 lines 19-20, shipping ports are located in the coastline along the U.S. east coast. Based on the 2008 National Emissions Inventory, commercial marine vessels in Maine emitted 0.1 kg in 2008 which is relatively small compared to point sources, but it is a source of Hg emissions. But because this potential source area was absent in the CWT PBM plots, we suggested in the ACPD paper in section 3.5 p. 4200

lines 4-8 that photochemical production may be involved. If shipping port activities was a source, there should be effects on PBM since marine diesel engines emit particulate Hg.

Cheng, I., Zhang, L., Blanchard, P., Dalziel, J., Tordon, R., Huang, J., and Holsen, T. M.: Comparisons of Mercury Sources and Atmospheric Mercury Processes between a Coastal and Inland site. J. Geophys. Res. Atmos., 118, 2434-2443, doi: 10.1029/2012JD018419, 2013.

Original comment: 3.4 Effects of industrial Hg sources on CWTs: Again it is strange that only industrial sources have been taken into account. Besides this I consider this to be the key paragraph of the paper. Unfortunately, the CWT methodology seems unable to give a conclusive answer. The main problem is that each grid cell, a trajectory has passed, is considered a source location. Thus a low correlation between emissions and CWT values is to be expected (page 4197 lines 4-10). A much better approach would be to correlate CWT values against the total mercury that has been emitted into a trajectory before it reaches the measurement station. Possibly a dilution factor for the distance as well as a dependency on the altitude (using stack height and average plume rise to determine whether the trajectory came in contact with point sources and only counting non elevated sources if the air mass is relatively close to the surface) of the air parcel need to be incorporated into the method too.

Response: The CWT model and similar trajectory statistical model was focused on identifying known industrial Hg point source emissions because precise locations of these sources and updated Hg emissions data are available. This allowed us to conduct statistical analysis between the modeled source areas and industrial Hg emissions from each grid cell (ACPD paper section 3.4). Source areas were also compared with non-point sources (local and regional) reported in previous literature findings and 2008 National Emissions Inventory (ACPD paper section 3.5 and 3.6). In the revised paper (section 3.6), we compared CWT results over the ocean with those from a recent modeling study suggested by the reviewer (Soerensen et al., 2010). The questions raised

in the results are due to model uncertainties and limitations, which have been added to the revised paper in section 3.7.

We don't agree with the comment that "The main problem is that each grid cell, a trajectory has passed, is considered a source location. Thus a low correlation between emissions and CWT values is to be expected." The first comment applies to trajectory statistical model that examines only the trajectory segment endpoints (e.g. Potential Source Contribution Function). But it doesn't apply to CWT model because it is a function of concentrations and residence times of the trajectory endpoints in the grid cells as mentioned in the ACPD paper on p. 4189 lines 9-11. The concentration needs to sufficiently high so that the calculated CWT is in the upper 10th percentile of seasonal CWTs to be considered a source location (p. 4191 lines 5-8, p. 4193 lines 26-27). We included the locations of the trajectory segment endpoints for each seasons in the revised paper (Figure 7) to show how they are different from the CWT source areas (orange colour grid cells). This point has been clarified in the revised paper (1st paragraph of section 3.5).

The CWT model equation is based on pollutant concentrations corresponding to the arrival of the trajectory at the site. The approach suggested by the reviewer would be different than the conventional model equation and could be tested in future work. The addition of a dilution factor and filtering out the results at different altitudes require a sensitivity analysis to be conducted to see if it a better correlation is obtained. Applying a dilution factor and examining trajectories at different altitudes may introduce more uncertainties because there may be vertical mixing and turbulence in the boundary layer, which was a source of trajectory uncertainties discussed by Stohl (1998). Changes in the boundary layer height throughout the day and night affect vertical mixing, which has subsequent effects on the diurnal patterns of atmospheric Hg concentrations (Sigler et al., 2009; Nair et al., 2012).

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

Nair, U. S., Wu, Y., Walters, J., Jansen, J., and Edgerton, E. S.: Diurnal and seasonal variation of mercury species at coastal-suburban, urban, and rural sites in the southeastern United States. Atmos. Environ., 47, 499–508, doi:10.1016/j.atmosenv.2011.09.056, 2012.

Original comment: Page 4197, line 11-14: "Correlations between industrial Hg emissions and modeled source areas may be dependent on the trajectory duration, use of total versus Hg species-specific emissions for comparison (Choi et al., 2008), and receptor location (Kabashnikov et al., 2011)." This is one example of the many questions raised in the results, that should have been answered. You could use longer trajectory durations for an epsiode with low wind speeds. You could use the above describe methodology with different emission estimates. Using ensemble trajectories will help to reduce dependency of receptor location. Please note that the mercury speciation in emission inventories is subject to large uncertainties and concentrations of GOM and PBM might be dominated by oxidation in the atmosphere.

Response: The potential factors that can affect the agreement between trajectory statistical model results and emissions inventory data suggested in the studies by Choi et al. (2008) and Kabashnikov et al. (2011) can be examined in future applications of the CWT model. Neither studies had used the CWT model for speciated atmospheric Hg. These questions raised are more appropriately answered in a model sensitivity analysis study. There are several reasons for keeping the trajectory duration to 48 hours, e.g. reducing wind field errors with longer trajectories and deposition effects of short-lived Hg species, GOM and PBM. As the reviewer had emphasized, mercury speciation in emission inventories is subject to large uncertainties and concentrations of GOM and PBM might be dominated by oxidation in the atmosphere. Potential dependency on receptor location discussed in Kabashnikov et al. (2011) was referring to where a receptor is located and not the small offsets in meteorological data in ensemble trajectories (there's no change in the receptor location, only offsets in meteorological data points in the HYSPLIT model). They were alluding to how three European sites in the

same region could have different source areas. In the revised paper (section 3.7), a more detailed discussion on the model uncertainties and limitations have been added.

Original comment: Page 4198, line 3-7: "The major source areas that were identified from the CWT plots were often associated with areas that have no known industrial Hg sources. The analysis of CWTs and known Hg point source emissions revealed that overall 94% of elevated CWTs for GEM (defined as $\geq$ 90th percentile of CWTs from 2010–2011) were not associated with known industrial Hg emissions." Considering 48 end points per trajectory this means that on average each trajectory could be associated to 3 major point sources. This again shows, that the CWT method is unable to identify individual sources because of its tendency to create false positives. It would give much more insight to look at whole trajectories and see how many of them have never touched a point source.

Response: The estimate of the number of point sources associated with each trajectory seems to be oversimplified; we didn't use the trajectory residence time as the only criterion to identify point sources. The analysis was conducted on CWT, which is a function of concentrations and residence time of trajectories in each grid cell (p.4189 lines 9-11 in ACPD paper). Concentration is a major factor in the CWT model. If there are trajectories passing over an area without a Hg point source, the concentrations need to be high enough so that the calculated CWT in the grid cell are in the top 10 percentile of seasonal CWTs (criteria for determining major source areas, p.4191 lines 5-8). This has been emphasized in the 1st paragraph of section 3.5 of the revised paper. If the concentration was not included, such as in Potential Source Contribution Function, it would be appropriate to examine whole trajectories. This was why we tried to answer how many elevated CWTs (or major source areas) were associated with different levels of Hg emissions in each grid cell.

Many of the back trajectories were expected not to pass over areas with a Hg point source because of the location of the site and the model geographical domain. About 1/3 of the model geographical domain is the Atlantic Ocean, which does not have Hg

point sources. The plots of trajectory segment endpoints for each season (included in Figure 7 in the revised paper) illustrates that the trajectories traced back to the Atlantic Ocean; therefore it is not unusual that the trajectories had passed over areas with no Hg point sources. Because of these reasons, the CWT model is not reporting false positives on Hg point sources. It is recognized from literature that the ocean is the largest natural source of GEM globally. In the revised paper (section 3.6), the CWT results over the ocean were compared with the net GEM evasion result from a previous modeling study (Soerensen et al., 2010).

Original comment: Page 4198, line 12-18: "When the analysis was conducted separately for each season (Table 3), a higher percentage of elevated CWTs for GEM, GOM, and PBM were associated with industrial Hg emissions in the fall than other seasons. This was previously observed in the fall CWT plots, which illustrated that the major source areas were in regions with the highest density of industrial Hg sources (northeastern US). The percentages were lowest in the winter and summer for GEM and PBM, and lowest in the summer for GOM." How does this fit to the overall low concentrations in Fall? A further analysis of this would be interesting.

Response: The seasonal CWT plots for Hg (Fig. 2 to 4 in previous ACPD paper) shows which areas are more likely to be sources than other areas in a particular season. CWTs above the 90th percentile of the CWTs in each season were considered major source areas, but the value is different for each season. Unlike the seasonal concentrations, the 90th percentile CWT can't be directly compared between seasons. A further analysis has been included in the revised paper (Fig. 8) showing which season had the maximum CWT value for GEM, GOM, and PBM in each grid cell. This analysis allows the source areas to be compared between different seasons. It verified that the region with industrial Hg sources (U.S. northeast) had larger impacts to the Dartmouth site in the fall than other seasons. Although the speciated atmospheric Hg concentrations were lowest in the fall, trajectories travelled over the region with industrial Hg sources more frequently in the fall than other seasons, resulting in a larger CWT. This

explanation was included in the revised paper (section 3.5).

Original comment: Page 4198, line 20-24: This is a very good method to test for false negatives. It would be interesting to see whether the results of this test improve when incorporating the trajectory altitude and ensemble trajectories into the methodology.

Response: Analyzing the CWT model at different trajectory endpoint altitudes would introduce more uncertainties in the results because of vertical mixing in the boundary layer as mentioned in our response for a previous comment. This has been added to the discussion of model uncertainties and limitations in section 3.7 of the revised paper. Similarly, the use of ensemble trajectories is a good way to show the uncertainties in trajectory position due to small offsets in the meteorological data points, but it doesn't help to improve the model accuracy (Stohl, 1998).

Original comment: 3.3 Summary: In the methodology used for this chapter there is a very convincing test for false negatives but not for false positives. The method itself is prone to false positives. This is the reason this paper fails to actually link mercury concentrations to emission sources. Additionally, there are many assumptions about the influence of emissions not incorporated into the model (e.g. residential combustion, oceanic emissions).

Response: As mentioned in a response to a previous comment, the CWT model is not prone to reporting false positives because it is not based only on the trajectory residence time in each grid cell. Concentration is an important factor in the CWT model. Concentrations affect the CWT value, which we used the criterion of the top 10 percentile CWT in each season to identify potential source areas. Since the sampling site was located in a coastal area, back trajectories originating from the Atlantic ocean were expected and it wouldn't be unusual that the back trajectories did not travel over any Hg point sources. This is not an indication of false positives because evasion of GEM from the ocean is a significant source of Hg. In the revised paper (section 3.6), the CWT results over the ocean were compared with a previous modeling study

(Soerensen et al., 2010). Previously (section 3.5 in ACPD paper), source areas were also compared with residential combustion reported in previous literature findings and 2008 National Emissions Inventory.

Original comment: Page 4200, line 28,29: “The results have shown concentration-weighted trajectory (CWT) is a very quantitative and objective method of locating potential sources areas affecting a receptor site.” I do not agree with this sentence.

Response: The sentence was deleted.

Original comment: Page 4201, line 5-10: “Hg emissions from oceans, forests, and different types of residential combustion, the CWT method does require having more precise locations of these sources due to the nature of the grid cells, which is not available from these inventories. Since sources like soil, wildfires, and oceans can occupy a large area (and numerous grid cells), there are also some uncertainties on whether the Hg emissions occur uniformly over the entire area.” There are gridded emissions for emissions from residential combustion. Also oceanic GEM sources can be (although with a high degree of uncertainty) estimated based on publications. The US EPA NEI inventory also includes gridded data for natural mercury emissions from land and ocean. Finally, there are global emissions on 0.5o x0.5âŮę available from AMAP.

Response: There are Hg emissions data from 2008 National Emissions Inventory (NEI) from non-point sources (e.g., residential combustion) and on road (vehicles) and commercial marine vessels, which we used in section 3.5 and 3.6 of the ACPD paper to interpret the CWT model and conditional probability function results. The data was also not in a gridded format. To our knowledge, Hg emissions data from forest fires, land, or oceans from the 2008 NEI were not available. Gridded Hg emissions inventory from the AMAP website may be too outdated (most recent is from 2000) compared to the speciated atmospheric Hg data (2010-2011) and may introduce more uncertainties. In the revised paper (section 3.6), CWT model results over the ocean were compared

with estimates from the recent modeling study by Soerensen et al. (2010).

Original comment: Page 4202, line 1: “The only known industrial Hg source is a cement plant located...” Obviously the word ’local’ is missing in front of the word ’source’

Response: Revised according to your suggestion.

Original comment: Page 4203, line 9,10. The sentence starts with Although and suggests a connection between gypsium mining emissions and artisanal gold mining. Line 9 should probably just be removed to form a sentence like: “Artisanal gold mining is a significant source....”

Response: Revised according to your suggestion.

Original comment: 4. Conclusions: Page 4203, line 27: “The sources where sometimes associated with known industrial sources...” Sometimes is a very unspecific word for a conclusion.

Response: The sentence was revised to, “Some of the source areas were associated with known industrial sources...”.

Original comment: Page 4204, line 19-24: “Large CWTs were potentially in regions where there are Hg emissions from residential wood and oil combustion, forest fires, shipping ports, and oceans as indicated in National Emissions Inventory (USEPA, 2012b) and research- derived Hg emission inventories (Pirrone et al.,2010), but precise locations of these sources are necessary to conduct statistical comparisons with model results.” There are gridded data for mercury emissions from residential combustion (e.g. AMAP) Locations of shipping lanes for the US-Canadian east coast are available in the US EPA NEI. There are high resolution land-use datasets which can be used to identify port areas. There are estimates for the GEM flux from the Atlantic (see comments above). Arguably forest fire are the most problematic emission source. There are satellite based products that determine forest fires based on temperature measurements. However precise emission factors are not available.

Of course the non-point source emissions are subject to much larger uncertainties than the industrial mercury emissions. However, this is not a reason to not incorporate the available data into the methodology.

Response: Gridded Hg emissions inventory from the AMAP website was too outdated (most recent is from 2000) compared to the speciated atmospheric Hg data (2010-2011). Local source areas identified from conditional probability function were compared with commercial marine vessel Hg emissions data from 2008 NEI previously on p. 4202 lines 2-9 of the ACPD paper. In the revised paper (section 3.6), we compared the CWT model results over the ocean with the net evasion modeling results from previous publications. We had previously used information from literature and websites to gather information about the known locations of forest fires and compared them to the locations of modeled source areas (ACPD paper p. 4199 lines 13-20). We had also discussed about the uncertainties with from estimating Hg emission from forest fires in p. 4199, lines 20-23.

Uncertainties in Hg emissions data from non-point sources is a major issue because these data are being used to assess the accuracy of the CWT model at identifying Hg sources affecting Dartmouth. A detailed comparison between the CWT model source areas and industrial Hg emissions from the grid cells were conducted because point source emissions data are updated annually and the precise locations provided are compatible with the sampling period of the speciated atmospheric Hg measurements and the high resolution grid of the CWT model. Even with the absence of this data for non-point sources, the modeled source areas were compared with non-point sources reported in other emissions inventory, literature, and model simulations.

Original comment: Page 4204, line 28: “CWT is a very quantitative model...” Following the methodology proposed in this paper CWT is not able to identify source regions because of a too high rate of false positives. Possibly the analysis of whole trajectories as proposed above could improve the results significantly.

Response: The sentence was changed to, “CWT identifies potential source areas affecting a particular site based on ambient air concentrations and back trajectory data, but the interpretation of sources is still necessary without a comprehensive Hg emissions database”, in the revised paper (see last paragraph of Conclusions). As mentioned in a previous comment, the CWT model is not reporting a high rate of false positives because it is not based only on the trajectory residence time in each grid cell (unlike some trajectory statistical models which are based entirely on trajectory residence time). Concentration is an important factor in the CWT model (ACPD paper p. 4189 lines 9-11). Concentrations affect the CWT value, which we used the criterion of the top 10 percentile CWT in each season to identify potential source areas. As shown in the locations of trajectory segment endpoints in the revised paper (Figure 7), they are completely different from the CWT source areas. Since the sampling site was located in a coastal area, back trajectories originating from the Atlantic ocean were expected and it wouldn’t be unusual that the back trajectories did not travel over any Hg point sources. This is not an indication of false positives because evasion of GEM from the ocean is a significant source of Hg. In the revised paper, the CWT results over the ocean were compared with a previous modeling study (Soerensen et al., 2010) that was suggested by the reviewer.

Original comment: Page 4205, line 1: “future applications of Trajectory Statistical Methods or Hybrid Receptor Models on speciated atmospheric Hg should develop a better method of incorporating Hg emissions from all types of sources...” I think that it is not an appropriate result for this paper to show that the chosen methodology does not work.

Response: The application of Trajectory Statistical Methods or Hybrid Receptor Models for identifying potential sources of atmospheric Hg had worked in past studies (see literature review in the Introduction). There may be a perception that the methodology did not work in this study because of the emphasis on evaluating the model against Hg emissions data, which had not been a focus in previous studies using similar types

of models but needs to be done. We think the results are appropriate because we identified potential source areas from the CWT model and CPF analysis, compared the CWT source areas with known industrial Hg point source data (applying statistical analysis when applicable) and with non-point sources discussed in previous literature, modeling studies (added to revised paper), and 2008 National Emissions Inventory, and discussed the major sources of uncertainties (uncertainties due to trajectory simulations and uncertainties and limitation with Hg emissions inventories in the revised paper), and potential alternative methods of assessing the accuracy of a model like this.

Original comment: This reviewer's conclusion: The paper is promising but needs a significant rework of the underlying methodology as it does not satisfy the goal of "Identifying sources of speciated atmospheric mercury at Dartmouth".

Response: In the revised paper (section 3.7), there is a greater emphasis on the uncertainties from back trajectory modeling and how it relates to the model parameters that were selected. Hopefully, we can clarify that this is a model for identifying potential sources of speciated atmospheric mercury at Dartmouth and like any other air quality model, it is subject to uncertainties and data limitations.

Interactive comment on Atmos. Chem. Phys. Discuss., 13, 4183, 2013.