

Regional Patterns of Wet Mercury Deposition

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Most of the mercury contamination in lakes and streams of nonindustrialized regions of the United States and Canada is derived from atmospheric deposition. In order to determine the regional patterns of these inputs, seven mercury-in-precipitation monitoring sites were established in Minnesota, North Dakota, and Michigan. A 3-year study showed that the magnitude of mercury deposition was dominated by the quantity of precipitation. Regional variations of mercury concentrations in precipitation were mostly explained by precipitation rate with higher concentrations occurring in the summer. Statewide (Minnesota) annual mercury emission estimates exceeded depositions for 1990, 1991, and 1992 by a factor of approximately 2 and indicated long-range transport of mercury. Significant correlations were observed between concentrations of mercury and other ions in precipitation.

Introduction

Recent findings from mercury (Hg) research in Minnesota indicate that (a) the major source to Minnesota lakes is atmospheric deposition (1, 2); (b) significant sources to the atmosphere (and surface water) are fossil fuel combustion and incineration of municipal solid waste and sludge (3-5); and (c) sediment strata indicate that mercury flux to lakes has been increasing throughout this century (6, 7).

The 1988-1989 mercury-in-precipitation study by Glass *et al.* (2) involved three monitoring stations in northeastern Minnesota used to investigate areal depositional patterns, washout mechanisms, correlations with other ions, and storm back-trajectories. The results showed similar mercury depositions at each location and suggested that a wider network of stations was needed to characterize any regional variations such as the south-north gradient observed in Sweden (8). Mercury washout from precipitation was shown to remove only a small fraction of the total mercury in the air column for a given event (2, 9). Thus, long-range transport from mercury emission sources occurs. This may result in slowly varying gradients across the region, especially away from industrialized areas.

Storm back-trajectories of air parcels (2) over long distances (72-h; greater than 1500 km) were difficult to interpret because of incomplete knowledge on a storm's history of precipitation rates. This is important because of the relationship between mercury in rain concentrations and the amount of precipitation along the storm track that may have previously "washed" the air parcel.

For this study (1990-1992), the number of precipitation monitoring sites was expanded from three to seven in order to better study mercury deposition in terms of regional patterns. The larger number of stations was also useful for investigating seasonal dependencies and the presence

of deposition hot spots, while providing wide-area data useful for estimating a state-wide depositional average.

Study Region

Seven precipitation sampling stations (Figure 1) were located in rural settings (except the Duluth site which was at the residential edge of the city) near the following cities or towns: Bethel (Cedar Creek), MN; Cavalier, ND; Duluth, MN; Ely (Fernberg Road), MN; International Falls (Voyageurs National Park), MN; Lamberton, MN; and Raco, MI. These sites were selected to establish regional mercury deposition patterns on a statewide scale.

Each site (except Duluth) was chosen to be collocated with other precipitation sampling efforts for comparison purposes. The stations at Cavalier, Ely, Lamberton, and Raco are collocated with National Atmospheric Deposition Program (NADP) sites. Those collocated with Minnesota Pollution Control Agency (MPCA) sites are Bethel and International Falls. Data regarding calcium, magnesium, potassium, sodium, ammonium, nitrate, chloride, and sulfate ion concentrations as well as pH, electrical conductance, and precipitation depth were provided by the NADP and MPCA for the corresponding sites.

Sampling Methods

Sampling was accomplished using an automatic sensing collector (MIC Co., Thornhill, Ontario, Canada) with a double sensor head (40 cm²), movable roof, and a Teflon-lined funnel (0.212 m² collection area). Additional details are described by Glass *et al.* (2, 3). Collected precipitation passes out the bottom of the funnel through a Teflon fitting and tubing into a sample container which has 12 mL of an acid dichromate preservative (2.5% K₂Cr₂O₇ and 25% HNO₃) to minimize mercury losses from reduction and degassing (2, 8, 10) and 40 mL of distilled deionized water (DIW) to reduce Hg sorption from the air. Sorption was also minimized by covering the container with a loosely fitting polyethylene cover to reduce air circulation. The sampling vessel was contained in the enclosed base of the MIC sampler, which was heated during winter months to about 4 °C. Sample collection was performed, and meteorological observations were recorded weekly at each station on Tuesday mornings.

From January 1990 to September 1992 (July 1992 for the Duluth site) 2-L Teflon (Nalgene) bottles were used for sample collection. The large collection area of the MIC sampler caused these bottles to overflow during moderate to large precipitation events into a graduated bucket provided to catch and quantify the volume of these overflows. To avoid overflows, 20-L polyethylene sample containers were used when the bottle/overflow bucket system was discontinued at all sites except Duluth. At the Duluth site, the 2-L bottle was used for another year (July 1992-July 1993), but the overflows were collected in a 20-L sample container instead of an overflow bucket.

The purpose of this special protocol at Duluth during 1992-1993 was to characterize the differences between mercury concentrations observed in the 2-L bottle versus

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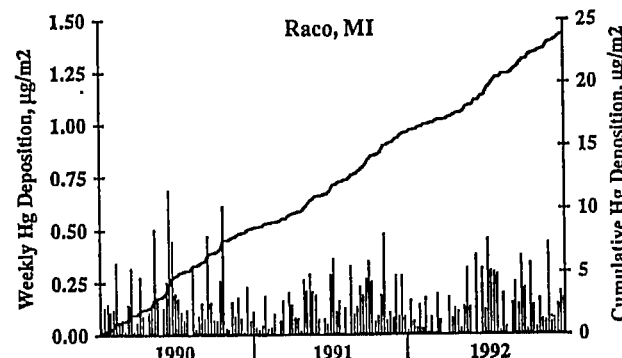
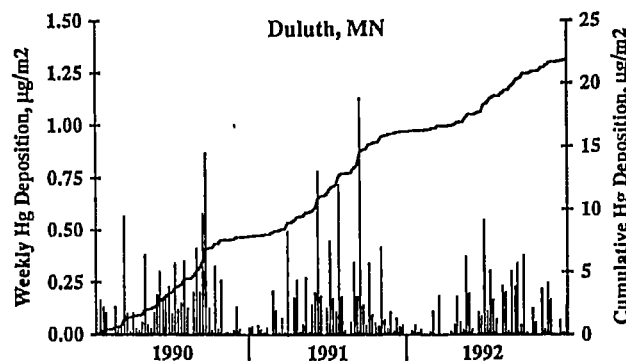
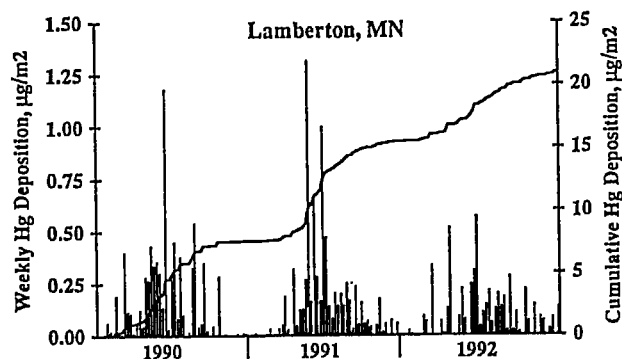
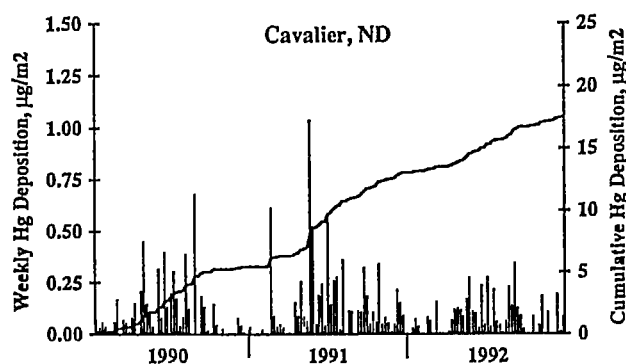
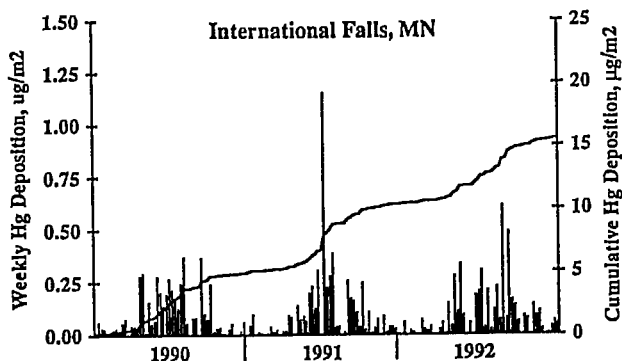
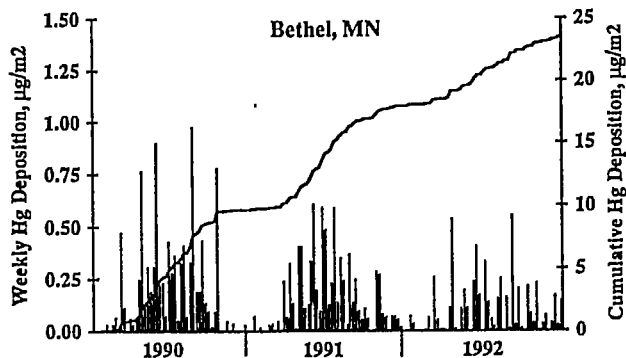
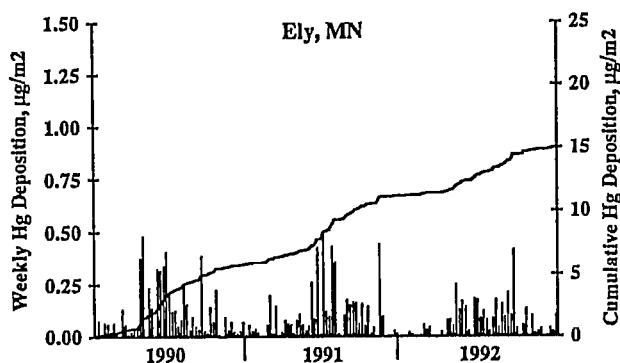


Figure 1. Map of precipitation monitoring sites in the upper Midwest and plots of weekly mercury wet depositions and their cumulative summations for 1990–1992.

those in the overflowed sample. This was needed to assess the accuracy of using the concentrations in the 2-L bottle to represent the entire event. Results of this sampling are discussed below in Data Analysis Methods.

Precipitation samples were also collected at Bethel, Cavalier, Ely, International Falls, Lambertson, and Racoon using Aerochem Metrics (Miami, FL) Model 301 automatic sensing precipitation collectors as part of the NADP and

Table 1. Analytical Characteristics of Mercury Measurements in Precipitation^a

no. of runs	flask averages (ng/L)		precision (ng/L)	ref recovery ^{b,c} (%)	spike recovery ^b (%)
	blank	det lim			
156	3	2	1 (328)	102 ± 1 (417)	103 ± 3 (172)

^a Values in parentheses are the number of samples or sample pairs associated with the entry. ^b Uncertainty expressed as standard error. ^c Value relative to NBS No. 1641b certified water (diluted to 30 ng/L).

Table 2. Summary of Some Collector Statistics and Mercury Analyses Less Than the Detection Limit

site	MIC collector efficiencies ^a (%)	sum of precip. depths when Hg data were not available ^b (% of total)			analyses less than detection limit (dl) ^c	
		1990	1991	1992	n < dl / n > dl	% of wet Hg deposition from cases < dl
Bethel	88	0.7	0.1	4.6	4/129	0.1
Cavalier	91	0.8	1.6	2.6	3/123	0.3
Duluth	93	0.0	0.0	0.0	4/141	0.5
Ely	88	0.1	16.4	4.9	8/135	1.3
Int'l Falls	93	7.7	8.6	1.3	11/141	0.6
Lamberton	90	0.2	0.7	0.4	7/125	1.1
Raco	83	2.2	0.5	6.7	2/143	0.8

^a Collected volume compared to volume predicted by precipitation gauge. ^b A result of MIC collector malfunctions or power failures yielding insufficient sample to represent the precipitation event. ^c Cumulative data for 1990–1992.

the MPCA networks. Samples were collected on the same weekly schedule as Hg samples by site operators, who measured volume, pH, and conductivity on site and sent the rest of the sample to the Illinois Water Survey–Central Analytical Laboratory at Champaign, IL (NADP sites), or to the MPCA (MPCA sites) for additional analyses of major ion concentrations. The precipitation gauge and major ion concentrations data were obtained from the NADP coordinator in Boulder, CO, and the Air Quality Division, MPCA. Further details of the sampling and analysis using an Aerochem Metrics sampler are given in Glass and Loucks (11). Gauge measurements did not begin at the Duluth site until August 1992.

Analytical Methods

Mercury measurement methodology for precipitation samples utilized cold vapor atomic absorption spectrometry (CVAAS) approved by U.S. EPA Method 245.1 (12) with modifications (3, 13). Analysis of Hg was performed on 150-mL aliquots. Unused sample portions were stored for possible future analyses. Table 1 summarizes the analytical characteristics of mercury measurements using CVAAS in this study.

Tests for Hg contamination were conducted by pouring distilled deionized water (DIW) over the entire MIC collection funnel surface and collecting the rinse water in a sample bottle containing a preservative solution. Samples (N = 26) collected in this fashion were analyzed and found to be less than the detection limit (2 ng of Hg/L).

Data Analysis Methods

Because MIC sample collector efficiencies were approximately 90% (Table 2), the mercury deposition for each precipitation event was computed based on the

Table 3. Summary of Some Low and High Sample Volume Statistics for Each Monitoring Site

site	Hg deposition due to events <200 mL sample volume (%)			collections without overflows ^a (% of total)
	1990	1991	1992	
Bethel	0.8	0.6	6.9	55
Cavalier	12.0	9.8	9.5	70
Duluth	4.7	1.7	2.3	53
Ely	4.0	1.8	1.9	63
Int'l Falls	1.4	2.0	1.2	64
Lamberton	3.2	2.2	1.1	65
Raco	1.9	2.4	0.8	54

^a Applicable periods with possible bottle overflows: Duluth, 1/90–5/92; other sites, 1/90–9/92.

product of the measured mercury concentration and the precipitation gauge depth. For Duluth, the gauge value was estimated from the collected sample volume and the collector efficiency for events before August 1992.

Special considerations that may affect deposition calculations are given to the following cases: (a) events when the MIC sampler malfunctioned; (b) analyses below detection limit; (c) low-volume events; and (d) high volume events. Summaries of data and statistics concerning these items are given in Tables 2 and 3 and are discussed below.

MIC Sampler Malfunctions. On occasion, the MIC sampler would fail to collect sufficient precipitation for mercury analyses as a result of mechanical or power failure. A summary of those instances is given in Table 2. For purposes of estimating the total annual wet deposition of mercury, the deposition for such events was estimated by the product of event depth and the yearly average mercury concentration for each site.

Analyses Less Than Detection Limit. The number of events with analyses less than detection limit was small (about 1%) and contributed little to the total annual wet deposition of mercury (Table 2). For analyses resulting in a measurement less than the detection limit, the actual estimated value of the mercury concentration was used rather than the method detection limit value.

Low-Volume Events. Low-volume events present two concerns that need to be addressed. The first, evaporation, can concentrate mercury to yield extreme overestimates in deposition if they are based on the product of concentration and gauge depth. For weeks of no precipitation, it was found that the average amount of evaporation of preservative solution ranged from 2 to 17 mL, of the original 52 mL, across all sites. We therefore chose to calculate mercury deposition as the total collected mercury mass divided by the collection area for all events less than 200 mL (200 mL ≈ 0.1 cm precipitation depth) in order to keep errors from evaporation typically less than 10%.

The second concern, mercury sorption, stems from the accumulation of mercury in the preservative solution from mercury present in ambient air. Previous studies of this phenomenon by Glass *et al.* (2) showed that mercury sorption was appreciable at high preservative concentrations but decreased significantly as the preservative was diluted with water.

To further investigate sorption effects for this study, we examined all samples where no measurable precipitation was collected. The average sorption for those samples was about 2 ng of Hg/wk (average of all sites) or effectively 0.009 μg of Hg/m²-wk if included in the deposition

Table 4. Summary of 1990–1992 Mercury in Precipitation Data for Seven Monitoring Sites

site	1990			1991			1992			long-term precip depth rate ^c (cm/yr)
	precip depth (cm)	wet Hg depos ^a ($\mu\text{g}/\text{m}^2$)	av Hg concn ^b (ng/L)	precip depth (cm)	wet Hg depos ^a ($\mu\text{g}/\text{m}^2$)	av Hg concn ^b (ng/L)	precip depth (cm)	wet Hg depos ^a ($\mu\text{g}/\text{m}^2$)	av Hg concn ^b (ng/L)	
Bethel	90.4	9.7	10.7	106.7	8.2	7.7	54.6	5.5	10.1	67.8
Cavalier	34.9	5.5	15.7	58.7	7.6	12.9	41.4	4.5	10.8	48.0
Duluth	74.5	7.8	10.5	84.3	8.3	9.9	65.5	5.7	8.7	66.0
Ely	66.2	5.8	8.8	68.0	5.4	7.9	61.6	3.8	6.2	68.7
Int'l Falls	60.8	4.9	8.1	70.9	5.4	7.6	59.6	5.2	8.8	59.2
Lamberton	61.8	7.6	12.3	73.8	7.9	10.7	67.0	5.4	8.1	63.8
Raco	94.5	8.5	9.0	83.3	7.5	9.0	83.8	7.9	9.4	76.2

^a For events where mercury data were unavailable, the deposition was estimated based on the yearly average mercury concentration and the precipitation depth. ^b Volume weighted. ^c Geraghty *et al.* (14).

calculations. According to previous results (2), this sorption decreases to approximately a 0.5-ng contribution for a 200-mL event. This is less than 8% of the 6.4-ng average collected mercury mass per 200-mL event (average of all events between 180 and 220 mL for all sites, $n = 22$). For increasingly larger events, the precipitation-derived mercury mass increases while sorption continues to decrease.

In deciding whether or not to correct low-volume events for mercury sorption, we first assess the contribution of low-volume events to total deposition, which are summarized in Table 3. We observed in most cases that the contribution was negligible with the highest values occurring for Cavalier, where the annual precipitation depths were the lowest. Considering that mercury sorption makes up only a fraction (i.e., $\approx 8\%$ @ 200-mL volume) of the low-volume deposition sum and that low-volume deposition in turn contributes less than 5% to the total in most cases, we concluded that an adjustment of the data for sorption was unnecessary.

High-Volume Events. Table 3 indicates that the number of events with sample bottle overflows was appreciable and that overflow effects on deposition calculations may be important. A test was conducted at the Duluth site (July 1992–July 1993) to determine if mercury concentration differences between the 2-L bottle and the overflow samples were significant. The results showed slightly higher concentrations in the 2-L bottle that depended on the amount of overflow volume. The reasons for this are probably a result of the decreasing mercury concentrations in precipitation with time for most events (2) and the configuration of sample collection. First, the higher concentrations occurring at the beginning of an event fill the 2-L bottle. Later, as more precipitation (lower in mercury concentration) enters near the top (upper half) of the bottle, it may overflow before completely mixing with the contents of the bottle, thus resulting in lower concentrations in the overflow.

The ratio of the mercury concentrations in the 2-L bottle to the average computed for the event ranged (approximately linear, $r = 0.62$) from 1.0 to 1.3 for overflows ranging from 0 to 10 L, respectively. Therefore, the average mercury concentration for each overflow event was calculated by adjusting the measured bottle concentrations by a factor linear with overflow volume. The consequence of this adjustment can be seen by comparing computed annual mercury depositions based on adjusted vs unadjusted bottle concentrations. This comparison showed that adjusted deposition values were about 15% lower than unadjusted values (average of all sites).

Results and Discussion

Mercury Concentrations and Depositions. The results of monitoring (weekly) mercury in precipitation at seven monitoring sites for 1990–1992 are shown in Figure 1 and Table 4. In general, these mercury concentrations and/or depositions are lower than those found previously in Minnesota (1, 3, 13), England (15), and the majority of Scandinavian sites that were highly variable (16) and approximately the same as those observed in Canada (17) and Italy (9). The apparent decrease in values observed for Minnesota may be due to a change in sampling procedures and/or to a number of actions taken by that state since 1989 to reduce or eliminate mercury emissions from products such as batteries, paints, fungicides, switches, and light bulbs. Additional time and study are needed to better evaluate this possible trend.

The highest mercury concentrations were observed at Cavalier and Lamberton in 1990 and 1991 and at Cavalier and Bethel in 1992. A combination of factors may explain these observations. Significant differences in annual precipitation depths exist between monitoring sites and mercury concentrations show an inverse dependence on precipitation depth rate (see Mercury Concentration vs Precipitation Depth). Another factor contributing to higher concentrations at these sites may be washout of higher amounts of soil-derived or other particulates (containing mercury) in the air associated with a prairie setting and/or agricultural activity (11). Proximity of emission sources and air parcel trajectories are also important (2) in considering differences among individual monitoring sites.

Mercury Concentration vs Precipitation Depth. Figure 2 illustrates the strong dependence of weekly mercury concentrations in rain on the amount of precipitation depth and is consistent with the results of Glass *et al.* (2). The data shown in Figure 2 consist of all sites and the combined sampling years (1990–1992) for rain events only (May 15–September 30, see Seasonal Effects). Events with collected volumes less than 0.1 L (≈ 0.05 cm depth) were excluded to reduce low-volume concentration errors (see Low-Volume Events).

The regression line ($n = 370$, slope = -0.32 , $r = -0.63$, $p < 0.001$) in Figure 2 suggests that the log of mercury varies approximately linearly with the square root of depth. Snow events gave similar but less correlated results ($n = 188$, $r = -0.31$, $p < 0.001$) and were, therefore, considered separately here. Other differences noted between snow and rain events are discussed under Seasonal Effects.

The correlations and slopes for individual years were

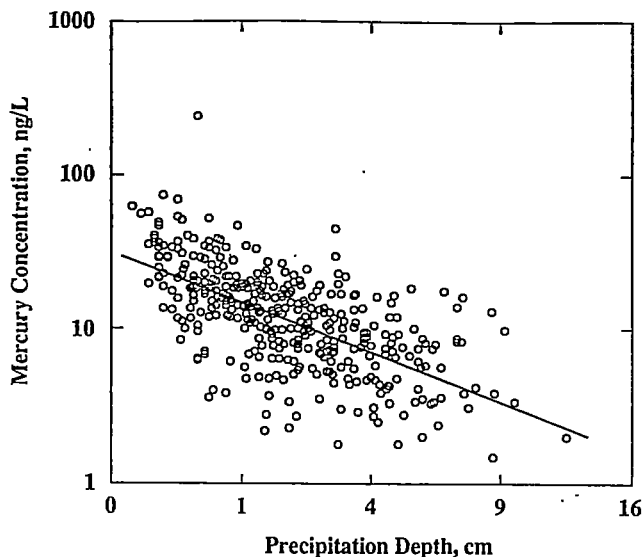


Figure 2. Weekly mercury concentrations (logarithmic scale) in precipitation as a function of precipitation depth (square root scale) showing an approximate linear relationship between the transformed axes. The data shown consists of all sites and the combined sampling years (1990–1992) for rain events only (May 15–September 30). Events with collected volumes less than 0.1 L (≈ 0.05 cm depth) were excluded to reduce low-volume concentration errors.

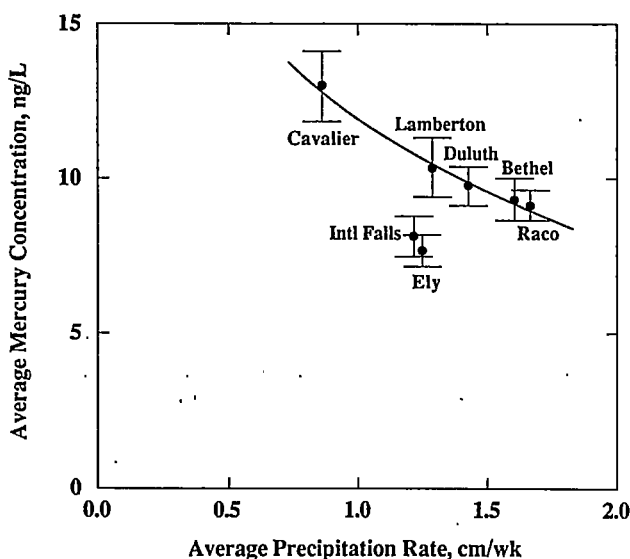


Figure 3. Average volume-weighted mercury concentrations in precipitation for combined years (1990–1992) as a function of the average precipitation rate for each site. Error bars represent the volume-weighted standard errors. The line represents a logarithmic least-squares fit applied to five of the seven sites.

similar to those for the combined years with slopes of -0.33 , -0.32 , and -0.31 and correlation coefficients of -0.68 ($p < 0.001$), -0.57 ($p < 0.001$), and -0.63 ($p < 0.001$) for 1990–1992, respectively. When individual sites were considered separately for the combined years, similar correlations and significances were observed but with more varied slopes.

Because of the strong relationship between mercury concentration and precipitation depth, the volume-weighted mercury concentration average was plotted against the average precipitation rate for each site for the combined years in Figure 3. It is interesting to note that for five of the seven sites a logarithmic regression line describes the data very well ($r = -0.99$). The figure suggests some important conclusions: (a) the highest concentrations

observed at Cavalier may result primarily from low precipitation depths rather than higher exposure to emission sources; (b) conversely, lower concentrations at Raco and Bethel may result from high precipitation depths diluting the overall concentration (but resulting in higher Hg depositions) and not lower emissions from contributing sources; and (c) the lower mercury concentrations at International Falls and Ely, as indicated by their lower positions relative to the regression line, may be associated with their remoteness from major emission source areas. Both sites are located in somewhat rural regions generally characterized by extensive forest cover and little urban development. However, unexplained high concentrations were recorded for Ely in an earlier study for 1989 (2). Possible regional mercury sources may come from activities such as iron ore mining and processing and pulp and paper production.

A paper products industry located in International Falls has recently increased emissions (18), including mercury, that have the potential to affect local mercury wet deposition. Sulfur-containing emissions may react with water-soluble atmospheric mercury forms (Hg^{2+}) to create water-insoluble forms resulting in a decreased washout (16), while periodic chlorine emissions may oxidize mercury (Hg^0) and increase local wet deposition. Evaluation of these hypotheses as well as others should be the subject of future site-specific work.

Because of the smaller concentrations at larger precipitation depths, it may not be obvious whether sites with more precipitation have higher mercury deposition. An observation of the data in Table 4, however, reveals that mercury depositions do increase with precipitation depth.

Seasonal Effects. In order to investigate seasonal effects, computations of the average volume-weighted mercury concentration for each site were made separately for winter and summer events. The definition of winter (primarily snow events) and summer (primarily rain events) time periods were December 1–March 15 and May 15–September 30, respectively. The data for the two intermediate periods (October 1–November 30 and March 16–May 14) were excluded to reduce the chance of mixing snow and rain events.

In comparing seasons, a difficulty arises where winter events have significantly lower precipitation depths than summer events. This is because mercury concentrations correlate inversely with precipitation depth as a result of washout mechanisms (2; Figure 2). Therefore, we chose subsets of events consisting of smaller precipitation depths (< 2 L of collected sample) for these comparisons so that precipitation rates for the two seasons were comparable. The low-volume events also comprise the most robust set of mercury concentration data because of overflows at larger volumes. The comparison subsets were further restricted by considering only collected volumes greater than 0.2 L to reduce sorption and evaporation effects (see Data Analysis Methods section).

These results, summarized in Table 5, show that the mercury concentrations of rain were higher than those of snow (average ratio 2.1:1) at all sites for the three years of record except for the 1990 Raco data. This suggests that more mercury is available for washout in the air during summer and/or that the washout of atmospheric mercury under rain conditions is more efficient than it is for snow. The former explanation would be consistent with higher amounts of soil-derived particulates occurring in the air

Table 5. Seasonal Mercury Concentrations (Volume Weighted, Low to Moderate Depth Events*) for 1990–1992 across All Sites

site	1990				1991				1992			
	rain		snow		rain		snow		rain		snow	
	Hg concn (ng/L)	n	Hg concn (ng/L)	n	Hg concn (ng/L)	n	Hg concn (ng/L)	n	Hg concn (ng/L)	n	Hg concn (ng/L)	n
Bethel	26	5	7	6	20	5	9	9	21	6	14	5
Cavalier	19	8	14	5	79	4	30	6	27	8	10	5
Duluth	19	7	16	6	16	3	8	6	14	6	10	5
Ely	16	8	6	9	9	8	8	9	7	10	7	6
Int'l Falls	20	7	6	9	9	5	4	6	15	7	6	9
Lamberton	26	8	12	3	30	7	6	5	17	7	13	6
Raco	14	9	15	9	19	7	10	7	19	4	12	7

* Pertains to subsets of events (numbers of which denoted by *n*) with collected volumes between 0.2 and 2 L.

Table 6. Pearson Correlation Coefficients between Mercury Concentrations and Indicated Parameters for Each Monitoring Site for 1990*

parameter	Bethel		Cavalier		Ely		Int'l Falls		Lamberton		Raco	
	correl.	n	correl.	n	correl.	n	correl.	n	correl.	n	correl.	n
depth	-0.46	16	-0.30	19	-0.51**	24	-0.52**	27	-0.42	15	-0.21	26
Ca ²⁺	0.67*	12	0.62**	17	0.66**	24	0.81**	17	0.87**	15	0.69**	28
Mg ²⁺	0.82**	13	0.68**	17	0.68**	24	0.77**	14	0.81**	15	0.73**	28
K ⁺	0.81*	7	0.20	17	0.56**	23	0.64**	17	0.80**	14	0.72**	27
Na ⁺	0.10	11	0.20	17	0.38	24	0.24	17	0.78**	15	0.36	27
NH ₄ ⁺	0.62*	13	-0.05	17	0.38	23	0.42	19	0.69**	15	0.61**	27
NO ₃ ⁻	0.08	14	0.09	17	0.40	24	0.45*	24	0.79**	15	0.68**	28
Cl ⁻	0.35	11	0.30	17	0.68**	24	0.56*	14	0.76**	15	0.59**	28
SO ₄ ²⁻	0.11	14	-0.04	17	0.36	24	0.62**	25	0.82**	15	0.55**	28
pH	0.82**	16	0.69**	17	0.47*	24	0.52**	26	0.39	15	0.26	28
cond	0.14	15	0.11	17	0.19	24	0.36	25	0.79**	15	0.53**	28

* Data subset with collected volumes greater than 0.2 L and less than 2 L. Significances are indicated as follows: (**) $p \leq 0.01$; (*) $p \leq 0.05$; (no designation) $p > 0.05$.

during summer (due to snow cover in the winter) and the correspondingly higher mercury concentrations that may be associated with them. The higher overall concentrations listed in Table 5 (compared to those in Table 4) are a result of using the smaller precipitation depth data subsets.

Relationships between Concentrations of Mercury and Major Ions. Table 6 summarizes weekly descriptive statistics and Pearson correlation coefficients for mercury concentrations and other precipitation parameters measured during 1990 (all seasons combined) at each individual NADP and MPCA site. The entries in this table were derived from the same nonoverflow data subset used in the seasonal comparisons but reflect the removal of values at the detection limit. Correlations were computed using transformed (log; except pH) variables to improve normality of the distributions.

Table 6 shows that the most consistent high correlates with mercury concentration were Mg²⁺ and Ca²⁺ concentrations. This indicates that contributions to mercury washout could be associated with soil-derived components as discussed above. Inverse correlations with precipitation depth were also observed for all sites with two being statistically significant at $p < 0.01$. These results are similar to 1988 and 1989 results for two sites in Minnesota (2).

Correlations between mercury and other precipitation components have also been calculated for Nordic sites by Iverfeldt (19) where high correlations were found with SO₄²⁻ and H⁺ ($r = 0.76$ and 0.69 , respectively) near industrial areas and low correlations ($r = 0.33$ and 0.24 , respectively) were observed for remote areas. The mercury vs SO₄²⁻ and pH correlations given in Table 6 show that

International Falls was the only site with highly significant correlations for both parameters. This may be explained by the influence of industrial air emissions from pulp and paper industries in an otherwise pristine setting.

Mercury Emission and Wet Deposition Inventories for Minnesota. A comparison between mercury emission and wet deposition inventories for Minnesota may contribute to understanding the phenomena of atmospheric mercury transport and deposition. White and Jackson (4) estimated 1990 mercury emissions in Minnesota at 4863 kg/yr for the sources they considered. Their calculated contributions (in kg/yr) were based on the following categories: fuel combustion (coal, oil, natural gas, and wood), 1677; incineration (municipal solid waste, medical waste, sewage sludge, and cremation), 1102; and noncombustion (petroleum refining, general industrial activity, landfills, dentistry, hospitals, labs, fluorescent lamps, paints, and fungicides), 2084. A similar estimate of 5620 kg/yr for Minnesota was also made by Cole *et al.* (5). Both inventories underestimate total emissions because they exclude a number of important sources such as lime and cement manufacturing kilns, iron foundries, explosives, pelletizing of taconite (iron ore), and non-anthropogenic sources.

Statewide mercury wet deposition inventories for 1990–1992 were determined by summing the depositions computed for each of nine climatological zones (20) within the state. These were based on the product of the average annual precipitation depth (20) and the estimated average annual mercury concentration for each zone. The average concentrations for each zone were estimated as follows: If a monitoring site(s) was located within a zone, then the

zone's concentration was defined as the annual average(s) for that site(s). If no site(s) was located within a zone, then the concentration was defined as the annual average(s) for sites in adjacent zones.

The results of these statewide annual wet mercury deposition budget calculations were 1600, 1700, and 1350 kg of mercury for 1990–1992, respectively. Corresponding values for precipitation depths were 64.1, 82.6, and 67.4 cm for the three years. These deposition values underestimate local contributions from emission point sources throughout the state and also do not reflect additional quantities from dry deposition. The difficulties surrounding dry mercury deposition measurements have resulted in a poor understanding of the phenomenon. However, it is known that the most significant contribution to dry deposition is the direct uptake from air into vegetation, which has been estimated to be generally less than half of the wet deposition magnitude (16).

If one estimates the mercury dry deposition as half of the wet deposition for each year, then the statewide total mercury deposition estimates for the three years of record are approximately half those of statewide emissions. Given the present data sets and dry deposition assumptions, this would indicate significant transport of mercury emissions from the state. It then also follows that a significant portion of the mercury deposition within Minnesota is most likely derived from emissions of other regions.

Mercury is mainly emitted from combustion sources as gaseous waste products of which some are in the form of water-soluble compounds (21). These compounds are subject to immediate precipitation washout (2) and may contribute significantly to total wet deposition within the region. However, incomplete data for mercury emissions and wet depositions as well as uncertainties in dry deposition suggest further study to refine these measurements and improve the present estimates.

Summary and Conclusions

Mercury in precipitation was measured in and near the state of Minnesota during 1990–1992 at seven monitoring sites located near the following cities and towns: Bethel, MN, Cavalier, ND; Duluth, MN; Ely, MN; International Falls, MN; Lamberton, MN; and Raco, MI. All sites, except for Duluth, were collocated with sites established by other monitoring programs (NADP and MPCA).

Average annual volume-weighted mercury concentration averages for the combined years (1990–1992) were found to be highest in the northwestern and southern extremes of the study region while lowest concentrations were observed at Ely and International Falls. Values ranged from 7.7 ng/L for Ely to 13.0 ng/L for Cavalier. However, much of the variation between sites may result from the inverse correlation between mercury concentration and precipitation depth rather than proximity to mercury emission sources.

Mercury wet depositions (μg of Hg/ $\text{m}^2\text{-yr}$) at each site were dependent on both concentrations and precipitation depths and found to be the following: Bethel, MN—9.7, 8.2, 5.5; Cavalier, ND—5.5, 7.6, 4.5; Duluth, MN—7.8, 8.3, 5.7; Ely, MN—5.8, 5.4, 3.8; International Falls, MN—4.9, 5.4, 5.2; Lamberton, MN—7.6, 7.9, 5.4; and Raco, MI—8.5, 7.5, 7.9, for 1990–1992, respectively.

Mercury concentrations averaged by season (volume weighted) showed concentrations for rain to be on the

average 2.1 times those for snow. This suggests that more mercury is available for washout in the air during summer and/or that the washout of atmospheric mercury under rain conditions is more efficient than it is for snow. The former explanation may be consistent with higher amounts of soil/vegetation-derived particulates occurring in the air for summer and the possibility of correspondingly higher mercury concentrations associated with them.

The mercury wet deposition budgets for Minnesota are estimated at 1600, 1700, and 1350 kg for 1990–1992, respectively. These values probably underestimate local contributions from sources in the Minneapolis–St. Paul metropolitan area and other major combustion sources and also do not reflect additional quantities from dry deposition, generally assumed to be less than half of the wet deposition in magnitude.

Comparisons between statewide estimates of total mercury depositions and emissions (4863 kg) from most of the anthropogenic sources in Minnesota indicate that emissions exceeded deposition by a factor of approximately 2. This would indicate significant transport of mercury emissions from the state and also that a significant portion of the mercury deposition within Minnesota is most likely derived from emissions of other regions.

Because mercury deposition from precipitation is dependent on meteorological patterns that are highly variable from year to year, it is difficult to characterize the phenomenon based on three years of observations. Further studies of mercury in precipitation with regard to geographic patterns, precipitation rates, seasonal variations, related ions, and emission and deposition inventories for sources not yet measured are needed in order to assess the long-term applicability of these findings and their relationships to the mercury contamination problem.

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