

Mercury TMDL for the State of Florida

Appendix F

Deterministic Atmospheric Modeling and Receptor Modeling

Watershed Evaluation and TMDL Section



July 5, 2012

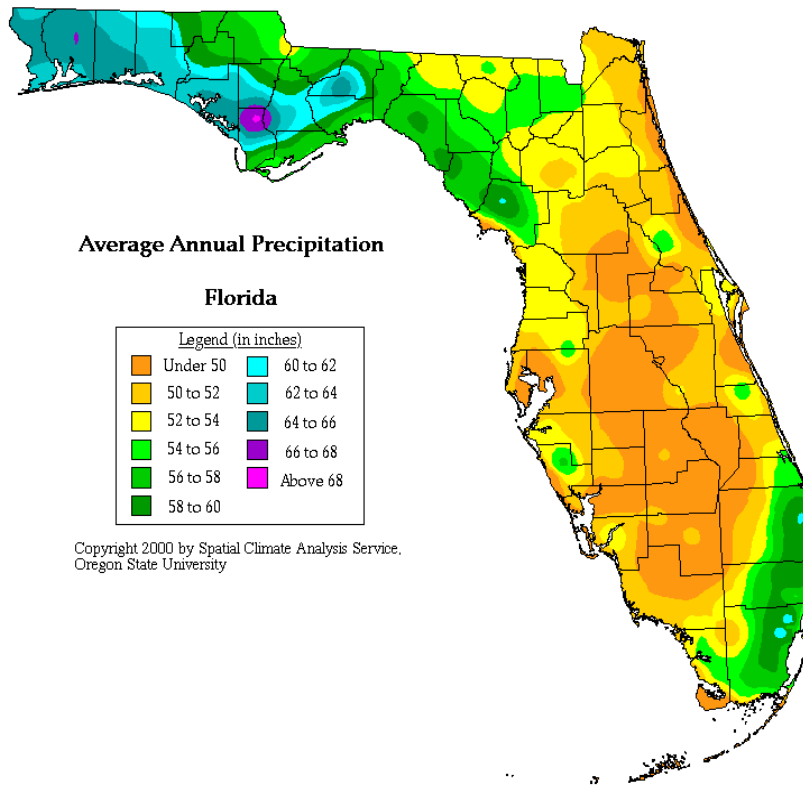
Appendix F: Atmospheric Modeling

CMAQ Model Evaluation – Draft Report

PMF Analysis of Wet Deposition Data – Draft Report

State of Florida Mercury Total Maximum Daily Load (TMDL) Project

CMAQ Model Evaluation – Draft Report



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June 25, 2012

CMAQ Model Evaluation

The following report synthesizes results of the Community Multiscale Air Quality (CMAQ) model evaluations conducted and reported as part of project Task Assignment 05 subtasks 5.1.1.A, 5.1.1.B, and 5.1.1.C. These include comparisons and evaluations of CMAQ output with observed (measured) ambient speciated mercury (Hg), observed mercury wet deposition, and inferentially modeled mercury dry deposition. Also included in this document are reporting on evaluations of CMAQ linearity and tagging scheme, results of which were also previously submitted as part of earlier project subtasks, as well as discussions on sensitivity to precursor emissions and applicability of model results for the TMDL project.

1. Statistics Used in Model-measurement Evaluations

The following standard performance statistics have been used to evaluate air quality models for mercury (e.g. *Bullock et al., 2009, EPA, 2008*), and have been used here.

Mean bias (in units for deposition, e.g. $\mu\text{g m}^{-2}$):

$$MB = \frac{1}{N} \sum_{i=1}^N (Dm_i - Do_i)$$

where

N = number of samples

Dm_i = model value for a specific time and location

Do_i = observed value for the same time and location as the model value

Mean error (in deposition units, eg. $\mu\text{g m}^{-2}$):

$$ME = \frac{1}{N} \sum_{i=1}^N |Dm_i - Do_i|$$

Normalized mean bias (relative units):

$$NMB = \frac{\sum_{i=1}^N (Dm_i - Do_i)}{\sum_{i=1}^N Do_i}$$

Normalized mean error (relative units):

$$NME = \frac{\sum_{i=1}^N |Dm_i - Do_i|}{\sum_{i=1}^N Do_i}$$

Coefficient of determination, r^2 (relative units):

$$r^2 = \frac{N \sum_{i=1}^N Dm_i Do_i - \left(\sum_{i=1}^N Dm_i \right) \left(\sum_{i=1}^N Do_i \right)}{N^2 \left(\sum_{i=1}^N Dm_i^2 - \left(\sum_{i=1}^N Dm_i \right)^2 \right) \left(\sum_{i=1}^N Do_i^2 - \left(\sum_{i=1}^N Do_i \right)^2 \right)}$$

2. Previous Mercury Model Evaluation Results:

Bullock et al. (2009) reported performance statistics for three different urban/regional-scale models (including CMAQ) combined with three different global-scale models, for a total of 9 comparisons. They evaluated results for a 1-year simulation for 2001 in comparison with weekly measurements of wet deposition and precipitation from the MDN network of 62 sites located throughout the U.S. (mostly in the eastern half).

They found normalized mean bias for the various model combinations ranging from -50% to +87%. There was significant variation between the three urban/regional models. CMAQ had relatively low mean bias, with values from -50% to +16% depending on the global background model. The REMSAD model tended to overpredict somewhat, with mean bias from +16% to +40%. The third regional model, TEAM, showed a major overprediction with mean bias +62% to +87%.

Normalized mean errors were 71% to 85% (CMAQ), 82% to 90% (REMSAD) and 105% to 130% (TEAM). Coefficients of determination (r^2) were relatively low for all models, ranging from 0.12 to 0.18. The relatively high mean errors and low coefficients of determination were driven largely by differences between the model and observed weekly precipitation (normalized mean error 62%, $r^2 = 0.35$).

Additionally, USEPA conducted mercury model evaluations with observed mercury wet deposition from the MDN network (USEPA, 2008). These included model results with REMSAD evaluated with three different sources of boundary conditions: CTM, GRAHM, and GEOS-CHEM.

This USEPA study utilizing REMSAD found a normalized mean bias of 60% using CTM with a normalized mean error of 66%, a normalized mean bias of 46% using GRAHM with a normalized mean error of 55%, and a normalized mean bias of 74% using GEOS-CHEM with a normalized mean error of 79%.

The performance statistics presented below for the current project differ from the previous studies in that (i) results are limited to evaluation sites in Florida, rather than for the U.S. as a whole, and (ii) the comparison is done on a monthly basis rather than weekly.

Other approaches to model evaluation:

A variety of approaches to evaluate model accuracy for mercury have been used in scientific studies. These are usually qualitative in nature rather than numerical. They include the following:

- * Evaluation of the geographical variation of wet deposition in comparison with measurements (e.g. Holmes et al., 2009, Selin and Jacob, 2008)
- * Evaluation of the vertical distribution of ambient mercury, especially above the boundary layer
- * Evaluation of the diurnal cycle of ambient mercury

Other suggested approaches include evaluation of predicted correlations between ambient Hg and other species (Hg⁰ versus RGM, Hg versus sulfate and nitrate, Sillman et al., 2007) and correlations between wet deposited species and or concentrations in rainwater (Hg versus sulfate, nitrate, and/or trace metals).

3. Model-Measurement Comparisons – Mercury Wet Deposition

CMAQ wet deposition results for calendar year 2009 were compared with results from measurement sites from this TMDL project, locations of which are illustrated in Figure 1. Figure 2 shows summed annual mercury wet deposition in the CMAQ model in comparison with measured values at the 6 Florida TMDL wet deposition measurement sites. Results show generally similar magnitudes for measured and model values. The model overestimates wet deposition at Davie (DVE) and underestimates at Pensacola (OLF). Model values at the four other sites [Tampa (TPA), Orlando (UCF), Everglades National Park (ENP) and Jacksonville (JKS)] all differ from measurements by less than 20%. Geographic variations are quite consistent between model and measurements. The model shows much higher wet deposition at Davie relative to other sites and lower wet deposition at Pensacola, neither of which appears in measurements. However, both the model and measurements show higher wet deposition at the southern sites (Davie and Everglades) relative to the other sites.

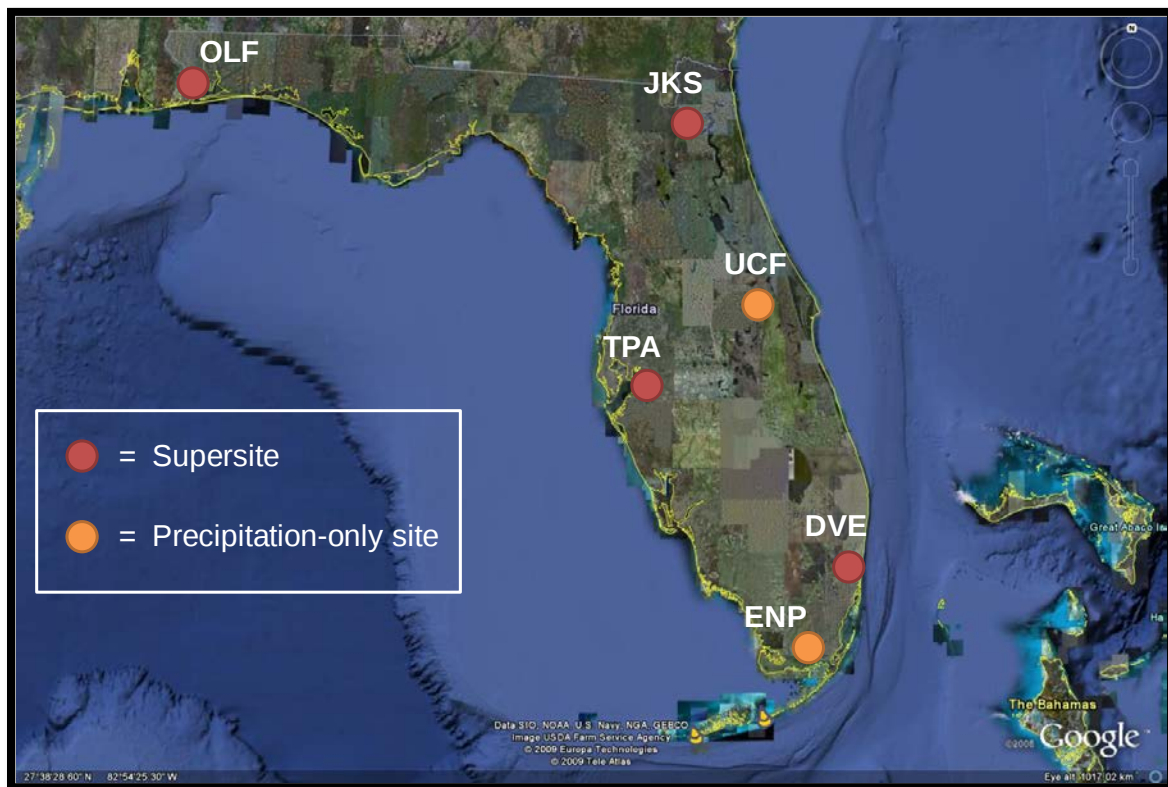


Figure 1. Location of the six TMDL project routine wet deposition monitoring sites.

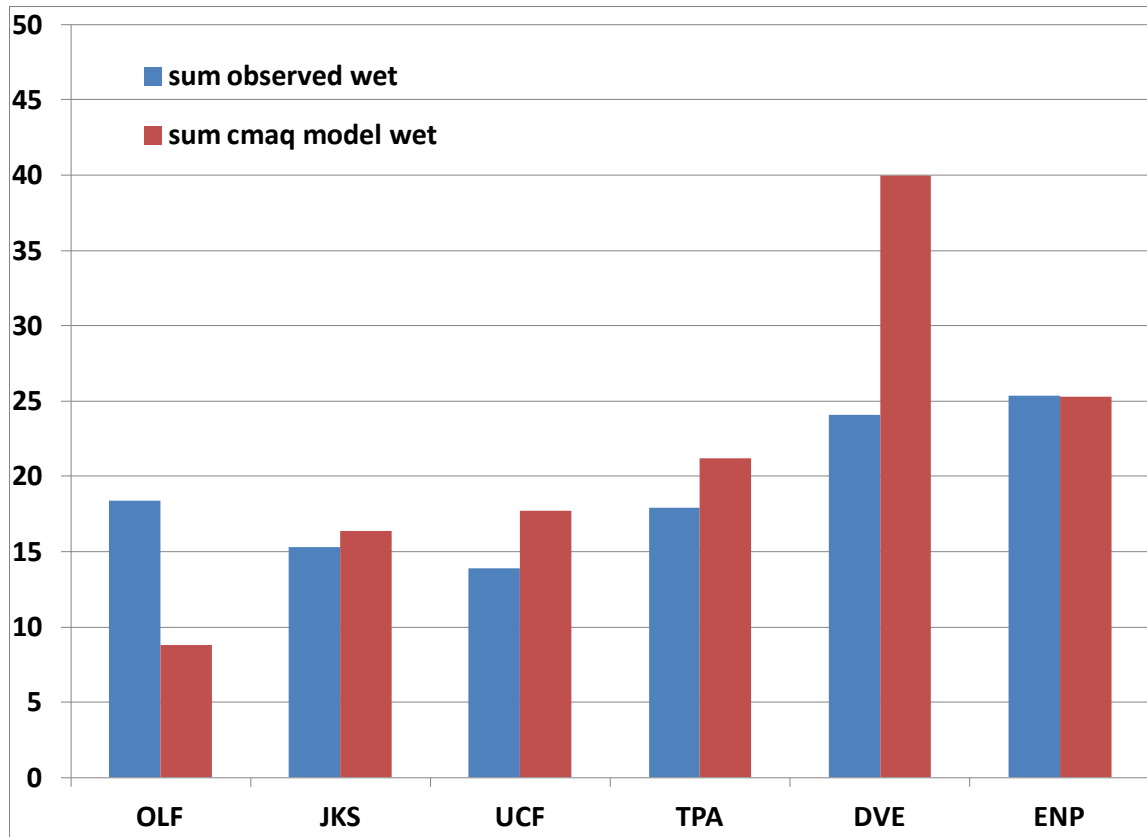


Figure 2. Summed annual (2009) mercury wet deposition ($\mu\text{g}/\text{m}^2$) in the CMAQ model in comparison with observed values at the 6 Florida TMDL wet deposition measurement sites.

Performance statistics for wet deposition evaluations, based on monthly values at each site over the 2009 year, include a normalized mean bias of 13%, and normalized mean error of 66%, and an r^2 of 0.36. While the normalized mean bias determined for this project evaluation (+13%) represents a significant improvement in performance for mercury wet deposition compared to previous studies, the determined normalized mean error and r^2 reported are very similar and quite typical of previous studies (see Section 2 above).

4. Model-Measurement Comparisons – Mercury Dry Deposition

Results of CMAQ mercury dry deposition for calendar year 2009 were evaluated with those determined using an inferential model based on surface measurements of ambient speciated mercury, meteorological and other variables (previously described and reported as part of an separate TMDL project subtask) measured at four TMDL project Supersites (Davie, Tampa, Jacksonville, and Pensacola, see Figure 1). Results of these comparisons show significant divergences between the CMAQ model and measurement-based (inferential) values. The CMAQ model dry deposition is biased low (normalized mean bias of -45%, with 51% normalized mean error over the four supersites) and the site-to-site variation tends to be different. CMAQ predicts the highest mercury dry deposition at Davie and Tampa, which likely reflect the large input from local emissions (see section below on sensitivity). CMAQ shows roughly 50% lower dry deposition for Jacksonville and Pensacola. By contrast, the inferential model shows highest dry deposition at Tampa and Pensacola, with lower deposition by 30% or more at Davie and Jacksonville. Figure 3 shows the summed annual mercury dry deposition in the CMAQ model in comparison with inferential model determined values at the 4 Florida TMDL Supersite measurement sites.

A complicating factor in this comparison is the ambiguity about the formal output for mercury dry deposition from CMAQ. The CMAQ model algorithm with bi-directional soil exchange of Hg includes release of Hg into the atmosphere from the soil as part of the dry deposition sum, so that reported dry deposition is actually the difference between direct deposition and release of Hg from soils (Jesse Bash, EPA, RTP North Carolina, personal communication, March 15, 2012). The soil release consists entirely of elemental Hg. Dry deposition of elemental mercury also differs from deposition of reactive gaseous mercury and particulate mercury in its relation to precursors. Deposition of elemental mercury is driven mainly by the global background, whereas dry deposition of reactive and particulate mercury is more sensitive to local emissions. For these reasons, and the lack of numerically quantified model-measurement based evaluations for mercury dry deposition from previous studies, it is much more difficult to contextualize the mercury dry deposition model performance compared to that presented above for mercury wet deposition. That said, this project is possibly the first to evaluate to this level of rigor the performance of CMAQ (or similar deterministic model) for mercury dry deposition compared to measurement-based approaches.

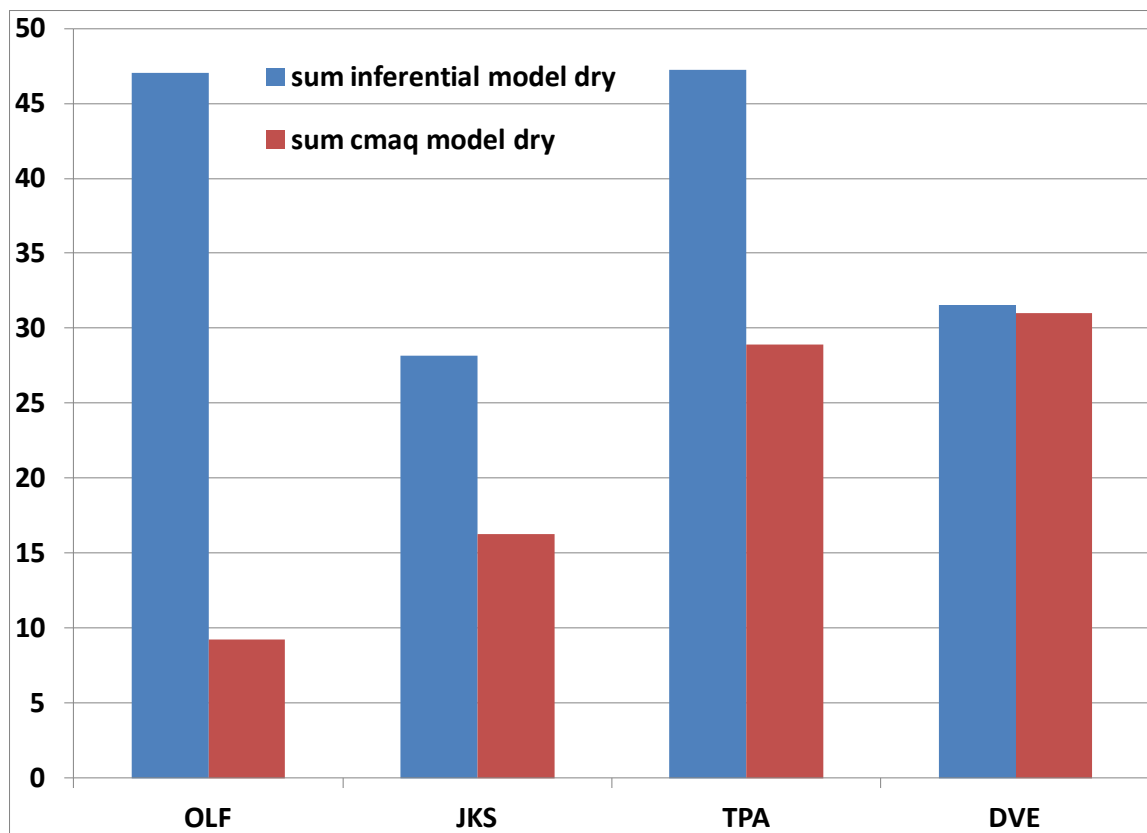


Figure 3. Summed annual (2009) mercury dry deposition ($\mu\text{g}/\text{m}^2$) in the CMAQ model in comparison with inferential model determined values for the 4 Florida TMDL Supersite measurement sites.

5. Model-Measurement Comparisons – Speciated Ambient Mercury Concentrations

Comparisons between CMAQ model results and measurements of elemental gaseous mercury (Hg₀), reactive gaseous mercury (RGM), and particulate mercury (HgP) were also conducted for calendar year 2009 for the four TMDL Supersite locations (Davie, Tampa, Jacksonville and Pensacola).

Model and measured elemental gaseous mercury show very reasonable agreement, with overall normalized mean bias of +15%, and normalized mean error of 16%. However, comparisons between model results and ambient measurements for reactive gaseous mercury and particulate mercury show large discrepancies. Model ambient concentrations are higher than measured values by factors of 10-15 for both RGM and HgP. Figure 4 shows the annual speciated ambient mercury concentrations in CMAQ in comparison with measurements from the 4 Florida TMDL Supersite measurement sites.

A distinctive feature of the measured ambient concentrations is the diurnal cycle. Measured RGM peaks during midday and declines to low values at night, with nighttime values typically lower than daytime values by a factor of 10. This strong diurnal cycle is not reproduced by the model. The RGM in the model decreases slowly at night, with the nighttime minimum just 20% below that daytime maximum. Measured particulate mercury also shows a daytime peak and nighttime minimum (lower than the daytime maximum by a factor of 3) but the nighttime decrease is not as strong as for RGM. The model also shows a diurnal cycle for HgP, but still not as strong as measured values. Elemental mercury shows less of a diurnal cycle but the measured values increase by 25% during the early morning hours (4-7am). This early morning increase does not appear in the model.

The annual cycle for reactive mercury generally shows highest values in May and in Sept-October, which correspond to the time of maximum photochemical activity in Florida. The higher reactive mercury appears in measurements and also appears in the model values.

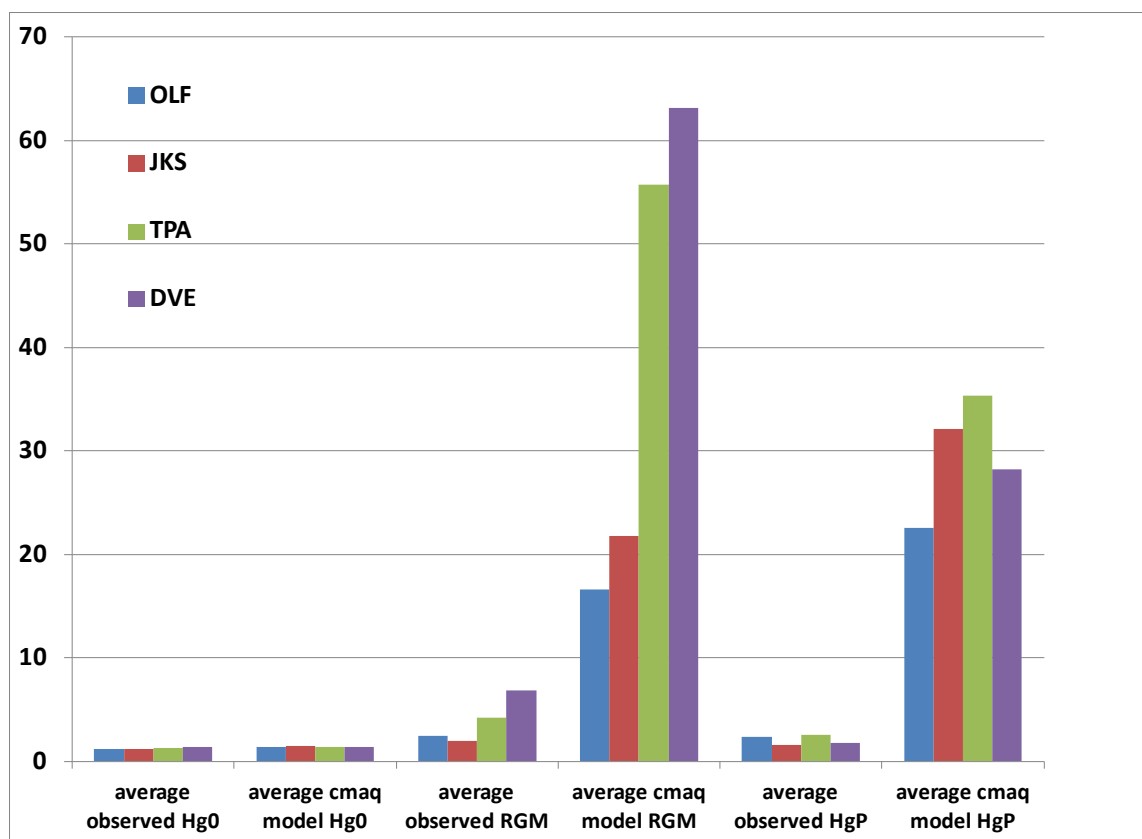


Figure 4. Annual (2009) concentrations of Hg0 (ng/m³), RGM (pg/m³), and HgP (pg/m³) in CMAQ in comparison with measurements from the 4 Florida TMDL Supersite measurement sites.

Interpretation: The strong diurnal cycle for reactive mercury combined with the seasonal peak in May and September suggest that photochemical production may have a large influence. However the very low nighttime concentrations also suggest that reactive mercury is rapidly removed at night, and that the removal process is omitted or underestimated by the model. The CMAQ model includes dry deposition of RGM with relatively high rates (2 cm s^{-1}). There is little decrease in ambient RGM in the model at Davie and other sites near emission sources because emitted RGM into the shallow nighttime boundary layer compensates for losses due to surface deposition. Consequently, dry deposition cannot explain the observed decrease in reactive mercury at night.

Possible explanations include the following:

- Rapid formation and removal of aqueous aerosols at night in association with very high humidity, fog and dew formation. This process may not be captured by the standard dry deposition representation in models.
- Conversion of reactive mercury to elemental mercury through aqueous reactions, which may be also associated with nighttime high humidity, fog and aerosol formation. Conversion from reactive mercury to elemental mercury has been suggested in association with sulfate aerosols (Seigneur et al., 2006).
- Overpredicted emissions of reactive mercury, possibly including errors in the partitioning of mercury emissions between elemental and reactive mercury.
- Overpredicted reactive mercury in the atmospheric background. However, previous comparisons between CMAQ and aircraft measurements showed relatively good agreement for RGM off the coast of Florida (Sillman et al., 2007).

Comparisons with other models:

The REMSAD simulation for the full US generally resulted in higher RGM and lower particulate mercury in comparison with CMAQ (Bullock et al., 2009a). Results from REMSAD for Florida showed surface RGM of 30-40 pg m^{-3} (annual average) and HgP 5-10 pg m^{-3} . By contrast, the earlier run of CMAQ reported by *Bullock et al.* (2009a) found approximately 20 pg m^{-3} RGM and 20-30 pg m^{-3} HgP in Florida. These values of RGM are somewhat lower than the CMAQ results found here (40-80 pg m^{-3} RGM, 20-40 pg m^{-3} HgP), possibly because the results here are for a model run with fine horizontal resolution and in source regions. Although ambient RGM from these other models are somewhat lower than the current simulation, they still exceed measured values in Florida by a factor of 5.

Selin et al. (2009) report results from the GEOS-Chem global model and measured RGM in Florida and elsewhere. GEOS-Chem showed RGM above 100 pg m^{-3} at higher elevations (above 1 km), which are also consistent with measurements. They did not discuss surface conditions in Florida but they reported that model RGM in the southwestern U.S. (100 pg m^{-3}) were much higher than measured values at the surface (6 pg m^{-3}).

We conclude that the high surface concentrations of RGM and HgP in CMAQ and the contrast with much lower measured values is a result shared by the current generation of models, and is not limited to Florida.

6. Sensitivity to Precursor Emissions

The following is an overview of the factors that affect the relative influence of local emission sources versus the global background and possible assumptions in CMAQ that influence model results.

In addressing the issue of local versus global impacts it is useful to view the behavior of mercury as consisting of two separate cycles: one for emission of elemental mercury; and the other for reactive and particulate mercury.

Elemental mercury, once emitted to the atmosphere, has a lifetime in the atmosphere of approximately one year. Species with such a long atmospheric lifetime are usually widely dispersed throughout the Northern Hemisphere and throughout the troposphere, with relatively little variation in species concentrations. The resulting deposition is therefore driven primarily by global sources as opposed to local emissions. Emissions from the U.S. represent approximately 5% of total global emissions (Selin, 2009).

Reactive mercury, by contrast, has a relatively short atmospheric lifetime. Reactive gaseous mercury has a lifetime of 5-10 hours (comparable to nitrate), while particulate mercury has a lifetime of 3-5 days (comparable to sulfate). These species are both removed rapidly by both wet and dry deposition. Consequently, transport is effectively limited to 500 km for RGM and 5000 km for HgP. Removal of directly emitted reactive species is strongly linked to local sources.

It is not possible to distinguish directly emitted elemental mercury from directly emitted reactive mercury because (except in the case of dry deposition of Hg⁰) elemental mercury is removed from the atmosphere through conversion to reactive mercury followed by removal of reactive mercury (via wet and/or dry deposition). Measured reactive mercury therefore consists of a combination of directly emitted elemental mercury (which has been converted to reactive form) along with directly emitted reactive mercury. However, this distinction can help identify critical assumptions that affect source-receptor allocation in models.

Factors that affect local versus global source attribution in CMAQ:

- *Speciation of emissions into elemental, reactive gaseous and particulate mercury:*
Emissions of reactive and particulate mercury have a much larger local impact relative to elemental.

- *Atmospheric processes that convert reactive mercury to elemental mercury:* Several mechanisms have been proposed, including conversion in cloud water (included in CMAQ) and conversion through contact with sulfate in plumes associated with large emission sources (included in the AMSTERDAM model but not in CMAQ). Conversion to elemental mercury would reduce the impact of local emission sources.
- *Wet versus dry deposition:* Wet deposition, especially through convective precipitation (thunderstorms), involves atmospheric mixing up to a very high depth (typically 10 km or more). As such, it includes mercury from the middle and upper troposphere, which represent mainly global background sources. Dry deposition, involves mercury that is near the ground, and consequently is likely to show greater sensitivity to local (ground-based) sources.
- *Model representation of vertical transport in clouds:* The exact transport pattern in convective clouds is complex and difficult to represent in models. CMAQ uses an approximate representation in which wet deposition is removed at a uniform rate from a vertical layer extending from the surface to the cloud top. If the actual removal of mercury follows a different distribution with respect to height the impact of local versus global sources could be changed.

Sensitivity of mercury wet and dry deposition to precursor emissions of mercury were investigated for this project in two ways.

1. The original model scenario was repeated for two alternate scenarios with changed emissions: (i) a 50% reduction in mercury emitted from all Florida sources; and (ii) a 100% reduction from all Florida sources. The reduction scenarios were performed for three individual months: January, May and July 2009.
2. A tagging system was implemented that tracks mercury from 14 different source categories, including 5 Florida categories and categories representing emissions in other individual states, the rest of the U.S., soil emissions and the global background.

The tagging system, if accurate, provides much more information than the individual control runs. Tags identify the impact of emissions from a broad range of categories, whereas results from each control run provide information only about the specific reductions used in the test. The tagging results are also available for the full year rather than for the specific months of the control test.

Use of the results from both the control runs and the tagging system also critically depend on the question of **linearity**. Conditions in the atmosphere do not always respond linearly to changes in emissions. For example: if mercury emissions in Florida are reduced by 100%, the resulting reduction in deposition is not necessarily twice as large as if mercury were reduced by only 50%. Similarly, it is not certain whether (for example) the result of a combined 60% reduction in emissions from coal-fired electricity generation along with a 30% reduction in emissions from other sources is equal to the sum of calculated reductions from each of these individually. If mercury deposition responds linearly to changes in emissions (assuming that the response to changes in elemental, reactive and particulate mercury are summed separately), then it becomes easier to infer the results of different control strategies, based on either tags for individual sources or from a small number of control scenarios.

Results here first show the response to emission changes in general (based on the more versatile tagging system as well as control runs), followed by more detailed tests for linearity and for the accuracy of tagging.

General results:

Figure 5 shows the annual mercury wet deposition partitioned into Florida and non-Florida sources, with the partition based on Florida and non-Florida tags. Results are shown for 7 sites: the four project Supersites (Davie, Tampa, Jacksonville and Pensacola), two extended sites (Everglades National Park and Orlando) and one additional site (Inglis, close to the Crystal River power plant) which is included to illustrate results in the vicinity of a largest point emission source in Florida.

Results show that wet deposition is attributed primarily to non-Florida sources, even at Crystal River. The highest Florida source attribution was at Davie and represented 25% of the total. This was followed by Crystal River (20%), Tampa (14%) and Jacksonville (11%). Florida source attribution at the other sites was 3% or less. The non-Florida source attribution consisted primarily of the global background. The amount attributed to emissions elsewhere in the U.S. were small except occasionally for locations close to state boundaries.

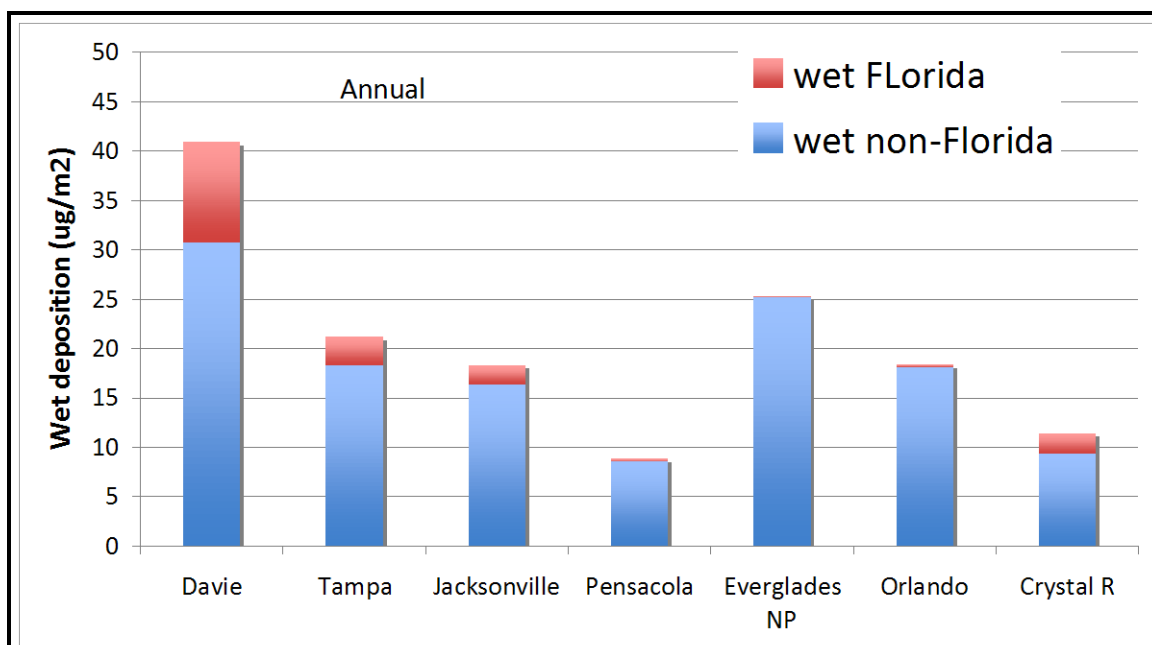


Figure 5. Annual (2009) mercury wet deposition ($\mu\text{g}/\text{m}^2$) results from CMAQ partitioned into Florida and non-Florida sources (partition based on Florida and non-Florida tags) for 7 sites.

Dry deposition, illustrated in Figure 6, shows a much larger attribution to Florida sources. The Florida source attribution accounts for more than 50% of total dry deposition at Davie and at Tampa, and approximately 30% of dry deposition at Crystal River and Jacksonville. The Florida source attribution was still relatively low elsewhere: 8% at Pensacola, 6% at Orlando and 1% at Everglades National Park. In general, CMAQ suggests that local emission sources have a large impact on local dry deposition but a much smaller impact on locations more than 100 km distant.

The variation in wet and dry deposition among sites shown in Figures 5 and 6 is also noteworthy. Dry deposition is predicted to be much higher at the sites with a large impact from Florida sources: Davie, Tampa and Crystal River. Model dry deposition for July at these sites is twice as large as dry deposition elsewhere. This enhanced dry deposition is most likely linked to the Florida source impact in the model. The site-to-site contrast provides a test for the accuracy of the model source attribution. By contrast, site-to-site variation for wet deposition does not appear to be influenced by proximity to local emission sources in the model.

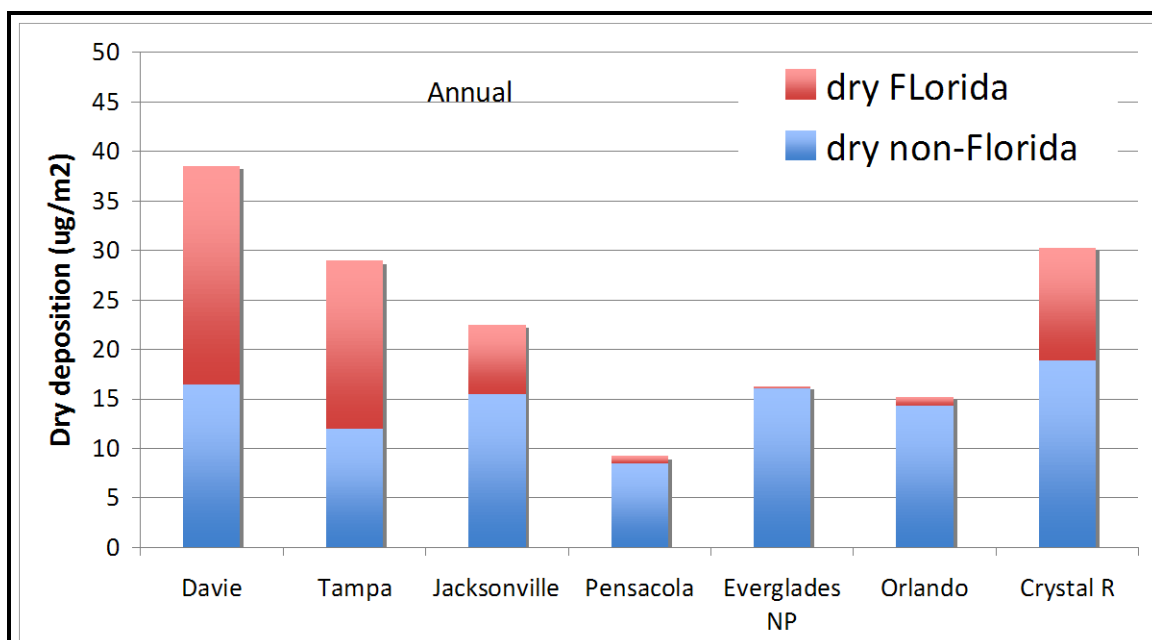


Figure 6. Annual (2009) mercury dry deposition ($\mu\text{g}/\text{m}^2$) results from CMAQ partitioned into Florida and non-Florida sources (partition based on Florida and non-Florida tags) for 7 sites.

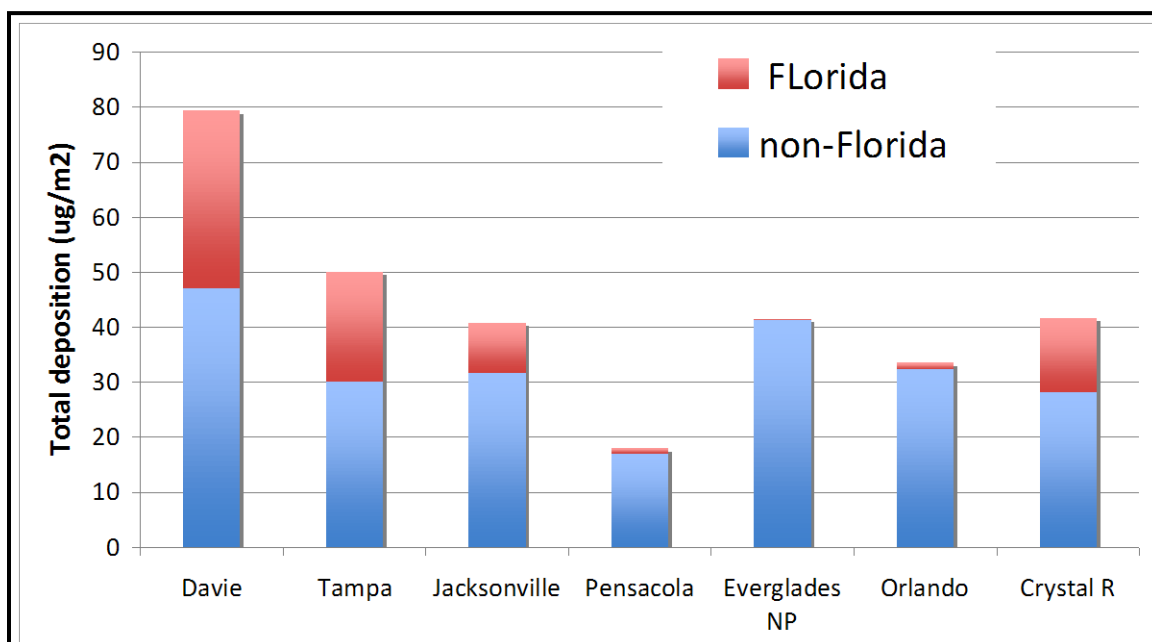


Figure 7. Annual (2009) total mercury deposition ($\mu\text{g}/\text{m}^2$) results from CMAQ partitioned into Florida and non-Florida sources (partition based on Florida and non-Florida tags) for 7 sites.

Total deposition for the year is shown in Figure 7. The Florida source attribution accounts for approximately 40% of total deposition at Davie and Tampa, 30% at Crystal River,

20% at Jacksonville, and 5% or less at the other sites. The above results are all based on the tagging methodology. Comparisons between the tags and results of control simulations are described below.

Emission reduction scenarios and tagging:

Comparisons between the tags and results of control simulations are shown in Figure 8. Here, we have calculated the CMAQ reduction in mercury wet and dry deposition associated with a 50% reduction in Florida emission sources (equal to the difference between results from the initial model scenario and the control scenario at each location). This is compared to the estimate from tagging, which is equal to the Florida tag source attribution multiplied by 50%. Results show a small degree of uncertainty, but the estimates based on tagging agree with the reduction derived from scenarios with reduced emissions to within 10% or better.

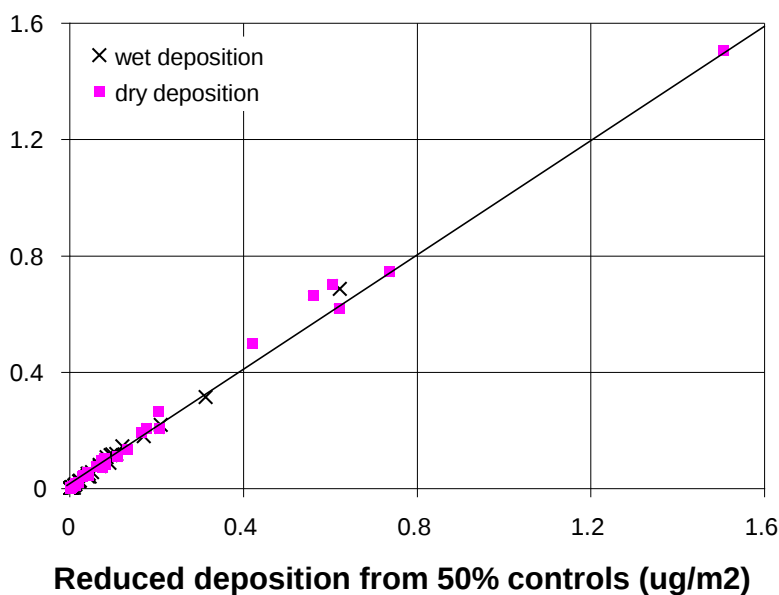


Figure 8. Calculated CMAQ reduction in mercury wet and dry deposition associated with a 50% reduction in Florida emission sources (equal to the difference between results from the initial model scenario and the control scenario at each location).

Linearity:

The question of whether the model wet and dry deposition responds in a linear way to reductions in emission rates is tested by comparing results from the 50% and 100% control scenarios.

For each scenario the reduction in deposition is calculated as the difference between deposition in the model base case and equivalent deposition in the control scenario. This method may be applied to monthly or annual sums or to results for individual days. If the model responds linearly to emissions changes, then the amount of the reduction for the scenario with 50% reduced emissions should be half as large as the reduction for the scenario for 100% reduced emissions.

Results in Figure 9 show that the model response is very close to linear. Deviations from a linear response occur for dry deposition on a few days, likely resulting from complications associated with the CMAQ bi-directional soil algorithm. These deviations are not significant in terms of monthly sums, which show deviations of less than 1% from the linear response.

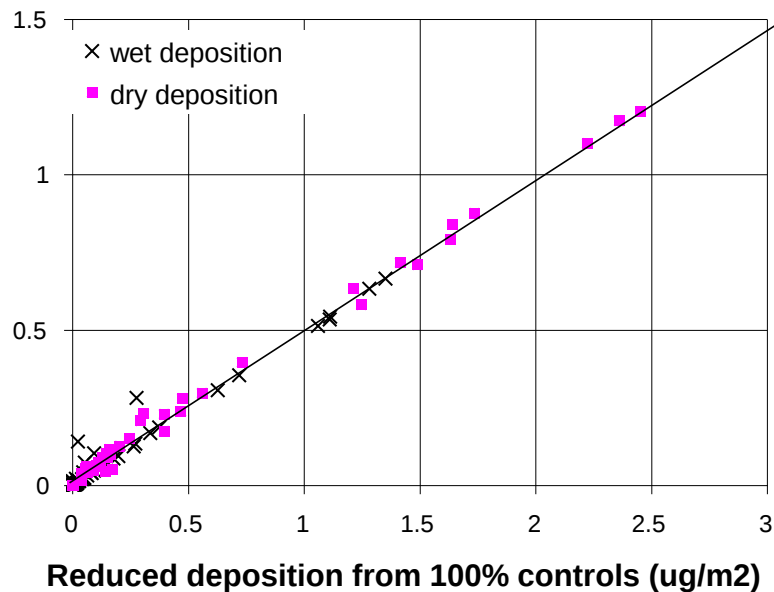


Figure 9. Linearity Tests: Reduction in Hg deposition (reduced deposition from 100% controls vs. reduction from 50% controls).

7. Sensitivity to Precursor Emissions: Conclusions and Implications from Model-Measurement Comparisons, and Applicability of CMAQ Results for TMDL Project

Results of the CMAQ evaluation of the sensitivity of mercury wet and dry deposition to Florida emissions yield the following conclusions.

CMAQ predicts the following:

- Wet deposition is attributed mainly to the global background. Impact of within Florida emissions are generally 10% or less.
- Florida emissions have a significant impact on dry deposition of Hg. At some locations more than 50% of dry deposition is attributed to Florida sources.
- The impact of Florida sources on dry deposition is mostly in locations close to the emission sources. The impact on rural areas more than 100 km distant is 20% or less.
- Dry deposition is predicted to be similar in magnitude to wet deposition, so that close to 50% of total deposition of mercury consists of dry deposition

Model-measurement comparisons provide an evaluation of CMAQ accuracy in general. In terms of ambient speciated mercury, CMAQ compared very well with gaseous elemental mercury, but significantly overestimated levels of reactive gaseous mercury and particulate mercury. These results are consistent with those presented as part of previous studies, and suggest that continued development and refinement of CMAQ and other similar models are needed to improve upon the models ability to better reflect observations based on measurements.

Model comparisons with measured mercury wet deposition are in good agreement, and for this project represent some of the best agreement observed when compared to previous studies. Model comparisons for mercury dry deposition compare less well than for wet deposition. However, a lack of any previous studies comparing these results for dry deposition somewhat complicates our ability to contextualize the dry deposition comparative results. One way to better contextualize and evaluate the CMAQ model deposition results is to compare total (wet + dry) deposition. When combined, CMAQ model results still compare well with total deposition based on measurements at the four project Supersites. Performance statistics for total mercury deposition evaluations, based on monthly values at each site over the 2009 year, include a normalized mean bias of 26%, and normalized mean error of 46%. These results are shown in a positive light even when compared to the wet-only deposition evaluations from

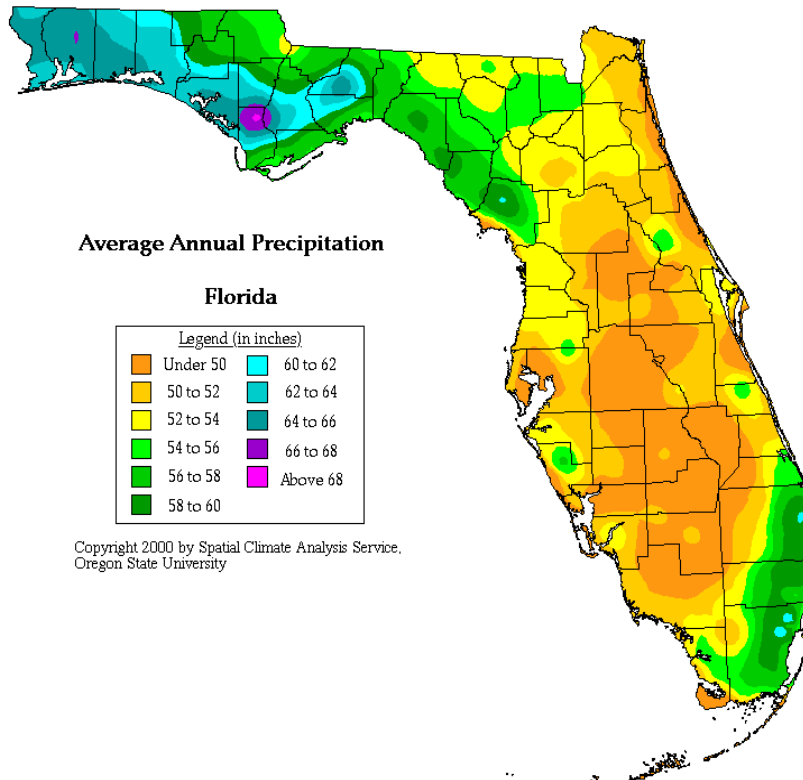
previous studies. Since total mercury deposition is the primary CMAQ output data that serves as input to the TMDL aquatic model, it can be concluded based on the performance statistics here that the CMAQ results are reasonably reflective of deposition observations from measurements, and appropriate for use in this TMDL project.

8. References

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State of Florida Mercury Total Maximum Daily Load (TMDL) Project

PMF Analysis of Wet Deposition Data – Draft Report



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The following report describes results of the application of the Positive Matrix Factorization (PMF) model analysis of Florida TMDL project wet deposition data collected at field monitoring sites. The wet deposition data collected was described and submitted as part of previous project subtasks. While the Community Multiscale Air Quality (CMAQ) model was utilized as a deterministic tool to estimate source contributions on a 4km grid across the state of Florida using an emissions tagging approach (submitted and discussed as part of previous project subtasks), this report summarizes results from source apportionment analyses using PMF for each of the six TMDL project wet deposition monitoring sites.

1. Precipitation Monitoring at Supersites/Satellite Sites

Four Supersite locations, combined with two Satellite site locations, formed a spatially diverse wet deposition monitoring network of operating sites for the Florida TMDL project. The four Supersites were located in Pensacola, Jacksonville, Tampa, and Davie, while the two Satellite sites were located in Orlando and Everglades National Park (Figure 1). The scope of this precipitation monitoring component of the project was to include the continuous characterization of key constituents of precipitation necessary for the mercury (Hg) TMDL assessment. The monitoring at the six wet deposition sites included sample collection for subsequent analysis for total Hg, major ions, and trace elements.

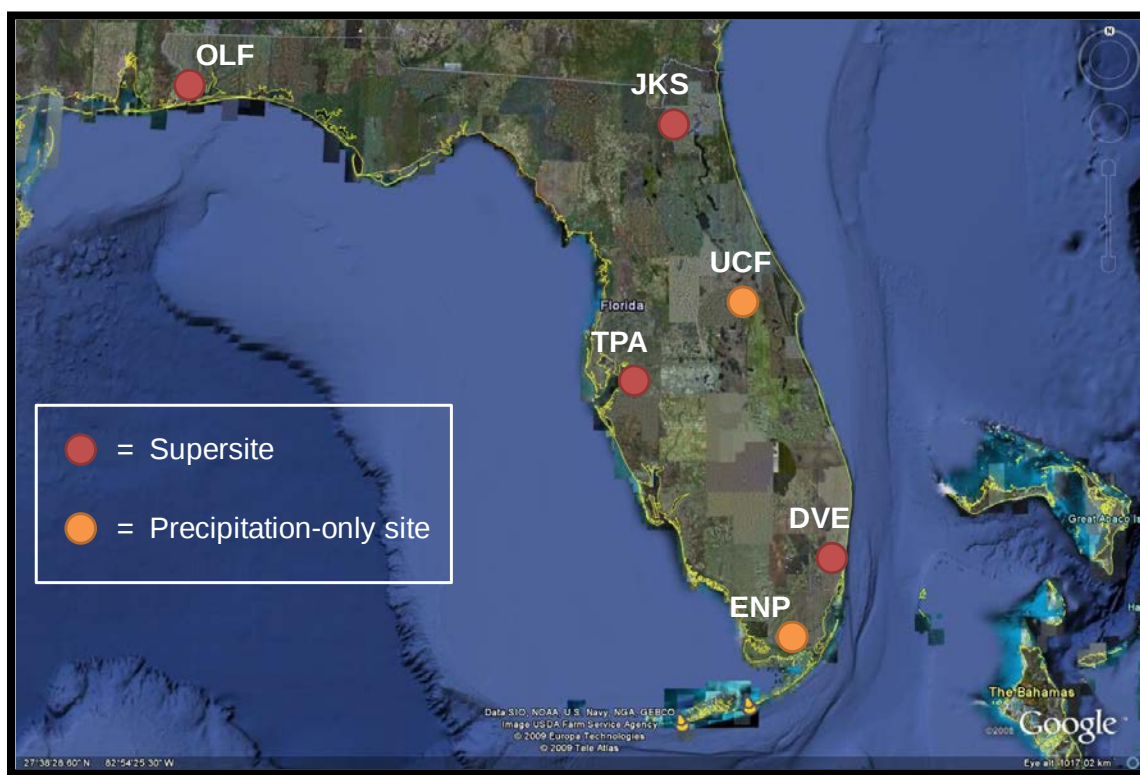


Figure 1. Location of the six TMDL project routine wet deposition monitoring sites.

The six wet deposition monitoring sites included the counties of Escambia, Duval, Orange, Hillsborough, Broward, and Miami-Dade:

- The Escambia County Supersite was located on U.S. Navy property approximately 19 km NW of downtown Pensacola (lat. 30.5500, long. -87.3751), and was a collaborative site with Southern Company Services. Precipitation

monitoring at this site (identified as OLF in Figure 1) began in October 2008 and continued through the end of August 2010.

- The Duval County Supersite was located on a farm managed by the City of Jacksonville-Parks and Recreation approximately 29 km WSW of downtown Jacksonville (lat. 30.2475, long. -81.9516). Precipitation monitoring at this site (identified as JKS in Figure 1) began in March 2009 and continued through the end of August 2010.
- The Hillsborough County site was located in private property approximately 8 km SE of the City of Tampa (lat. 27.9137, long. -82.3749), and was a coordinated site with staff at Hillsborough County. Precipitation monitoring at this site (identified as TPA in Figure 1) began in January 2009 and continued through the end of August 2010.
- The Broward County site was located at a county-operated air monitoring site (Site #8) located approximately 12 km SW of the City of Fort Lauderdale (lat. 26.0854, long. -80.2407), and was a coordinated site with staff at Broward County. Precipitation monitoring at this site (identified as DVE in Figure 1) began in February 2009 and continued through the end of August 2010.
- The Orange County site was a wet deposition-only site located on the property of the University of Central Florida (lat. 28.5921, long. -81.1903), and was a coordinated site with staff at Orange County. Precipitation monitoring at this site (identified as UCF in Figure 1) began in March 2009 and continued through the end of August 2010.
- The Miami-Dade County site was located within Everglades National Park at the Beard Research Center (lat. 25.3898, long. -80.6803), and was a coordinated site with staff of ENP. Precipitation monitoring at this site (identified as ENP in Figure 1) began in November 2008 and continued through the end of August 2010.

Automated Sequential Precipitation Samplers (ASPS)

The importance of collecting wet deposition on an event basis for receptor modeling and meteorological analysis is now well known (Ross 1990; Dvonch et al 1999; Landis et al 2002; Dvonch et al 2005). Wet deposition was collected on a daily-event basis using the University of

Michigan Automated Sequential Precipitation Sampler (ASPS). This sampler is a computer-controlled precipitation sampling system designed and built by the UMAQL that allows unattended wet-only event-precipitation collection (Figure 2). The Florida mercury TMDL atmospheric monitoring plan included deployment of one ASPS unit at each of the six monitoring locations. The ASPS allows for the concurrent automated collection of up to four different samples using independent sampling trains. The Hg sampling train was composed of



Figure 2. Photo of ASPS – Automated Sequential Precipitation Sampler – as deployed for TMDL project at Everglades National Park monitoring site.

glass and Teflon and samples were collected into acid-cleaned sampling bottles. A separate sampling train was used for trace elements and major ions. The sampler utilizes sampling racks that hold eight individual bottles connected to discrete sampling trains, and automatically sequences to a new sampling bottle each day to allow for discrete precipitation events to be characterized on a daily basis. Each bottle is sealed before and after the precipitation sample is collected using the computer controlled rack module and valves. The sample racks are housed in the base of the sampler in a temperature-controlled chamber that is kept between 5-8°C.

Sample Shipment and Processing, and Laboratory Analysis for Mercury, Trace Elements, Major Ions, and Mercury Isotopes

All sample preparation, handling, and processing employed ultra-clean techniques as described by Landis and Keeler (1997) and Hoyer et al. (1995). All supplies for wet deposition collection were acid-cleaned at the UMAQL, and were subsequently shipped to the six individual monitoring sites on a routine basis during the period October 2008 through August 2012. After field sample collection, samples were shipped from the monitoring sites to FDEP Central

Laboratory for total mercury analysis, and to UMAQL for analysis of trace elements and major ions.

Mercury. Laboratory determinations for total Hg in precipitation were conducted at the FDEP Central Laboratory. After oxidation with BrCl, total Hg in precipitation was purged from solution in a Hg-free argon stream after reduction with NH₂OH and reduction of divalent Hg by SnCl₂ to Hg⁰, and concentrated onto a gold trap. Total Hg was then quantified using a dual amalgamation technique followed by cold-vapor atomic fluorescence spectrometry (CVAFS).

Trace Elements. Laboratory analyses of trace elements in precipitation were carried out at the UMAQL. Samples were acidified with concentrated HNO₃ to a 0.2% solution (v/v) in the sample bottle and stored in a dark cold room for a minimum of 14 days before analysis to provide adequate time for optimal leaching (Graney et al 2004). Precipitation samples were analyzed for a suite of trace elements using a Finnigan MAT Element magnetic sector field high resolution ICP-MS using a method similar to that previously described (Keeler et al 2006).

Major Ions. Laboratory analyses for major ions were completed at the UMAQL. Precipitation samples were analyzed for major anions using a Dionex (Sunnyvale, CA) ion chromatography system.

2. Positive Matrix Factorization

While one of the primary goals of the Florida Mercury TMDL was to estimate the loading of Hg to the State freshwater bodies, of equal importance was an improved understanding of the relative impact of source types and source regions (within-state, out-of-state) contributing to the total deposition. Previously, the Community Multiscale Air Quality (CMAQ) model was utilized as a deterministic tool to estimate these source contributions on a 4km grid across the state of Florida using an emissions tagging approach (submitted and discussed as part of previous project subtasks).

An additional source apportionment approach described here is carried out utilizing the observed wet deposition data collected at project measurement sites, and a multivariate receptor modeling technique, the major advantage of which being the ability to identify and apportion the impact of major source types on a receptor site with lack of source information. Among the multivariate receptor modeling methods, Positive Matrix Factorization (PMF) is a recently developed factor analysis technique where the factor score matrix and factor-loading matrix are constrained to non-negative values (Paatero 1997). The PMF model is a weighted least-squares fit, with weights based on the known standard deviations of the elements of the data matrix. The PMF model is described in detail by Paatero (1997). Since PMF uses realistic error estimates, the PMF approach offers improvements over the Principal Components Analysis (PCA) approach. One of the critical steps in PMF modeling is the identification of source types with the chemical composition profile of each factor, and the determination of the appropriate number of factors. The identification of specific source types contributing to a factor is accomplished using known indicator species or elemental ratios. PMF allows the calculation of factor contributions for the major sources impacting the site. In many instances the co-mingling of source contributions on one factor occurs and further analysis is required to determine the source types contributing. Identification of the major source contributors (and the relative proportion of their contribution) is possible in many cases as the major sources or combinations of sources have distinct major and trace elemental signatures that distinguish themselves from each other (Gordon, 1988). PMF compares well with other source receptor modeling approaches in use, giving quite similar results (Hopke et al, 2006; Keeler et al., 2006). Utilizing this receptor modeling technique, observed data provided for analysis and determination of source contributions to the measured wet deposition during the study period at each of the project wet deposition monitoring sites (Figure 1).

3. Results

Davie monitoring site (DVE in Figure 1):

PMF analysis of data from the Davie site identified five significant factors, or source types. The first factor was identified as a marine contributor, with significant loadings of Sr and Mg. The second factor, including a strong loading of Ca, was identified as associated with cement production. The waste incineration factor was identified by loadings of Pb and Sb. An oil combustion factor was identified by significant loadings of V and Ni. The last factor was identified as a crustal contributor, with loadings of Rb and Mn. Of these five identified source types, three of these factors contributed significantly to Hg wet deposition, based on the 5th percentile of the bootstrap uncertainty. As illustrated in Figure 3, the waste incineration factor accounted for 50% of the measured Hg wet deposition at the Davie site, while the oil combustion factor contributed 25%, and the crustal factor accounted for 13%, with 11% of the measured Hg left unexplained by this analysis.

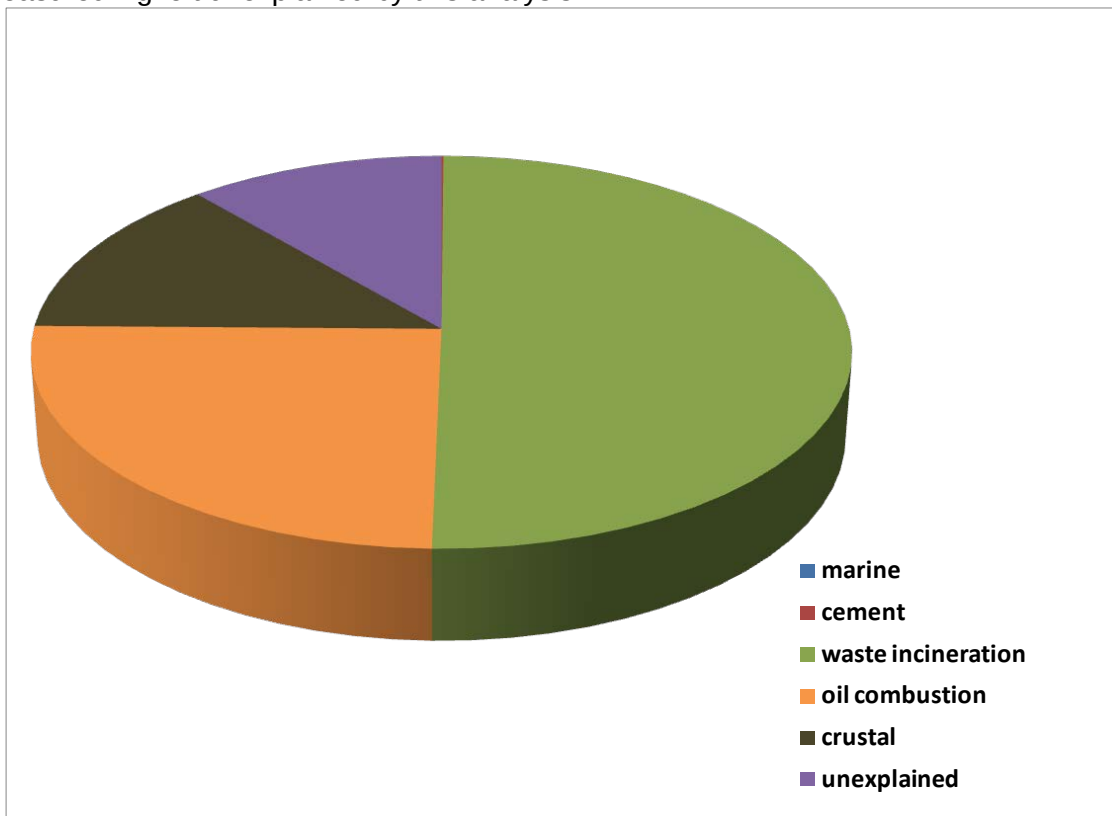


Figure 3. Percent contributions by PMF identified source types to measured Hg wet deposition at the Davie TMDL project monitoring site ($r^2 = 0.70$).

Everglades National Park monitoring site (ENP in Figure 1):

PMF analysis of data from the Everglades National Park site identified four significant factors. The first factor was identified as a combined oil combustion/industrial source contributor. The second factor represented a crustal source, the third factor a marine source, and the last factor was identified as waste incineration. Of these four identified source types, only the oil combustion/industrial source factor contributed significantly to Hg wet deposition, based on the 5th percentile of the bootstrap uncertainty, accounting for 69% of the Hg wet

deposited at the ENP site. 31% of the measured Hg was left unexplained by this analysis, as illustrated in Figure 4.

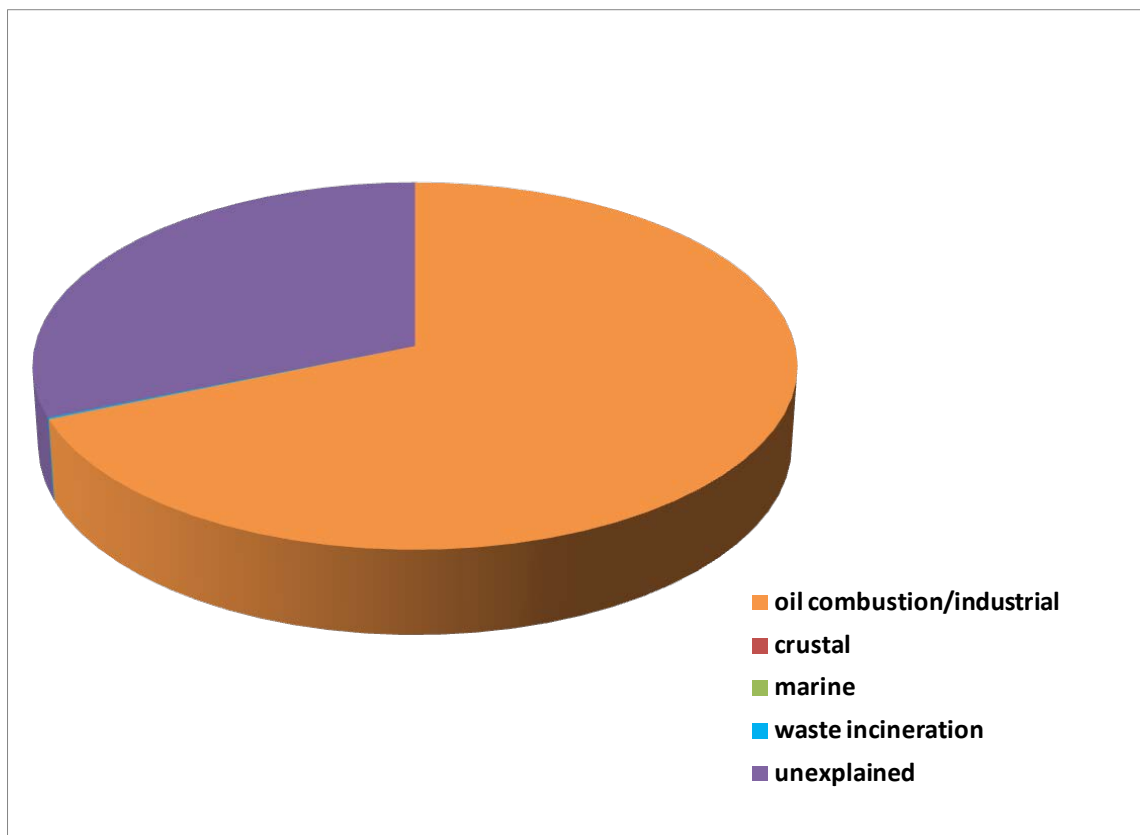


Figure 4. Percent contributions by PMF identified source types to measured Hg wet deposition at the Everglades National Park TMDL project monitoring site ($r^2 = 0.60$).

Tampa monitoring site (TPA in Figure 1):

PMF analysis of data from the Tampa site identified six significant factors, or source types. The first factor was identified as a fertilizer source, with a strong loading of P. The second factor was identified as a waste incineration factor, the third factor as oil combustion, the fourth factor as a marine source, and the fifth factor as a crustal contributor. The last factor was identified as a coal combustion source, with significant loadings of S and Se. Of these six identified source types only the coal combustion factor was found to contribute significantly to measured Hg wet deposition at the TPA site, based on the 5th percentile of the bootstrap uncertainty, contributing 81%. 19% of the measured Hg was left unexplained by this analysis, as illustrated in Figure 5.

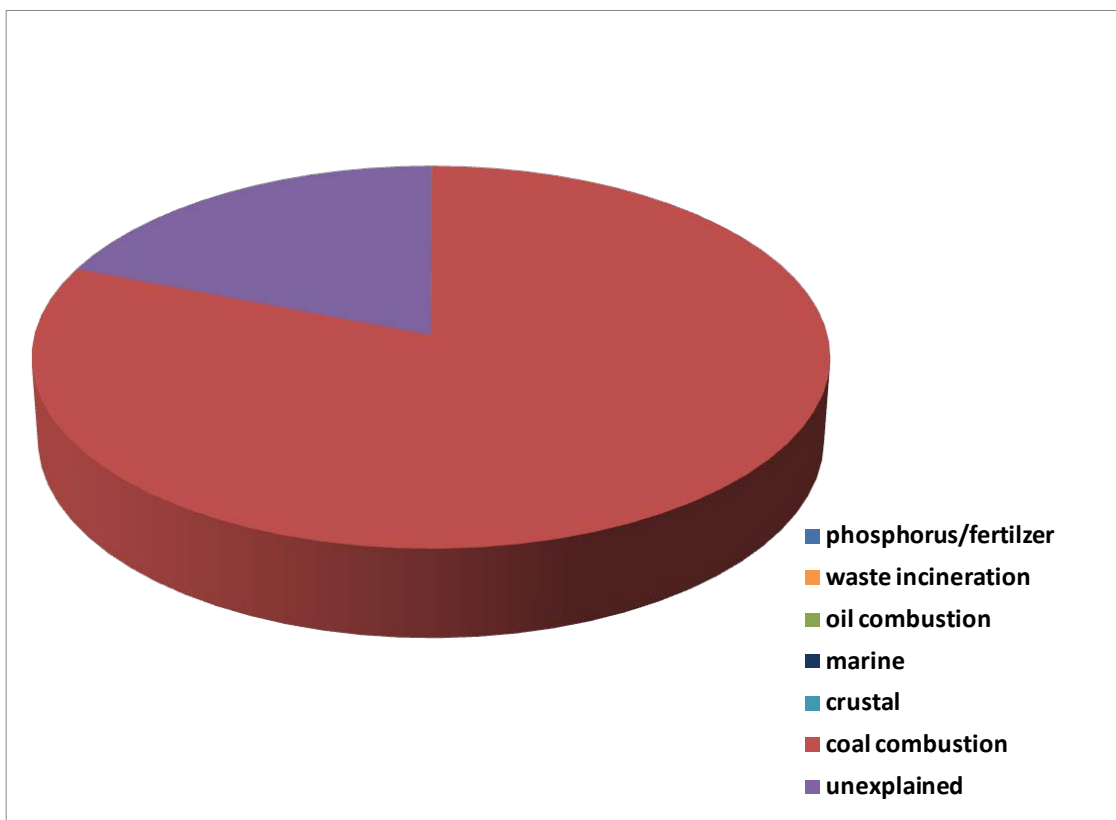


Figure 5. Percent contributions by PMF identified source types to measured Hg wet deposition at the Tampa TMDL project monitoring site ($r^2 = 0.77$).

Orlando monitoring site (UCF in Figure 1):

PMF analysis of data from the Orlando site identified four significant factors, or source types. The first factor was identified as a crustal contributor, the second factor a coal combustion source, the third factor a marine contributor, and the last factor from waste incineration. Of these four identified source types only the coal combustion factor was found to contribute significantly to measured Hg wet deposition at the UCF site, based on the 5th percentile of the bootstrap uncertainty, contributing 37%. While the waste incineration factor did contribute a large amount to Hg deposition, the analysis did not identify this as statistically significant, resulting in 63% of the measured Hg as left unexplained by this analysis, as illustrated in Figure 6.

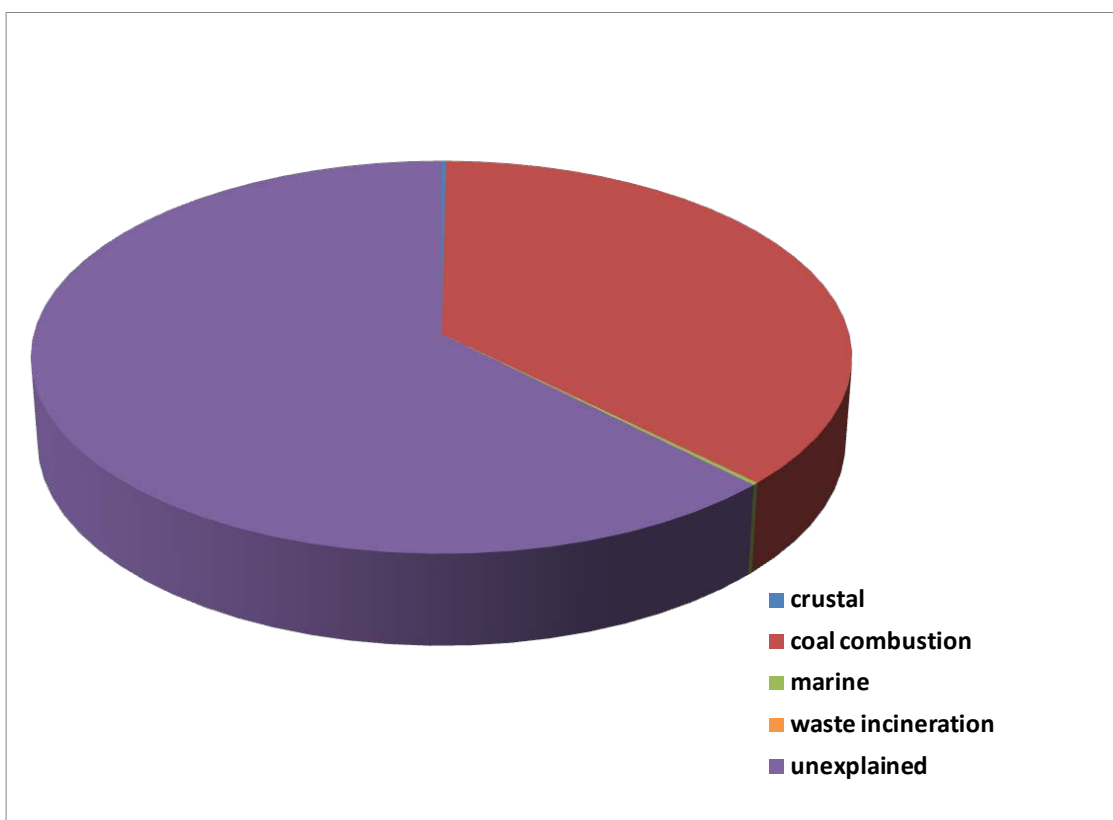


Figure 6. Percent contributions by PMF identified source types to measured Hg wet deposition at the Orlando TMDL project monitoring site ($r^2 = 0.69$).

Jacksonville monitoring site (JKS in Figure 1):

PMF analysis of data from the Jacksonville site identified five significant factors, or source types. The first factor was identified as a combined waste incineration/oil combustion source. The second factor was identified as a crustal contributor, with the third factor as a combined cement production/industrial source contributor. The fourth factor was identified as a marine source, and the fifth factor as coal combustion. Of these five identified factors, only the coal combustion factor was found to contribute significantly to measured Hg wet deposition at the JKS site, based on the 5th percentile of the bootstrap uncertainty, contributing 74% and leaving 26% of the measured Hg left unexplained by this analysis, as illustrated in Figure 7.

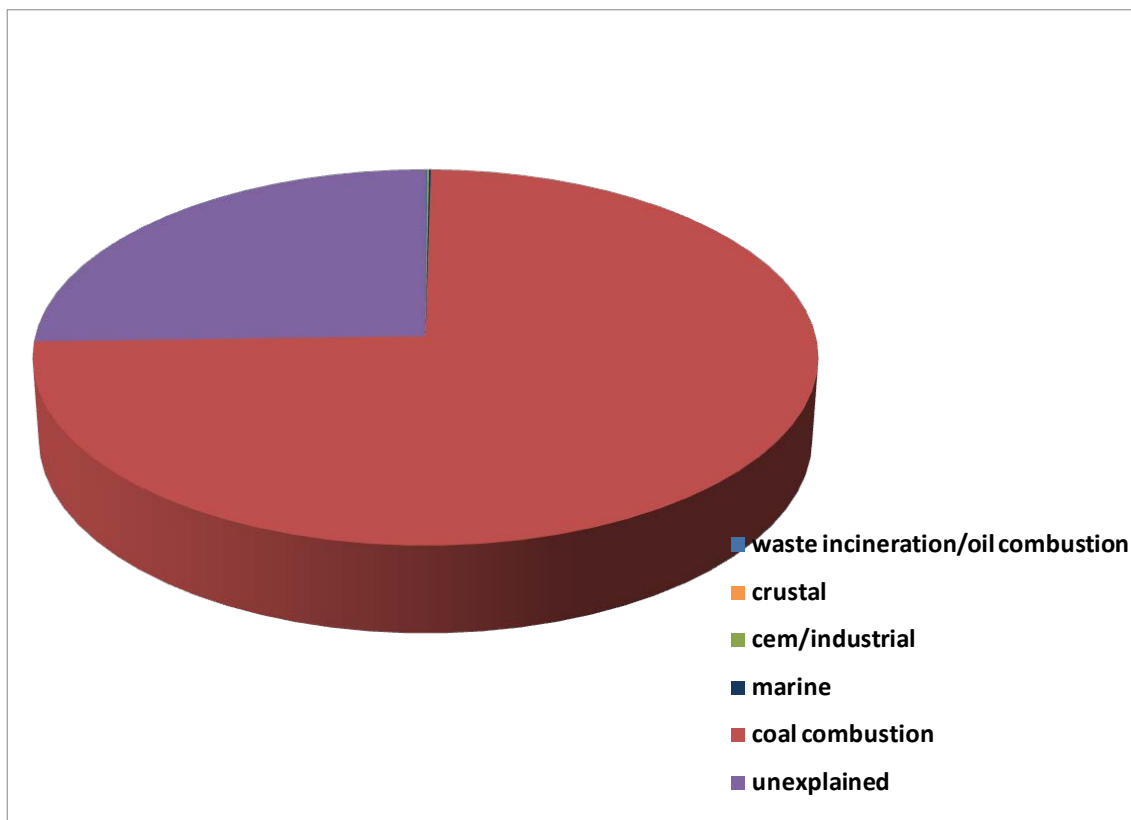


Figure 7. Percent contributions by PMF identified source types to measured Hg wet deposition at the Jacksonville TMDL project monitoring site ($r^2 = 0.60$).

Pensacola monitoring site (OLF in Figure 1):

PMF analysis of data from the Pensacola site identified five significant factors, or source types. The first factor was identified as a marine contributor, and the second factor as coal combustion. The third factor was identified as a combined crustal/refinery contributor, with the fourth factor as a combined cement production/industrial source contributor. The fifth factor was identified as waste incineration. Of these five identified factors, only the coal combustion factor was found to contribute significantly to measured Hg wet deposition at the OLF site, based on the 5th percentile of the bootstrap uncertainty, contributing 60% and leaving 40% of the measured Hg left unexplained by this analysis, as illustrated in Figure 8.

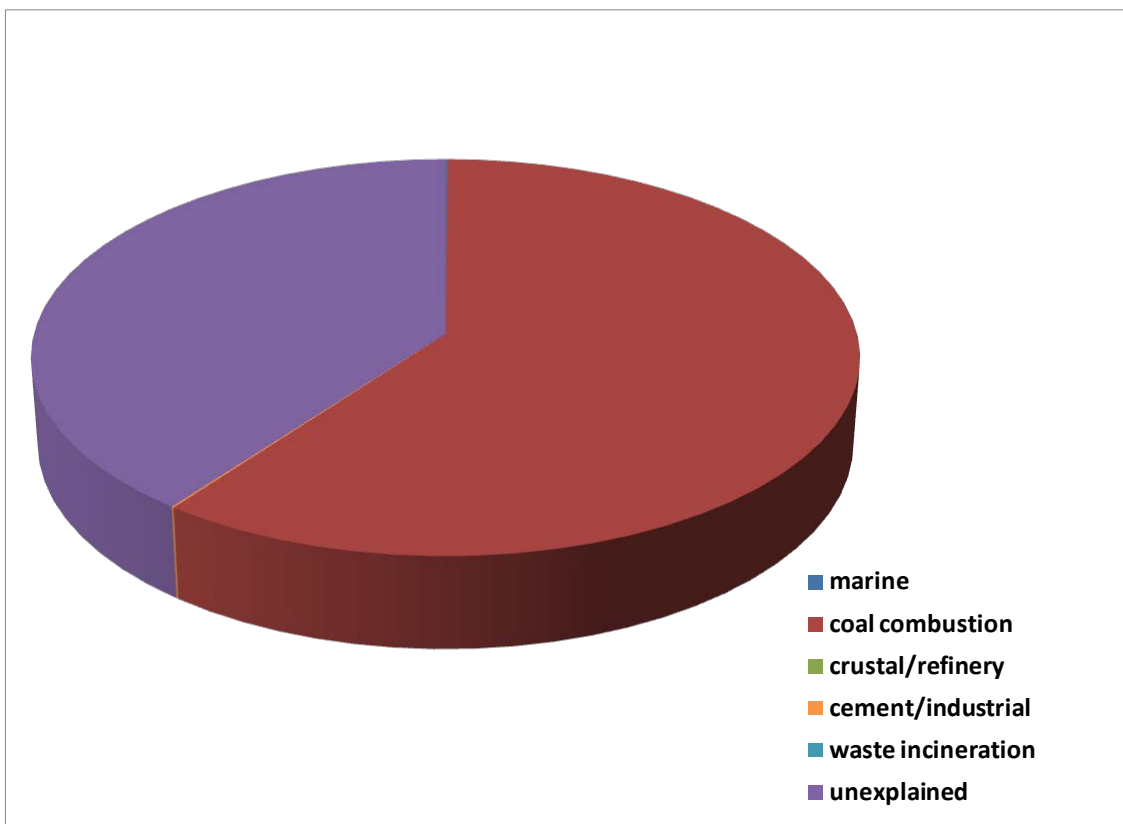


Figure 8. Percent contributions by PMF identified source types to measured Hg wet deposition at the Pensacola TMDL project monitoring site ($r^2 = 0.70$).

4. Summary

While one of the primary goals of the Florida Mercury TMDL was to estimate the loading of Hg to the State freshwater bodies, of equal importance was an improved understanding of the relative impact of source types and source regions (within-state, out-of-state) contributing to mercury deposition. The Community Multiscale Air Quality (CMAQ) model was utilized as a primary deterministic tool to estimate these source contributions on a 4km grid across the state of Florida using an emissions tagging approach (submitted and discussed as part of previous project reports). While CMAQ was the primary model utilized for source attribution analysis on a statewide basis, field measurement data also collected as part of the project allowed for an independent source apportionment analysis utilizing a multivariate receptor modeling approach.

This current report described results of the application of the U.S. Environmental Protection Agency (EPA) Positive Matrix Factorization (PMF) model (version 3.0), a receptor model and multivariate statistical analysis software developed specifically for air quality management applications, for analysis of Florida TMDL project field measurement-based wet deposition data collected at project field monitoring sites. Receptor models provide scientific support for air quality management by identifying and quantifying contributions for source apportionment. To ensure that receptor modeling tools are available for use in the development and implementation of air quality standards, the U.S. EPA's Office of Research and Development (ORD) has and continues to develop a suite of receptor modeling tools that are freely distributed to the air quality management community. EPA-PMF is one of the receptor models that ORD has developed, and has been utilized as part of this TMDL project. The algorithms used in the EPA-PMF model to compute profiles and contributions have been peer reviewed by leading scientists in the air quality management community and have been certified to be scientifically robust.

Application of EPA-PMF to the TMDL measurement data-sets revealed a range of source apportionment observations. Identified source types across the measurement sites primarily included coal combustion, waste incineration, oil combustion, cement production, crustal, and marine contributors. In terms of quantified contributions to Hg wet deposition, measurement sites located closest to large local emission point sources, or dense urban areas, were found to have the largest local contributions to measured mercury wet deposition. These included local source contributions of greater than 70% of the total measured mercury wet deposition at several of the monitoring sites located nearest to the local emission sources and dense urban areas. This finding is similar to previous mercury source apportionment studies in areas near local emission point sources, including one conducted in Steubenville, Ohio (Keeler et al., 2006). These observations are also consistent with those found within the CMAQ-derived source attribution analyses previously completed for the project using an emissions tagging approach, which found local emission sources to have the largest impact on mercury deposition at locations nearest to the sources, within 50-100 km, with much smaller local source impacts at locations beyond these distances.

8. References

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