Trans-Pacific Chemical Transport of Mercury: Sensitivity Analysis on Asian Emission Contribution to Mercury Deposition in North America Using CMAQ-Hg

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1. INTRODUCTION

Mercury is a global pollutant subject to long-range transport, due to the long atmospheric lifetime of gaseous elemental mercury (GEM, 0.5-2 years) [*Lin and Pehkonen*, 1999; *Schroeder and Munthe*, 1998]. Recently, there are concerns of the potential long-range transport from East Asia to North America [*Jaffe et al.*, 2005], which may lead to enhanced dry and wet depositions in the continental United States (US). An earlier modeling study for global attribution of mercury deposition in the US using the Trace Elements Analysis Model (TEAM) in the 1998 modeling year indicates that Asian anthropogenic emission can contribute 5-36 % of mercury deposition in the US, depending on the locations [*Seigneur et al.*, 2004]. In this study, we report the modeling evidence of trans-Pacific chemical transport of mercury, and the Asian emission contribution to mercury deposition in North America using an updated research version of CMAQ-Hg from [*Bullock and Brehme*, 2002]. This study is a part of the modeling efforts of the USEPA's Intercontinental transport and Climatic effects of Air Pollutants (ICAP) Program to understand the effect of emissions outside of the US to regional air quality through long-range transport.

2. APPROACH

2.1 Emission Scenarios

We performed CMAQ-Hg simulation for GEM, reactive gaseous mercury (RGM) and particulate mercury (PHg) with the global emission inventory of criterion pollutants and speciated mercury in a 108-km Lambert Conformal trans-Pacific domain (74×180 grids). The modeling year is 2001. The mercury emission inventory includes the updated anthropogenic emission, natural emission and re-emission [*Pacyna et al.*, 2006; *Pacyna et al.*, 2003; *Seigneur et al.*, 2004; *Streets et al.*, 2005]. Annual simulation using six mercury emission scenarios were performed to study the relative contribution from various emission sources on the dry and wet mercury depositions:

Case 1: the base case including anthropogenic and natural/re- emission of mercury,
Case 2: zeroing out the natural/re- emission in the entire domain to study the impact of non-anthropogenic mercury emission,
Case 3: zeroing out the anthropogenic emission in East Asia,
Case 4: zeroing out all mercury emission from East Asia (i.e., anthropogenic, and natural/re- emission),
Case 5: zeroing out the anthropogenic emission in North America, and
Case 6: zeroing out *all* emission to study the chemistry forcing on mercury deposition from initial and boundary conditions.

2.2 CMAQ-Hg Model and Data

CMAQ-Hg model – A research version of CMAQ-Hg was used in the simulation. The CMAQ is based on CMAQ release v4.5. The mercury model is as described in *Bullock and Brehme* [2002], with revisions in the chemical mechanism of atmospheric mercury. The revisions include speciating the oxidation products of GEM by ozone and OH to 50/50 RGM and PHg (as

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opposed to 100 % PHg), and slightly lowering the GEM oxidation rate by OH (to 7.7×10^{-14} cm^3 $molec^{-1}$ s^{-1}). The oxidation speciation is important, since it has been shown that it can strongly affect the model results of mercury deposition [*Lin et al.*, 2006]. In this version of CMAQ-Hg, it is assumed that the dry deposition of GEM is balanced by the natural/re- emission of elemental mercury from the earth's surface. Therefore, GEM dry deposition is not treated explicitly as in the CMAQ-Hg release v4.5.1. Furthermore, the dry deposition (V_d) of gaseous nitric acid is used as a surrogate V_d for calculating the dry deposition of RGM.

Meteorological data – The Year 2001 MM5 meteorology generated by the ICAP project was used. The model-ready met fields were processed by the meteorology-chemistry interface processor (MCIP) v2.2. The dry deposition of GEM and RGM were not treated extensively as in MCIP v3.1.

Initial and boundary conditions – the initial and boundary conditions (IC/BCs) were interpolated from the GEOS-CHEM global chemical transport simulation of mercury in Year 2001 [*Selin et al*., 2006]. The ICs and annual average of BCs for various mercury species is shown in Figure 1. High mercury concentrations are observed in China and India, which may lead to elevated dry deposition in the regions.

Based on the above model configuration and input data, the spatial distribution of total mercury concentration and deposition of the base-case simulation are presented. The based-case results are verified with the total annual wet mercury deposition reported by MDN in 2001 after correcting the MM5 precipitation fields. The impact of the long-range transport from Asia on the mercury deposition in the continental US is assessed in terms of the source contribution of the wet and total depositions at 13 selected MDN sites. The implications of the simulation results are discussed.

3. RESULTS AND DISCUSSION

From our base-case simulation, several trans-Pacific transport events of GEM from Asia to the West Coast of North America were identified in March-April and October-November of 2001. The transport event in April 2001 is particularly strong. It takes 7-15 days for the Asian plume of GEM to transport to North America. The plume usually enters the US through the States of Oregon and Washington, although the intensity of the plume has been much diluted during the transport process, leading to an increase of surface GEM concentration by only 0.1-0.3 ng/m^3. We feel that more simulations in multiple modeling years should be performed to determine the frequency and intensity of such long-range transport events. Nevertheless, our results show convincing model evidence that long-range transport of Asian mercury emission indeed occurs. This adds to the recent measurement evidence of "mercury export from China" [*Jaffe et al.*, 2005].

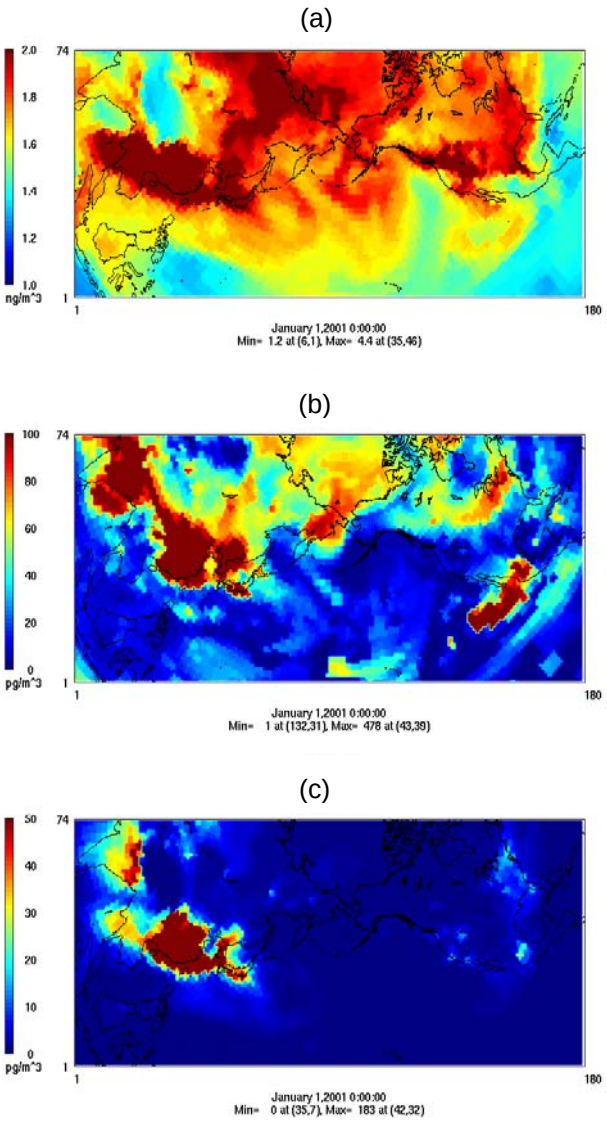


Fig. 1: The initial and average boundary conditions of (a) GEM, (b) RGM and (c) PHg in the trans-Pacific domain.

Figure 2 shows the spatial distribution of annual average mercury (GEM+RGM+PHg) concentration, and the total annual dry and wet depositions. The total mercury concentration is dominated by GEM, typically ranging from 1.4-1.7

ng/m^3 except near anthropogenic emission sources. The mercury plume is strong in east China and Japan compared to other regions in the domain, typically ranging between 2-6 ng/m^3 (Figure 2a). The dry deposition is primarily caused GEM oxidation followed by RGM deposition removal (Figure 2b). The wet mercury deposition is closely correlated with the precipitation field in the domain. The simulated annual wet deposition in the continental US agrees reasonable well with the MDN data, ranging from 4-25 μg/m^2 with elevated deposition in the Gulf of Mexico and the Great Lakes in 2001 (Figure 2c).

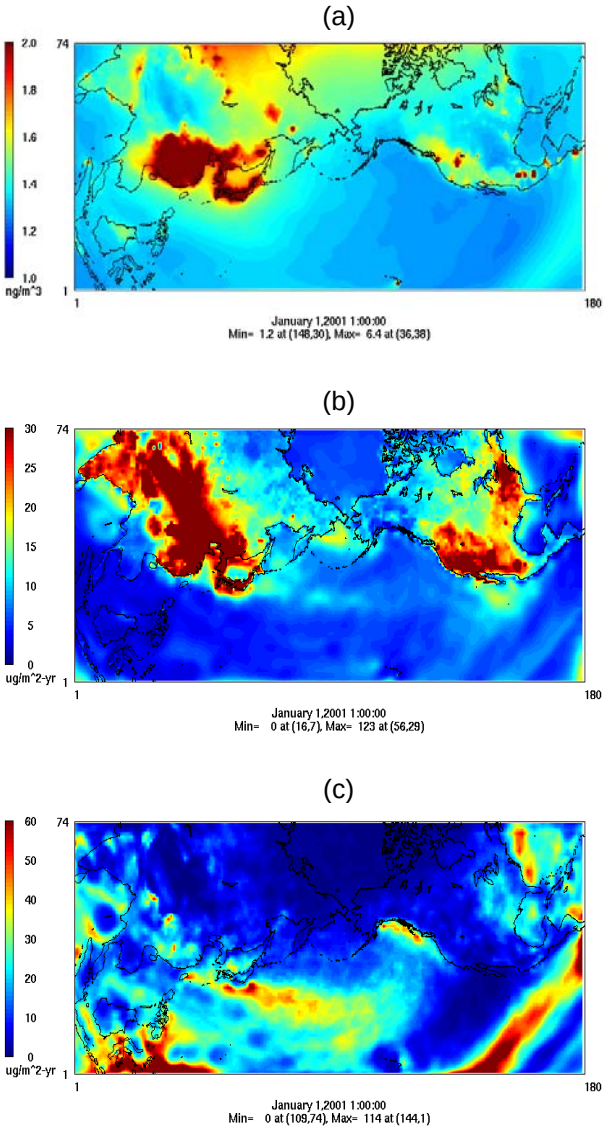


Fig. 2: Simulated spatial distribution of the (a) annual average concentration (GEM+RGM +PHg), (b) total dry deposition and (c) total wet deposition, of mercury.

Figure 3 shows the domain-wise source contribution for mercury concentration and deposition. The anthropogenic emission does not significantly modify ambient concentration of mercury except near emission sources [*Lin et al.*, 2006]. The IC/BCs contribute to the greatest fraction to the modeled mercury concentration and deposition, indicating the importance of mercury background and chemistry forcing on dry and wet depositions. The results are consistent with those reported in Seigneur and co-workers [*Seigneur et al.*, 2003b; *Seigneur et al.*, 2004]. Among the considered EI scenarios, Asian anthropogenic mercury emission contributes to greatest fraction to mercury deposition compared to other emission sources. It may also significantly contribute to the global mercury background that leads to an indirect impact on the deposition.

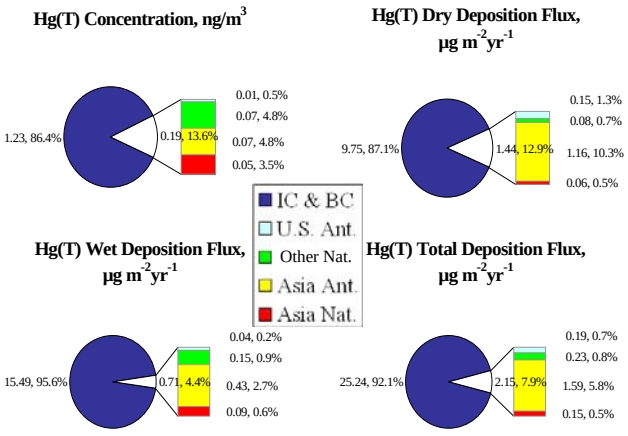


Fig. 3: The domain-wise source contribution for mercury concentration and deposition in the trans-Pacific domain.

We also assessed the source contribution to wet mercury deposition in the United States at selected MDN sites using our model results. The criteria for the site selection were based on that the modeled annual precipitation fields have comparable values (± 50 %) to the site-measured precipitation. These selected thirteen MDN sites are shown in Figure 4 in blue circles, which show representative urban and rural monitoring locations.

The results of source contribution of mercury wet and total depositions at the selected MDN sites are shown in Figure 5. As seen, the background mercury (i.e., IC/BCs) with chemistry forcing remains as the greatest contributor for both wet and total deposition observed at the sites (79-95 % of wet and 64-96 % of total deposition).

However, in certain industrial locations (for example, Site PA37), the contribution from the US anthropogenic emission sources can be significant (up to 17 % for wet deposition and up to 34 % for total deposition). The direct contribution from the intercontinental transport of Asian mercury emission is not significant (< 3 %, Figure 5) in the one-year simulation. The incorporation of natural/re- emission of mercury in the chemical transport modeling does not significantly affect mercury deposition produced by the model (< 2 % total, Figures 3 and 5). This also agrees with an earlier modeling analysis [*Lin et al.*, 2005].

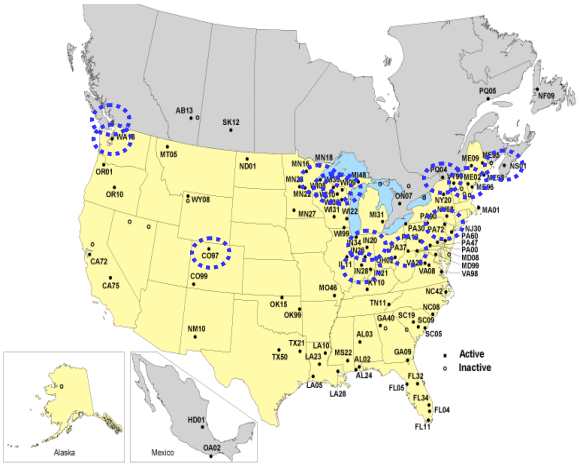
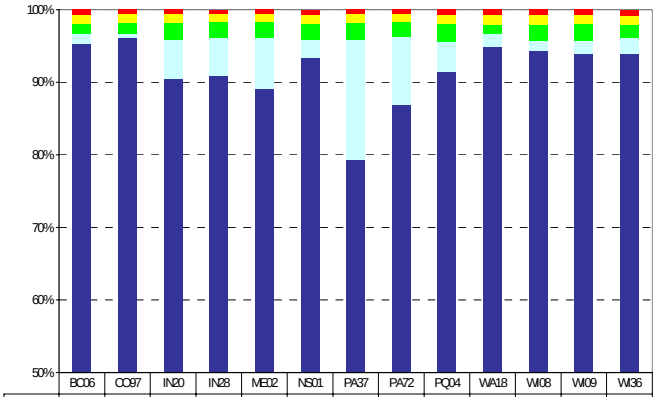


Fig. 4: The selected MDN sites for source contribution analysis.

These source attribution results have several important implications. First, controlling local anthropogenic mercury emission in the US would be important for reducing both dry and wet mercury depositions in the regions near the emission sources. The grid resolution in this study is relatively coarse (108 km), which can cause much dilution of the emitted mercury [*Seigneur et al.*, 2003a]. Because of this reason, we feel that the source contribution of the US anthropogenic emission should be regarded as a lower bound.

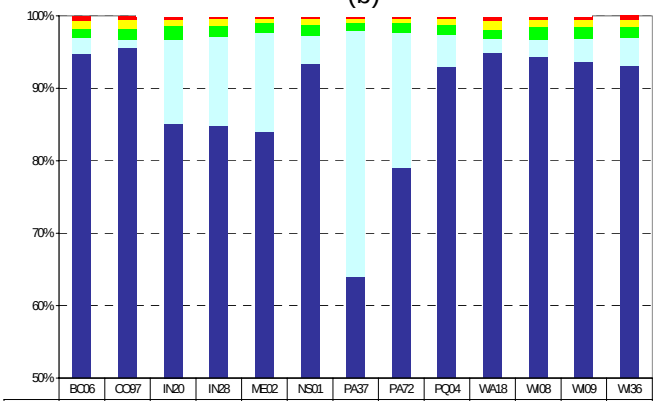
Secondly, although the intercontinental transport of mercury from Asia to North America is clearly shown in our model output, the *direct* impact from the trans-Pacific transport on mercury deposition in the US is not likely to be significant given the occasional transport events. However, since Asian emission makes up about one-third (1/3) of elemental mercury input into the domain, its contribution to the background GEM (and thus to mercury deposition in the US *indirectly*) should not be overlooked. Furthermore, the increasing atmospheric input of mercury from Asian emission, especially in China [*Streets et al.*, 2005], could slowly force a slow increase of background concentration of mercury if not properly controlled. Since chemistry forcing is the primary factor driving mercury deposition based on our current understanding of atmospheric mercury, Asian mercury emission may gradually impose a more significant *indirect* impact on mercury deposition observed in North America.

(a)



	BC06	CO97	IN20	IN28	ME02	NS01	PA37	PA72	PQ04	WA18	WI08	WI09	WI36
Asia.Nat.	0.74	0.63	0.63	0.56	0.59	0.68	0.62	0.59	0.70	0.76	0.75	0.76	0.82
Asia.Ant.	1.23	1.13	1.19	1.11	1.04	1.24	1.18	1.07	1.22	1.29	1.37	1.25	1.24
U.S.Nat.	1.32	1.54	2.31	2.17	2.24	2.22	2.29	2.09	2.46	1.34	2.19	2.25	1.84
U.S.Ant.	1.34	0.59	5.40	5.32	6.94	2.51	16.64	9.35	4.24	1.76	1.27	1.87	2.10
IC&BC	95.36	96.11	90.47	90.84	89.19	93.36	79.26	86.90	91.38	94.85	94.42	93.87	94.01

(b)



	BC06	CO97	IN20	IN28	ME02	NS01	PA37	PA72	PQ04	WA18	WI08	WI09	WI36
Asia.Nat.	0.64	0.55	0.49	0.43	0.34	0.43	0.32	0.36	0.41	0.68	0.54	0.55	0.57
Asia.Ant.	1.16	1.23	0.92	0.84	0.60	0.77	0.61	0.65	0.74	1.24	1.00	0.93	0.93
U.S.Nat.	1.22	1.58	1.80	1.67	1.36	1.56	1.12	1.27	1.45	1.20	1.69	1.73	1.51
U.S.Ant.	2.18	1.02	11.71	12.17	13.67	3.78	33.95	18.74	4.37	2.02	2.45	3.11	3.87
IC&BC	94.80	95.63	85.08	84.88	84.03	93.47	64.00	78.99	93.03	94.86	94.32	93.68	93.12

Fig. 5: The source contribution of (a) wet, and (b) total mercury deposition at the selected MDN sites shown in Figure 4.

Finally, the above model results represent the analysis from the annual simulation in 2001.

Additional analysis performed in multiple years and model advancements in CMAQ-Hg will be helpful to further verify the conclusions in this study. It will be of particular interest to study how Asian emission sources would modify the background mercury concentration, and contribute *indirectly* to the US mercury deposition over a longer simulation period.

4. SUMMARY

We performed CMAQ-Hg simulation with the global emission inventory of criterion pollutants and mercury in a 108-km trans-Pacific domain for Year 2001. Several long-range transport events of GEM from Asia to the North America were identified, increasing the surface layer GEM concentration by 0.1-0.3 ng/m^3 in the West Coast of US. Six mercury emission scenarios were implemented in a series of sensitivity simulations to study the source contribution from various anthropogenic and natural/re- emissions on the dry and wet mercury depositions in North America. The model results show that atmospheric mercury chemistry of background mercury is the most dominant factor leading to the dry and wet depositions, contributing 65-95 % of total mercury deposition at selected MDN sites. The inclusion of natural/re- emission of mercury in the emission inventory does not significantly affect mercury deposition (< 2 % in total deposition), while local anthropogenic emission can have a significant contribution to the deposition in the US (up to 34 %). The *direct* contribution from the trans-Pacific transport of Asian mercury emission to the deposition in the US may not be significant based on our one-year modeling results. However, since Asian mercury emission constitutes an important fraction of global mercury input to the atmosphere, its *indirect* contribution, i.e., the accumulative contribution to the global background, should not be overlooked and requires further modeling analysis using a long-term simulation period.

5. ACKNOWLEDGMENTS

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