

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.

Anonymous Referee #2

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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

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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.

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, NO_x, 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.

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

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are estimates about the air-sea flux of mercury in the Atlantic Ocean (e.g. Soerensen 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.

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 $1^\circ \times 1^\circ$ 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

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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.

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.

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.

Scheele, M.P., et al., Sensitivity of trajectory 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, (1997).

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.

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.

3.1 Overall concentrations :: It would be good to also give median concentrations and

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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 detailed analysis of these events)

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.

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?

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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.

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 episode 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.

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

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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.

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.

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.

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).

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.

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 in-

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ventories. 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 0.5°x0.5° available from AMAP.

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'

Page 403, line 9,10. The sentence starts with Although and suggests a connection between gypsum 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....'

4. Conclusions ::

Page 4203, line 27: 'The sources where sometimes associated with known industrial sources...' Sometimes is a very unspecific word for a conclusion.

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.

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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.

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.

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.

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".

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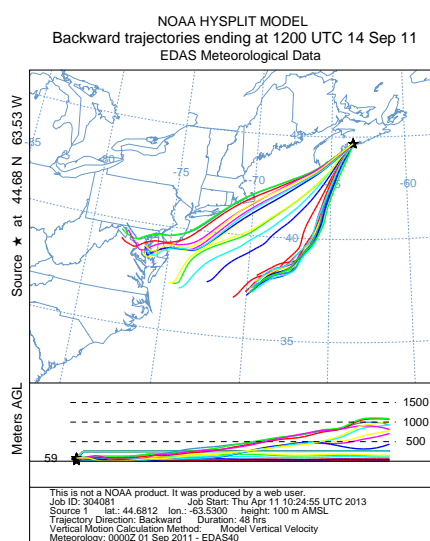


Fig. 1. Uncertainty of HYSPLIT trajectories.

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