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Mercury Wet Scavenging and Deposition Differences by Precipitation Type

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ABSTRACT: We analyze the effect of precipitation type on mercury wet deposition using a new database of individual rain events spanning the contiguous United States. Measurements from the Mercury Deposition Network (MDN) containing single rainfall events were identified and classified into six precipitation types. Mercury concentrations in surface precipitation follow a power law of precipitation depth that is modulated by precipitation system morphology. After controlling for precipitation depth, the highest mercury deposition occurs in supercell thunderstorms, with decreasing deposition in disorganized thunderstorms, quasi-linear convective systems (QLCS), extratropical cyclones, light rain, and land-falling tropical cyclones. Convective morphologies (supercells, disorganized, and QLCS) enhance wet deposition by a factor of at least 1.6 relative to nonconvective morphologies. Mercury wet deposition also varies by geographic region and season. After controlling for other factors, we find that mercury wet deposition is greater over high-elevation sites, seasonally during summer, and in convective precipitation.



INTRODUCTION

Atmospheric mercury is a toxic pollutant that causes nervous system disorders in humans and wildlife and is especially harmful during gestational development and childhood.^{1–3} Human exposure to mercury occurs primarily through consumption of fish and rice,^{4,5} with deposition of atmospheric mercury being the main source of mercury to most marine and aquatic ecosystems. Thus, it is important to understand the transport and fate of atmospheric mercury. In this context, there is a need to understand processes responsible for the observed geographical patterns of mercury wet deposition.

Within the continental United States, the eastern United States and especially the Ohio River Valley have the highest density of atmospheric mercury emissions (Figure 1). In this area, local emissions account for a large fraction of observed mercury wet deposition.^{6–8} However, the highest mercury wet deposition in the continental United States occurs along the Gulf Coast, where local emissions are lower than in the Ohio River Valley. Even higher wet deposition is observed in Puerto Rico,⁹ an island with no substantial mercury emissions. While Hg deposition is generally low in the arid western United States, concentrations in rain can be high.¹⁰ The discrepancy between local emissions and wet deposition patterns suggests the importance of long-range and global atmospheric mercury cycling in depositing mercury to these regions.

Mercury exists in the atmosphere in three forms: gaseous elemental mercury (GEM), gaseous oxidized mercury (GOM), and oxidized particle-bound mercury (PBM). The oxidized species collectively comprise Hg(II). The majority of atmospheric mercury (95%) exists as GEM, which has low solubility and high volatility compared to the oxidized forms. Due to its low solubility and slow chemical oxidation, GEM has a long atmospheric residence time $(0.5-1 \text{ year})^{14,15}$ and can be transported globally. The oxidized species are quickly removed from the lower troposphere by dry and wet deposition, but oxidized mercury can accumulate in the upper troposphere and stratosphere.^{11,16-24}

Prior studies suggest that this high-altitude reservoir of oxidized mercury could sustain high mercury deposition in regions without significant mercury emissions. Since the reservoir is thought to be widespread in the upper troposphere and lower stratosphere, deposition from it is likely determined by patterns of subsidence and precipitation.^{11,25} Although the stratosphere contains high concentrations of Hg(II),^{17,24} transport across the tropopause is generally slow, which limits its relevance to surface deposition. However, strong convective storms can force subsidence in the surrounding clear air that can transport stratospheric ozone, and possibly stratospheric Hg(II), down into the troposphere.^{26,27} Observations and simulations show that convective storms extending to higher altitudes have higher mercury concentrations.^{28,29} In addition, idealized numerical models suggest that mercury scavenging efficiency is sensitive to the thermodynamic and meteorological conditions that control convective system morphology. These conditions vary regionally, and Nair et al.²⁸ found that storms forming in low-shear, high-instability environments, which frequently occur around the Gulf Coast in the summer and

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Figure 1. Mercury emissions, rainfall, and wet deposition over the continental United States. (a) Mercury emissions are based on the 2011 National Emissions Inventory (NEI). (b) Monthly mean mercury wet deposition for 1996–2013 is interpolated from Mercury Deposition Network (MDN) observations. Different markers indicate MDN sites associated with the seven regions discussed under Data and Methods: (\blacktriangle) Northeast, (\bigcirc) Southeast, (\bigstar) Ohio River Valley, (\blacksquare) Midwest, (+) Great Plains, (\blacksquare) Mountain West, and (*) West Coast).

tend to produce disorganized convection, are more efficient at mercury wet removal than storms formed in some other environments.

Event-based precipitation samples provide the best opportunity to study how mercury is scavenged from the atmosphere,³⁰ but such observations are currently rare, while weekly collections are much more common. We extracted 525 event-based precipitation samples from the Mercury Deposition Network archive and used them to understand the role of storm type, as well as seasonal and geographic differences, on Hg deposition.

DATA AND METHODS

The Mercury Deposition Network (MDN) monitors mercury wet deposition across North America with uniform analytical methods.¹⁰ MDN sites are generally located in rural areas, so that measurements are regionally representative, but they may miss high deposition in urban areas or near point sources.³ Most MDN sites collect weekly deposition samples, which often contain several precipitation events but sometime only one. A limited number of network sites collect precipitation samples after each precipitation event (within 24 h). Since the primary goal of this study requires event-based analysis, all MDN observations from January 2005 to August 2013 were examined to identify wet deposition measurements that come from a single precipitation system.⁵² In order to make this determination, manual analysis of radar reflectivity and precipitation rates from U.S. National Weather Service WSR-88D radar (5 min temporal resolution level II reflectivity and level III one hour precipitation total)^{32,53} and colocated surface rain gauges (U.S. 15 Minute Precipitation Data, created by the National Climatic Data Center)54 were utilized. MDN observations were excluded if precipitation rates did not indicate a single continuous rain event. Rainfall events spanning two or more MDN collection periods were also excluded. By use of the procedure described, we found 525 wet deposition samples that could be linked to a single precipitation event (Figure 2a).

After the single-event samples are identified, radar observations are used to classify the precipitation type. We use classification criteria developed by Smith et al.³³ for convective storms, with additional nonconvective categories. These radarbased criteria were chosen because they provide objective radar definitions for a comprehensive list of storm types and are appropriate for the entire United States.³³ The precipitation types are (1) supercell thunderstorms, which have low-level radar reflectivity values greater than 35 dBZ, a peak rotational velocity of at least 10 m/s below 7 km altitude and extending through at least one-fourth of the storm's depth, and persistence of these features for at least 10 min; (2) quasilinear convective systems (QLCS), which have low-level reflectivity greater than 35 dBZ, length exceeding 100 km, and a length-to-width aspect ratio aspect of 3:1 or greater; (3) disorganized thunderstorms, which have low-level reflectivity greater than 35 dBZ but do not meet the requirements of supercell and QLCS categories; (4) extratropical cyclones, which are large-scale and characterized by nonconvective precipitation; (5) tropical cyclones, which are organized cyclonically rotating precipitation systems originating in the tropics; and (6) light precipitation, defined as precipitation below the 35 dBZ threshold and less than 50 km in size. While QLCS and tropical cyclones can contain both convective and stratiform precipitation, QLCS precipitation is mostly convective, whereas stratiform precipitation dominates in landfalling tropical cyclones.

For each storm type we calculate the mean precipitation depth $(\langle p \rangle)$ and mean deposition $(\langle D \rangle)$ per event (Table 1). When mercury concentration or deposition in precipitation is compared between different events, confounding effects of differences in amount of precipitation need to be taken into account. As with other soluble trace gases and aerosols, the relationship between mercury concentrations in precipitation (C) and precipitation amount (p) roughly follows a power-law relationship:^{29,34–38}

$$C(p) = C_0 (p/p_0)^{-\gamma} \tag{1}$$

The coefficients C_0 and γ are fitted to observations for each precipitation type, where C_0 represents the Hg concentration in an event per unit precipitation, $p_0 = 1$ mm, and γ is typically positive, meaning that concentrations are diluted in large rain



Figure 2. Mercury concentration versus precipitation as a function of precipitation system morphology. (a) Scatter plot of individual observations: (yellow) supercell, (red) disorganized thunderstorm, (green) QLCS, (blue) extratropical cyclone, (black) light rain, and (brown) tropical cyclone. (b–e) Mercury concentrations for (b) disorganized thunderstorm, (c) QLCS, (d) extratropical cyclones, and (e) light rain. (f) Similar plots for supercells and tropical cyclones are shown together; open circles are used to distinguish data points associated with tropical cyclones. Lines show ordinary least-squares regression described in eq 1 and summarized in Table 1.

events. The power law implies a linear relationship between log(C) and log(p). In order to quantify the dilution curves for each precipitation system morphology, estimates of parameters γ and C_0 for each type of precipitation system were determined by ordinary least-squares regression (Table 1).

Geographical and seasonal differences can also influence Hg deposition. To account for these factors, a robust linear model (RLM), implemented by use of the robustbase R package,³⁹ is constructed from observations of the individual precipitation events. The regression model is

$$D(p, i, j, k) = D_0 (p/p_0)^{\nu} R_i S_j T_k$$
(2)

where D(p, i, j, k) is the Hg deposition resulting from precipitation depth p in region i, season j, and from storm type k; D_0 is the deposition for $p_0 = 1$ mm precipitation; R_i is a multiplicative factor for region i; S_j is a multiplicative factor for season j; and T_k is a multiplicative factor for storm type k. The regression fit is preformed on the logarithm of eq 2, which is a linear equation, and the results are transformed back (Table 2). Season, region, and storm type are all discrete predictors. Seasons are categorized as winter (December, January, and February; DJF), spring (March, April, and May; MAM), summer (June, July, and August; JJA), and fall (September, October, and November; SON). Geographical regions are the Southeast, Mountain West, West Coast, Northeast, Ohio River Valley, Midwest, and Great Plains. The MDN sites that fall within these regions are shown in Figure 1. The RLM also tests for interactions of precipitation depth with precipitation type, season, or region, although these are not shown in eq 2 because they were not found to be significant. Interactions of precipitation type with region and season were excluded from the RLM because some precipitation types do not occur in all regions and seasons. Similarly, interactions between region and season are excluded, since observations for some combinations of these variables are not present in our data set. The optimal set of predictors is selected with a backward, stepwise model selection approach based on Akaike information criterion (AIC) implemented in the AICcmodavg R package.⁴⁰ This method sequentially discards predictors from the regression model to minimize the AIC value and thus identifies the most parsimonious model that maximizes the explained variability of Hg concentration with the fewest predictors.

Table 1. Mercury	Concentration and	l Deposition f	or Multip	e Precipitation	Types"
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morphology	n	$C_0 (ng \cdot L^{-1})$	γ	r	p_{χ^2}	$D (ng \cdot m^{-2})$	$\langle D \rangle ~({ m ng}{\cdot}{ m m}^{-2})$	$\langle p \rangle$ (mm)
supercell	7	$20.4 \pm 1.47^*$	-0.04 ± 0.15	0.12	0.79	2800	393 ± 119	17.2 ± 5.16
disorganized	61	$26.7 \pm 1.26^*$	$0.35 \pm 0.09^*$	-0.46	< 0.01	11 000	182 ± 21	16.8 ± 1.99
QLCS	160	$22.4 \pm 1.09^*$	$0.26 \pm 0.05^*$	-0.40	< 0.01	21 000	133 ± 15	9.26 ± 1.04
extratropical cyclones	255	$12.4 \pm 1.09^*$	$0.34 \pm 0.04^*$	-0.59	< 0.01	18 000	70 ± 5	12.5 ± 1.10
light rain	29	$15.9 \pm 1.22^*$	$0.28 \pm 0.15^*$	-0.34	0.06	1700	60 ± 21	4.24 ± 1.54
tropical cyclones	13	1.31 ± 3.19	-0.07 ± 0.27	0.08	0.79	2000	154 ± 345	77.1 ± 11.0

^{*a*}*n* is the number of events, C_0 and γ are parameters for eq 1 with correlation coefficient *r*, $p_{\chi^2}^2$ is the *p* value for the χ^2 goodness-of-fit test, *D* is total wet deposition, $\langle D \rangle$ is mean Hg deposition per precipitation event, and $\langle p \rangle$ is mean precipitation depth. The uncertainty ranges are standard errors for C_0 , γ , D_c , $\langle D \rangle$, and $\langle p \rangle$. Asterisk indicates statistical significance at the 0.05 level.

RESULTS

For most storm types, mercury concentrations decline with increasing precipitation depth; however, there is large scatter apparent for all storm types in Figure 2. The scatter is due to many processes that are not explicitly accounted for in the statistical model, including initial Hg(II) concentration before the rain event, distance to Hg(II) sources, airmass trajectory, rain heterogeneity within a single storm, and other meteorological variability. Despite the scatter within the data, the power law reasonably describes the dilution effect based on χ^2 goodness-of-fit test ($p \leq 0.06$ for all but tropical cyclones and supercell thunderstorms), and lack of structure (e.g., trends, skewness) in the fit residuals. The regression coefficients (Table 1) describing this dilution cluster around γ = 0.3 for disorganized thunderstorms, QCLS, light rain, and extratropical cyclones (all within 1 standard error, SE). This value is within the range of past dilution estimates for mercury, other trace metals, and sulfur.^{29,36,41} The remaining storm types, supercell thunderstorms and tropical cyclones, exhibit less dilution that is statistically indistinguishable from $\gamma = 0$ (no dilution) but at the upper end of the coefficient uncertainty (2 SE) is also consistent with $\gamma = 0.3$. The data set contains few (*n* = 7, 13) of these storm types, so it is unclear whether the apparent lack of dilution in these storms reflects real differences in scavenging. The C_0 coefficients, which specify the Hg concentration in a 1 mm precipitation event, have clear differences between precipitation types (Table 1). Convective storms have the highest concentration coefficients ($C_0 = 20-27$ $ng \cdot L^{-1}$; light rain and extratropical cyclones have intermediate values $(C_0 = 12-16 \text{ ng} \cdot \text{L}^{-1})$; and tropical cylones have the lowest $(C_0 = 1.3 \text{ ng} \cdot \text{L}^{-1})$. The uncertainties in C_0 estimates are around 1.3 ng $\cdot \text{L}^{-1}$, so these differences are statistically significant.

The mean and total deposition for each storm type is sensitive to the particular events that happen to be observed, although some patterns related to storm type emerge. The mean wet deposition $(\langle D \rangle)$ per event ranges from a low of 60– 70 $\text{ng}\cdot\text{m}^{-2}$ in extratropical cyclones and light rain to a high of 390 $ng \cdot m^{-2}$ in supercell thunderstorms (Table 1). The other storm types (QLCS, disorganized thunderstorms, and tropical cyclones) have similar mean deposition of $130-180 \text{ ng} \cdot \text{m}^{-2}$ per event, despite their clear differences in concentration and precipitation amount (Figure 2). In general, the storm types with high mean precipitation depth $(\langle p \rangle)$ tend to have high mean deposition (e.g., tropical cyclones and supercell and disorganized thunderstorms), but the tendency is weak. The tropical cyclones in our data set produced over 4 times more rain on average than the supercell storms but less than half the mean Hg deposition, because of the low Hg concentrations in these tropical cyclones. Due to the large number (n) of disorganized, QLCS, and extratropical cyclones in our database, the total wet deposition from these morphologies (Table 1) contributes the majority of the total wet deposition in the events considered.

In the discussion above on the variability of mercury wet deposition as a function of precipitation system morphology, the confounding effects of geographic and seasonal variability were neglected. The RLM approach (see Data and Methods) addresses these effects, with the optimal model selected using a backward, stepwise approach. The resulting optimal RLM model has predictors of precipitation depth, season, geographic region, and precipitation system morphology. Stepwise construction of the RLM showed that the most important variable, determined by the change in AIC as predictors are removed from the RLM, is precipitation depth (ΔAIC = 534.2), followed by precipitation type ($\Delta AIC = 134.8$), season (Δ AIC = 26.4), and region (Δ AIC = 11.6). The Δ AIC values for interactions between precipitation depth and all other predictors (season, region, and precipitation type) were positive, meaning that they degraded model performance, so these terms were excluded. The precipitation exponent b in eq 2 should be related to the dilution exponent γ in eq 1 via $b = \gamma$ + 1. The value of b = 0.69 (log₁₀ 4.93, Table 2) is consistent with $\gamma = 0.3$ (Table 1) for most storm types. Since the γ values in Table 1 appear to differ between storm types, the lack of interaction between precipitation depth and storm type in the RLM means that the apparent differences in dilution effect (γ) between storm types are likely due to confounding effects of region and season. After controlling for these season and region effects, we found that all storm types have the same precipitation exponent (b) coefficients. Mercury emissions, transport, and atmospheric chemistry do not explicitly appear in the regression model, but they influence the baseline deposition (D_0) through the concentrations of GOM and PBM and also influence the geographic and seasonal differences

RLM analysis (Table 2) shows that storm morphology impacts mercury wet deposition independent of precipitation amounts, seasonality, and location. Compared to extratropical cyclones, mercury wet deposition is significantly greater in supercell thunderstorms, disorganized thunderstorms, and QLCS (p < 0.01). Tropical cyclone morphologies have significantly lower mercury deposition than extratropical cyclones (p < 0.01), and light rain is not significantly different from extratropical cyclones (p = 0.81). As a group, convective storms have greater mercury wet deposition than nonconvective types (extratropical cyclones and light rain) by a multiplicative factor of at least 1.6 (= 10^x , where $x \ge 0.21$ is the fit coefficient for QLCS, disorganized, or supercell; Table 2). This is similar to the factor of 1.48 ± 0.07 increase previously

Table 2. R	egression	Model	of Hg	Wet	Deposition
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predictor	value ^a	std error ^b	P^{c}				
D_0	15.51 ng·m ⁻²	1.93 ng·m ⁻²	< 0.01*				
b (precipitation)	0.69	0.32	< 0.01*				
	Season (S)						
DJF	0.62	0.07	< 0.01*				
MAM	1.01	0.09	0.95				
JJA	1						
SON	0.81	0.07	0.01*				
	Region (R)						
Mountain West	2.05	0.71	0.02*				
Great Plains	1.28	0.17	0.05*				
Midwest	1.03	0.11	0.79				
Southeast	1						
Ohio River Valley	0.99	0.11	0.92				
Northeast	0.74	0.07	< 0.01*				
West Coast	0.69	0.31	0.31				
Storm Type (T)							
supercell	2.54	0.71	< 0.01*				
disorganized	1.68	0.20	< 0.01*				
QLCS	1.62	0.15	< 0.01*				
light rain	1.04	0.18	0.81				
extratropical cyclone	1						
tropical cyclone	0.57	0.09	< 0.01*				

"All values are unitless except D_0 . Values for season, region, and storm type are multiplicative factors. Values are defined as 1 for the reference season (JJA), region (Southeast), and storm type (extratropical cylcone). ^bStandard error of regression parameter values. ^cP is the probability that the coefficient value is 0 (for precipitation b) or 1 (for all others, which is 0 in log transform). For the discrete categorical variables, this determines whether the season, region, or storm type differs from the reference category. Asterisk indicates statistical significance at the 0.05 level.

found for summer thunderstorms in the eastern United States. $^{\rm 29}$

After control for precipitation depth, region, and morphology, the RLM analysis (Table 2) shows that wet deposition is highest during summer and lowest during the winter. For a given precipitation amount, storm type, and season, mercury wet deposition is also highest over the Mountain West region, followed by the Great Plains, then by a group consisting of the Southeast, Midwest, and Ohio River Valley (Table 2). The lowest deposition after controlling for other factors is found in the Northeast and West Coast. Relative to the Southeast, the differences are statistically significant only for the Mountain West (p = 0.02), Northeast (p < 0.01), and Great Plains (p = 0.05).

DISCUSSION

We have identified samples in the MDN archive that originate from single precipitation events, providing the most geographically diverse database of mercury wet deposition events to date. After accounting for dilution effects, we find that the variability of mercury concentrations in rainfall is best explained by precipitation system morphology, season, and region. The regression model shows that mercury deposition tends to be greater in convective precipitation than in stratiform precipitation, greater in summer than winter, and greater in the highelevation regions of the western states than the rest of the United States.

The following discussion considers the processes that are consistent with statistical differences in mercury deposition between seasons, regions, and precipitation system types. Seasonal variation, with greatest deposition in summer and lowest in winter, is consistent with past studies of Hg wet deposition.^{10,42} These have previously been attributed to the emissions, dispersion, and atmospheric chemistry that drive seasonal cycles of GOM and PBM at the surface^{43,44} and throughout the troposphere,²¹ as well as greater scavenging efficiency of rain than snow.^{45,46}

Regional differences in Hg wet deposition have also been studied previously,^{8,10,25,47,48} but our results provide some new insights. The interior western United States has lower total Hg wet deposition than the eastern United States or West Coast because of the small amounts of precipitation.¹⁰ After controlling for the precipitation depth and storm type, however, we show that the Mountain West and Great Plains have the highest Hg wet deposition $(2.0 \pm 0.3 \text{ and } 1.3 \pm 0.14 \text{ times})$ higher than the Southeast, respectively; Table 2). High volumeweighted Hg concentration in precipitation has previously been observed throughout the Mountain West,¹⁰ but our results, which control for precipitation depth, show that the deposition is high even after accounting for dilution. Past work has found that the free troposphere is an important source of surface GOM and PBM^{23,49} in the western United States, and within that region, wet deposition increases with altitude.⁵⁰ Our results are consistent with the free troposphere as an important source of Hg wet deposition throughout the Mountain West. The same process may also enhance Hg wet deposition, to a lesser extent, at the intermediate altitudes of the United States Great Plains.

The most unique aspect of this work is that we have characterized Hg wet deposition in multiple storm types. Differences between storms remain statistically significant after we control for precipitation depth, season, and region, so we believe they represent the influence of storm dynamics and precipitation formation on wet scavenging. The convective storms have higher deposition than nonconvective storms, which has been previously seen,²⁹ because convective storms can scavenge Hg(II) from the upper and lower troposphere,² while nonconvective storms scavenge only from near the surface. Convection is not all the same, however. Deposition from supercell storms is about 1.5 ± 0.25 times greater (= 2.5/1.7, Table 2) than that from disorganized thunderstorms or QLCS, although the small number of supercell storms makes it difficult to draw firm conclusions. Deposition from disorganized thunderstorms and QLCS is an additional 1.6 \pm 0.2 times greater than that from light rain, after control for other factors (Table 2). This pattern is consistent with organized thunderstorms having greater inflow and entrainment that resupplies Hg(II) to precipitating regions. Extratropical and tropical cyclones have much greater air inflow than thunderstorms⁵¹ but lower Hg deposition, after control for other factors. This behavior may be caused by Hg(II)-depleted outflow air recirculating through the precipitating regions of these large, long-lived cyclones. Air recirculation is greater in land-falling tropical cyclones than extratropical cyclones, which is consistent with tropical cyclones having the lowest Hg deposition, after control for other factors, of any storm type investigated here.

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Notes

The authors declare no competing financial interest.

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