ATMOSPHERIC CONCENTRATIONS AND DEPOSITION OF Hg TO A DECIDUOUS FOREST AT WALKER BRANCH WATERSHED, TENNESSEE, USA

S. E. Lindberg, R.R. Turner, T. P. Meyers[1], G. E. Taylor Jr.[2], and W. H. Schroeder[3] Environmental Sciences Division, Oak Ridge National Laboratory[4], PO Box 2008, Oak Ridge, TN 37831 USA

ABSTRACT. Aerosol and total vapor-phase Hg concentrations in air have been measured at Walker Branch Watershed, Tennessee for ~2 yr. Airborne Hg at this site is dominated by vapor forms which exhibit a strong seasonal cycle, with summer maxima that correspond to elevated air temperature. Concentrations in this forest are near background levels; however, concentrations at a site within 3 km are significantly elevated due to emissions from Hg-contaminated soils. The concentration data have been combined with a recently modified dry deposition model to estimate dry deposition fluxes to the deciduous forest at Walker Branch. Weekly mean modeled V_d values for Hg° ranged from <0.01 (winter) to > 0.1 (summer) cm s^{-1}. Weekly dry deposition fluxes ranged from <0.1 μg m^{-2} during winter to >1.0 μg m^{-2} in the summer. Our dry deposition estimates plus limited measurements of wet deposition in this area indicate that dry deposition may be the dominant input process in this forest, at least during the summer.

1. Introduction

Progress has been made in recent years in understanding the cycling of Hg in aquatic and terrestrial ecosystems, such that the importance of atmospheric

---

[1] NOAA Atmospheric Turbulence and Diffusion Division, Oak Ridge, TN.

[2] Desert Research Institute, Reno, NV.

[3] Atmospheric Environment Service, Downsview, Ontario, Canada.

[4] Research sponsored by the Atmosphere and Climate Research Division, U.S. Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. Environmental Sciences Division Publication No. 3595, ORNL.

Water, Air, and Soil Pollution **56**: 577–594, 1991.

Hg to these cycles is now well recognized (e.g. Schroeder *et al.*, 1989; Lindqvist *et al.*, 1984). Because atmospheric Hg species may be altered in response to changes in regional tropospheric chemistry (e.g. Lindberg *et al.*, 1987; Ottar *et al.*, 1989), the role of dry deposition needs to be better understood. There are few recent data on Hg dry deposition, particularly in forested watersheds. However, experimental data have demonstrated the ability of plants to accumulate Hg vapor directly from the air (e.g. Browne and Fang, 1978; Lindberg *et al.*, 1979). Since wet deposition may not account for all of the Hg apparently accumulating in fish and lakes in forested watersheds, the potential for an important Hg dry deposition component must be considered.

Dry deposition has been shown to be a significant atmospheric pathway to forests for many major atmospheric species and trace metals (e.g. Lindberg *et al.*, 1982, 1986). Mercury in the atmosphere is dominated by vapor forms (Brosset, 1982), and new models have been published to estimate dry deposition velocities (V_d) for several atmospheric gases and vapors to forests (Hicks *et al.*, 1987; Meyers *et al.*, 1989). In a companion paper, we describe some modifications of these models and others (Bondietti *et al.*, 1984) to develop a routine for estimating dry deposition of Hg in both fine aerosol and vapor form to forests (Lindberg *et al.*, in review). We describe here our air chemistry data for Hg, and summarize some of the results of the model estimates of dry deposition at Walker Branch Watershed in Tennessee.

2. Study Area and Methods

Samples of aerosols and total Hg vapor in air were collected at and near the Walker Branch Watershed in Oak Ridge, Tennessee (Turner *et al.*, 1989). The watershed is a 100 ha catchment in moderate terrain (elevations range from 265 to 365 m) covered with a deciduous forest of mature oak and hickory species, and is located at Lat. 35° 58' N, Long. 84° 17' W (Johnson and Van Hook, 1989). Weekly integrated samples were collected from February, 1988 to September, 1989 in a forest clearing. For comparison, samples were also collected for the period July, 1986 through April, 1989 at a site ~3 km from the forest near an area known to contain Hg-contaminated soils (Turner *et al.*, 1989). The sampling train consisted of a teflon aerosol filter followed by an iodated, activated carbon absorption tube through which air was drawn via a critical flow orifice at a rate of 1.0 L min^{-1}. The absorption tube collects total vapor-phase Hg, regardless of speciation (Lindberg, 1980), but this phase is dominated by elemental Hg vapor (Hg°) (Brosset, 1982; Schroeder and Jackson, 1987). Hereafter we refer to the Hg collected with this method as Hg°. While the possibility of gas-particle artifacts cannot be ignored during extended sampling periods such as those used here, comparisons between simultaneous, sequential daily samples of Hg° collected on gold traps (supplied by N. Bloom) and weekly samples collected using our methods yielded comparable concentrations (Turner *et al.*, 1989).

As part of another study, we measured standard meteorological parameters at the Walker Branch collection site during the period 4/88-10/89 for use with a modified dry deposition model for Hg, and measured concentration gradients of Hg° within and above this forest from a 43 m meteorological tower (Lindberg *et al.*, in review). The approach for estimating the dry deposition velocities for Hg is briefly discussed in a following section. We also collected a limited number of samples of precipitation for Hg analysis, using pre-baked and acidified glass bottles and funnels placed in acid-washed wet-only collectors (eg. Lindberg, 1982).

Samples were analyzed by long-path flameless atomic absorption following wet digestion. The efficiency of this sampling system, the recovery of the wet digestion procedure, and the accuracy and precision of the analytical methods for Hg have been published (Turner *et al.*, 1989; Lindberg, 1980, 1981). The detection limit for Hg in air ranged from 0.01 ng m^{-3} for aerosol Hg to 0.5 ng m^{-3} for Hg°, depending on the air volume sampled; for water the detection limit was ~1 ng L^{-1}. Typical blank values for the carbon traps were in the range of 1-2 ng/tube, while those of the teflon filters were consistently <1 ng/filter. During one gradient experiment and during four weekly sampling periods, from 2-3 adjacent replicate sampling trains were operated. The results of these tests indicated that we could measure Hg° in air with an average precision of ± 6% at concentrations of 4 to 15 ng m^{-3}.

3. Results and Discussion

3.1 FACTORS INFLUENCING AIR CONCENTRATIONS OF Hg

The Hg data from the Walker Branch site indicate that concentrations were generally near continental background levels, and that total atmospheric Hg was dominated by vapor forms, as expected (Table 1). The overall mean concentration of Hg° in air was 5.5 ng m^{-3} for the 19-mo period 2/88 to 9/89. For the year 4/88-3/89, when particle-associated Hg was also analyzed, the mean concentration of aerosol Hg was 0.03 ng m^{-3}, or ~0.5% of the total Hg in air. Seasonal trends in the Hg° concentrations were apparent at both measurement sites, with the highest concentrations generally occurring during the warmer summer months (Figure 1). The mean concentration of Hg° in air during the 1988 forest growing season (4/88-10/88) was over twice that during the colder dormant season (Table I). The similar temporal trend of airborne Hg° concentrations at both sites ($r=0.61$; $P<0.01$) suggests a relationship with ambient air temperature, reflecting the volatility of many Hg species and compounds, particularly elemental Hg. The temperature-concentration relationship was best fit with an exponential curve (Figure 2), which is the same

Table 1. Statistics on weekly air concentrations of Hg at sites in Walker Branch Watershed (WBW), Tennessee, and ~3 km to the northeast near a storage area for Hg-contaminated soils (W-2).

		Hg Concentration (ng m^{-3})				
Site[1]	Species	Mean	σ	N	Range	Sampling Period
WBW	Hg°	5.5	3.1	84	0.8-16	2/9/88-9/12/89[2]
W-2	Hg°	9.4	7.1	153	2.9-58	7/18/86-4/18/89[2]
WBW	Hg°	5.9	3.6	52	0.8-16	One year (4/88-3/89)
WBW	Hg-p[3]	0.03	0.02	12	0.01-0.07	One year (4/88-3/89)
W-2	Hg°	12	6.2	52	3.4-36	One year (4/88-3/89)
WBW	Hg°	7.8	3.6	30	3.1-16	GS[4] (4/88-10/88)
WBW	Hg°	3.3	1.4	22	0.8-7.5	DS[4] (11/88-3/89)
WBW	Hg-p	0.03	0.02	12	0.02-0.07	GS (4/88-10/88)
WBW	Hg-p	0.03	0.02	12	0.01-0.06	DS (11/88-3/89)

---

[1] WBW = Walker Branch Watershed; W-2 = area with Hg-contaminated soils.
[2] Complete data record.
[3] Hg-p = particle-associated Hg (from monthly samples).
[4] GS = forest growing season; DS = forest dormant season.

relationship as that between temperature and the equilibrium vapor pressure of elemental Hg. Interestingly, a similar relationship might be expected between soil microbial activity and temperature, suggesting the possibility of biotic and/or abiotic influences. In a linear regression model of log (Hg°) on temperature for the annual data from Walker Branch for the period 4/88-3/89, the variance in weekly mean air temperature accounted for 59% of the variance in the log of the weekly mean concentrations of Hg° (see Figure 2). The aerosol data for this period did not exhibit similar seasonal trends. While the mean concentrations of aerosol Hg (Hg-p) were the same for each season (Table I), the individual values were characterized by considerable variability, including peaks during July and February (Figure 3). Our data for seasonal trends in Hg° are in strong contrast to those reported in Sweden which exhibited a clear winter maximum and summer minimum (Brosset, 1982). However, the Swedish trends were related to aerosol soot content and to SO_2

concentrations, suggesting the peaks to be influenced by seasonal emissions in central and eastern Europe.

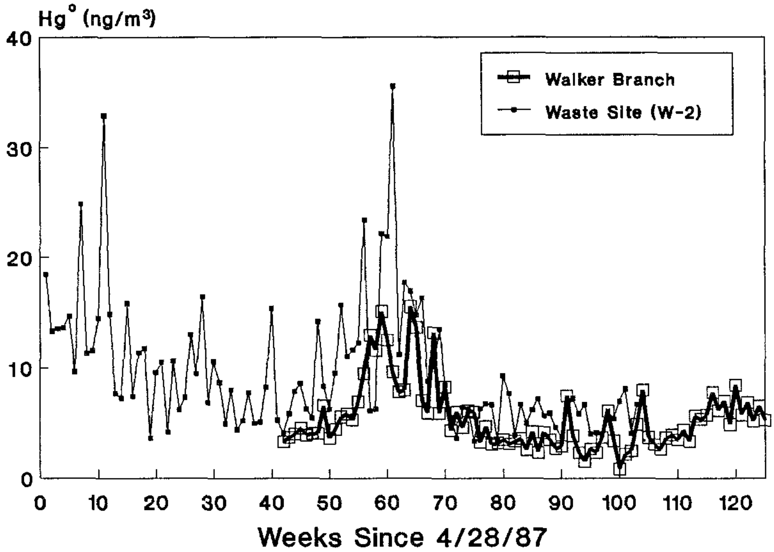

Figure 1. Temporal trends in the measured air concentration of Hg° vapor at Walker Branch Watershed (WBW) and in the vicinity of a nearby storage site for Hg-contaminated soils (W-2) for the period April, 1987 - August 1989. The values represent weekly means. The mid-summer periods include those weeks numbered 1-19 (1987), 53-71 (1988), and 112-125.

Sources of Hg° at these continental sites include natural soil emissions (microbially or chemically controlled) and releases from industrial processes such as power plants and incinerators. Coal combustion dominates the industrial atmospheric emissions of Hg in this region (Lindberg, 1980). However, in this mild climate, coal combustion does not exhibit the same seasonality in emissions that is illustrated in Figure 1 for the atmospheric concentrations of Hg°, suggesting that temperature-controlled surface emissions are indeed important at this site. In addition to the natural soil surface emissions, there are also surface emissions of Hg° from Hg-contaminated soils stored ~3 km north-northeast of this site (Turner *et al.*, 1989). The effect of these sources on Hg° in air at site W-2 is apparent from a comparison of the time series data for each site in Figure 1. Over a comparable time period, the annual mean concentration at this site exceeds that at the Walker Branch site by a factor of two (Table I). Although Hg emissions from this area are influenced primarily by the contaminated soil deposits, we cannot rule out the influence of a small nearby steam plant which burned coal until December, 1988.

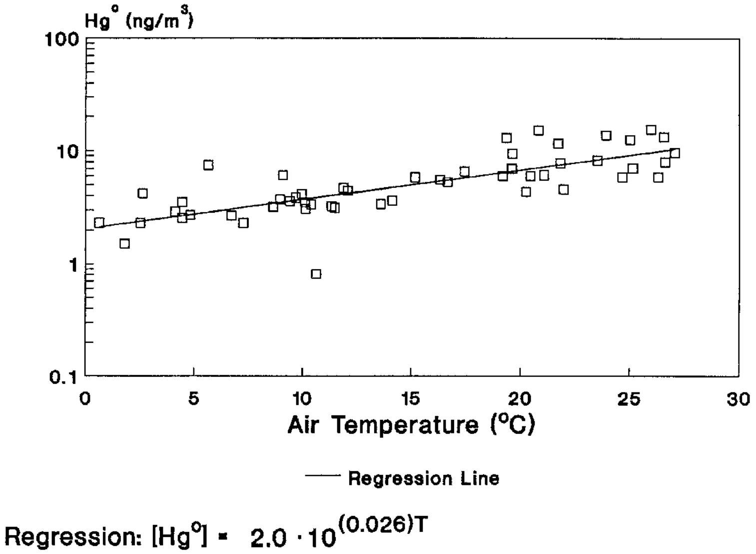

Figure 2. The relationship between air temperature and the measured atmospheric concentrations of Hg° vapor at Walker Branch Watershed, and the best-fit exponential regression line. The values represent weekly means from the year April 1988 to March 1989. The linear regression of log(Hg°) on temperature exhibited an $r^2 = 0.59$.

The influence of the area source near W-2 on concentrations measured at Walker Branch is also apparent as shown by the Hg° concentration and wind direction data in Figure 4. The mean concentration of Hg° at Walker Branch was clearly higher for periods dominated with wind directions from the 0-45° sector. However, despite these local sources, adding the wind direction frequency data to the regression model of log [Hg°] on temperature (Figure 2) explained only an additional 3% of the variance in the concentration of Hg°. By itself, wind direction frequency explained <1% of the variance in the weekly mean concentrations of Hg° at Walker Branch. This seems to imply an overriding role of regional, and not site-specific, soil surface or other emissions which are influenced by air temperature in controlling airborne Hg° at this site. The influence of air temperature is apparent on the concentrations of Hg in air both near and removed from Hg-contaminated soils. This influence may be a function of the vapor pressure of many Hg compounds, especially Hg°, and/or the increased soil microbial activity under conditions of increased temperature. Soil microbes are known to reduce Hg^{2+} to Hg° (Landa, 1978).

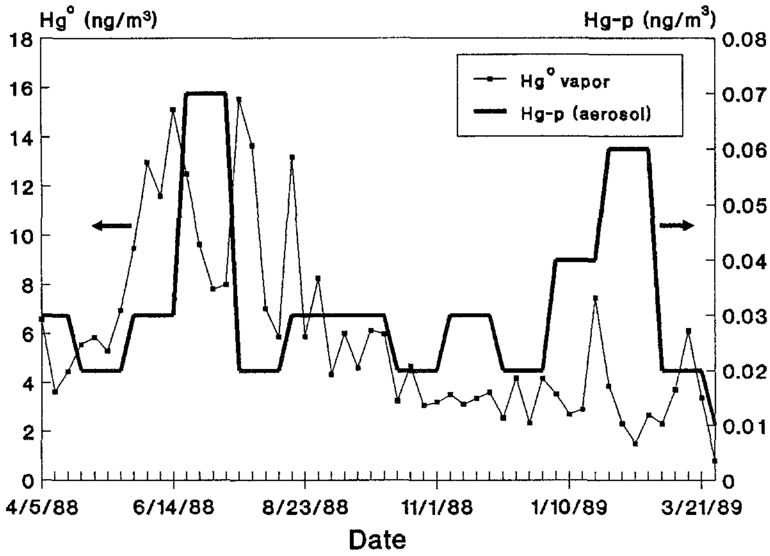

Figure 3. Temporal trends in the measured air concentrations of Hg° vapor and particle-associated Hg (Hg-p) for the year April 1988 to March 1989 at Walker Branch Watershed. The values represent weekly means for Hg° and monthly means for Hg-p.

The Hg° data at Walker Branch from the summers of 1988 and 1989 provide an interesting comparison which may reflect the influence of local climate conditions on airborne Hg°, as well as the influence of the operating status of the nearby coal-fired steam plant. For the period April - August 1988, the mean concentration of Hg° at Walker Branch was 8.8 ng m^{-3} (SE=0.8), while the mean concentration for the same period in 1989 was significantly ($P<0.01$) lower (5.1 ng m^{-3}, SE=0.4). Summer 1988 was marked by dry, hot weather, during a record two-year drought in the southeastern U.S. The total rainfall was 37 cm, and the monthly mean air temperature was 21° C. The drought ended in early 1989, which was marked by cooler weather and above-average rainfall. For April - August, 1989 rain totaled 72 cm, and the monthly mean air temperature was 19° C. These climatic conditions in 1989, plus the conversion of the nearby steam plant to natural gas in December 1988, may partially the lower levels of Hg° during 1989. Higher rainfall and lower temperatures may lead to reduced soil emissions of volatile Hg°. The influence of the steam plant conversion from coal to gas cannot be separated from the climatic influence, but the facility is expected to have its greatest impact at Walker Branch during the colder months, and not during summer.

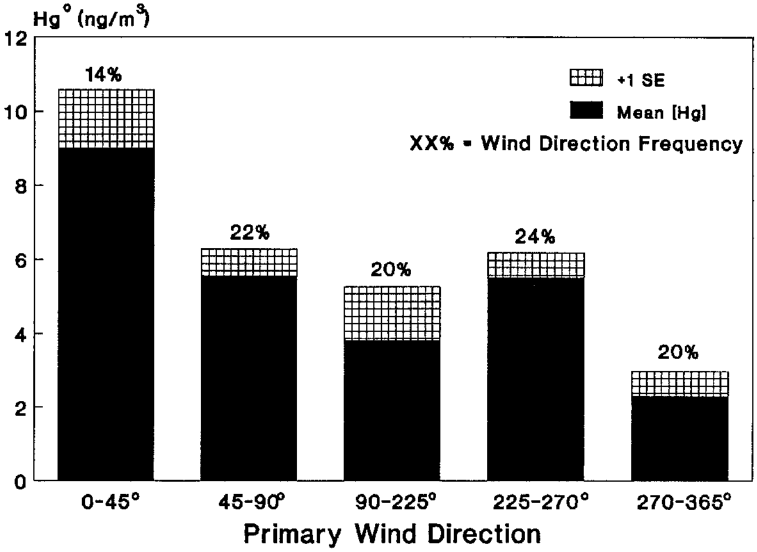

Figure 4. The influence of primary wind direction sector on the weekly mean concentration of Hg° in air at Walker Branch Watershed for the year April 1988 to March 1989. (SE = standard error).

3.2 COMPUTING THE DRY DEPOSITION OF AIRBORNE Hg

There have been only limited studies of the plant physiological processes which control the air/surface exchange of Hg°. Based on the early work of Fang and co-workers (Du and Fang, 1982; Browne and Fang, 1978), it appears that the dry deposition of Hg° vapor to plant canopies is governed almost exclusively by the leaf's physiology and biochemistry. The principal site of Hg° deposition is probably tissues of the leaf interior, indicating a dominant role for processes controlling gas exchange at the leaf surface via stomata, and Hg assimilation at the gas-liquid interface within the leaf mesophyll. These observations are consistent with the limited water solubility of Hg° (Sanemasa, 1975), and suggest very low deposition velocities (V_d) for Hg° to plant canopies. The few experimental measurements of V_d for Hg° which have been published support this idea. Barton *et al.*, (1981) reported values in the range 0.06 to 0.1 cm s^{-1} for a tall grass canopy based on gradient measurements in the field, and values of 0.03 to 0.1 cm s^{-1} can be derived for an alfalfa canopy from the chamber studies of Lindberg *et al.*, (1979).

We have recently modified the "big leaf" multiple resistance model of Hicks *et al.*, (1987) to infer hourly mean dry deposition velocities for Hg° (Lindberg *et al.*, in review). These values have been used with the weekly mean air concentration data to estimate the long-term dry deposition of Hg° to the deciduous forest at Walker Branch. Hourly meteorological data for each sampling period were used with canopy structure measurements (leaf area index and its distribution with height) to estimate the aerodynamic, boundary layer, and canopy resistance terms, which then were used to compute the mean total resistance and its reciprocal, V_d. The work of Fang and co-workers suggests that the dry deposition of Hg° is predominantly controlled by the overall leaf resistance (R_l), which consists of stomatal (R_s), cuticular (R_{cut}), and mesophyll resistances (R_m). R_s was modeled by analogy with molecular diffusion of water vapor through stomates, corrected for the molecular diffusivity of Hg° (Mikhailov and Kochegarova, 1967), while R_m was modeled from the temperature response curves of Du and Fang (1982). A value for R_{cut} was also deduced from Browne and Fang (1978). R_l was scaled to the full canopy using seasonally measured values of the Walker Branch forest leaf area as described in Hicks *et al.*, (1987). A parallel soil resistance (R_{soil}) was deduced from limited flux chamber measurements on forest soils in Sweden (Xiao *et al.*, 1990). Details on the modifications of the model for Hg° and estimation of the terms R_s, R_{cut}, R_m, and R_{soil} for Hg° are given in Lindberg *et al.*, (in review).

The values of V_d for Hg° derived from the resistance model were small, as expected. Weekly mean values increased from a winter minimum of 0.006 cm s^{-1} to 0.02 cm s^{-1} in early summer, then reached a maximum of 0.10 to 0.12 cm s^{-1} for several weeks in mid summer. The influence of stomatal response to light on the modeled hourly V_d's is clearly shown in Figure 5, which illustrates the diurnal cycles in V_d for a typical summer week in June. The importance of the mesophyll resistance for Hg° can be seen by comparison with the modeled values of V_d for SO_2 in Fig. 5. SO_2 has a molecular diffusivity similar to that of Hg°, and the model assumes that SO_2 exhibits a mesophyll resistance of zero. Our sensitivity tests of the resistance model for Hg° indicated that V_d was most sensitive to the inclusion of a non-zero R_m, that air temperature had an important influence on daytime V_d via its control over R_m, and that the modeled V_d was relatively insensitive to the very limited range of published experimental values that could be assigned to R_{cut}, R_m, and R_{soil} (Lindberg *et al.*, in review).

Aerosol Hg, which generally comprises less than ~5% of total airborne Hg (Schroeder and Jackson, 1987) and exists primarily in the fine fraction (Lindqvist *et al.*, 1984), is dry deposited to foliage by eddy diffusion, a process which may be traced using natural radionuclides such as ^{214}Pb. We used the air/vegetation transfer model of Bondietti *et al.*, (1984) with seasonal measurements of foliar biomass to estimate weekly mean V_d values for fine aerosol Hg (Lindberg *et al.*, in review). These values were generally in the same range as those for Hg°. During the forest growing season, the mean V_d

for aerosol Hg was 0.087 cm s^{-1} (range 0.02 to 0.11), while during the dormant period the mean was 0.003 cm s^{-1}.

It is important to note that if other, more soluble, vapor phase Hg species such as $HgCl_2$ exist, they may exhibit more efficient removal by dry deposition. Highly soluble atmospheric vapors are more surface reactive than Hg°, and are not as strongly controlled by the stomatal and mesophyll pathways. Such species (e.g. HNO_3 vapor) can exhibit large values of V_d, being controlled primarily by aerodynamic resistance (Meyers *et al.*, 1989). If soluble, gas-phase Hg-II compounds actually exist and exhibit a significant lifetime in the troposphere, they may dominate Hg dry deposition. Similarly, moisture films at the leaf surface are known to enhance the dry deposition of some gases (e.g. SO_2, Meyers and Baldocchi, 1988). If Hg° is oxidized in the aqueous phase at the leaf surface (e.g., Iverfeldt and Lindqvist, 1986), this could also result in a net increase in its dry deposition to foliage. It is beyond the scope of this paper to consider the fluxes by these alternative pathways, and for the purposes of this discussion we will assume that Hg vapor dry deposition is dominated by plant uptake of Hg°.

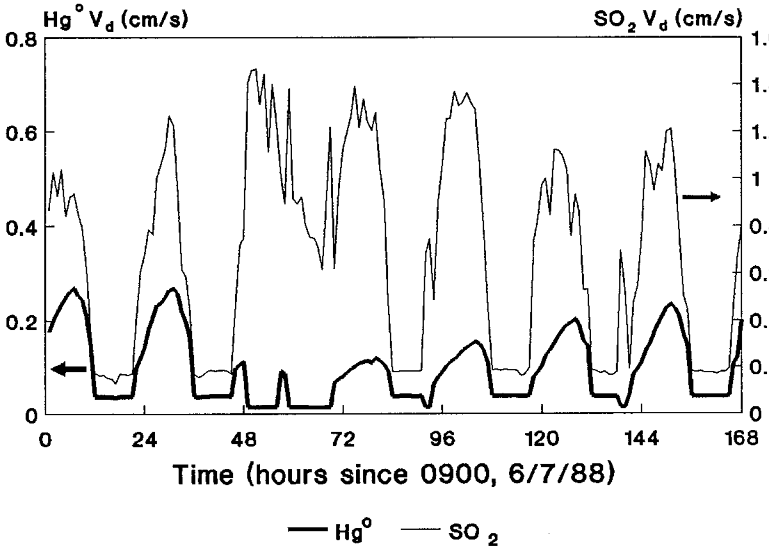

Figure 5. Modeled values of dry deposition velocities (V_d) for Hg° vapor and for SO_2 to the deciduous forest canopy at Walker Branch Watershed. These values represent hourly mean V_d's computed for the period June 6-14, 1988.

3.3 ESTIMATES OF SEASONAL AND ANNUAL DEPOSITION TO THE WALKER BRANCH FOREST

The seasonal trend in the modeled V_d for Hg° (Figure 6) exhibited a similar pattern as that shown by the concentration of airborne Hg° (Figure 3). This resulted in a strong seasonal cycle in the dry deposition of Hg° as well (Figure 6). Weekly winter fluxes averaged ~0.03 μg m^{-2} wk^{-1} (~4 ng m^{-2} d^{-1}). Summer fluxes were significantly higher, and more variable, averaging ~1 μg m^{-2} wk^{-1} (~140 ng m^{-2} d^{-1}) in mid-summer and ranging over a factor of three from week-to-week. Most of the variance in summer dry deposition rates (>90%) was explained by the variance in weekly mean summer air concentrations of Hg°, which were more variable than were the weekly mean values of V_d. Overall, aerosol Hg contributed an insignificant portion of the total Hg dry deposition because of its low air concentration. Its contribution to the total dry deposition ranged from 0.1 to 1.5%.

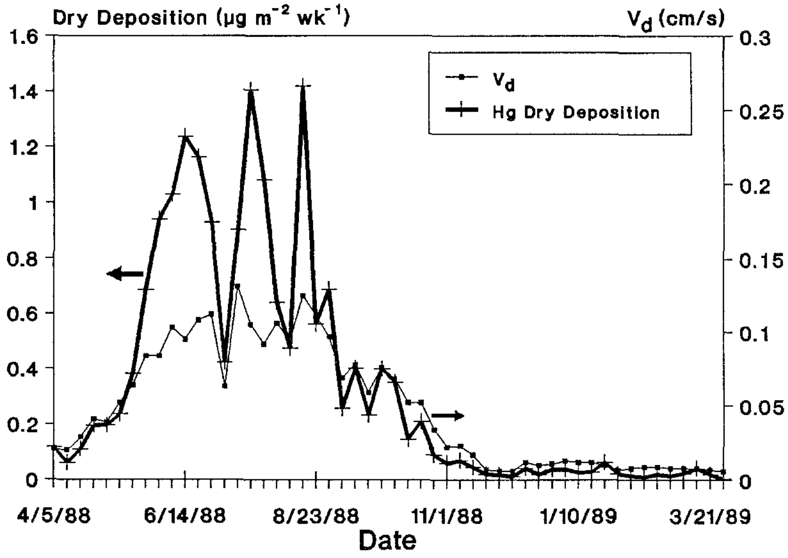

Figure 6. Temporal trends in the modeled weekly mean dry deposition velocities (V_d) for Hg° vapor and in the computed dry deposition rates of airborne Hg to the deciduous forest at Walker Branch Watershed for the year April 1988 to March 1989.

Summing the estimates of weekly fluxes yields an estimate of the annual dry deposition of Hg on the order of 20 μg m^{-2} y^{-1} for the period 4/88-3/89 (a mean flux of ~50 ng m^{-2} d^{-1}). It appears that aerosol dry deposition contributed less than 0.5% of the total flux. Over 90% of the input occurred during the summer growing season (April through October) when both air concentrations and modeled deposition velocities were highest. It is difficult to place an uncertainty on our calculated fluxes because of the nature of the assumptions involved in the model. The overall sampling and analytical uncertainty in the concentration of airborne Hg was <10%, but this is negligible compared to the uncertainty in the modeled V_d values which we estimated to be about a factor of 2 based on model sensitivity tests (Lindberg *et al*, in review). This would yield an overall range in estimated annual dry deposition to this forest of ~10 - 40 μg m^{-2} y^{-1}.

During the period June-August, 1989, we performed limited sampling of precipitation at Walker Branch, collecting three large-volume events comprising ~25% of the total 3-mo rainfall of 49.6 cm. The concentrations in these samples ranged from 1-5 ng L^{-1}, and the weighted mean concentration was ~3 ng L^{-1}. We estimate that the wet deposition of Hg at this forest was on the order of 1-2 μg m^{-2} for this period. Because we sampled relatively large events (the mean rainfall volume sampled was ~4 cm) and only 25% of the total precipitation, this estimate must be considered a rough approximation. It may also be a conservative estimate because of the typical inverse relationship between rain volume and metal concentrations (Lindberg, 1982), including Hg (Lindberg and Harriss, 1985). Based on the air concentration data in Figure 1 and dry deposition model runs for June - August 1989, the estimated dry deposition of Hg° was ~6 μg m^{-2} for this period. Thus, dry deposition could have been the dominant pathway of air to ground transport in this forest during the summer of 1989, contributing over 70% of the total atmospheric deposition of Hg.

There are limited published data with which to compare our estimates. Total dissolved Hg concentrations in unpolluted rain water are considered to be in the range of 2 to 10 ng L^{-1} (Fogg and Fitzgerald, 1979; Brosset, 1987), those in rain at rural sites are reported in the range <10 - 40 ng L^{-1} (Iverfeldt and Rodhe, 1988; Glass *et al.*, 1988), while those in urban or industrialized areas range from 10 to 85 ng L^{-1} (Lindqvist *et al.*, 1984). Wet deposition was reported to be 10 to 20 μg Hg m^{-2} y^{-1} in the Muskoka area of south-central Ontario (Canada) (Barton *et al.*, 1981; Mierle, 1990), and to average ~14 μg Hg m^{-2} y^{-1} at 9 sites in Scandinavia (Iverfeldt, 1990a). If these fluxes are representative of background continental locations, then the annual dry deposition of Hg at Walker Branch may be comparable in magnitude to that of wet deposition.

By comparison to wet deposition, experimental determination of dry deposition for atmospheric Hg is more difficult, and reliable values for dry deposition velocities or rates are scarce. For the Kobe area of Japan, Kobayashi (1984) reported seasonal mean dry deposition rates ranging from 12 to 27 ng m^{-2} d^{-1}, and an annual flux of ~7 μg Hg m^{-2} y^{-1}. Total annual input at this high rainfall site was dominated by wet deposition (~40 μg Hg m^{-2} y^{-1}; annual rainfall = 146 cm). Barton *et al.*, (1981) estimated Hg° dry deposition from measured gradients over a grassy field near Muskoka, Ontario to be in the range of ~40-100 μg Hg m^{-2} y^{-1}. Compared to wet deposition (~20 μg Hg m^{-2} y^{-1}), dry deposition was the dominant input process. Kobayashi (1984) summarized mean total (wet plus dry) deposition rates reported for 10 different locations, which ranged from 0.055 μg m^{-2} d^{-1} in Greenland to 0.67 μg m^{-2} d^{-1} in Wraymires, UK. However, most of the values were in the range of ~0.08 to 0.15 μg m^{-2} d^{-1} (~20 to 50 μg Hg m^{-2} y^{-1}), comparable to our estimates of total deposition for Walker Branch.

Our dry deposition estimates represent atmospheric fluxes in the downward direction, but upward fluxes of Hg° occur simultaneously in forests, most probably originating from the soil (e.g. Xiao *et al.*, 1990). We measured gradients in Hg° concentrations at this site during four experiments in 1989 (Lindberg *et al.*, in review). In each case, the concentration of Hg° generally decreased with increasing height above the ground, suggesting the important effect of a ground-level source. Figure 7 illustrates the overall mean gradient in Hg° for several of the sampling periods, with concentrations expressed relative to the concentrations at an above-canopy reference level. These data indicate this forest to be a net source of Hg° to the overlying atmosphere, and

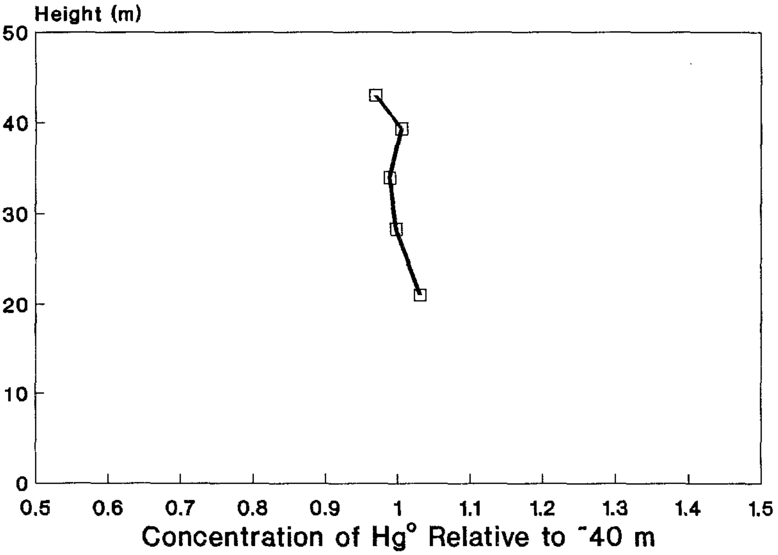

Figure 7. The mean gradient in the air concentration of Hg° within and above the deciduous forest canopy at Walker Branch Watershed from four experiments during the summer of 1989. The concentrations at each level have been expressed relative to the concentration measured at ~40 m. The mean air concentration of Hg° at ~40 m was 3.9 ng m^{-3} (σ = 1.1). The average canopy height surrounding this tower is 22-23 m.

not a net sink. This does not imply that dry deposition is not occurring, only that dry deposition over the periods of the gradient measurements was less than the emission of Hg° from the canopy/soil system, most likely the soil.

The slopes of these gradients were very small, and near the precision of the overall sampling and analytical process for Hg° (the mean relative gradient from below to above the canopy was ~12%). However, the trends were consistent over several experiments. We applied a modified version of the micro-environment turbulence model for the forest canopy at Walker Branch (Meyers and Baldocchi, 1988) to model the measured gradients. This allowed separation and quantification of the canopy exchange and soil emission rates, and yielded V_d values for Hg° at 30m on the order of 0.1 cm s^{-1}, comparable to those described above. A detailed interpretation of the gradients and the modeling results of the deposition/emission process, are presented in Lindberg *et al.*, (in review).

4. Summary and Implications

Our atmospheric data from Walker Branch suggest that the near-background concentrations of atmospheric Hg° at this continental site display a strong seasonal cycle, possibly in response to surface temperature. These concentrations are also influenced by local sources to some extent. Aerosol Hg does not show the same trends, and is only a very minor component of the atmospheric burden. The multiple resistance model yielded dry deposition velocities (V_d) for Hg° to the forest canopy at Walker Branch which were generally low. Hourly values of V_d were in the range of 0.1 to 0.3 cm s^{-1} during optimum summer daylight conditions, averaging ~0.1 cm s^{-1} during mid-summer. The seasonal cycles in both V_d and the concentrations of Hg° resulted in significantly higher dry deposition of Hg during the summer months. Based on limited samples of precipitation, we speculate that dry deposition dominates the atmospheric flux of Hg to this forest during the summer months. The few published data available (generally from the early 1980's) indicate that, on an annual basis, the rate of Hg dry deposition is a highly variable fraction of total input, but that wet and dry deposition are of the same magnitude. A similar conclusion was reached by Iverfeldt (1990b) based on more recent data from Sweden.

As a result in the increased interest in the biogeochemical cycling of Hg in the environment, the knowledge base on the behavior of this element has improved significantly in recent years. However, understanding the factors influencing its cycling between the troposphere and the Earth's surface remains a major research need. There are a number of specific research needs in this field before we fully understand the dry deposition process and its role in the biogeochemical cycle of Hg. Further physiological studies of Hg exchange mechanisms at the leaf level are needed with forest species. These should include research on factors which control the leaf uptake of Hg°, as well as other Hg species, both external and internal to the leaf or needle. Field studies of Hg accumulation and fate in foliage and of Hg fluxes in throughfall are also necessary to understand the behavior of Hg deposited to plant canopies. The existence of transient atmospheric vapor species of Hg-II which exhibit high solubility must also be confirmed. These species may control dry deposition fluxes under some conditions. Similarly, the ability of Hg° to be oxidized to more soluble Hg-II species directly on canopy surfaces must be understood to fully appreciate the overall pathway of Hg dry deposition. Finally, the problem of co-occurring upward and downward fluxes of Hg in forests confuses the already difficult issue of quantifying the sink strength of forests. The degree to which downward fluxes are balanced by soil emissions, and the role of internal cycles of Hg° emitted from the soil but dry deposited to the canopy must be quantified in order to develop accurate balances of Hg in forested catchments.

The data reported here have some interesting implications for the role of possible changes in the Earth's physical and chemical climate on the tropospheric cycle of Hg. The atmospheric concentration of Hg° at this site appears to be strongly related to air temperature, suggesting the importance of surface soil emissions. A similar relationship may exist between the dry deposition of Hg° and air temperature, with modeled dry deposition velocities increasing with temperature due the strong physiological control over the mesophyll pathway for uptake of Hg° (Du and Fang, 1982). If these relationships are universal, a general increase in global temperature would have profound implications on the global biogeochemical cycle of Hg, possibly resulting in increased rates of transfer of Hg from the geosphere to the biosphere. Because of the unique chemistry of Hg and its compounds, it is clearly among those trace metals whose cycling is sensitive to global change.

5. References

Barton, S.C., Johnson, N.D., and Christison, J.: 1981, Atmospheric mercury deposition in Ontario. Proc. Air Pollut. Control. Assoc. 74th Annual Meeting, Paper JAPCA 81-60.4. Philadelphia, June 21-26, 1981.

Bondietti E.A., Hoffman, F.O., and Larsen, I.L.: 1984, J. Environ. Radioact. 1,5.

Brosset, C.: 1982, Water, Air, Soil, Pollut. 17,37.

Brosset, C.: 1987, Water, Air, Soil Pollut. **34**,145.

Browne, C.L. and Fang, S.C.: 1978, Plant Physiology **61**,430.

Du, S. and Fang, S.C. 1982. Uptake of elemental mercury vapor by C_3 and C_4 species. Environmental and Experimental Botany **22**:437-443.

Fogg, T.R. and Fitzgerald, W.F. 1979. Mercury in Southern New England Coastal Rains. J. Geophys. Res. **84**:6987-6989.

Glass, G., Leonard, E.N., Chan, W.H., and Orr, D.B. 1988. Airborne Mercury in Precipitation in the Lake Superior Region. J. Great Lakes Res. 12:37-51 (1988).

Hicks, B.B., Baldocchi, D.D., Meyers, T.P., Hosker, R.P. Jr, Matt, D.R. 1987. A preliminary multiple resistance routine for deriving deposition velocities from measured quantities. Water, Air, Soil, Pollut. **36**:311-330.

Iverfeldt, A., and Rodhe, H. 1988. Atmospheric Transport and Deposition of Mercury in the Nordic Countries. IVL Report No. L87/285; Swedish Environmental Research Institute, Box 47086, S-40258 Göteborg, Sweden.

Iverfeldt, A. 1990a. Occurrence and turnover of atmospheric Hg over the Nordic countries. (in preparation).

Iverfeldt, A. 1990b. Hg in canopy throughfall and its relation to atmospheric dry deposition. (in preparation).

Iverfeldt, A. and Lindqvist, A. 1986. Atmospheric oxidation of elemental Hg by ozone in the aqueous phase. Atmos. Envir. **20**:1567-1573.

Johnson, D. W. and Van Hook, R. I.: (Eds.). 1989, Analysis of Biogeochemical Cycling in Walker Branch Watershed, Springer-Verlag, Berlin.

Kobayashi, T.: 1984, Deposition of atmospheric mercury to the ground through the precipitation and the fallout -- A method for estimating the deposition rate of mercury. Reports of the Environmental Science Institute of Hyogo Prefecture. **16**,35.

Landa, E. R.: 1978, J. Environ. Qual 7,84.

Lindberg, S.E., Jackson, D.R., Huckabee, J.W., Janzen, S.A., Levin, M.J. and Lund, J.R.: 1979, J. Environ. Qual. **8**,572.

Lindberg, S.E., Stokes, P.M., Goldberg, E., and Wren, C.: 1987, Rapporteur's report on mercury. In T. C. Hutchinson and K. Meema (Eds.), Lead, Cadmium, and Mercury in the Environment, United Nations Scientific Committee on Problems in the Environment Series, John Wiley, NY, p. 17-34.

Lindberg, S.E.: 1982, Atmos. Environ. **16**,1701.

Lindberg, S.E. and Harris, R.C.: 1985, Mercury in rain and throughfall in a tropical rain forest. Proceedings Fifth International Conference on Heavy Metals in the Environment, CEP Consultants Ltd. Publishers, Edinburgh, UK, Vol. 1, 527-529.

Lindberg, S.E. , Harriss, R.C., and Turner, R.R.: 1982, Science **215**, 1609.

Lindberg, S.E.: 1981, Atmos. Environ. **15**, 631.

Lindberg, S.E., Lovett, G.M., Richter D.R., and Johnson, D.W.: 1986, Science **231**, 141.

Lindberg, S. E.: 1980, Atmos. Environ. **14**, 227.

Lindberg, S.E., Meyers, T.P., Taylor, G.E., Turner, R.R., and Schroeder, W.H. Atmosphere/surface exchange of mercury in a forest: Results of modeling and gradient approaches. J. Geophys. Res. (in review).

Lindqvist, O., Jernelov, A., Johansson, K., and Rodhe, H.: 1984, Mercury in the swedish Environment -- Global and Local Sources. SNV Report no. 1816; Swedish Environmental Protection Board, Box 13021, S-17125, Solna, Sweden.

Meyers, T.P., Huebert, B.J., and Hicks, B.B.: 1989, Boundary-Layer Meteor. **49**, 395.

Meyers, T.P., and Baldocchi, D.D.: 1988, Tellus, **40B**, 270.

Mierle, G.: 1990, Aqueous Inputs of Mercury to Precambrian Shield Lakes in Ontario. Environ. Toxicol. Chem. in press.

Mikhailov, V.K. and Kochegarova, M.I.: 1967, Chem. Abstr. **69**, 5777.

Ottar, B., Lindberg, S.E., Voldner, E., Lindqvist, O., Mayer, R., Steinnes, E., and Watt, J.: 1989, Special topics concerning interactions of heavy metals with the environment. In Pacyna, J. and Ottar, B. (Eds.). Control and Fate of Atmospheric Trace Metals, NATO Advanced Science Institute Series, Kluwer Academic Publishers, Dordrecht, Holland, pp. 365-372.

Sanemasa, I.: 1975, Bull. Chem. Soc. Japan **48**, 1795.

Schroeder, W.H. and Jackson, R.A.: 1987, Chemosphere **16**, 182.

Schroeder, W.H., Munthe, J., and Lindqvist O.: 1989, Water, Air, Soil Pollut. **48**, 337.

Turner, R.R., Bogle, M.A., Heidel, L., and McCain, L.: 1989, Mercury in ambient air at the Oak Ridge Y-12 plant July 1986 through April 1987. Laboratory Technical Report Number YTS-574 (in press).

Xiao, Z.F., Munthe, J., Schroeder, W.H., and Lindqvist, O.: 1990, The transfer of mercury between the atmosphere and lake or soil surfaces. In Ross, H.B. (Ed.), Proc. Nordic Symposium on Atmospheric Chemistry. Report CM-78, University of Stockholm, March, 1990.