

Six-Year Trend (1990–1995) of Wet Mercury Deposition in the Upper Midwest, U.S.A.

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Total wet mercury deposition was monitored weekly at six Upper Midwest, U.S.A. sites for a period of six years, 1990–1995, to assess temporal and spatial patterns and contributions to surface waters. Annual wet mercury deposition averaged $7.4 \mu\text{g Hg/m}^2\cdot\text{yr}$ and showed significant variations between sites and increased trends averaging $0.60 \mu\text{g Hg/m}^2\cdot\text{yr}$ [8%/yr] over the period ($p < 0.0001$). Warm (rain) season wet mercury deposition was found to average 77% of total annual wet deposition. Warm (rain) and cold (snow) season trends showed increases of 0.31 [5.5%/yr] and $0.29 \mu\text{g Hg/m}^2\cdot\text{yr}$ [17%/yr], respectively ($p < 0.01$). Average annual precipitation depth showed a nonsignificant increase of 0.25 cm/yr [0.4%/yr] for the period. Differences in precipitation depth, mercury concentrations, and wet mercury deposition among sites were noted. Methylmercury wet deposition, measured in 36 weekly samples, averaged about 0.18 ng/L [1.5% of total mercury] in rain and strongly correlated with total mercury, major ions, and precipitation depth.

Introduction

Atmospheric mercury deposition is one of the primary sources of mercury contamination of the fisheries in the Upper Midwest (1–5) where fish consumption advisories have now been extended to all lakes in Minnesota and Michigan and many more in Wisconsin and Ontario. Mercury sources and impacts are of interest to other regional researchers as well (6–9), and, currently, eight Minnesota and Wisconsin sites are being monitored as part of the 37-site NADP Mercury Deposition Network (10). The importance of atmospheric mercury as a contamination source in that region was established when an examination of surface sediments revealed that wet mercury deposition could account for most of the sediment mercury loadings (4). Since then, studies of dated core stratigraphy have been used to estimate that preindustrial mercury in the atmosphere was about 25% of today's levels (11, 12), while another study (13) showed that mercury concentrations in forest soils increased toward more industrialized regions. Among topics of more recent interest are the importance of global vs local and regional mercury emission sources to atmospheric loadings, deposition, and mercury speciation.

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Near vs Distant Atmospheric Sources. One method of inferring the importance of near vs distant mercury source contributions is to study spatial gradients in deposition rates. One early observation of a gradient in mercury deposition rates was in Sweden where somewhat pristine northern sites were found to receive significantly less deposition than those in the south (14), nearer to industrial sources of northern Europe. A similar circumstance was observed for Michigan by Hoyer et al. (6). Another method of comparing source inventories was conducted by Engstrom and Swain (15) where mercury levels in sediments were compared between northern Minnesota and Alaska. In that study it was estimated that global sources had a slightly greater contribution to mercury deposition rates in northern Minnesota than regional sources.

In this work we report wet mercury deposition data, spanning six years, from six monitoring sites in and near Minnesota, and use it to investigate spatial and temporal patterns and make qualitative comparisons with predicted deposition results from a comprehensive regional model.

Mercury Speciation: Methyl-Hg(II). The importance of the methylated form of mercury in toxicity and as the active species in bioaccumulation mechanisms of the aquatic food chain is well established. However, the primary mechanisms and/or sources for the formation of methylmercury(II) in the total environment are not well understood (16), and few studies have been directed toward identifying the possible sources of alkyl mercury species in the atmosphere and in wet deposition. Dimethyl mercury has been reported in the waters of the equatorial Pacific below the thermocline ($>200 \text{ m}$) (17) and in the Alboran Sea and the adjacent Strait of Gibraltar (18). The measured profiles in seawater suggested flux to the atmosphere or decomposition in the surface waters. Terrestrial sources of dimethyl mercury from soils have been suggested, but few reports are available. Dimethyl mercury is assumed to be of short duration in the atmosphere with expected decomposition products that include monomethyl mercury cations (19). Brosset and Lord (20) have reported preliminary measurements of methylmercury in ambient Swedish air near 0.01 ng/m^3 . Other methylated compounds have been reported in the atmosphere including di- and trimethylarsenic and methanesulfonic acid originating from the Sea of Japan (21).

The identification of atmospheric processes and mechanisms that control and participate in the formation and deposition of total- and methylmercury is of intense interest (22). The factors governing wet deposition of total mercury and relationships to possible emission sources have been presented in previous papers (3–5). This report presents information describing methylmercury wet deposition and correlations with the major ions present in precipitation. Comparative information suggesting source relationships and mechanisms for total and methylmercury formation, deposition, and cycling are discussed. Methods for measuring total mercury in water by cold vapor atomic fluorescence and atomic absorption are evaluated, and wet deposition samplers are also compared.

Methods and Measurements

Extent of Study. From 1990 through 1995 precipitation was collected for monitoring total mercury deposition at nine sites located in Minnesota, North Dakota, and Michigan (Figure 1). Six of those sites have six years of continuous weekly sampling data which are the main focus of this paper. Also presented are results of methylmercury measurements

TABLE 1. Summary of Comparisons between UMD and Alternate Samplers at Three Sites

alt site (data source ^a)	dates	sample inventory ^b UMD/alt		no. of matching wks ^c	alt sample preservative ^d	vol wtd Hg concn (ng Hg/L)		av Hg deposition ^e ± SD (ng Hg/m ² -wk)		collector effic ^f av	
		single wk	no. Hg			UMD	alt	UMD	alt	UMD (%)	alt (%)
Duluth no. 2 (UMD)	3/26/96–6/11/96	10/10	0/0	10	HNO ₃ /K ₂ Cr ₂ O ₇	13.6	13.2	163 ± 103	158 ± 93	81	83
	12/27/94–4/4/95	14/14	7/7	7	HNO ₃ /HAuCl ₄	10.7	12.0	155 ± 82	173 ± 92	67	69
	6/14/94–12/27/94	27/27	5/5	22	none	12.5	6.9	247 ± 233	138** ± 109	100	98
	4/4/95–3/26/96	48/48	10/10	38	none	11.7	8.3	238 ± 240	167** ± 173	87	81
Marcell (NADP)	5/23/95–2/27/96	40/28	8/5	23	HCl/BrCl	8.5	10.1	233 ± 190	277 ± 301	93	90
Ely (NADP)	3/28/95–3/19/96	44/39	15/17	21	HCl/BrCl	9.5	8.6	193 ± 142	180 ± 168	83	96

^a Source for alternate data. ^b Single wk = total number of samples representing a single week; no. Hg = number of 1 wk samples for which a mercury concentration is not reported (volume too low or invalid sample [e.g. sampler efficiency < 25% with respect to rain gauge]). ^c A matching alternate vs UMD sample is defined as a 1-week collection for which both have a Hg value. ^d All UMD samples are preserved with HNO₃/K₂Cr₂O₇ except as stated. ^e Statistical significances of *t*-tests for deposition differences (square root transformed): ** = *p* < 0.01; no symbol = *p* > 0.10. ^f Calculated from collector area and regression slope of collected volume vs gauge depth.



FIGURE 1. Map of precipitation monitoring sites (named for the nearest city but usually located outside city limits by several kilometers) in the Upper Midwest. Latitudes and longitudes for each site are as follows: Bethel, MN – 45.4125, 93.2125; Cavalier, ND – 48.7825, 97.7542; Duluth, MN – 46.8403, 92.0094; Ely, MN – 47.9464, 91.4961; Finland, MN – 47.3875, 91.1958; International Falls, MN – 48.5917, 93.1875; Lamberton, MN – 44.2372, 95.3006; Marcell, MN – 47.5311, 93.4686; Minneapolis, MN – 44.9484, 93.3438; and Racoon, MI – 46.3742, 84.7414.

conducted for selected dates in 1993 from seven monitoring sites.

Sampling Protocol. Procedures for sampling were described previously (3, 5). A brief summary along with some additional information are presented here. Precipitation collection for mercury and major ion analyses was accomplished using MIC (Thornhill, Ontario, Canada; Teflon coated funnel; area = 0.21 m²) and Aerochem Metrics (Miami, FL; area = 0.070 m²) wet deposition samplers, respectively. Samples from both samplers were collected on the same weekly schedule along with precipitation depth readings using a Belfort recording gauge. Major ions and precipitation depth measurements were made by either the Minnesota Pollution Control Agency (MPCA) or the National Atmospheric Deposition Program (NADP, 23), depending on the monitoring site.

Mercury samples were collected in 2-L Teflon bottles from 1/3/90 to 9/15/92 and 20-L polyethylene containers from 9/15/92 to 1/2/96 that were each initially charged with 12 mL of preservative consisting of HNO₃ (25%)/K₂Cr₂O₇ (2.5%) and 40 mL of distilled water to reduce mercury sorption from air. For the Duluth site, however, the 2-L bottles were used in conjunction with a larger container (to collect overflows) for an extra year in order to assess implications of the protocol change (5). Both types of sample containers were stored in plastic bags for clean handling and shipping.

TABLE 2. Precipitation Collector Efficiencies for Seven Monitoring Sites^a

monitoring site	all dates (%)		warm season (%)		cold season (%)	
	effic	SE	effic	SE	effic	SE
Duluth	92.4	0.9	92.1	1.1	70.8	1.5
Ely	88.6	1.3	90.4	1.5	57.3	2.8
Int'l Falls	92.7	0.9	94.4	1.5	89.6	3.0
Lamberton	89.6	0.7	92.7	1.0	63.8	2.7
Cavalier	87.5	1.5	91.7	1.1	15.0	1.1
Bethel	95.5	0.9	96.7	1.1	48.3	3.2
Finland	87.2	0.9	91.3	1.1	73.7	2.7
av	90.5	1.2	92.7	0.8	59.8	8.9

^a Computed from volume vs depth slopes for collection dates 1/93 to 12/95.

The MIC sampler components (funnel and drain tube) were cleaned every 3 months using distilled water, sponges, and cotton swabs. After cleaning, distilled water was run through the system and collected for analyses. All rinse-water mercury analyses were less than the detection limit (1–2 ng/L).

Sampling Protocol Tests. Several tests were conducted at the Duluth site to assess influences of sampling protocol on observed mercury concentrations in precipitation.

Background Blanks. Because ambient mercury can be absorbed by the mercury preservative even during non-precipitation conditions, a second “background blank” container was placed within the MIC sampler along with the actual sampling container at the Duluth site in order to quantify this phenomenon. The two 20-L containers were equal in all respects except that the tube entering the top of the background blank was not connected to the MIC funnel. Results of 109 weeks of this testing yielded a background blank average of 2.0 ± 1.3 (SD) ng per sample. This corresponds to 92 ng per year and would correspond to an overestimate in annual deposition of about 0.4 μg/m² (assuming 46 weeks [site average] of measurable precipitation) if not corrected. No statistically significant seasonal difference was observed. Results for all sites are adjusted for the 2.0 ng/sample background blank.

An alternate method was used to determine the background blank for the 2-L Teflon bottle protocol. This was accomplished by analyzing nonevent samples for each monitoring site. The average blank across all sites was found to be 1.0 ng per week or one-half the background blank value found for the 20-L container. For comparison, the average

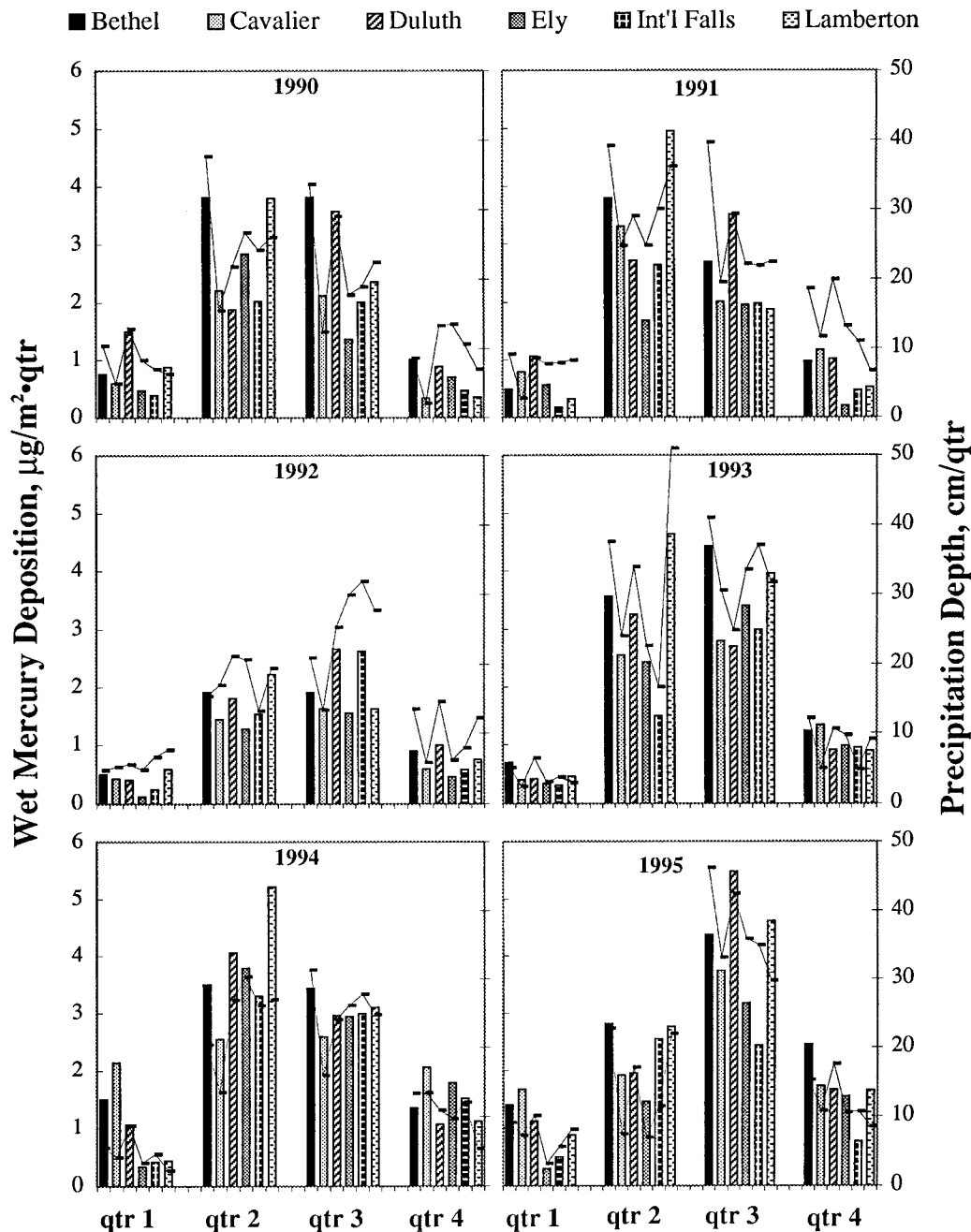


FIGURE 2. Quarterly wet mercury deposition (bars) and precipitation (lines) rates at each long-term monitoring site from 1990 to 1995 (qtr 1 = Jan–Mar; qtr 2 = Apr–Jun; qtr 3 = Jul–Sep; and qtr 4 = Oct–Dec). The estimated uncertainties in individual quarterly precipitation and deposition rates, based on measurement precision, are 1.8 ± 0.5 (sd) % and 4.8 ± 0.2 (sd) %, respectively (site means).

background value, as determined by averaging nonevents for the 20-L container, was 2.4 ng per week at the Duluth site. Results for 2-L bottle collections are adjusted for the site specific background blank.

Recovery from 20-L Sample Container. To quantify any residual mercury left in a sample container after analysis, a rinse test was devised for a subset of precipitation samples. After the sample was poured from the 20-L container, two successive rinses, using fresh preservative solution and vigorous shaking for several minutes, were also analyzed for mercury. The average mass of mercury collected in the first and second rinsates ($n = 49$ samples) were 0.7 ± 0.7 (SD) ng and 0.5 ± 0.5 (SD) ng, respectively. For comparison, a typical weekly collection is about 30 ng of total mercury for precipitation samples. This indicates either a small amount of carryover from the last event or contribution to the following event depending on various conditions. This may

slightly influence the accuracy of weekly results but should not significantly affect quarterly or annual results.

Alternate Sampling: Preserved vs Preserved Samples. At the Duluth site colocated samplers were also used to compare $\text{HNO}_3/\text{K}_2\text{Cr}_2\text{O}_7$ vs HNO_3 (25%)/ HAuCl_4 (9%) and replicated $\text{HNO}_3/\text{K}_2\text{Cr}_2\text{O}_7$ preserved samples. Results for 19 sample pairs shown in Table 1 indicate no significant difference for either comparison.

Alternate Sampling: Preserved vs Unpreserved Samples. At the Duluth site preserved and unpreserved samples were collected in two, colocated MIC samplers using 20-L containers. A summary of data for 67 matching weeks grouped by different time periods are shown in Table 1. Volume weighted concentrations computed for each grouping indicate that unpreserved samples were significantly different and had mercury levels that averaged from about 60–70% of the preserved samples. When more stringent data screening

TABLE 3. Annual Mercury Concentrations, Wet Mercury Depositions, and Precipitation Depths from 1990 to 1995 for Monitoring Sites in and Near Minnesota^a

site	1990			1991			1992			1993		
	av concn ^b	wet depos ^c	precip depth	av concn ^b	wet depos ^c	precip depth	av concn ^b	wet depos ^c	precip depth	av concn ^b	wet depos ^c	precip depth
Bethel	10.4	9.4	90.4	7.4	7.9	106.7	9.5	5.2	54.6	10.3	9.9	95.8
Cavalier	15.1	5.3	34.9	12.4	7.3	58.7	9.9	4.1	41.4	11.3	7.1	62.0
Duluth	10.2	7.8	77.0	9.6	8.3	86.8	8.8	5.9	66.8	9.6	7.3	75.8
Ely	8.1	5.4	66.3	7.3	4.4	68.0	5.5	3.4	61.6	10.4	7.1	68.9
Int'l Falls	7.8	4.9	60.8	7.5	5.3	70.9	8.4	5.0	59.6	9.2	5.7	62.3
Lamberton	12.0	7.4	61.8	10.4	7.7	73.8	7.7	5.2	67.0	10.4	9.9	95.2
six site av	10.6	6.7	65.2	9.1	6.8	77.5	8.3	4.8	58.5	10.2	7.9	76.7
Finland							8.7	7.2	83.1	9.2	7.9	86.0
Raco	7.9	8.6	92.5	7.3	8.5	85.4	7.5	8.9	83.8			

site	1994			1995			1990–1995 summary							
	av concn ^b	wet depos ^c	precip depth	av concn ^b	wet depos ^c	precip depth	concn ^d		depos		precip depth		slope (vs yr)	
							av	SD	av	SD	av	SD	depos	depth
Bethel	13.9	9.8	70.6	11.6	11.0	93.4	10.5	2.2	8.9	2.1	85.2	19.1	0.53	-1.50
Cavalier	19.5	9.3	47.1	14.9	9.0	58.5	13.8	3.4	7.0	2.1	50.4	11.0	0.80	2.97
Duluth	13.0	9.1	70.5	11.7	10.2	87.3	10.5	1.6	8.1	1.5	77.4	8.4	0.45	0.33
Ely	12.7	8.8	69.5	11.5	6.5	56.4	9.3	2.7	5.9	2.0	65.1	5.1	0.64	-1.08
Int'l Falls	11.7	8.2	71.0	10.0	6.2	62.6	9.1	1.6	5.9	1.3	64.5	5.1	0.47	0.29
Lamberton	16.5	9.9	59.4	14.5	9.9	68.3	11.9	3.2	8.3	1.9	70.9	12.9	0.68	0.50
six site av	14.6	9.2	64.7	12.4	8.8	71.1	10.9	1.8	7.4	1.3	68.9	12.0	0.60	0.25
Finland	11.2	8.7	78.0	8.8	8.7	99.0								
Minneapolis	13.1	9.7	74.6	14.7	10.5	71.4								

^a The average estimated uncertainties in annual wet mercury deposition and precipitation rates, based on measurement precision, are 2.5 ± 0.1 (SD) % and 0.5 ± 0.1 (SD) %, respectively. Units are as follows: concn – ng/L; depos – $\mu\text{g}/\text{m}^2$; depth – cm. ^b Volume weighted. ^c Depositions for events with missing mercury analyses (av across sites = 2% of total precipitation) were estimated as the depth (cm) multiplied by the average concentration (ng/L) for the current quarter/100. ^d Average of six yearly values.

criteria were invoked (i.e. collector volume agreement within 20%, precipitation depth > 0.25 cm, and exclusion of two possible overflow cases), mercury in 42 unpreserved samples averaged 66 ± 4 (SE) % that of preserved samples. Grouping data by seasons indicated no seasonal differences.

A comparison of mercury levels in container rinsates (see rinsate methods described under "Recovery from 20-L Sample Container" above) from 13 unpreserved and preserved sample pairs resulted in an average difference (unpreserved – preserved) of 0.3 ± 0.3 (SE) ng. This indicates that the mercury lost from an unpreserved sample cannot be accounted for by the rinsate recovery from container walls and suggests that either evasion from the water surface is important or that the preservative rinse was not effective at removing adsorbed mercury. Another study comparing HCl preserved to unpreserved bulk samples using Teflon bottles and vapor lock found no significant difference when a "whole bottle" digestion for the unpreserved sample was used (24).

Alternate Sampling: NADP. At two sites, Marcell and Ely, sampling by the NADP mercury monitoring program overlapped for a period of time with our efforts. NADP samples were collected using a modified Aerochem Metric sampler using a preservative of HCl/BrCl (25). Comparisons of paired data, matching collection weeks, showed no significant difference (Table 1). Results at Marcell indicate that NADP values are slightly higher and, at Ely, slightly lower than ours. Considering the differences in sampling equipment, collector efficiency, operational techniques, and analytical methodology, the estimations of wet mercury deposition at these two sites are in reasonable agreement.

Collector Efficiency. Collector efficiencies as determined by comparisons between MIC volumes and predicted volumes based on Belfort gauge values are given in Table 2. Note that the cold season efficiencies are highly variable and low compared to the warm season and overall efficiencies. This may be a result of the lack of sensor response and the

uneven nature of snowfall accumulation, especially in windy conditions or near objects disrupting wind currents. Another contributing factor could be the funnel heater used to melt collected snow. Evaporation induced by this process could be appreciable for the small events more common in the winter. For those samples (total volumes < 200 mL), the total mercury mass present in the sample was used to compute the weekly mercury deposition rate.

Because of the variable collection efficiencies, we chose to multiply measured Hg concentrations in the collection samples (total volume > 200 mL) by the rain gauge precipitation depth in order to calculate total mercury wet deposition. For periods when gauge depth data were not available, depth was estimated from MIC collected volumes and measured efficiency. For samples missed due to power outages or sampler malfunction (about 2% of samples per year, all sites), the gauge depth and volume weighted average mercury concentration for the same season were used to estimate missing deposition values.

Analyses Methods. Analyses for total mercury were performed on precipitation and surface water samples using EPA Method 245.1 (26, 27), employing cold vapor atomic absorption (CVAA). Method 1631 (28), employing atomic fluorescence (CVAf) techniques, was used for selected sample analyses comparisons. Methylmercury analyses (reported as Hg) were performed using CVAf methods described by Liang et al. (29) on a subset of samples collected from the second or third week of each month, June–October, 1993 (exceptions: the Duluth site had one May and two extra June samples). CVAf results for methylmercury analyses were verified by comparing measured species using both extraction and distillation procedures. The method of standard additions was used to quantify analyte concentrations. Total and methylmercury recoveries were 104 ± 8 (SD) % and 79 ± 8 (SD) %, respectively. Methyl impurities in the derivatizing reagent, sodium tetraethylborate, were measured as a

TABLE 4. Seasonal Wet Mercury Deposition and Precipitation Depths from 1990 to 1995 for Six Monitoring Sites in and Near Minnesota

yr	total deposition (ug/m ²)							total depth (cm)						
	Bethel	Cavalier	Duluth	Ely	Int'l Falls	Lamb	mean	Bethel	Cavalier	Duluth	Ely	Int'l Falls	Lamb	mean
Warm Season														
1990	7.63	4.32	5.45	4.20	4.03	6.15	5.30	71.4	27.9	50.9	44.5	43.2	48.4	47.7
1991	6.47	5.31	6.23	3.63	4.61	6.82	5.51	78.8	44.2	58.4	47.0	52.0	58.7	56.5
1992	3.82	3.07	4.47	2.83	4.16	3.84	3.70	36.3	30.3	46.6	50.6	45.1	47.2	42.7
1993	8.00	5.34	5.95	5.83	4.49	8.59	6.37	78.5	54.6	58.8	56.2	53.8	83.1	64.2
1994	6.92	5.14	7.02	6.74	6.29	8.32	6.74	51.8	29.6	51.0	56.4	53.8	51.8	49.1
1995	7.18	5.65	7.43	4.63	4.98	7.37	6.21	69.0	40.5	59.6	42.7	46.3	51.7	51.6
slope vs yr	0.093	0.239	0.393	0.413	0.290	0.438	0.31	-1.46	1.23	0.96	0.71	0.86	0.91	0.54
Cold Season														
1990	1.76	0.93	2.38	1.17	0.85	1.24	1.39	19.0	7.0	26.1	21.9	17.7	13.4	17.5
1991	1.46	1.97	2.08	0.77	0.64	0.84	1.29	27.8	14.4	28.5	21.0	18.9	15.1	21.0
1992	1.39	1.01	1.40	0.58	0.82	1.33	1.09	18.3	11.1	20.2	11.0	14.5	19.8	15.8
1993	1.93	1.74	1.33	1.32	1.25	1.35	1.49	17.3	7.4	17.0	12.8	8.6	12.1	12.5
1994	2.85	4.20	2.12	2.11	1.93	1.54	2.46	18.8	17.5	19.6	13.0	16.6	7.6	15.5
1995	3.85	3.40	2.78	1.83	1.25	2.53	2.60	24.4	18.0	27.7	13.7	16.3	16.6	19.4
slope vs yr	0.433	0.564	0.058	0.231	0.180	0.245	0.29	-0.04	1.73	-0.63	-1.80	-0.57	-0.41	-0.29

function of adding increasing amounts of reactive Hg(II), stepwise, from 0.5 to 4.0 ng Hg. An average value of the fraction of methyl to ethyl present was found to be 0.15 ± 0.01 (SE) %. This value would make a negligible (<10%) contribution to the methylmercury analyte concentrations reported. The number of precipitation samples less than detection was 2–3% for CVAA (detection limit 1–2 ng Hg/L for total Hg) and none for CVAF (detection limit typically < 0.1 ng Hg/L for MeHg).

The method detection limit for CVAA methodology was computed using the procedure described in USEPA 40 CFR (30) and found to be 1.2 ng/L. For this work, some average measurement characteristics and standard errors were as follows: precision (average % difference between original and duplicate analysis) = 11% (493 samples); standard addition recovery = 100.2 ± 0.7 (SE) %, (327 samples); and certified standard recovery = 99.6 ± 0.4 (SE) % (413 samples), relative to NBS No. 1641b certified water (diluted to 30 ng/L).

As part of this study a comparison was made between measurements derived from CVAF (EPA Method 1631) and CVAA (EPA Method 245.1) on split precipitation and surface water samples sent to three other laboratories. These methods have never before been compared at concentrations less than 100 ng/L. Although EPA Method 245.1 states a detection limit of 200 ng/L, it was shown by Glass et al. (2) that a method detection limit of $\approx 1-2$ ng/L could be achieved with minor modifications and clean techniques, thus making such a comparison possible. Combined results of 140 samples from all laboratories indicated a slope (CVAA vs CVAF) slightly greater than 1 [1.07 ± 0.04 (SE)] and a near-zero intercept, 0.7 ± 0.4 (SE).

We also participated in an interlaboratory comparison test (organized by Bloom and others, (31)) of water sample analyses using CVAA, EPA methodology, and clean techniques. The overall mean value for the intercomparison sample for the 23 participating laboratories was 1.3 ± 0.4 (sd) ng/L and compared well with a reference laboratory which obtained a value of 1.27 ± 0.14 (sd) ng/L. The value we reported for the study was 1.3 ± 0.3 (sd) ng/L (based on nine measurements of which two were less than detection limit).

Statistical analyses were performed using Systat and Excel software and Apple Macintosh computers. To compute correlations some variables were transformed (log or square root) to satisfy normalcy requirements. The uncertainties in seasonal and annual deposition rates were calculated by propagation of errors in all underlying measurements. The

variances derived from measurements precision, background blanks, and precipitation depths for each weekly event were taken into account. As a result, the uncertainties in annual wet mercury deposition and precipitation rates were found to average 2.5 ± 0.1 (SD) % and 0.5 ± 0.1 (SD) %, respectively, across years and sites. The uncertainties for precipitation depths were estimated using a precision value of 0.05 cm depth uncertainty per week (23).

Results and Discussion

Measurement and Sampling Comparisons. Independent analytical methods for measuring environmentally occurring concentrations of mercury in the range from 1 to 35 ng/L in precipitation and surface waters are compared and found to be in reasonable agreement. Both the U.S. EPA official old (atomic absorption) and new (atomic fluorescence) methods for water can be used satisfactorily to measure total mercury for ambient surface and atmospheric waters with detection limits near (CVAA) or below (CVAF) 1 ng/L.

Precipitation sampling and subsequent analyses using two colocated samplers, independently operated, gave comparable results in estimating wet mercury deposition at three different monitoring sites.

Regional and Temporal Deposition Patterns. *Seasonal Patterns.* Seasonal variations in precipitation and mercury wet deposition rates are shown in Figure 2, where it is clearly seen that the warmer months (second and third quarters) are associated with the higher precipitation and mercury deposition rates. Greater precipitation depths occur for the warmer seasons, when the source of moisture originates more from southern areas (Gulf of Mexico) (32, 33). In the cold season, the dominant wind patterns are more westerly and north and bring colder drier air into the region. Significant differences in atmospheric washout phenomena also occur for the different seasons (33); warm rain is more efficient compared with cold snow events (34). This results in different "washable" atmospheric mercury lifetimes and thus transport ranges of ionic emissions are likely to be different for the seasons (35, 36), with higher air concentrations of vapor-phase mercury occurring in the winter as compared to the summer (37). A consistent seasonal pattern of higher precipitation and mercury deposition rates in the warm season, as compared with the cold season, is observed, year to year, over the six years of study (see Figure 2). For these reasons, trend and pattern analyses of mercury deposition by season is of interest in understanding and interpreting its environmental behavior.

TABLE 5. Summary of *t*-Test Comparisons of Wet Mercury Deposition among Monitoring Sites

data type	selected site	<i>p</i> -value for comparing selected site vs indicated site					
		Bethel	Cavalier	Duluth	Ely	Int'l Falls	Lamberton
annual	Ely	0.003	0.11	0.021		0.73	0.001
deposittn	Int'l Falls	0.011	0.091	0.009	0.73		0.009
annual	Ely	0.11	0.004	0.12		0.83	0.006
concn	Int'l Falls	0.013	0.006	0.010	0.83		0.024
warm season	Ely	0.009	0.74	0.026		0.78	0.001
deposittn	Int'l Falls	0.030	0.91	0.007	0.78		0.015
warm season	Ely	0.18	0.011	0.024		0.64	0.006
concn	Int'l Falls	0.11	0.011	0.002	0.64		0.025
cold season	Ely	0.010	0.049	0.029		0.18	0.43
deposittn	Int'l Falls	0.017	0.042	0.025	0.18		0.18
cold season	Ely	0.060	0.002	0.83		0.50	0.009
concn	Int'l Falls	0.14	0.001	0.69	0.50		0.12

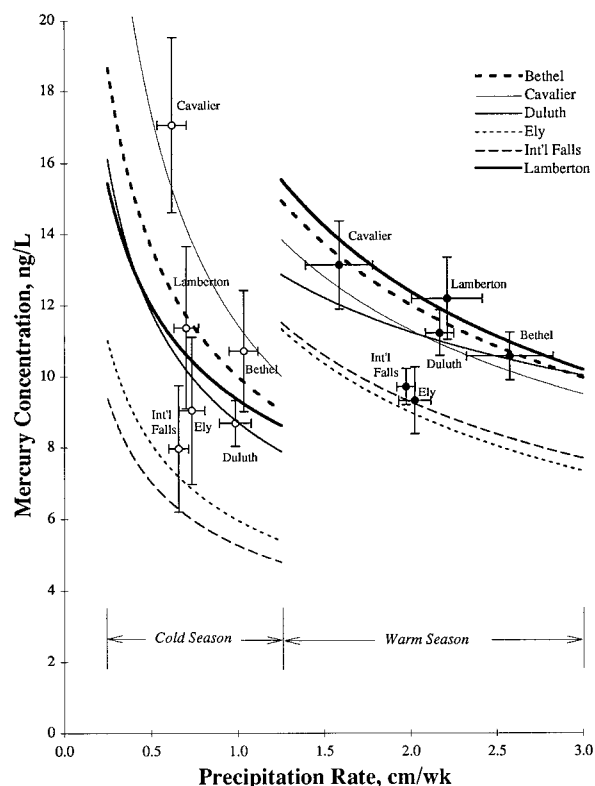


FIGURE 3. Each point represents the average of six concentrations and precipitation rates that were derived from seasonal (warm; cold) averages (volume weighted for concentration) computed for each year. Bars represent standard errors. Lines show individual site power curve regressions for weekly measured precipitation mercury concentrations (*C*) vs weekly precipitation depth rates (*d*). Example regression equations for warm and cold seasons at Bethel are as follows: $C = 16.6 \cdot d^{-0.464}$, $r^2 = 0.47$ ($n = 137$), and $C = 10.0 \cdot d^{-0.451}$, $r^2 = 0.30$ ($n = 95$), respectively.

Wet Deposition Trends. Average values of mercury concentration (volume weighted), mercury deposition, and precipitation depth, for the six long-term monitoring sites from 1990 to 1995, are listed for each year in Table 3. Also presented in Table 3 are summary statistics across years which include the computed (linear regression) rates of change of both deposition and depth vs time.

Considering the annual six-year trends, deposition vs year regressions yielded positive slopes for each site. Although the individual slopes were not statistically significant, the average slope across sites (representing greater statistical power) yielded a highly significant ($p = 0.0001$) nonzero result

of 0.60 ± 0.056 (SE) $\mu\text{g Hg}/\text{m}^2 \cdot \text{yr}$ [8.1 ± 0.76 (se) %/yr]. The corresponding set of regressions of precipitation depth vs year yielded a nonsignificant average annual increase of 0.25 ± 0.64 (SE) cm/yr [0.36 ± 0.93 (SE) %/yr] in the amount of precipitation ($p = 0.71$).

A similar treatment of trend analyses for seasonal data, presented in Table 4, indicates that wet deposition for both warm and cold seasons showed statistically significant increases for the six-year period. Average increases in wet mercury deposition were $0.31 \mu\text{g Hg}/\text{m}^2 \cdot \text{yr}$ [5.5 ± 0.95 (SE) %/yr] ($p = 0.002$) and $0.29 \mu\text{g Hg}/\text{m}^2 \cdot \text{yr}$ [17 ± 4.3 (SE) %/yr] ($p = 0.01$) for warm and cold seasons, respectively. Seasonal precipitation showed nonsignificant changes of 0.54 ± 0.41 (SE) cm/yr [1.0 ± 0.78 (SE) %/yr] ($p = 0.24$) and -0.29 ± 0.47 (SE) cm/yr [-1.7 ± 2.8 (SE) %/yr] ($p = 0.57$) for warm and cold seasons, respectively.

In comparison, increases in atmospheric mercury (1.46%/yr) for the Northern Hemisphere were reported (38) for the time period 1977–1990, and coal consumption increased by 2%/yr in the Upper Midwest over the period 1990–1995 (39). Earlier declines in lake sediment deposition were indicated for the 1980s vs 1970s for measurements in sediment cores from eight of 12 Minnesota lakes, while increases were seen in the surface sediments from the other four lakes (15).

The lowest values of mercury deposition occurred in the warm season for all sites in 1992 and corresponds to the lowest precipitation depth values for the period. The highest values of mercury deposition occurred in 1994 and did not correspond to the highest precipitation depth.

Regional Patterns. The data presented in Tables 3 and 4 may be used to examine regional patterns of wet mercury deposition. Table 3 shows that the lowest average (six-year) annual values of concentration and deposition occurred for sites at Ely and International Falls. This was also the case for seasonal concentrations (Figure 3) with the exception of Ely having slightly higher concentrations than Duluth for the cold season. Statistical significances of deposition and concentration comparisons between Ely and International Falls vs other sites are given in Table 5. These differences were significant ($p < 0.05$) for most annual and seasonal comparisons showing a strong north–south gradient. The cold season comparisons showed the least number of significant differences as can be seen by the larger standard error bars in Figure 3.

Comparisons with Predicted Wet Deposition. The north–south differences in observations may be a consequence of the southern monitoring sites being closer to mercury emission sources than those in the north, and where predicted wet deposition is higher for Duluth and Bethel vs Ely and International Falls sites, see Figure 4 ((40), R. Bullock, NOAA, personal communication). The predicted deposition result

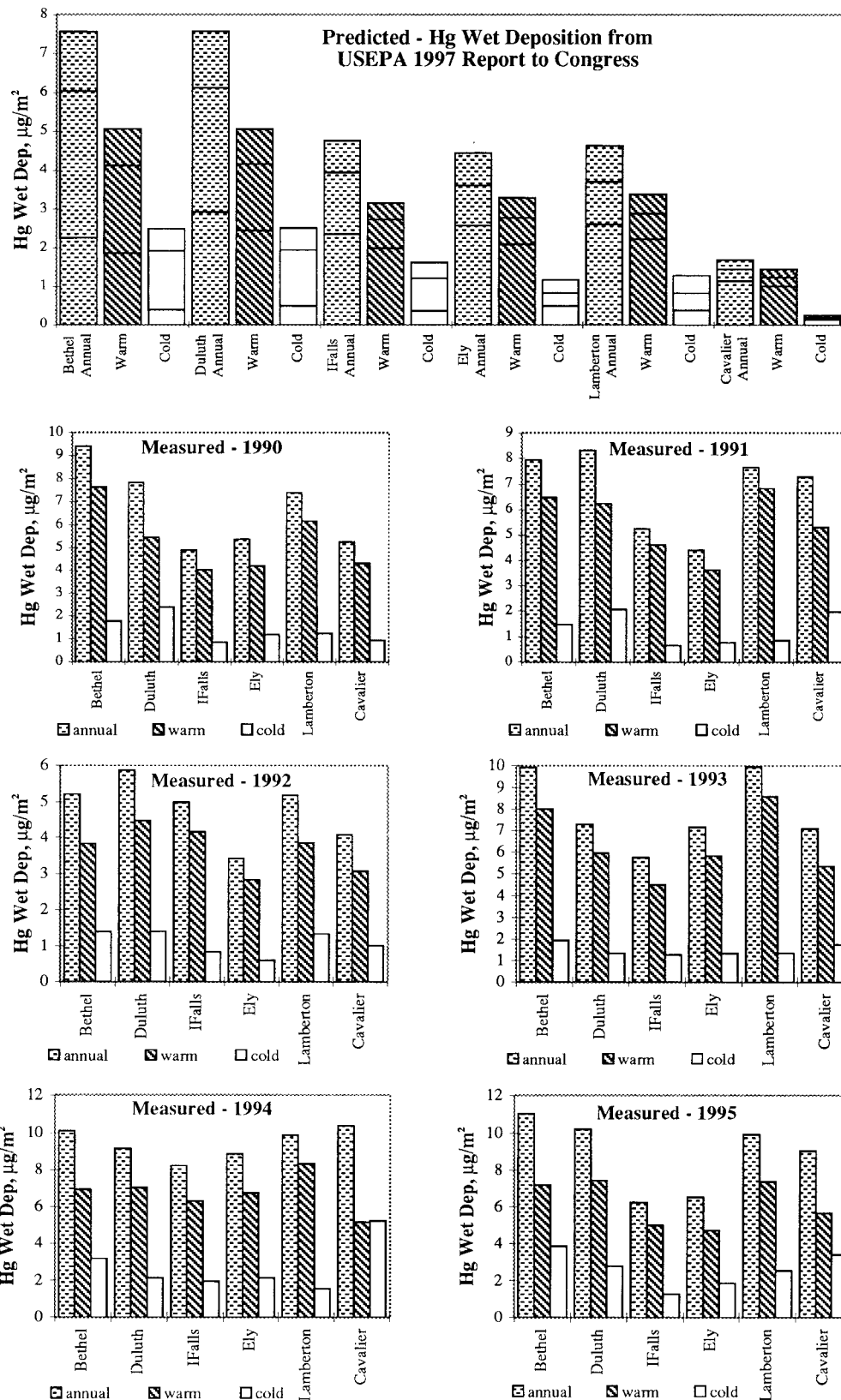


FIGURE 4. Predicted patterns of wet mercury deposition for annual, warm, and cold seasons for six precipitation monitoring sites (upper panel) vs measured patterns of wet deposition for annual, warm, and cold seasons for the same sites, 1990–1995 (lower panels). Predicted wet deposition bars are each composed of three sections representing predicted contributions from wet deposition of Hg(0), lower; Hg(II), middle; and Hg(particulate), top, respectively, using a comprehensive regional model (40, R. Bullock, NOAA, personal communication).

from a comprehensive regional Lagrangian model used to analyze mercury emission, transport, and fate over the continental U.S. using 1989 meteorological data. The deposition rates predicted for the Lamberton and Cavalier sites

are lower than those observed, are most likely influenced by mercury inputs from soil-derived particulates (containing previously deposited mercury) in the air associated with a prairie setting and extensive agricultural activity, and indicate

TABLE 6. Descriptive Statistics of Methyl and Total Mercury and Major Ion Concentrations and Calculated Depositions for 36 Samples from Seven Sites for Selected Dates of 1993^a

parameter	mean	median	SD	min.	max.	no. of samples at det lim
Concentrations						
methylmercury (ng/L)	0.184	0.169	0.088	0.044	0.48	0
total mercury (ng/L)	14.3	12.5	6.9	4.3	28.9	0
Ca ²⁺ (mg/L)	0.194	0.130	0.217	0.020	1.04	7
Mg ²⁺ (mg/L)	0.082	0.030	0.211	0.003	1.27	9
K ⁺ (mg/L)	0.056	0.014	0.170	0.008	1.03	13
Na ⁺ (mg/L)	0.032	0.020	0.034	0.010	0.165	13
NH ₄ ⁺ (mg/L)	0.499	0.425	0.600	0.010	3.73	0
NO ₃ ⁻ (mg/L)	0.957	0.880	0.458	0.018	2.07	0
Cl ⁻ (mg/L)	0.052	0.050	0.038	0.008	0.150	7
SO ₄ ²⁻ (mg/L)	0.954	0.845	0.476	0.360	2.20	0
Depositions						
methylmercury (ng/m ²)	3.37	3.30	2.04	0.37	9.58	0
total mercury (ng/m ²)	269	186	190	40	754	0
Ca ²⁺ (mg/m ²)	2.97	1.99	3.02	0.193	10.24	7
Mg ²⁺ (mg/m ²)	0.881	0.574	0.975	0.087	4.19	9
K ⁺ (mg/m ²)	0.535	0.298	0.832	0.072	4.14	13
Na ⁺ (mg/m ²)	0.563	0.384	0.531	0.033	2.69	13
NH ₄ ⁺ (mg/m ²)	7.76	5.73	6.20	0.033	28.3	0
NO ₃ ⁻ (mg/m ²)	19.3	16.5	14.8	0.058	62.7	0
Cl ⁻ (mg/m ²)	0.903	0.692	0.848	0.048	4.07	7
SO ₄ ²⁻ (mg/m ²)	18.8	13.8	15.1	3.05	63.6	0
Others						
methyl to total Hg ratio	0.015	0.013	0.008	0.004	0.037	0
precip depth (cm)	2.19	1.78	1.56	0.31	6.78	0
conductivity (μS/cm)	9.40	7.20	5.31	3.4	29.9	0
pH	5.50	5.43	0.66	4.43	7.21	0

^a Collection dates of weekly samples for indicated sites: Bethel, MN: 6/15, 7/13, 8/10, 9/14, 10/26; Cavalier, ND: 6/15, 8/17, 9/14, 10/26; Duluth, MN: 5/11, 6/15, 6/22, 7/13, 8/17, 9/14, 10/26; Ely, MN: 6/15, 7/13, 8/17, 9/14, 10/26; Finland, MN: 6/15, 7/13, 8/10, 9/14, 10/26; International Falls, MN: 6/15, 7/13, 8/10, 9/14, 10/26; Lamberton, MN: 6/15, 7/13, 8/17, 9/14, 10/26.

a north-south gradient in five of the six years studied. Note also that the predicted deposition differences for warm and cold seasons generally follow the observed seasonal patterns at each site.

Methyl and Total Mercury and Major Ion Concentrations and Deposition. The values obtained for total and methylmercury (as Hg) and major ions in 1993 precipitation samples averaged across all sites and dates are shown in Table 6 along with calculated weekly wet deposition values. No significant differences were found among individual sites for total Hg, MeHg, and the methyl-to-total ratio. Methylmercury and total mercury concentrations were found to be 0.18 ± 0.09 (SD) ng/L and 14.3 ± 6.9 (SD) ng/L, respectively, for weekly samples of precipitation. Maxima in methylmercury wet deposition occurred during July, 1993, when total mercury wet deposition and temperature maxima occurred. Monthly averages across all sites from June to October were 0.15, 0.22, 0.20, 0.17, and 0.17 ng/L, respectively, for methylmercury and 0.015, 0.018, 0.015, 0.014, and 0.013, respectively, for the ratios of methylmercury to total mercury. These ratios showed no statistically significant differences among sampling dates and are comparable to an average ratio (0.013) found by St. Louis et al. (7) in northwestern Ontario, Canada.

Correlations Among Wet Deposition Components. Correlations among wet deposition (June-October) components, including methylmercury, were conducted on both a mass and concentration basis for 36 samples, are summarized in Table 7, and were reported on in earlier studies of total mercury and major ions (3, 5). The strongest concentration correlates with methylmercury are total mercury, precipitation depth, Cl⁻, conductivity, and SO₄²⁻. These correlations were positive with the exception of that with precipitation depth, which was negative indicating a component "dilution" effect. For deposition rate correlations, best correlates were

the same as those listed for the concentration correlations with the exception of NO₃⁻ which was not significant for concentrations.

The significant positive correlation between methyl and total mercury is consistent with the maxima observed for the monthly averages as described above and suggests that the mechanisms by which methylmercury is present in the atmosphere is related to a large environmental "pool" of total mercury which could be 1) co-emitted from terrestrial and aquatic sources, and/or 2) be formed in the atmosphere by free radical reactions such as: $Hg^0 + CH_4 + 2HO \cdot \rightarrow MeHgOH + H_2O$ (41-43).

The significant negative correlation between the methyl-to-total Hg ratio with total Hg provides further information. That is, as total Hg levels increase, methylmercury levels also increase, but at a lower rate. This behavior is consistent with emissions or evasion from a larger "pool" of volatile inorganic forms rather than organic forms, and has been attributed to dilution by anthropogenic inorganic mercury sources (44). Significant correlations between total mercury and major ions suggest a common source such as combustion emissions or deposition on soil derived particulate. While strong relationships of methyl and total mercury with sulfate, and chloride could also suggest that a combination of anions may be important in heterogeneous reaction process(es) operating on atmospheric gaseous Hg⁰ by reactive gaseous radicals and electron-seeking compounds (43, 45).

High correlations between total mercury and major ions suggest relationships such as a common source of origin (dust from soils: Ca²⁺ and Mg²⁺, Na⁺ and Cl⁻), heterogeneous neutralization reactions (acid-base, HSO₄⁻ + NH₃⁺: SO₄²⁻ and NH₄⁺) (46), and mercury formation/redox transfer reactions, see example given above (43, 45, 47). Studies of homogeneous gas reactions in Teflon containers have thus

TABLE 7. Summary of Pearson Correlation Coefficients between Mercury Concentration and Deposition and Other Components in Upper Midwest Precipitation Collected in 1993^a

variable	xform	n ^b	skewness	Pearson correlation ^c		
				MeHg	total Hg	ratio ^e
Concentration vs Concentration^d						
MeHg	sqr	36	0.23		0.55**	0.39*
total Hg	sqr	36	0.24	0.55**		-0.50**
Ca ²⁺	log	29	0.11		0.62**	-0.38
Mg ²⁺	log	27	0.24		0.42*	
K ⁺	log	23	1.35	0.36	0.46*	
Na ⁺	log	23	0.78		0.54**	-0.38
SO ₄ ²⁻	log	36	0.15	0.40*	0.63**	-0.32
NH ₄ ⁺	none	35 [†]	0.11		0.58**	-0.31
NO ₃ ⁻	none	36	0.64		0.45**	-0.28
Cl ⁻	log	29	-0.05	0.45*	0.51**	
depth	sqr	36	0.25	-0.52**	-0.46**	
pH	none	36	0.62		0.34*	
conductivity	sqr	35 [‡]	0.54	0.41*	0.60**	
longitude	none	36	1.06		0.30	
Deposition vs Deposition^d						
MeHg	sqr	36	-0.01	-	0.68**	0.30
total Hg	sqr	36	0.46	0.68**	-	-0.45**
Ca ²⁺	log	29	-0.39	0.47**	0.74**	
Mg ²⁺	log	27	-0.15		0.33	
K ⁺	log	23	0.69		0.44*	
Na ⁺	log	23	-0.44	0.40	0.69**	
SO ₄ ²⁻	log	36	0.016	0.70**	0.83**	
NH ₄ ⁺	sqr	36	0.49	0.46**	0.64**	
NO ₃ ⁻	sqr	36	0.26	0.63**	0.84**	-0.29
Cl ⁻	log	29	0.19	0.59**	0.71**	
depth	sqr	36	0.25	0.73**	0.80**	
pH	none	36	0.62	-0.40*		
conductivity	sqr	35 [‡]	0.54			

^a Stepwise multiple regression results (fwd, rev = method of variable addition, removal, respectively)—MeHg predictors: *concentration* total Hg, depth, and pH ($r^2 = 0.43$; fwd and rev); *deposition* depth removed: SO₄²⁻ ($r^2 = 0.49$; fwd); total Hg and pH ($r^2 = 0.53$; rev) and depth included: depth and SO₄²⁻ ($r^2 = 0.56$, fwd); pH, depth, and NH₄⁺ ($r^2 = 0.60$, rev). ^b Numbers less than 36 indicate data removed that were less than the detection limit with two exceptions: [†]one extreme measurement was removed and [‡]one sample failed qa criteria. ^c Correlation significances are indicated as follows: ** - $p < 0.01$; * - $p < 0.05$; and no symbol - $p < 0.10$. Correlations with $p \geq 0.10$ are left blank. ^d One set of values for ratio, depth, pH, and conductivity are used for computing correlations under both concentration vs concentration and deposition vs deposition headings. ^e Ratio = methyl Hg/total Hg.

far yielded negative results in identifying formation mechanisms of methylmercury in the atmosphere (48).

Additional studies are needed to identify sources of increasing atmospheric mercury and subsequent mechanisms for their reduction, especially if the recently established quality criterion limit of 1.3 ng/L mercury for Great Lakes and tributary water is to be achieved for the protection of aquatic resources and wildlife (49).

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