Mercury Deposition and Sources for the Upper Great Lakes Region

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Abstract. Mercury concentrations and depositions for northeastern Minnesota were measured in precipitation to investigate depositional trends, relationships with major cations and anions, and possible source emission regions. Results for 1987-1990 showed that environmentally significant amounts of Hg are present in precipitation and air and are subsequently deposited to remote lake watersheds. Volume-weighted concentrations of total Hg in precipitation averaged about 18 ng Hg L^{-1} with calculated annual depositions near 15 μg Hg m^{-2}. Mercury concentrations in precipitation are positively correlated with the major ions, conductivity, and pH, and are negatively correlated with precipitation volume. The best predictor equation from stepwise regression has an r^2 of 0.65 with Mg and chloride concentrations as predictor variables. From measurements of Hg in rain concentrations as a function of time within events, scavenging ratios for "washable" Hg were calculated to be 140 ± 80 (mass based at a 1 mm hr^{-1} precipitation rate). Up to about 10% of the total Hg in air is subject to washout by precipitation for a given event. Air parcel back-trajectories indicate that possible source regions within 72-hr travel time were located mostly to the south, southeast, and southwest, up to 2500 km distance away but local sources may also be important.

1. Introduction

Fish consumption advisories that restrict full utilization of the resource because of high levels of Hg in fish tissue are listed for many of the lakes in Minnesota, Wisconsin, Michigan, and Ontario. Levels as high as 5 ug Hg g^{-1} have been observed in large game fish from remote lakes where the primary Hg source was found to be of atmospheric origin (Sorensen *et al.*, 1990). The Minnesota Health Advisory cites that sensitive high risk individuals (children 6 yr of age and younger, pregnant women, and nursing mothers) should consume no more than one meal of fish per month with Hg concentrations of 0.16 to 0.66 μg Hg g^{-1}, and no consumption of fish measuring above 0.66 μg Hg g^{-1} (MDH, 1989; Shubat, 1990).

Fish from the lakes of northeastern Minnesota have not always been high in Hg. The rate of change (not compounded) of Hg concentrations in fish over time was found to be + 3% per year comparing museum samples from the 1930s, and + 5% per year comparing samples collected at 5- to 16-yr intervals during the 1970s and 1980s (Swain and Helwig, 1989). That study also compared increasing Hg accumulation in sediments from lakes in the same area, and found the rates to be consistent with the fish comparisons. The present fractions of 65 study lakes whose standard size (55 cm, 1.0 kg) northern pike (Sorensen *et al.*, 1990) exceeds Minnesota health advisories are 97, 11, and 2%, respectively, for 0.16 ug Hg g^{-1} (one meal / week), 0.66 ug Hg g^{-1} (one meal /

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month), and 1 ug Hg g^{-1} (FDA limit). These percentages would have been only 9, 0, and 0% 50 yr ago based on calculations using a compounded + 3% per year increase (approximate average of non-compounded 3 and 5% rates), and could reach 100, 80, and 45% in 30 yr, respectively, if the current rate of increase persists. The present levels of Hg in the environment of northeastern Minnesota have been recently reported by Glass *et al.* (1990) and Sorensen *et al.* (1990).

The objectives of this research were to determine the nature, magnitude, and seasonal variation of atmospheric Hg inputs and to document any relationships between Hg concentrations and that of major cations and anions present in precipitation. In addition, atmospheric transport from possible emission source regions, precipitation scavenging mechanisms, and geographic patterns and deposition rates had to be investigated.

2. Experimental

2.1. Precipitation Sampling and Measurement Methods

Three precipitation monitoring stations were set up at Duluth, Marcell, and Ely, MN. Sampling was accomplished using an automatic sensing collector (MIC Co., Thornhill, Ontario, Canada) with a double sensor head (40 cm^2), movable roof, and a teflon-lined funnel (0.212 m^2 collection area). Additional details are described by Glass *et al.*, 1990. Collected precipitation passes out the bottom of the funnel through a teflon fitting and tubing into a 1-L polyethylene (Nalgene) sample collection bottle containing 6 mL of an acid dichromate preservative (2.5% $K_2Cr_2O_7$ and 25% HNO_3) and 20 mL deionized water (DIW) to reduce Hg sorption from air. Sorption was also minimized by loosely covering the bottle to protect against air circulation. Sample collection bottles were changed weekly at each station and/or at shorter intervals corresponding to individual precipitation events and several times during heavy events at the Duluth station. At each site, bottle overflow was captured in a graduated bucket to allow the recording of precipitation volumes in addition to collection times and meteorological observations. Analysis of Hg was performed on 150-mL aliquots with a duplicate analysis for more than 40% of the samples.

Rain samples were also collected using four 600-mL (0.00739 m^2 collection area) Pyrex beakers (Glass *et al.*, 1986) that contained 3 mL of preservative and from 0 to 150 mLs of DIW to assess Hg sorption from air and Hg loss from collected precipitation. Inverted Pyrex funnels (with ends sealed) were placed 2 cm above two of the four beakers as a rain shelter while allowing for air circulation and dry Hg deposition and sorption.

Precipitation samples were also collected at Marcell and Ely using Aerochem Metrics (Miami, FL) Model 301 automatic sensing precipitation collectors as part of the National Atmospheric Deposition Program (NADP). 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 for additional analyses of major ion concentrations. The data for 1988-1989 were obtained from the NADP Coordinator in Boulder, CO. Further details of the sampling and analysis are given in Glass and Loucks (1986).

Mercury measurement methods utilized cold vapor atomic absorption spectrometry (CVAA) approved by USEPA (1983) with modifications for standardizing operating procedures and screening reagents for lowest levels of Hg content to reduce the blank value. The details for the analysis and quality assurance are published in Glass *et al.*, (1990) and Sorensen *et al.*, (1990). The detection limit for the precipitation sample analysis was about 2 ng Hg L^{-1}.

2.2. Air Sampling and Measurement Methods

Air sampling for Hg was accomplished by drawing air through 2 or 3 (most cases) parallel and/or series dosimeters (Arizona Inst., Jerome, AZ) and flowmeters using a diaphragm pump (Neptune Co., Dover, NJ) at flow rates typically near 1.0 L min^{-1}. The majority of sampling intervals were from 12 to 24 hours. Dosimeters were analyzed for Hg content using a gold film resistance analyzer (Model 431, Arizona Inst., Jerome, AZ).

The dosimeters have a specified capture efficiency of 100% for flow rates up to 0.05 L min^{-1}. However, atmospheric air sampling requires much larger flow rates (~1.0 L min^{-1}) for measurable 1 day accumulations. These higher flow rates yield efficiencies from 30 to 75% (depending on actual flow rate and age of dosimeter) and, therefore, introduce significant calibration concerns. Because it is only with great difficulty that these low (and therefore highly variable) efficiencies can be monitored (using parallel and series comparisons between dosimeters), the use of higher efficiency dosimeters is strongly recommended for environmental studies.

2.3. Air Parcel Back-Trajectory Calculations

Air parcel back-trajectories were calculated by the method outlined in Yap and Kurtz (1986). Representative horizontal winds in the atmospheric boundary layer are obtained from the surface and 850-mb geostrophic winds with modifications for surface frictional effects. Calculations are based on an objective analysis scheme using synoptic weather data from approximately 300 stations on a 30 x 30 grid system (grid length 127 km) for the surface level and using the height fields on an 11 x 11 grid system (grid length 381 km) for the 850-mb level. This trajectory model is coupled to a meteorological data acquisition system that collects and stores the input raw data supplied by Environment Canada from the North American network of weather stations via a satellite link to the Air Resources Branch, Ontario Ministry of the Environment. To obtain air parcel back-trajectories for a specific location, the 3-hr wind vectors (surface) and the 12-hr wind vectors (850-mb) were integrated with backward time-steps over 72 hr.

In this study, the air parcel trajectories were calculated for individual precipitation events where two or more subsamples were available from the Duluth (Lester Park) Monitoring Site during 1988 and 1989. Synoptic weather maps were also used to determine whether or not precipitation (and presumed Hg washout) had occurred previously (within the 72-hr period) along the calculated air trajectory in order to interpret the Hg concentrations and loadings observed at Duluth.

3. Results and Discussion

3.1. Precipitation Collection Methods

The difficulties of making quantitative measurements of Hg in precipitation in addition to within-event samplings were identified in a previous study (Glass *et al.*, 1986). Need was demonstrated for an automated sampler (such as the MIC type) with sensitive response to capture low levels of precipitation. Tests for Hg contamination were conducted by pouring DIW into the MIC collection funnel. Samples (N = 7) collected in this fashion were analyzed and found to contain less than the detection limit (~2 ng Hg L^{-1}).

To further examine our collection methods we ran a comparison study between beakers and the MIC sampler. Before comparisons could be made it was necessary to determine the proper amount of preservative and DIW to add to each beaker to avoid excessive dry absorption from gaseous Hg during the precipitation collection period.

Hg Sorption during Precipitation Collection. Because the beakers were exposed to wind-driven air circulation, there was concern over excessive scavenging of Hg from the air. Table I shows the results of Hg sorption for the sheltered beakers at the values of added DIW. The Table shows that the addition of 150 mL of DIW substantially reduces the mean sorption and its variability. Because Hg collected from rain in unsheltered beakers ranged from 0.5 to 8.6 ng, it was necessary to adopt the 150 mL DIW addition protocol. The sorption dependence on preservative concentration is further illustrated by a regression involving sheltered beakers yielding $\log_{10}$ (sorption rate) = 0.353 (± 0.098) - 0.719 (± 0.073) x $\log_{10} [(V_f + V_i) / 2]$ ($r^2 = 0.51$; N = 92) where sorption rate is in ng Hg day^{-1} and V_f (final volume after evaporative loss) and V_i (initial volume) are in mL.

Table I. Average Hg Mass Collected in Sheltered Beakers for Different Amounts of Added DIW.

Added DIW (mL)	Hg Mass (ng)	Number of Samples	Collection Period (days)
0	2.9 (± 1.9)	6	< 1
10	2.5 (± 2.3)	63	5.6
150	0.5 (± 0.3)	33	7.0

The MIC collection bottle, with 20 mL of DIW added to 6 mL of preservative, showed an average of 0.5 ± 0.03 ng (N = 16; average collection period = 6.3 days) of sorbed Hg for zero volume events. This is lower than beaker sorption (for the same preservative concentration) because of the relatively small air circulation exposure within the MIC bottle. For comparison, the average amount of Hg collected by the Duluth MIC during precipitation events (1987-1990) was 17 ± 50 ng (range: 0.2 to 746 ng).

Beaker vs MIC Comparisons. Table II summarizes the comparisons between the unsheltered beaker and MIC samples. For precipitation volumes we see that the regression of beaker (not evaporation corrected) vs MIC yields an intercept of -105 mL. This indicates a substantial evaporative loss for the beakers. After correcting for beaker evaporation using sheltered beaker data, we note an intercept of -26 mL. This could be the result of more evaporation occurring for unsheltered vs sheltered beakers from differences in sun shading and air circulation. The regression slope (0.0355) compares well with that expected from the collection area ratio (0.0349).

The regression of total Hg mass collected in the beaker vs the MIC sampler yields a slope of 0.0353 and is also close to the ratio of collection areas. A sorption adjustment to the unsheltered beaker mass by the amount collected in the sheltered beaker was not feasible because of the volume differences and the sorption vs preservative concentration dependence. It is also evident that the sorption vs volume equation stated above is inadequate for correction purposes because of high uncertainties.

Because the zero event sorption for the beaker and MIC samples is about the same (0.5 ng), we feel that the slope yields a reasonably accurate assessment that the MIC sampler is adequate for precipitation collection for Hg analysis.

Table II. Regression Equations (Y = A + B x X) Relating Volumes and Hg Masses (ng) for the Precipitation Collection Methods at the Duluth Station[a].

Y	X	A ±S.D.	B ±S.D.	r^2 N	Mean Y Median Y	Low Y High Y	Mean X Median X	Low X High X
Vol_{B}	Vol_{MIC}	-105	0.0376	0.94	43.7	-146	3950	-10
		±9	±0.0014	47	-9.7	539	1836	15300
Vol_{BC}	Vol_{MIC}	-26.2	0.0355	0.97	113.9	-56.1	3950	-10
		±5.3	±0.0009	47	32.1	591.2	1836	15300
Hg_{BP}	Hg_{MIC}	1.01	0.0353	0.93	3.0	0.6	56.5	0.2
		±0.17	±0.0019	27	1.6	8.8	26.6	237.6
Hg_{BUP}	Hg_{BP}	-0.31	0.693	0.79	2.08	0.10	3.45	0.20
		±0.38	±0.088	17	1.10	7.00	3.20	8.80
Hg_{BUP}	Hg_{MIC}	0.21	0.0245	0.75	2.34	0.20	86.8	6.1
		±0.42	±0.0036	16	1.25	7.00	66.3	238

[a] Abbreviations used are as follows:

Vol_{B} - final minus initial volumes in beaker (mL)
Vol_{MIC} - volume of precipitation collected using the MIC sampler (mL)
Vol_{BC} - volume of precipitation in beaker after correcting for evaporation (mL)
Hg_{BP} - mass of mercury collected using an open beaker with a preservative (ng)
Hg_{MIC} - mass of mercury collected using an MIC sampler (ng)
Hg_{BUP} - mass of mercury collected using an open beaker without a preservative (ng)

Storage Effects. In some cases samples from Marcell and Ely were stored for over a month before analysis; hence there was a need to determine storage effects on the Hg content. To do this we examined two types of samples: those for zero precipitation events (high preservative concentration) and those for moderate to high volume events (low preservative concentration).

There were 27 zero precipitation events with storages ranging from 0 to 64 days. A regression for these samples indicated an increase of 0.094 (± 0.011) ng Hg day^{-1} ($r^2 = 0.73$). This rate is in close agreement with the sorption rate of Hg during actual sample collection (0.5 ng) discussed above. To test the significance of these sorption rates, we computed the total mecury depositions (1988-1989) for each collection site with and without correcting for sorption (up to 200 mL events). The maximum difference across sites was 2%.

For precipitation events ranging from 400 to 12,000 mL of collected volume we analyzed 25 samples at two different times ranging from 50 to 290 days apart. Results showed that the samples lost Hg at about 0.098 (± 0.019) ng day^{-1} ($r^2 = 0.53$). We computed total Hg depositions (1988-1989) for each site both with and without correcting for this effect on storage (samples > 400 mL) and found that the maximum difference was again only 2%.

Given the small impact of storage effects, offsetting gains and losses, and the high uncertainties associated with the correction equations, we have presented all results as unadjusted for storage effects.

Precipitation samples were also collected for 4 months using the beakers without preservative to determine the "volatility" of Hg in rain. Seventeen pairs of samples showed a 31% loss compared to preserved samples based on the slope of the regression shown in Table II. The difference may not be all caused by volatilization, as Hg sorption onto the Pyrex beaker is a possibility.

MIC vs Gauge. For the Marcell and Ely stations (1988 and 1989) it was found that the collected MIC volumes were both 31% less than that expected based on NADP gauge data. We believe that this results from: 1) inefficiencies in MIC collection from aerodynamics and its effect on wind currents (Lynch *et al.*, 1990); 2) evaporative losses experienced by the overflow portion of the MIC collected sample; and 3) inefficient sensor triggering for low precipitation rate events (Lynch *et al.*, 1990).

Because the collection system was optimized for integrated Hg sampling and not an accurate precipitation volume measure, we chose to base our deposition calculations on the NADP gauge readings for these two sites.

For the Duluth site the nearest precipitation gauging station (operated by NOAA) is located about 15 km away at the Duluth International Airport. A comparison of the yearly totals between the MIC collected volumes and these gauge data indicated a 32% inefficiency for the MIC volumes, similar to that found for the other two sites. Although these results are consistent and suggest that the NOAA gauge data could be used for deposition calculations at Duluth, we felt that a simple adjustment of the MIC volumes would be more appropriate.

3.2. Mercury Wet Deposition

The results of monitoring precipitation and Hg analysis for 1988 and 1989 are shown in Figure 1 and summarized in Table III. The wet deposition values are weekly composites for Marcell and Ely, and calculated weekly averages for Duluth from individual event and sub-event collections. Continuous sampling was begun using MIC samplers in December 1987 in Duluth, January 1988 in Marcell, and February 1988 in Ely. Pyrex beakers were also used at the Duluth monitoring site from July 1987 through October 1988.

Table III. Annual Depositions and Volume Weighted Concentration Averages for Hg in Precipitation at the 3 Monitoring Stations for 1988 and 1989[a].

Site	Year	Deposition (ug m^{-2})[b]	Concentration (ng L^{-1})	Precipitation Depth (cm)[b]	Sampling Period (weeks)
Duluth	1988	19.9	22.6	88.5	52
Marcell	1988	15.7 (16.4)	17.7	88.8 (92.5)	48
Ely	1988	16.7 (17.1)	19.7	84.9 (86.8)	47
Duluth	1989	6.5	10.5	62.1	52
Marcell	1989	13.0 (13.5)	18.0	72.2 (75.2)	41
Ely	1989	41.9	81.4	51.4	52

[a] Based on adjusted MIC data for the Duluth site and NADP gauge data for Marcell and Ely.

[b] Full year estimates for incomplete Hg sampling years, shown in parentheses, are based on gauge data and average concentrations.

Table III shows a surprising degree of variability in annual depositions and average concentrations for both Duluth and Ely when comparing data from the 2 yrs. Of particular interest, though, are the anomalously high depositions occurring in the spring of 1989 at Ely (Figure 1) with 13 consecutive events averaging 200 ng Hg L^{-1} and no event < 100 ng Hg L^{-1}. For that season it is

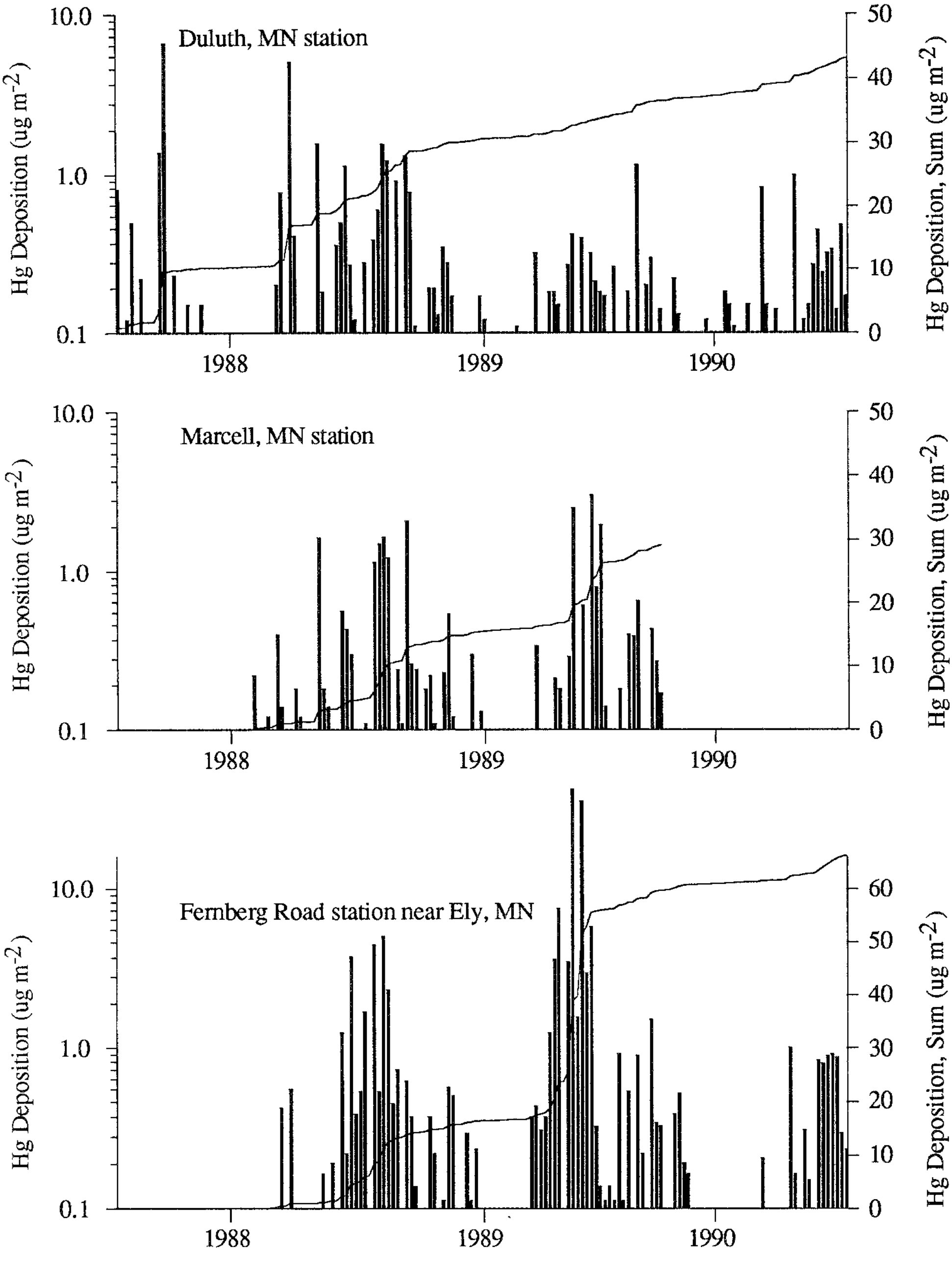

Figure 1. Mercury wet deposition (weekly totals) and deposition summation for precipitation monitoring sites in Minnesota at Duluth (near Lester River), Marcell, and Ely (Fernberg Road).

apparent that the Ely site received significantly more Hg deposition than Marcell and Duluth combined. Because the distances between all monitoring sites are relatively small (120 to 150 km), the pattern of increased wet deposition at Ely suggests the possibility of significant local source contributions rather than a more general pattern of elevated deposition at all sites from more distant sources of Hg emissions. This may also explain the lack of a corresponding increase in other ions (discussed below). Additional research on source identification and source-receptor relationships along with continued precipitation monitoring is needed to determine the cause of this anomaly (see Section 3.5).

For the purpose of expressing overall deposition and concentration averages for the study region across all three monitoring sites (1988 and 1989) we hesitate to include the 1989 Ely data until more is understood about the nature of those spring observations. Using the balance of the data we report an average annual deposition of 15 ug m^{-2} and an average concentration of 18 ng Hg L^{-1}.

3.3. Mercury-Major Ion Relationships

The correlations between Hg concentrations and major ion concentrations for two NADP monitoring sites at Marcell and Ely are given in Tables IV and V. For Ely, the 1989 spring data were again excluded. The major ion interrelationships have been discussed previously by Glass and Loucks (1986). The relationship of Hg to the ionic components of atmospheric washout is strongly indicated because of the significant positive correlations, ranging from 0.2 to 0.7 for all major ions and conductivity. The negative correlations (-0.3, -0.5) with event precipitation depth are expected for atmospheric washout. The differences in correlations when comparing Marcell and Ely may reflect both similarities in relationships for regional Hg inputs and differences in relationships caused by local contributing sources.

Table IV. Measured Hg Concentrations (ng L^{-1}) in Precipitation Compared with Values of Other Parameters[a]. Data are from the NADP Site at Marcell MN for 1988 and 1989.

Component	No. of Samp.	Mean	Std. Dev.	Median	Min.	Max.	Best Corr.[b]	Hg Conc. Corr.[b]
Ca	58	0.26	0.25	0.19	0.03	1.61	0.94 (Mg)	0.66
Mg	58	0.042	0.038	0.030	0.004	0.235	0.94 (Ca)	0.70
K	58	0.044	0.062	0.026	0.003	0.351	0.63 (Mg)	0.52
Na	58	0.10	0.14	0.048	0.012	0.76	0.75 (Cl)	0.61
NH$_4$[c]	47	0.38	0.28	0.30	0.03	1.26	0.69 (SO$_4$)	0.56
NO$_3$	58	1.29	0.88	1.08	0.03	4.83	0.77 (CndL)	0.45
Cl	58	0.092	0.060	0.075	0.030	0.340	0.75 (Na)	0.68
SO$_4$	58	1.14	0.81	0.99	0.17	5.29	0.73 (CndL)	0.62
pHL	56	5.13	0.51	4.98	4.29	6.31	0.46 (CndL)	0.20
CndL	56	10.7	5.7	9.6	4.0	38.1	0.77 (NO$_3$)	0.58
NADPg	69	23.0	29.6	4.4	0.8	151.1	-0.72 (Na)	-0.47
Hg Conc.	66	23	20	17	5	98	0.70 (Mg)	-

[a] All in mg L^{-1} except as follows: pHL- laboratory measured pH; CndL - laboratory measured conductivity, uS cm^{-1}; NADPg,- precipitation depth as measured by the NADP gauge, mm.
[b] Variable transformations used in correlations: logarithm - Ca, Mg, K, Na, NH$_4$, Cl, CndL, Hg Conc., and NADPg; square root - NO$_3$ and SO$_4$. [c] Eleven values at detection limit (0.02 mg L^{-1}) not included.

Stepwise regression analysis performed on the Marcell dataset showed that the best predictor equation, log([Hg]) (ppt) = 2.37 + 0.372 x log[Mg] (mg L^{-1}) + 0.55 x log[Cl] (mg L^{-1}), has an r^2

Table V. Measured Hg Concentrations (ng L^{-1}) in Precipitation Compared with Values of Other Parameters[a]. Data are from the NADP Site Near Ely MN for 1988 and 1989.

Component	No. of Samp.	Mean	Std. Dev.	Median	Min	Max	Best Corr.[b]	Hg Conc. Corr.[b]
Ca	60	0.23	0.32	0.12	0.01	2.22	0.94 (Mg)	0.49
Mg	60	0.034	0.046	0.018	0.003	0.287	0.94 (Ca)	0.54
K	60	0.019	0.031	0.010	0.003	0.208	0.52 (Mg)	0.25
Na	60	0.086	0.14	0.043	0.007	0.840	0.72 (Cl)	0.40
NH$_4$[c]	51	0.31	0.23	0.27	0.03	0.84	0.66 (SO$_4$)	0.20
NO$_3$	60	1.13	0.66	1.05	0.03	3.98	0.63 (Ca)	0.26
Cl	60	0.078	0.045	0.060	0.030	0.240	0.72 (Na)	0.36
SO$_4$	59	0.97	0.64	0.87	0.14	3.39	0.69 (Mg)	0.27
pHL	53	4.87	0.30	4.81	4.40	5.75	0.52 (Mg)	0.29
CndL	55	10.2	3.4	10.2	4.8	18.5	0.65 (SO$_4$)	0.03
NADPg	60	18.5	22.3	11.7	0.5	120.6	-0.70 (Na)	-0.30
Hg Conc.	59	25	22	17	3	123	0.54 (Mg)	-

[a] All in mg L^{-1} except as follows: pHL- laboratory measured pH; CndL, - laboratory measured conductivity, uS cm^{-1}; NADPg,- Precipitation depth as measured by the NADP gauge.
[b] Variable transformations used in correlations: logarithm - Ca, Mg, K, Na, NH$_4$, Cl, CndL, Hg Conc., and NADPg; square root - NO$_3$ and SO$_4$. [c] Eight values at detection limit (0.02 mg L^{-1}) not included.

of 0.65 (N = 52). Similar analysis on the Ely data set resulted in only one (Mg) significant predictor variable.

Wet deposition was found to be the most important deposition mechanism for atmospheric trace metal loadings measured by Chan *et al.*, (1986) for Fe, Al, Pb, Mn, Cu, Ni, V, Zn, and Cd. Annual wet loadings ranged from 100 μg Cd m^{-2} to 47,500 μg Fe m^{-2} at Lac La Croix, Ontario in 1982. The values for these metals are all significantly higher than our measured Hg loadings.

3.4. Mercury Washout

During the period from January 1988 to October 1989, 24 precipitation events were sampled with two to five samples taken within each event. The results of these samplings and analyses for Hg concentrations, mass, and volumes are given in Table VI. Subsequent samplings within each event typically showed a marked decrease in Hg concentration compared to the first sampling. Only 4 cases exhibited a significant increase for the second sampling and 8 cases showed an increase for the last sampling. These observations are in general agreement with other studies regarding sequential sampling of Hg (Ferrara *et al.*, 1986) and major ions (dePena *et al.*, 1984) in precipitation.

Two events are shown in Figures 2a and 2b that clearly exhibit a decrease of Hg in rain with time. The Hg in air concentrations are also shown over the same period for comparison purposes. These plots both indicate that Hg in air increases at the onset of the event and then decreases with time. The final air concentration after the event, however, shows no significant reduction compared to before the event. Although Figure 2c suggests that these changes may be statistically insignificant compared to normal variations, it is interesting to note that for 18 of the events sampled where Hg in air data exists, a total of 12 events showed this initial rise in air Hg concentration while only 2 events showed a decrease and 4 events showed no change.

Table VI. Mercury in Precipitation Data Showing within Event Sampling for the Duluth, MN Station (1988-1989).

Event Sampling Period Start/Stop		Hg Conc. (ng L^{-1})	MIC Vol. (mL)	Hg Mass (ng)	Event Sampling Period Start/Stop		Hg Conc. (ng L^{-1})	MIC Vol. (mL)	Hg Mass (ng)
Date	Time				Date	Time			
01/11/88	1700/2000	100.9	> 300.0	> 30.3	01/15/89	1600/2000	6.1	874.0	5.3
01/11/88	2000/2200	17.4	271.1	4.7	01/17/89	1200/1700	3.6	1117.9	4.0
01/11/88	2200/0600[a]	30.9	> 300.0	> 9.3	01/17/89	1700/2200	< 2.2	264.0	< 0.6
01/12/88	0600/1200	16.0	> 300.0	> 4.8	03/12/89	1600/0600[a]	41.4	26.8	1.1
01/12/88	1200/1445	7.9	259.3	2.0	03/14/89	0500/0740	11.1	264.0	2.9
05/08/88	1640/0750[a]	19.7	4221.3	83.0	03/14/89	0740/1200	4.6	1031.7	4.8
05/09/88	0750/1225	< 2.8	1348.1	< 3.8	03/14/89	1200/1700	4.2	324.0	1.4
05/09/88	1245/1445	< 4.7	987.0	< 4.6	03/24/89	0200/0600	10.1	349.0	3.5
05/09/88	1445/1530	6.1	897.0	5.5	03/24/89	1700/2200	17.2	274.0	4.7
05/09/88	1720/0730[a]	< 4.9	887.0	< 4.3	03/29/89	1300/2330	< 3.9	849.0	< 3.3
06/28/88	0200/0950	28.9	1035.1	29.9	03/29/89	2330/0100[a]	10.5	724.0	7.6
06/28/88	0950/1410	7.9	1308.2	10.3	04/01/89	1300/1500	9.6	624.0	6.0
07/13/88	0100/0500	11.3	1897.3	21.4	04/01/89	1500/2100	8.2	1204.2	9.2
07/31/88	0648/0718	33.7	222.0	7.5	04/03/89	1300/2300	8.2	1386.2	11.3
07/31/88	0718/0858	28.9	187.0	5.4	04/03/89	2300/0730	2.6	714.0	1.9
07/31/88	0858/0920	39.0	137.0	5.3	04/29/89	0300/1545	14.2	964.0	13.7
08/01/88	2000/2100	44.4	377.0	16.7	04/29/89	1545/1000[a]	4.3	1213.8	5.2
08/02/88	1500/1900	29.9	797.0	23.8	04/30/89	1600/1800	12.4	574.0	7.1
08/04/88	0100/0650	6.1	2673.7	16.4	05/01/89	1700/1800	39.4	42.7	1.7
08/04/88	0650/0800	< 1.5	897.0	< 1.4	05/08/89	0700/0900	44.7	115.9	5.2
08/04/88	0800/1100	4.5	357.0	1.6	05/18/89	0200/0945	29.0	774.0	22.5
08/04/88	2300/0800[a]	< 1.5	3128.9	< 4.7	05/18/89	1600/2030	8.4	1022.1	8.6
08/13/88	0100/0200[a]	17.8	2218.6	39.5	05/24/89	1300/1800	8.2	5593.1	46.1
08/16/88	2300/0300[a]	9.6	10493.0	100.9	05/24/89	1800/2300	32.4	344.0	11.1
09/15/88	0900/0800[a]	21.2	1681.9	35.6	06/12/89	0645/0750	6.2	2140.5	13.1
09/16/88	0800/2230	18.1	3128.9	56.6	06/12/89	0750/1220	3.1	1204.2	3.7
09/18/88	1400/1500	23.8	1308.2	31.2	06/12/89	1220/0745[a]	9.7	1841.4	17.9
09/19/88	1500/2030	13.0	2683.3	34.8	06/21/89	0745/0600[a]	21.0	1022.1	21.5
09/19/88	2030/2230	5.0	2055.7	10.3	08/26/89	1200/1500	3.0	2406.8	7.3
09/19/88	2230/0200[a]	7.0	3512.2	24.7	08/28/89	2000/2100	5.7	174.0	1.0
11/15/88	0700/1218	17.0	787.0	13.4	09/04/89	0300/1000	9.4	5309.6	49.9
11/15/88	1218/2125	15.7	1054.3	16.5	09/04/89	1000/1100	7.2	434.0	3.1
11/26/88	0800/2020	12.0	1955.0	23.4	09/19/89	1100/1700	10.3	2488.3	25.6
11/26/88	2020/0730[a]	0.9	1226.8	1.1	09/20/89	1600/2200	6.5	3398.6	22.3
12/26/88	1200/0600[a]	5.1	787.0	4.0	09/20/89	2200/2400	< 2.7	2852.4	< 7.8
01/07/89	0100/0900	3.7	1327.4	5.0	09/21/89	2100/2200	21.4	334.0	7.2
01/07/89	0900/1250	7.5	1054.3	7.9	10/04/89	2300/0100	31.0	224.0	6.9
01/07/89	1250/2200	10.2	947.0	9.7	10/05/89	1200/1400	14.8	364.0	5.4

[a] Stopped on following day.

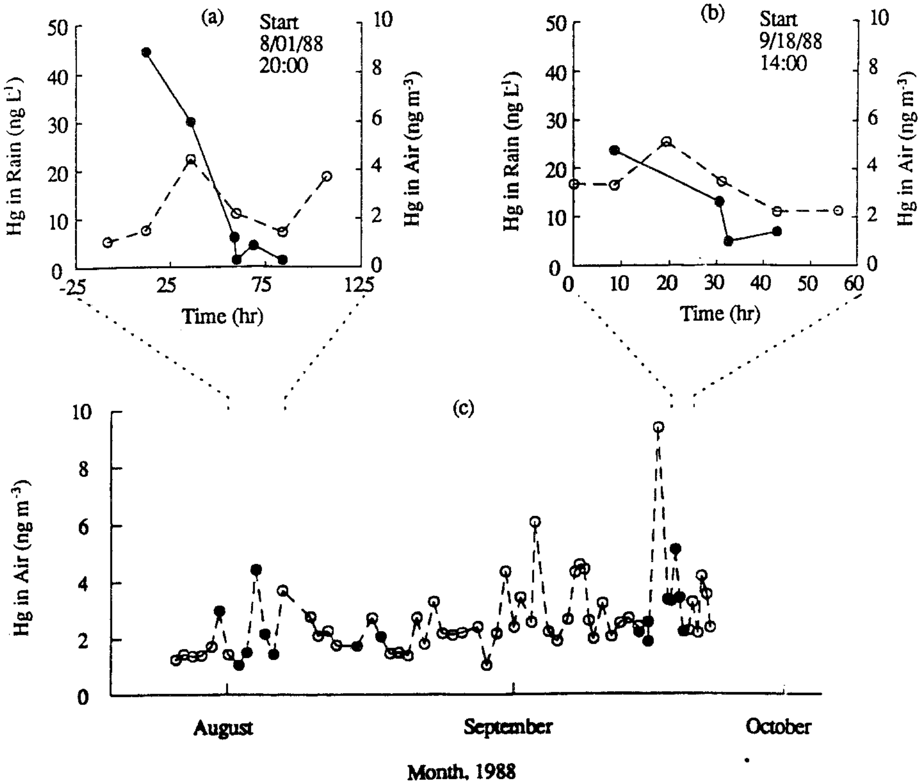

Figure 2. Panels (a) and (b) show a comparison between Hg in rain (——) and Hg in air (— —) concentrations as a function of time for two events in Duluth, MN. Panel (c) shows Hg in air concentrations for a 2-mo period spanning these two events and others where periods of rain and no rain are represented by closed and open circles, respectively.

These observations suggest two important conclusions: 1) The onset of a rain event temporarily enriches the near ground Hg in air concentrations. This may be a result of revolatilization and is consistent with observations of Hg loss from rain collected in unpreserved beakers. 2) The "washable" portion of Hg in air (Hg_w) is only a small fraction of the relatively insoluble total (primarily Hg(0)). Hg_W probably consists mainly of Hg bound to particulates and Hg oxidized by ozone (Iverfeldt and Lindqvist, 1986).

If we use Hg_w as a basis for defining a scavenging ratio (S) then

$$S = Hg_p / Hg_w \qquad (1)$$

where Hg_p (Hg concentration in rain) and Hg_w are expressed in terms of a mass per mass basis.

Although Hg_w is unknown throughout each event summarized in Table VI, we may still estimate S by using a simple model (e.g. NRC, 1983). Writing the time rate of change of Hg_w we get

$$\partial Hg_w / \partial t = -\rho\, R\, S\, Hg_w / h$$

where ρ is the ratio of the density of water to that of air, R is the precipitation rate, and h is the effective air column height being washed out. Assuming that S, R, and h are constant over each precipitation sample taken within the event, this may be solved for each sample period to yield

$$Hg_w = Hg_{w0} \exp(-\rho\, S\, R\, t / h)$$

where Hg_{w0} is Hg_w at time $t = 0$ (beginning of each sample period). Using the definition of S we may write

$$Hg_p = Hg_{p0} \exp(-\rho\, S\, R\, t\; / h) \tag{2}$$

where Hg_{p0} is Hg_p at time $t = 0$.

Now since S varies with R (estimated for each sample period), we use the graphical results of Scott (1978) for a Bergeron-Findeison process (EPA, 1980) to write

$$[\ln(S) - \ln(S_1)] / \ln(R) \cong -0.26 \qquad (0.1 < R < 10\ \text{mm hr}^{-1}) \tag{3}$$

where S_1 (assumed constant throughout the event) is the value of S for a precipitation rate of 1 mm hr^{-1}. Using equations (2) and (3) and data from Table VI we solve (non-linear least squares) for the values of S_1 and Hg_{p0} for each event with h taken to be 2000 m (EPA, 1980) and the effective cross section of the MIC collector equal to 0.16 m^2.

After omitting samples that increased in Hg_P (near end of event) and using only those events where a minimum of 3 samples were taken, we computed an average scavenging ratio (at 1 mm hr^{-1} precipitation rate) of 140 ± 80 and an average value of Hg_{p0} of 29 ± 19 ng Hg L^{-1} (N = 5 events). These do not include the high outlier of $S_1 = 2550$ for the event starting on 3/12/89.

Using our estimated values of Hg_{p0} and S_1 we computed Hg_w from equation (1). Comparing with our total Hg in air measurements (existing for 4 of the 5 events) we find that the "washable" portions of Hg in air were 11, 10, 1, and 7% of the total for the events starting on 8/01/88, 9/18/88, 1/15/89, and 9/19/89, respectively. This compares with about 20% measured over Italy by Ferrara *et al.* (1986) and 3-20% of the total Hg existing as "water soluble" measured by Brosset (1987) over Sweden.

3.5. Mercury Air-Source Pathways

Sampling within the period of a precipitation event is required to better define weather conditions in relation to calculations of air parcel back-trajectories. In many cases, the within event Hg concentration (Table VI) decreased with time and total precipitation volume. However, in some cases, the Hg concentration did not decrease and may have actually increased, possibly as a result of contributions of Hg from different source regions. In order to investigate this observed variability in Hg concentrations, loadings, and possible origins of Hg sources, 72-hr air parcel back-trajectories were computed for each event at its beginning and every 3 hr thereafter until the end of the precipitation period. Examples of the trajectories are shown in Figure 3 for four of the

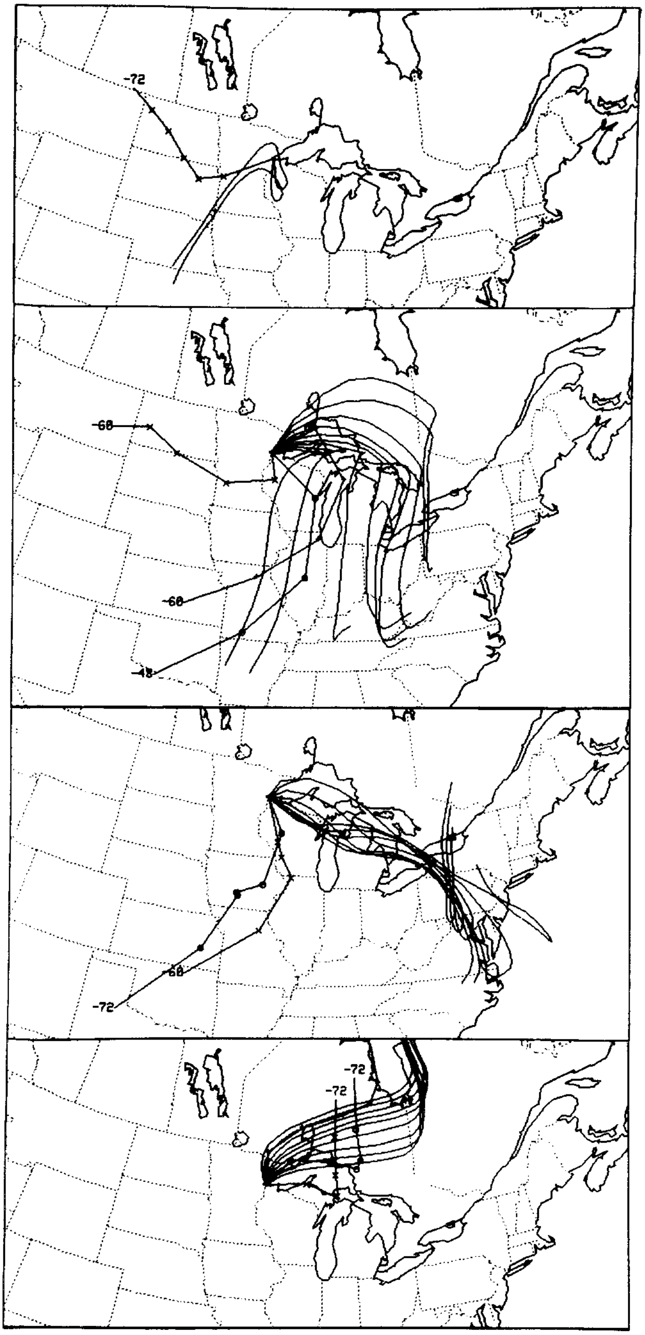

Figure 3. Examples of air parcel trajectories going to Duluth. Surface geostrophic 72-hr pathways at 3-hr intervals (solid lines) and upper level (850-mb) 48-72-hr pathways (dotted lines) are shown for 4 precipitation events listed in Table VI (top to bottom: 7/31/88, 11/26/88, 1/7/89, and 4/30/89).

events in Table VI to illustrate the large variety of patterns and geographical regions traversed. One of the more interesting results was that the apparent air pathway experienced in Duluth as a Lake Superior "northeaster" can actually originate from the central states region to the south and east.

Relatively higher Hg concentrations were recorded with trajectory pathways over the Ohio River Valley region on May 18, 24, and June 21, 1989 where no precipitation had occurred along the trajectories. In one additional case, June 12, 1989, the Hg concentration was low but the Hg loading was high because of the large volume of the event. This can be compared with pathways over or through the Ohio River Valley region that experienced rain along the trajectories so that the resulting precipitation at Duluth showed relatively low concentrations of Hg for May 9-10, November 26, and December 26-27, 1988, and January 4 and March 4, 1989. These findings indicate that prior storm activity, in addition to the actual pathway taken, should be an important consideration.

Wide regions of the central states provide pathways for air trajectories that co-occur with precipitation events in Duluth and Western Lake Superior. Air emissions containing Hg from these pathways (Van Horn, 1975) are most likely to contribute to the regional loading of Hg to the atmosphere and to result in measured Hg concentrations and masses being deposited on northeastern Minnesota.

Local and regional sources of Hg from northeastern Minnesota could also contribute to the Hg concentrations and deposition from precipitation. Local activities in the region that could contribute significantly are the mining of iron ore, using about 45 million Kg of explosives per year, the processing and sintering of taconite ore into 42 million tons (1988) of marketable pellets (Lipp, 1989), and the assaying of iron in ores (Kolthoff and Sandell, 1958). These possible sources and those from local energy production and garbage incineration should be evaluated in detail as possible contributors to the high Hg precipitation events observed, especially at the Ely site .

4. Conclusions

Mercury deposition and precipitation volume were measured at three sites in northeastern Minnesota: Duluth, Marcell, and Ely. Wet deposition values were 20, 16, and 17 μg Hg m^{-2}, respectively, in 1988, and 6, 14, and 42 μg Hg m^{-2}, respectively, in 1989. Significant amounts of Hg are present in precipitation and are thus deposited in remote lake watersheds. The pattern of increased wet deposition at Ely suggests the possibility of significant local source contributions rather than a more general pattern of elevated deposition at all sites from more distant sources of Hg emissions. Additional research on source identification and source-receptor relationships is needed to determine the cause of the variability in wet Hg deposition.

Across the region, volume-weighted concentrations of total Hg in precipitation averaged about 18 ng Hg L^{-1} while annual depositions averaged 15 ug m^{-2}. Mercury concentrations in precipitation are positively correlated with the major ions, conductivity, and pH, and negatively correlated with precipitation volume. The best predictor equation from stepwise regression has an r^2 of 0.65 and shows that Hg concentrations are related to magnesium and chloride concentrations.

From measurements of Hg in rain concentrations as a function of time within events, scavenging ratios for "washable" Hg were calculated to be 140 ± 80 (mass based at a 1 mm hr^{-1} precipitation rate). The "washable" portion of mercury in air was calculated to be up to approximately 10% of the total for the study region and the events sampled.

Individual precipitation events were sampled one to five times on twenty-four occasions during 1988-1989. Air parcel back-trajectories and residence time analyses indicate that possible source regions within 72-hr travel time were located mostly to the south, southeast, and southwest, up to a distance of 2500 km but local sources may also be important.

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