ATMOSPHERIC MERCURY IN NORTHERN WISCONSIN: SOURCES AND SPECIES

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Abstract. The atmospheric chemistry, deposition and transport of mercury (Hg) in the Upper Great Lakes region is being investigated at a near-remote sampling location in northern Wisconsin. Intensive sampling over two years and various seasons has been completed. A multi-phase collection strategy (gas-, particle- and precipitation-phases) was employed to gain insight into the processes controlling concentrations and chemical/physical speciation of atmospheric Hg. Additional chemical and physical atmospheric determinations (e.g. ozone, particulate constituents, meteorology) were also made during these periods to aid in the interpretation of the Hg determinations. For example, correlations of Hg with ozone, sulfur dioxide and synoptic-scale meteorological features suggest a regionally discernible signal in Hg. Comparison to isosigma backward air parcel trajectories confirms this regionality and implicates the areas south, southeast and northwest of the site to be sources for Hg. Particle-phase Hg (Hg_p) was found to be approximately 40% in an oxidized form, or operationally defined as "reactive". However, this was quite variable from year-to-year. Hg_p and other particle constituents (esp. sulfate) show significant correlation and similarity in behavior (concentration ratios in precipitation and in particles). These observations are part of the growing evidence to support the hypothesis that precipitation-phase Hg arises in large part from the scavenging of atmospheric particulates bearing Hg. Observed concentrations of rain and particle-Hg fit broadly the theoretical expectations for nucleation and below-cloud scavenging. Significant increases in the Hg/aerosol mass ratio appear to take place during transport. Enrichment of aerosols is taken as evidence of gas/particle conversion which could represent the step linking gas-phase Hg with rain. The refined budget indicates ca. 24% of total deposition is from summer particle dry deposition, and that this deposition also contributes ca. 24% of all reactive Hg deposition. Additionally, almost all (86%) deposition (wet and dry) occurs during the summer months.

1. INTRODUCTION

Recent budgets of the biogeochemical cycling of mercury (Hg) in temperate latitudes have increased understanding of Hg accumulation in sensitive lakes (Fitzgerald *et al.*, 1991, 1994; Lindqvist *et al*, 1991; Mason *et al.*, 1994; Watras *et al.*, 1994). In north central Wisconsin, the budget (Fitzgerald *et al.*, 1991) outlined a total deposition of 10.3 $\mu g/m^2/yr$, with 66% arriving from precipitation and 34% from dry deposition. While such budgets unequivocally implicate the atmosphere in the transport of Hg to the aquatic environment, little is known about Hg's atmospheric chemistry. Determinations of Hg species in source plumes and in laboratory experiments (Meij, 1991; Prestbo, 1995; Munthe, 1992) have offered critical information about the chemical nature of Hg when released to the atmosphere and presented chemical-based mechanisms for its incorporation into rainwater. Extensive receptor-based chemical investigation is required, however, to assess the importance of various Hg transformation pathways to Hg deposition.

The University of Connecticut, with aid from the Wisconsin Department of Natural Resources and as a part of EPRI's Mercury Accumulation Processes and Pathways Project (MAPP) has established the Crab Lake Atmospheric Mercury Station (CLAMS) in north central Wisconsin to specifically address the need for receptor-based chemical information on atmospheric Hg. Here, we are presenting some of the results from the on-going investigations.

2. METHODS

The bulk of the results reported below were obtained at the Crab Lake Atmospheric Mercury Station (CLAMS). CLAMS is located in north central Wisconsin (Vilas County) near the town of Presque Isle (49.6° N, 89.0° W). The station consists of a 60' aluminum tower, field laboratory and pump enclosure. The field laboratory is outfitted with a class 100 clean bench and

Cold Vapor Atomic Fluorescence Spectrometer. During Aug. 1992, additional sampling was done at Max Lake, a small naturally acidic lake, approximately 30 Km south of CLAMS. This sampling was carried out at the end of a short 7m pinewood dock. The sampler inlets were approximately 1.5m from the lake surface.

At both sites, the following Hg collection procedures were used: 1) Gas-phase Hg (TGM) was collected on Au-coated quartz sand traps systems as described elsewhere (Fitzgerald and Gill, 1979; Fitzgerald, *et al.*, 1991) and the samples analyzed in the field. Samples for particle-phase Hg (Hg_p) were collected on polycarbonate (Nuclepore®) or quartz-fiber filters (Pallflex®), both capable of high efficiency collection of > 0.2 μm diameter particles, and moderately efficient for .2-.05 μm particles. All filter handling took place in the CLAMS cleanbench.

Precipitation was collected using ultraclean protocols and an acid-cleaned, manually-operated Teflon®-film funnel (Mason *et al.*, 1992; Fitzgerald, *et al.*, 1991). Snow was collected at CLAMS (and nearby Carlin Lake) by scooping up newly fallen material into acid-cleaned wide-mouth jugs, while the operator wore elbow-length gloves and stood downwind of the collection area. Some precipitation was filtered before analysis to study the physical distribution of the species present. This was done either with a peristaltic pump to remove liquid from the sample bottle and force it through a Teflon® in-line filter holder (Savillex®, for snow), or by suction through an aspirated polycarbonate filter funnel cassette (Nalgene®, for rain). In both instances, the precipitation was filtered using acid-cleaned 0.2 μm pore size polycarbonate filters (Nuclepore®)

Analysis of gas-, particle- and precipitation-phases of Hg was performed using techniques described elsewhere (Fitzgerald and Gill, 1979, Mason *et al.*, 1992; Lamborg *et al.*, 1994). Methylmercury (MeHg) analysis of particulates and precipitation was accomplished using the ethylation and chromatographic technique of Bloom and Fitzgerald (1988; Bloom, 1989). Inert distillation was used to separate the MeHg from precipitation and filter material (Horvat, 1993).

Sulfate determinations of precipitation or extracted filter material were made by ion chromatography (Miller and Nikolaidis, 1992). Isosigma air parcel back trajectories were prepared using the PC version of HySPLIT (Draxler, 1992) and interpolated meteorological data obtained from the National Climatic Data Center (NOAA). Aerosol mass was determined by gravimetric analysis of 47mm, 0.2 μm, Nuclepore® filters. Fine mass was selectively collected using a Teflon®-coated cyclone (University Research Glassware). Sulfur dioxide was collected behind the cyclone using a sodium carbonate-coated denuder (Koutrakis *et al.*, 1988). Ozone data were obtained from the Bureau of Air Management, Wisconsin Department of Natural Resources from Trout Lake Forestry Station, some 35 Km southwest of CLAMS. The sample inlet for the ozone determinations was located at approximately the same height as the Hg collection equipment at CLAMS.

3. RESULTS

Some results for gas-, particle- and precipitation-phase determinations of Hg at CLAMS are shown below in Figures 1-3 (where they are discussed). Summary statistics for Hg and other species for each sampling period can be found in Table I. Some values are missing from the figures, indicating voided samples. Error bars on the figures were generated in the following ways: for TGM, one standard deviation for duplicate or triplicate samples; for particle Hg, one standard deviation calculated as 15% of value from one system. Detection limits were nominally: TGM, 10 pg/m^3; particle Hg, 0.5 pg/m^3; precipitation Hg, 0.07 ng/L.

Table I. Summary of Hg measurements made during MAPP.

Sampling Period	TGM	Particle-Phase	Precipitation-Phase
Aug '92 (no gas & part figure)	1.21 ± 0.49 ng/m^3	total: 63 ± 32 pg/m^3 react: 38 ± 18 pg/m^3	total: 2.58 ± 2.23 ng/L react: 0.43 ± 0.51 ng/L
Jan. '93	1.79 ± 0.43 ng/m^3	total: 6 ± 4 pg/m^3 react: 5 ± 3 pg/m^3 methyl: 2 pg/m^3	total: 1.63 ± 0.91 ng/L react: 0.22 ± 0.11 ng/L methyl: n/a
Summer '93	1.8 ± 0.4 ng/m^3	total: 14 ± 23 pg/m^3 react: 1 ± 2 pg/m^3 methyl: 0.95 pg/m^3	total: 6.70 ± 5.55 ng/L react: 4.04 ± 4.74 ng/L methyl: 0.112 ± 0.423 ng/L
May '94 (no gas & part figure)	1.68 ± 0.26 ng/m^3	n/a	total: 8.74 ± 2.59 ng/L react: 2.94 ± 0.36 ng/L methyl: n/a

3.1 Gas-Phase

The high precision measurements (frequently with relative standard deviation of <5%) allow the temporal fine structure to be reliably documented. First it should be noted that the overall variability of gas-phase Hg is relatively low (rsd: 30%). This is consistent with the notion that Hg is a trace gas with a long residence time in the atmosphere (Slemr *et al.*, 1981; Fitzgerald *et al.*, 1981). However, the variability bears a connection with synoptic-scale meteorology (passage of fronts, etc.) as is noted on the January and Summer 1993 TGM time series (Figures 1 and 2). Frequently, the passage of fronts (noted by the arrows) was accompanied by rapid and significant changes in gas-phase Hg concentration. It should also be noted that these fronts were not always associated with precipitation (triangles) at the site or upwind of the site, and that changes in concentration cannot easily be attributed to a general cleansing of the air by rain.

Interestingly, there appeared to be little seasonal difference in the concentration and variability of TGM. The average value of 1.68 ng/m^3 is comparable to estimates made over the Pacific and Atlantic Oceans (Fitzgerald *et al.*, 1984, Slemr and Langer, 1992; Fitzgerald, 1995).

3.2 Particle-Phase

Unlike TGM, particle-phase Hg (Hg$_p$) shows a high level of temporal (60%) and seasonal (3-5x) variability. Wintertime collections made in January of 1993 (as well as previous measurements in Northern Wisconsin) suggest particulate mass which was dominated by fine fraction (< 2.5 μm) material. Indeed, collection of particles using a high-volume cascade impactor showed that the wintertime Hg resided entirely in the ultra-fine fraction (<0.5 μm). The dry deposition velocity for such material has been estimated to be 0.1 cm/s (Arimoto *et al.*, 1990). Analysis of the size distribution of summer Hg$_p$ indicated that some coarse fraction Hg (> 2.5 μm) is present during the summer, effectively increasing the mass mean diameter to 2 μm and deposition velocity of Hg$_p$ (0.5 cm/s). The amount of Hg observed in the coarse fraction during the summer was consistent with measurements of soil Hg made in the area (250 ng/g, Nater and Grigal, 1992) and amounts of total aerosol mass observed at the site (e.g. 250 ng Hg/g soil * 5 μg/m^3 = 1.25 pg Hg/m^3). While no direct observations are yet available, it can be assumed that the coarse/soil contribution to atmospheric Hg would be relatively constant throughout a season without snow cover (roughly 5 months of the year) with slight deviations due to soil moisture and local wind speed. Using this information, it can be estimated that dry
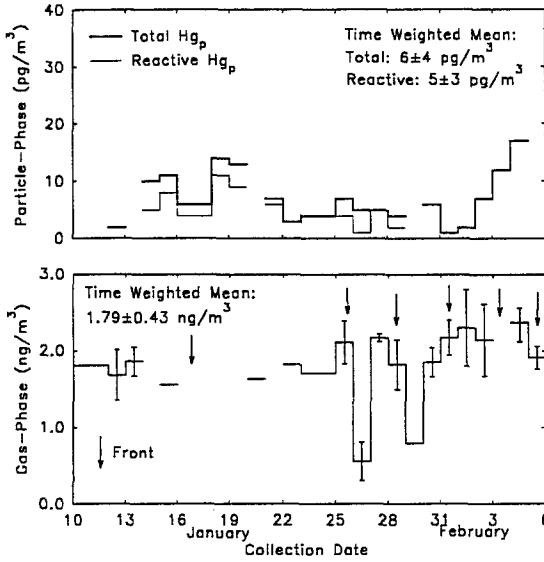
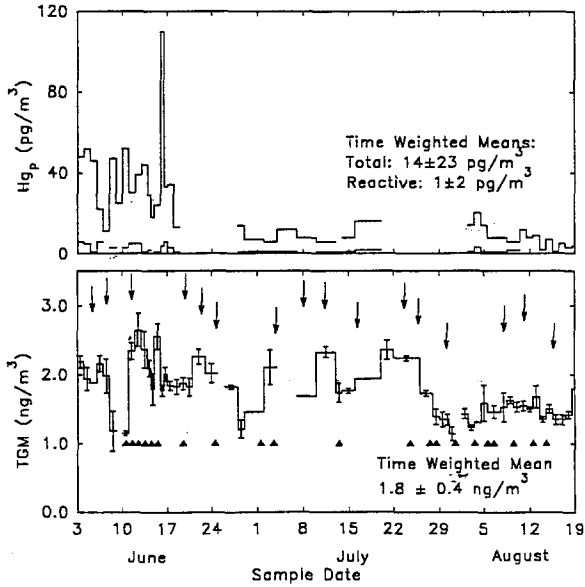Figure 1. Atmospheric Hg measurements at CLAMS, Winter 1993

Figure 2. Atmospheric Hg measurements at CLAMS, Summer 1993

deposition of Hg from recycled soil material would equal only 0.2 $\mu g/m^2/yr$, which represents roughly 2% of total deposition. This also implies that excursions, or "events" in Hg_p most probably arise as a result of increased fine fraction contribution. Fine fraction material, in general, has a relatively long atmospheric lifetime (3-5 days) and is usually the result of anthropogenic emissions (Finlayson-Pitts and Pitts, 1986). This, too, must be confirmed through observations.

Speciation of the particle-phase is an important component in the current study. Operationally defined reactive particle-phase Hg was demonstrated to make up a significant fraction of total Hg during the Summer 1992 and Winter 1993. In both these sampling sessions, reactive Hg_p was approximately 50% of total, and sometimes more. In contrast, this species made up generally less than 30% of the total at CLAMS during Summer 1993. These values are of the same scale as the percentage of reactive Hg which is observed in precipitation (see below). One explanation for the generally lower Summer 1993 levels might be the heavy rainfall associated with the "Flood of 1993" which fell primarily to the south of the site. The results from 1994 collections will aid in understanding this observation.

Particle samples were also analyzed for MeHg. Only a few samples have been completed (N=4) and gave the following results: one sample from Jan. '93 showed 2 pg/m^3 MeHg, while one from Summer '93 contained 0.95 pg/m^3. It should be noted that the technique used for the analysis is still under development. If further determinations confirm these findings, it is plausible that MeHg in rainwater could be explained by invoking washout of MeHg on particles. However, as has been demonstrated, the amount of MeHg arriving to Wisconsin lakes through deposition (dry and wet) is not sufficient to account for MeHg accumulation in fish (Fitzgerald *et al.*, 1991).

The results of sulfate and mass determinations in Summer 1993 are as follows: SO_4=2.12±2.06 $\mu g/m^3$ [0.24 - 10.62]; Total mass=5.0±3.8 $\mu g/m^3$ [2.0 - 25.1]; Fine Mass=3.6±1.5 $\mu g/m^3$ [2.2 - 9.8]. Hg_p and particulate sulfate were statistically significantly correlated, but with a low correlation coefficient (r^2=0.23 p>0.01 mean Hg/SO_4 = $2x10^{-5}$). However, as mentioned above, it appears that much of Summer 1993 may have been anomalous and obscured more striking connections between these two species. Hg_p likewise showed a weak but significant correlation with total aerosol mass (r^2=0.26, p>0.002) during Summer 1993 but no correlation during Winter 1993. It is interesting that particulate concentrations of Hg (mass/mass) were generally quite high (<1 - 30 ppm, avg.=7 ppm) during the summer. This is in stark contrast to primary particulate matter which was found to be < 1 ppm Hg after an electrostatic precipitator scrubbing coal-fired emissions (Meij, 1991) and to soil matter which may become entrained at the site (0.25 ppm; Nater and Grigal, 1992). Clearly, some enrichment of the aerosol takes place during transport and is assumed to be due to gas-to-particle conversion.

3.3 Regionality of Gas- and Particle-Phase Hg

During the Summer of 1993, both gas- and particle-phases of Hg at CLAMS showed weak but significant correlations with ozone (O_3) and sulfur dioxide (SO_2):

Hg-p and O_3: r^2= 0.14	Hg-p and SO_2: r^2=0.13
p>0.02	p>0.05
TGM and O_3:r^2=0.37	TGM and SO_2: r^2=0.16
p>0.001	p>0.02

Both of these species, particularly O_3, can be used as indicators for regional "air quality", or the general impact of anthropogenic activity on the atmospheric environment. Natural background levels of ozone (20 ppbv) and SO_2 (0.05 ppbv) were observed at CLAMS, as well as concentrations slightly elevated above these baselines (24h averages):

Species	Mean (ppbv)	Range (ppbv)
Ozone	30	10-50
Sulfur Dioxide	.1	<.05 - 10

While neither of these species were ever in "non-attainment" for their respective National Ambient Air Quality Standard (O_3: 120 ppb; SO_2: 30 ppbv), it is significant that maximum concentrations for ozone, SO_2 and Hg were coincident. This covariation is most probably the result of similar emission regions and transport. This example of atmospheric Hg's regional character is not a new observation (Lindqvist et al., 1991; Schroeder and Markes, 1994; Lamborg et al., 1994), but is perhaps more subtle (due to the site's remoteness) than those reported before.

      The regionality of Hg's behavior can be verified using meteorological tools as well. Using the HySPLIT model (Hybrid Single Particle Lagrangian Integrated Trajectory, Draxler, 1992), isosigma (constant pressure, terrain following) backward air trajectories can be generated which indicate the most probable travel path for air arriving at a site. Grouping trajectories by sector (8 in all) and generating average Hg concentrations for each group allows examination of chemical data for meteorologically-based trends. It should be noted that trajectories (and concentration information) which were found to cross fronts, as indicated by surface weather maps, were not included in the analyses. However, trajectories which likely had precipitation upwind of the site were included in the treatment, and may have therefore contributed to de-emphasizing the impact of certain sectors (Keeler and Samson, 1989). When this treatment was applied to samples from June 1993, the following results were obtained:

Species	N	NE	E	SE	S	SW	W	NW
Hg_p (pg/m^3.)	34		39	48	40	19	23	46
	n=5	n=0	n=1	n=2	n=2	n=3	n=1	n=2
TGM (ng/m^3)	1.83	1.85	1.82	2.22	1.39	2.01	1.94	1.86
	n=5	n=2	n=1	n=4	n=1	n=3	n=1	n=3

Although there are limited data, it appears that air arriving to northern Wisconsin from the industrial Midwest regions of southern Lakes Huron, Michigan and Erie may bear more Hg than from other regions. Interestingly too, Hg_p concentrations in air from the NW may be higher on average, indicating a source there as well. Here, the meteorological treatment has generally verified the correlation of Hg species with ozone and sulfur dioxide.

3.4 Precipitation-Phase

      The precipitation collected since January 1993 at CLAMS (as well as collections made previously in Wisconsin) is shown in Figure 3. Speciation for 1993 was fairly typical of past years, with approximately 47% of the Hg present in the form of reactive Hg. For May 1994, this speciation was more skewed toward total Hg, but the samples collected were from small sized events, and possessed a large amount of filterable material. MeHg can be found in rain and snow, but only in small amounts. Samples from 1993 also show this behavior.
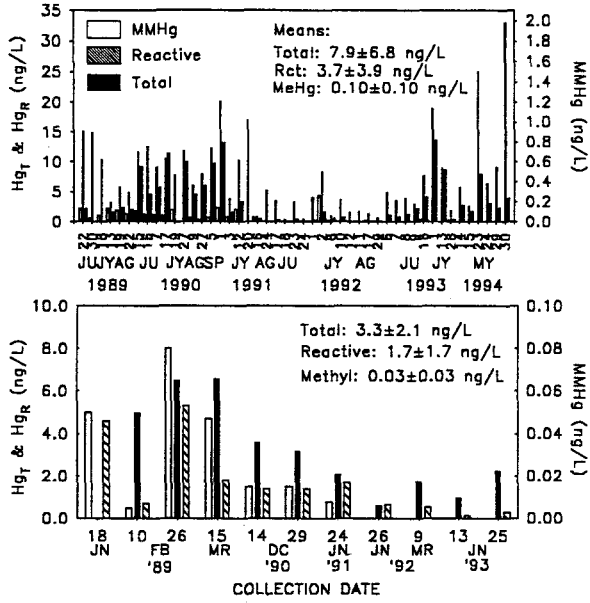
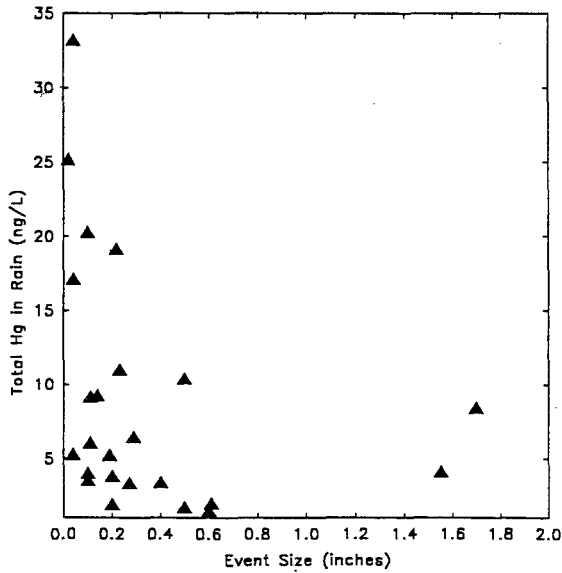Figure 3. Rain (above) and Snow Hg measurements from N. Wisconsin

Figure 4. Washout of Hg in rain from 1991-1994

Some samples from January 1993 and May 1994 were filtered through 0.2 μm pore, acid-cleaned polycarbonate filters and the filtrate analyzed for total and reactive Hg. (Table II). The results suggest that large fractions of Hg in precipitation can be removed along with particulate matter. The effect is greater for total than for reactive Hg, but some reactive Hg can be removed by filtration. This was very dramatically demonstrated with the May 1994 samples (not shown), which came from small sized events and perhaps more heavily impacted by scavenging of aerosols. If the concentration of rain collected is plotted versus event size (Figure 4), a dramatic nonlinear relationship can be observed. This relationship has been frequently observed between events and even within individual events (Bloom and Watras, 1989; Iverfeldt, 1991; Hoyer et al., 1993; Ferrara et al., 1986) and has usually been attributed to the impact of particle scavenging by rain. The washout ratio (w=Hg_{ppt} (ng/L) * 1.2 m^3/L /Hg_p (ng/m^3)) of samples collected during 1989 was 477±547. A similar value was found for 1993 (181±129). These values are similar to the range (200-2000) that might be expected for a precipitation-phase species which arises from particle scavenging (GESAMP Working Group 14, 1989).

Table II. Results from filtered precipitation Hg determinations.

Sample	Total Hg Unfiltered	Total Hg Filtered	Reactive Hg Unfiltered	Reactive Hg Filtered
Rain (N=3)	21.63±13.86 ng/L	5.08±1.55 ng/L	4.96±2.57 ng/L	2.76±1.29 ng/L
Snow (N=4)	1.42±0.74 ng/L	0.72±0.13 ng/L	0.40±0.23 ng/L	0.19±0.10 ng/L

There is a strong correlation between Hg and sulfate in rain from the 1993 collections (r^2=0.83 p>0.01, neglecting one outlier). Additionally, the Hg/SO_4 ratio in rain was 5±4x10^{-5}, and of the same order as that in the particulate matter. Charlson et al., (1983) using a parameterization scheme based on physical and chemical considerations, estimated that approximately 64% of the sulfate in rainwater in rural regions was the result of nucleation scavenging of particles bearing sulfate. Charlson et al. estimated that 3% of the sulfate arose from below-cloud scavenging by droplets, and the remaining 33% from in-cloud production from dissolving SO_2. Altogether then, particulate sulfate accounted for 67% of that which was found in rain. To the extent that Hg correlates with sulfate, it may be inferred that Hg in rain arises from perhaps analogous mechanisms. Not surprisingly, the end members of washout curves (appox. 40 ng/L at the start of, or for a small event and 2-6 ng/L at the end of, or for a large event), such as those from Wisconsin or Italy, reproduce fairly accurately the extreme predictions of Hg in rain from washout mechanisms (45 ng/L: Seinfeld, 1986) and in-cloud production (2-4 ng/L: Munthe, 1992).

3.5 Biogeochemical Budgetary Concerns

With winter, spring and summer determinations of all forms of atmospheric Hg now complete, a refined version of the budget for Hg (Fitzgerald et al., 1991) deposition in northern Wisconsin can be constructed. The relevant information used is listed below as a summary:

Season	Total Hg_p	React Hg_p	Methyl Hg_p	Total Hg_{ppt}	React Hg_{ppt}	Methyl Hg_{ppt}
Winter	7 pg/m^3 Vd=0.1 cm/s	7	2	3.27 ng/L 26 cm/yr	1.68	.03
Summer	26 pg/m^3 Vd=0.5 cm/s	10	0.95	7.86 ng/L 55 cm/yr	3.66	.1

These values yield the following:

Species Deposited	Dry ($\mu g/m^2/yr$)	Wet ($\mu g/m^2/yr$)	Total ($\mu g/m^2/yr$)
Total Hg	1.8 (93% Summer)	5.2 (84% Summer)	7.0 (86% Summer)
Reactive Hg	0.8 (84% Summer)	2.5 (82% Summer)	3.3 (82% Summer)
MethylHg	.01 (60% Summer)	.06 (88% Summer)	0.07 (84% Summer)

The refined budget is essentially identical to that from 1991. The total deposition was estimated to be 7.0 $\mu g/m^2/yr$. This value is somewhat lower that the 1991 estimate. Lower rain concentrations measured during 1992 lowered the wet depositional flux estimate. Wet deposition was found to furnish 74% of the deposition. This is a somewhat higher estimated contribution than calculated in 1991. This is due to the discovery that wintertime particulate Hg is located on ultrafine material, and therefore contributes less to dry deposition. The refined version demonstrates that the summer is the period when the majority (86%) of Hg is deposited. Furthermore, the refinements highlight the contribution of summertime dry deposition to annual reactive Hg fluxes (24%). This implies the existence of a supply of the substrate for methylation which is independent of precipitation amounts.

Acknowledgment

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