

MERCURY AIR/SURFACE EXCHANGE KINETICS OF BACKGROUND SOILS OF THE TAHQUAMENON RIVER WATERSHED IN THE MICHIGAN UPPER PENINSULA*

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Abstract. Air/surface exchange of mercury was investigated over background soils at five sites in the Tahquamenon River watershed in the Michigan Upper Peninsula in the summer of 1998. Measurements of Hg fluxes were performed during midday periods using the ORNL Teflon dynamic flux chamber. Mean Hg emission fluxes were 1.4 ± 0.3 – 2.4 ± 1.0 $\text{ng m}^{-2} \text{hr}^{-1}$ for three shaded forest sites and 7.6 ± 1.7 $\text{ng m}^{-2} \text{hr}^{-1}$ for an open field site. Hg dry deposition was observed at a heavily shaded forest site over wet soils (mean = -0.3 ± 0.2 $\text{ng m}^{-2} \text{hr}^{-1}$). The overall mean Hg flux was 1.4 ± 1.4 $\text{ng m}^{-2} \text{hr}^{-1}$ for the four shaded forest sites. The Hg fluxes observed at these sites are similar to those found at other northern background sites. Significant, rapid response of Hg emission to solar radiation was observed over these background soils. Artificial irrigation over these soils induced immediate and measurable increases in Hg emission. Soil temperature was found to be less influential to Hg air/surface exchange over these heavily shaded forest background soils than we have seen elsewhere.

Keywords: atmosphere, biogeochemical cycling, deposition, dynamic flux chamber, emission, forest, photochemistry

1. Introduction

Terrestrial surfaces are unequivocally important in mercury cycling between the atmosphere and the Earth's surface (Lindberg, 1996). Investigation into Hg air/terrestrial surface exchange, therefore, is critical to our construction of regional and global Hg budgets and to our understanding and modeling of Hg cycling on various scales. Field measurements of Hg air/soil surface exchange have been increasing in this decade, revealing the essential roles of soils in Hg regional and global cycling (Kim *et al.*, 1997; Carpi and Lindberg, 1998; Zhang and Lindberg, 1999). Soils naturally enriched with Hg have been considered to be important sources contributing to the atmospheric Hg load (Rasmussen, 1994; Gustin *et al.*, 1996). The latest field investigations indicate that these natural sources may be comparable to the anthropogenic sources in their impacts on regional and global atmospheric

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Hg pools (Gustin *et al.*, 1999a). Yet, our knowledge of Hg air/surface exchange at background soils (commonly $<0.5 \mu\text{g total Hg g}^{-1}$ soil) still remains insufficient. In particular, there has been a lack of the knowledge about background forest soils in the northern United States. The construction of regional and global Hg budgets can be compromised without a sophisticated knowledge of Hg exchange at background soils, including surface exchange kinetics, environmental factors, and physicochemical processes of Hg transformation and transportation in the soils.

As a joint field study by ORNL and UMI in the summer of 1998, the Lake Superior Mercury Air/Surface Exchange Project (LS-MASE) was aimed at estimation of Hg emission and deposition in the Lake Superior region. Hg air/surface exchanges were measured over the background soils of the Tahquamenon River watershed in the Michigan Upper Peninsula. Environmental factors affecting the exchange such as soil temperature, solar radiation, and precipitation were also investigated. This article reports the results of these measurements and studies, with comparison with previous data obtained over other background soils.

2. Sites and Methods

2.1. SITES AND SOILS

The field sites were located in the Tahquamenon River watershed in the Michigan Upper Peninsula (Chippewa County and Luce County, MI). Forested at both banks, the Tahquamenon river (~ 151 km long, discharging into the Whitefish Bay) drains an area of more than 2124 km^2 , a large proportion of which consists of wetlands, mostly various bogs. Two forest sites (the hardwood site and the pine site) and one open field site were chosen across the watershed, and two forest sites (the Upper Falls site ~ 1 km away from the river and the river mouth site ~ 1.5 km away from the Tahquamenon mouth) were chosen along the Tahquamenon river (Figure 1).

The hardwood site was in a hardwood forest with a well-closed canopy, dominated by beach, birch, spruce, and maple trees. The soil at this site is Rousseau fine sand (0–6% slope), which is located on upland flats, very deep and well drained. The pine site was in a pine forest with a moderately-closed canopy. The soil at this site is Deer Park fine sand (0–6% slope), an upland soil, very deep and excessively drained. The Upper Falls site was in a pristine forest with a well-closed canopy. The soil at this site is Alcona loamy fine sand (0–6% slope), well drained or moderately well drained. This soil typically has a litter layer ~ 3 – 4 cm thick, a surface covered by ~ 2.5 cm of undecomposed hardwood leaf litter. The site at the Tahquamenon River mouth was located in a secondary forest with a moderately-closed canopy. The soil at this site is Wainola fine sand (0–3% slope), an upland soil, very deep and somewhat poorly drained. The open field site is a cleared land currently covered with grass ~ 10 – 20 cm high. The soil at this site is the same as that at the pine site. A detailed soil description for each site can be referred to elsewhere (SCS USDA, 1990). Table I summarizes the descriptions of the sites and soils in this study.

TABLE I
General information of field sites and soils

| Data | Site | Location | County | Site description | Major vegetation | Soil | Total Hg ^b ($\mu\text{g g}^{-1}$ soil) |
|------|----------------------------------|------------------------------|----------|------------------|--------------------------------|---|---|
| 6/19 | Hardwood | In upland of the watershed | Chippewa | Forest, shaded | Beach, birch, maple, spruce | Rousseau fine sand dark soil, 0–6% slope | 0.069 (0–5 cm) 0.004 (5–8 cm) |
| 6/21 | Pine | In upland of the watershed | Chippewa | Forest, shaded | Pine | Deer Park-Kinross complex, 0–50% slope | 0.098 (0–2 cm) 0.006 (2–4 cm) |
| 6/24 | Upper Falls | ~1 km away from Taq. River | Luce | Forest, shaded | Beach, birch Maple, spruce | Wainola fine sand, 0–3% slope | <0.1 |
| 6/26 | Taq. ^a River mouth | ~1.5 km away from Taq. River | Chippewa | Forest, shaded | Mixed trees | Kinross-Wainola complex, 0–3% slope | <0.1 |
| 6/20 | Open field | In upland of the watershed | Chippewa | Open field | Grass, 10–20 cm | Deer Park fine sand 0–15% slope | 0.016 (0–3 cm) |

^a Taq.: Tahquamenon.

^b Total Hg in the soil samples was determined in Air Quality Laboratory of University of Michigan following the protocol detailed in Rea and Keeler (1998).

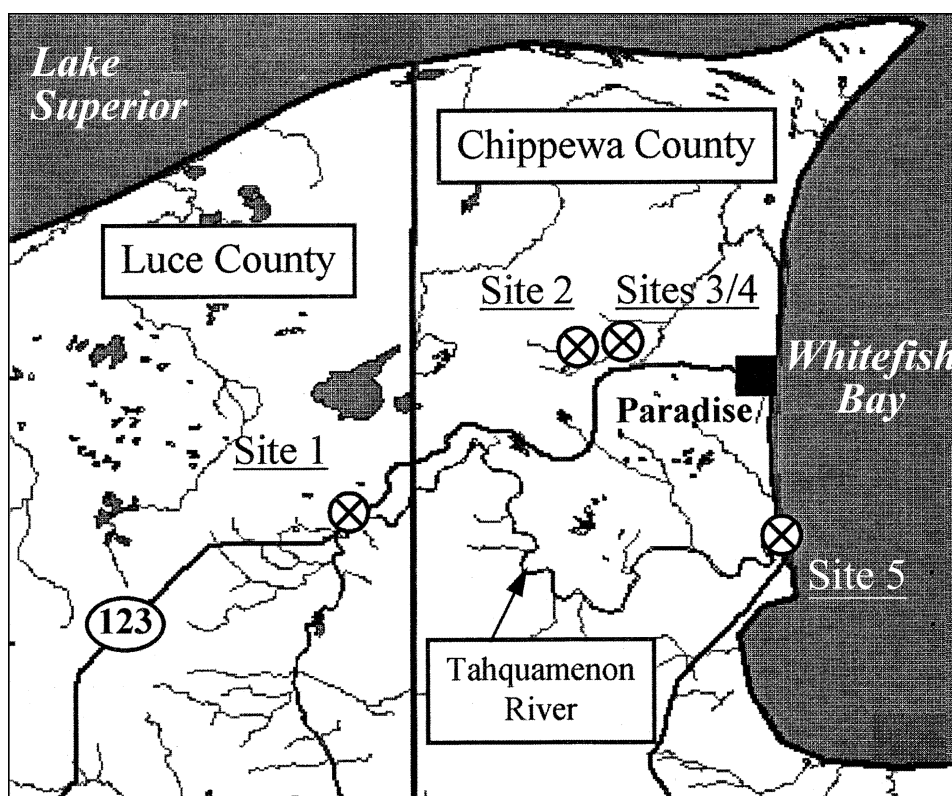


Figure 1. General site map for the Hg air/surface exchange study in the Tahquamenon River watershed in the Michigan Upper Peninsula in the summer of 1998 (Site 1: the Upper Falls site, Site 2: the pine site, Site 3: the open field site, Site 4: the hardwood site, and Site 5: the site at the Tahquamenon River mouth).

2.2. METHOD FOR FIELD MEASUREMENT OF SOIL Hg FLUX

Field measurements of Hg air/surface exchange kinetics were performed generally during daytime using the ORNL Teflon dynamic flux chamber (ORNL TFC) (dimension = $20 \times 60 \times 20$ cm³, $V = 0.024$ m³, surface area covered by TFC (footprint) $A = 0.12$ m²). Its design and performance along with the procedures for measuring Hg emission fluxes over soils were detailed elsewhere (Carpi and Lindberg, 1998). Ambient air was pulled through the TFC at a constant flow (Q) (total sweep gas flow rate $Q = 6$ L min⁻¹) using a mass flow controller/pump system to deliver a fraction of the emitted Hg to a Tekran automated mercury analyzer (sampling flow rate = 1.5 L min⁻¹, each air sampling time = 5 min). Both inlet (C_i) and outlet (C_o) Hg concentrations were continuously monitored alternatively by the Tekran Automated Dual Sampling System (TADS) method (Lindberg and Price, 1999). A

TABLE II

Hg concentrations (ng m^{-3}) of the air near ground (5–8 cm above) at different sites

| Site | Min. | Max. | Mean | S.D. | n |
|-------------------------|------|------|------|------|----|
| Hardwood | 2.1 | 2.2 | 2.1 | 0.08 | 7 |
| Pine | 2.0 | 2.9 | 2.4 | 0.30 | 16 |
| Upper Falls | 1.2 | 1.4 | 1.3 | 0.06 | 16 |
| Tahquamenon River mouth | 1.3 | 1.6 | 1.4 | 0.09 | 10 |
| Open field | 1.8 | 3.1 | 2.4 | 0.40 | 9 |

10 min-average of C_o (two 5-min samples) and a 10 min-average of C_i (two 5-min samples) were used to obtain a 20 min-averaged Hg flux (F) by Equation (1):

$$F = (C_o - C_i)Q/A \quad (1)$$

The blank of the new ORNL TFC used for these soil Hg flux measurements was tested in the field for a period of ~ 70 min both in shade and in the sun. The blank in shade ($1.6 \pm 0.7 \text{ ng m}^{-2} \text{ hr}^{-1}$) was close to that in the sun ($1.1 \pm 0.3 \text{ ng m}^{-2} \text{ hr}^{-1}$). The overall mean blank was $1.4 \pm 0.7 \text{ ng m}^{-2} \text{ hr}^{-1}$ and the blank was observed to be decreasing with time (by $\sim 50\%$ over a period of 35 min). Limited time in the field for sampling prevented us from obtaining more extensive data. Nevertheless, the blank of another new ORNL TFC of the same material was extensively tested before and a very low blank ($0.43 \pm 1.68 \text{ ng m}^{-2} \text{ hr}^{-1}$, where 1.68 is the 90% C.I.) was found during the first month of use (Carpi and Lindberg, 1998). Since more extensive FC blank data were not available for this study, since a new ORNL TFC was used, and since the blank is not statistically different from zero, the Hg fluxes reported here were therefore not corrected for the blank. This is consistent with our earlier studies (Kim and Lindberg, 1995; Carpi and Lindberg, 1998). Some Hg air/soil exchange events observed in this study could be interpreted as deposition if correction for the blank is made. Soil temperatures were manually measured at soil surface (~ 0 –2 cm). Total global solar radiation (R_g) was manually measured with a Li-Cor photometer.

3. Results and Discussion

3.1. TOTAL GASEOUS Hg CONCENTRATIONS OF THE AIR NEAR SOIL SURFACE

Table II summarizes the air Hg concentrations near soil surface (~ 5 –8 cm above ground) at the five background sites studied. Mean air Hg concentrations ranged

from 1.3 to 2.4 ng m⁻³. The mean concentrations at different sites correlated well with mean soil temperatures ($R^2 = 0.71$, not shown), suggesting that these background soils still functioned as moderate Hg sources, which influenced the air Hg level near the ground. This is supported by the positive correlation between mean air Hg concentrations and mean Hg fluxes at the five different sites ($R^2 = 0.52$, not shown). The R^2 value would be higher ($R^2 = 0.67$) if the data for the open field site is excluded. This could be due to the higher fluxes induced by higher solar radiation over the open field site.

3.2. Hg AIR/SURFACE EXCHANGE KINETICS AT THE FOREST SITES

Table III summarizes the Hg fluxes together with soil temperature and solar radiation at the five different sites monitored during midday periods, while Figures 2a–d and 3a show the Hg air/surface exchange kinetics at each site, respectively. Mean Hg fluxes ranged from -0.2 ± 0.3 to 2.4 ± 1.0 ng m⁻² hr⁻¹ at the four forest sites, and the overall mean fluxes for these sites was 1.4 ± 1.4 ng m⁻² hr⁻¹. These are extremely low fluxes, indicating that the soils studied in the Tahquamenon River watershed are background soils generally with very low contents of Hg. These fluxes were measured below the forest canopy where the solar radiation was significantly limited (Table III). Hence, they are considered as shaded background soil fluxes (e.g., Carpi and Lindberg, 1998). The fluxes at the forest sites were found to be almost the same at noon as in the early evening (Figures 2a–d).

The magnitudes of the fluxes at these background soils are consistent with the magnitudes of total Hg contents of these soils (Table I). Total Hg contents of the surface soils at these background sites were generally below 100 ng g⁻¹ soil, which are lower than those for the surface (humic) layers of background forest soils in Sweden (mean = 240 ng g⁻¹ soil, Lindqvist *et al.*, 1991), but higher than those for the background soils in southwest Siberia (mean = 45 ng g⁻¹ soil, Anoshin *et al.*, 1996). The higher Hg contents of the surface soils probably could be attributed to the presence of a rich organic horizon, which can strongly fix Hg (Lindberg and Harriss, 1974). The higher Hg content may also imply accumulation of deposited Hg in surface soils. Total Hg contents of the sub-layers (frequently typical E horizons) were extremely low, generally below 6 ng g⁻¹ soil (Table I), suggesting substantial removal of Hg from these layers (e.g. by eluviation).

The fluxes at the hardwood site (mean = 2.2 ng m⁻² hr⁻¹) were similar to those at the pine site (mean = 2.4 ng m⁻² hr⁻¹), fluxes at two different pine plots ~10 m apart were almost identical (Figure 2b), and fluxes at the Tahquamenon River mouth site (mean = 1.4 ng m⁻² hr⁻¹) were generally lower than those at the hardwood and pine sites (Table III). Fluxes at the Upper Falls site were unique among all the measured sites (mean = -0.2 ng m⁻² hr⁻¹). Hg emission was nearly absent, and deposition appeared to dominate the flux pattern at this site during the study. The soil at this site was covered with a thick, wet litter layer. We have only occasionally measured airborne Hg uptake by soils in earlier studies, generally at

TABLE III
Mercury emission fluxes of soils of the Tahquamenon River Watershed

| Soil site | Data | Mean T_{soil} | S.D. (n) | Mean R_g^a | S.D. (n) | Flux | | | S.D. | n |
|---------------------------------|------|------------------------|----------|---------------|-----------------------|---|------|------|------|-----------------|
| | | | | | | Max. | Min. | Mean | | |
| | | (°C) | | | (W m^{-2}) | — ($\text{ng m}^{-2} \text{hr}^{-1}$) — | | | | |
| Hardwood site | 6/19 | — | — | 50 (31–70) | 23 (5) | 3.7 | 0.6 | 2.2 | 0.9 | 10 |
| Pine tree site | 6/21 | 19.4 (18.1–20.2) | 0.8 (14) | 155 (80–330) | 274 (10) | 3.5 | 1.7 | 2.4 | 1.0 | 12 ^c |
| Upper falls site | 6/24 | 13.8 (13.1–14.2) | 0.4 (11) | 31 (13–55) | 61 (14) | 0.6 | –0.6 | –0.2 | 0.3 | 16 |
| Taq. R. ^b mouth site | 6/26 | 17.2 (16.9–17.2) | 0.3 (9) | 57 (42–135) | 15 (11) | 1.7 | 1.1 | 1.4 | 0.3 | 9 |
| Open field | 6/20 | 25.6 (20.6–27.6) | 1.9 (10) | 502 (250–812) | 205 (8) | 10.2 | 5.0 | 7.6 | 1.7 | 10 ^d |
| | | | | | | 10.2 | 3.2 | 7.1 | 2.0 | 14 ^e |

^a R_g : Measured global solar radiation.

^b Taq. R.: Tahquamenon River.

^c Data excluding those with artificial irrigation.

^d Data excluding those in artificial shade.

^e All data including those in artificial shade.

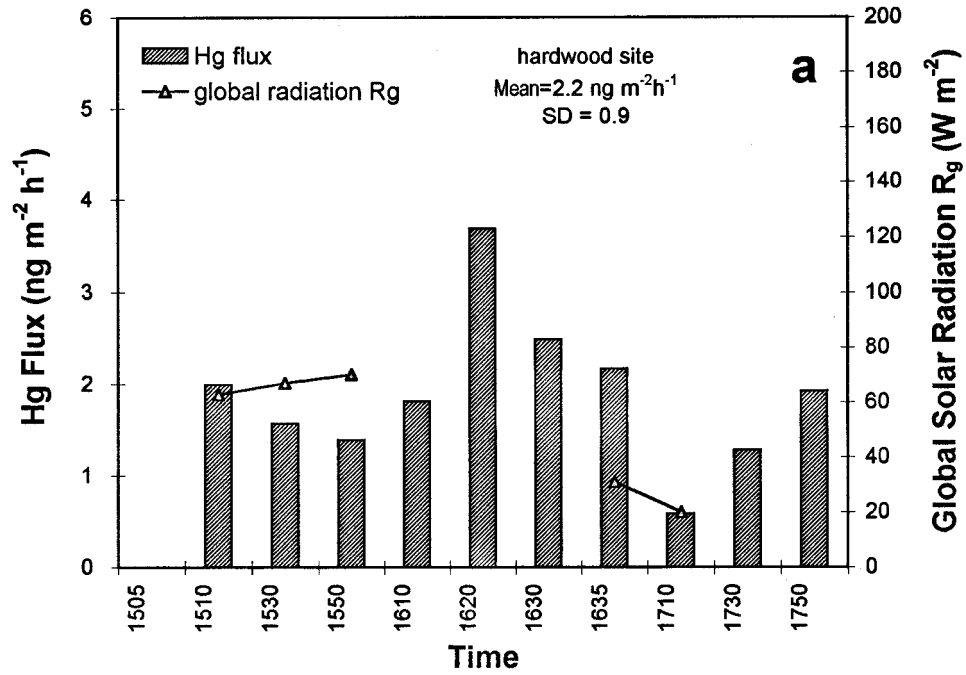


Figure 2a. Hg air/surface exchange kinetics and influence of environmental factors at the hardwood site.

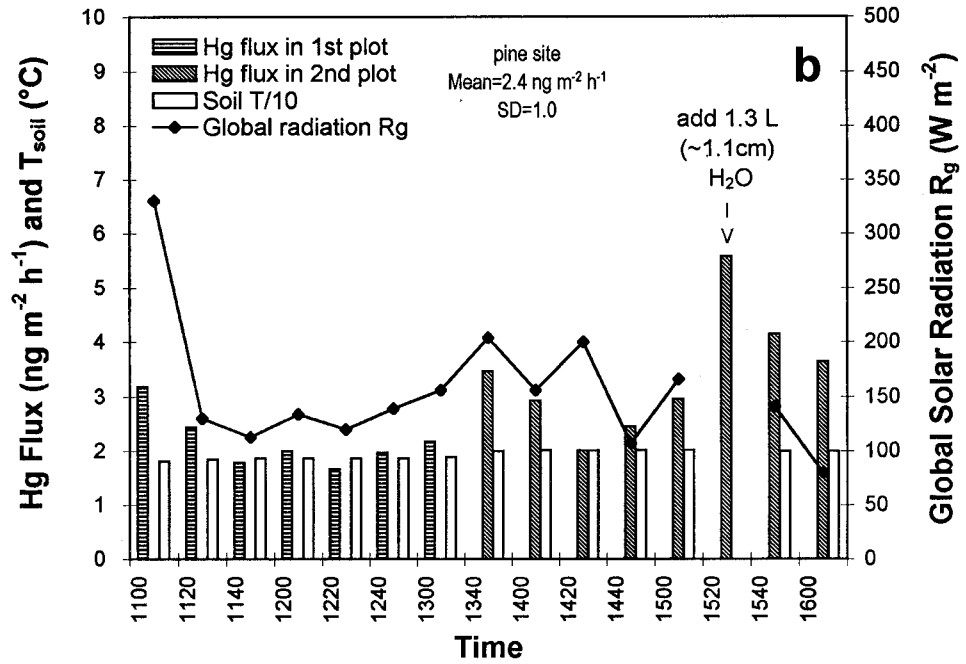


Figure 2b. Hg air/surface exchange kinetics and influence of environmental factors at the pine site.

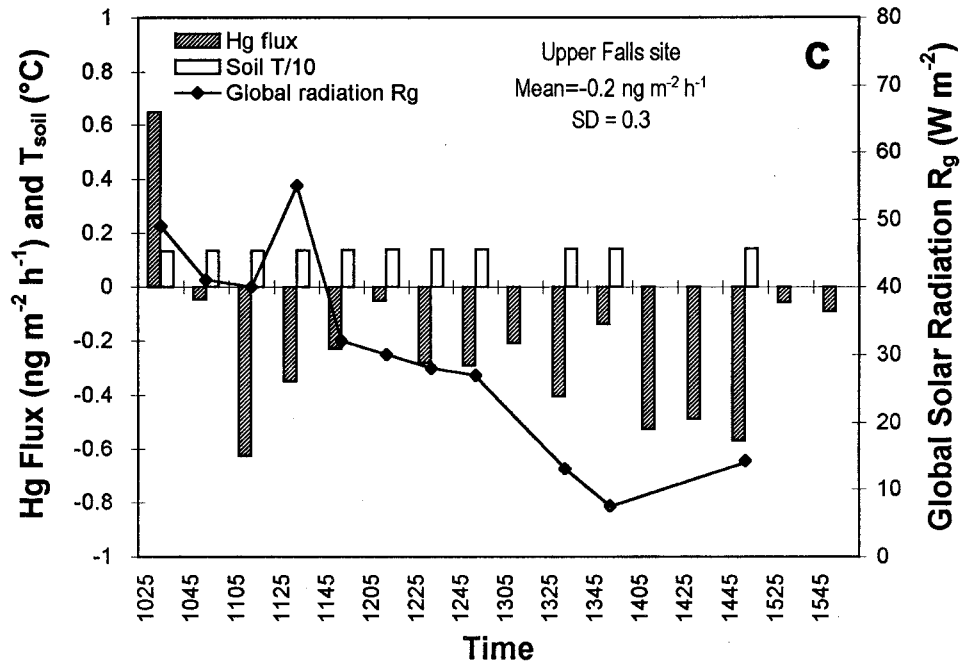


Figure 2c. Hg air/surface exchange kinetics and influence of environmental factors at the Upper Falls site.

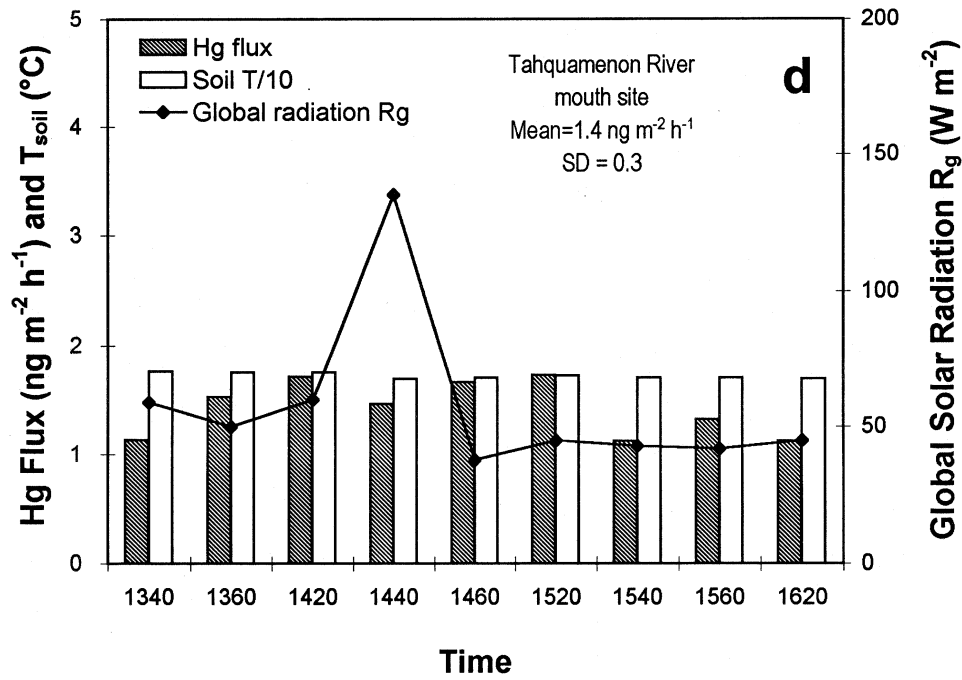


Figure 2d. Hg air/surface exchange kinetics and influence of environmental factors at the Tahquamenon River mouth site.

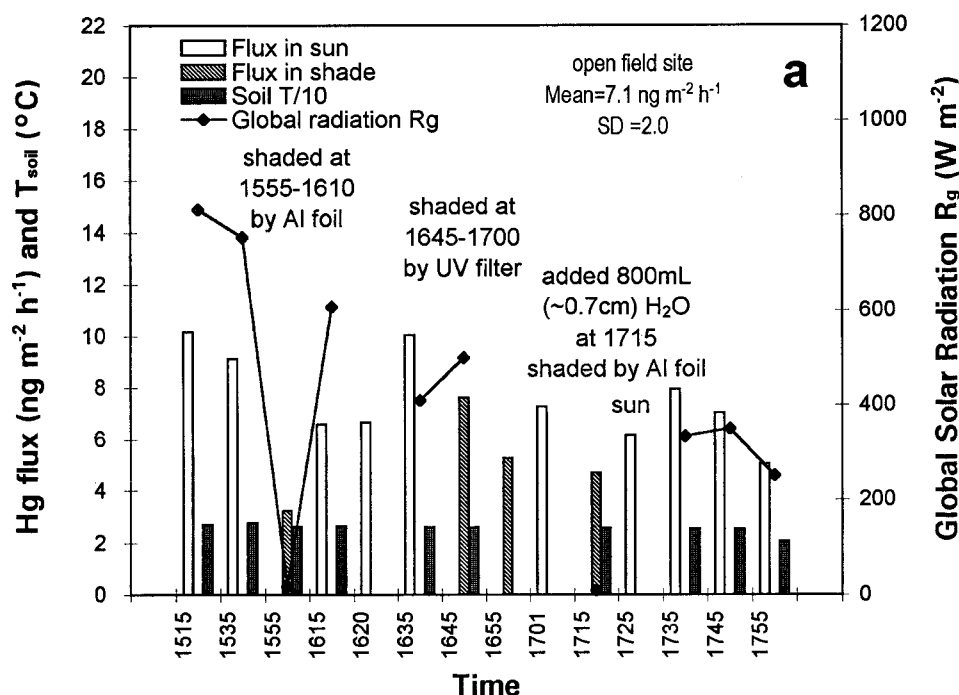


Figure 3a. Hg air/surface exchange kinetics and influence of environmental factors at the open field site.

night or over very wet soils (Kim *et al.*, 1995), and the fluxes reported here may not be representative for dryer conditions at the Upper Falls area. Very low Hg contents of the surface soils at the forest sites (Table I) and observations of very low Hg fluxes at these sites may be because of historically low Hg deposition or generally low throughfall such as reported for nearby Pellston Forest Stands (Rea, 1998). It is also possible that these sandy soils were conducive to transport of deposited Hg to deeper soil layers (below the leached layers) than would occur in finer soils.

3.3. Hg AIR/SURFACE EXCHANGE KINETICS AT THE OPEN FIELD SITE

Fluxes at the open field site (mean = $7.6 \text{ ng m}^{-2} \text{ hr}^{-1}$, data in artificial shade excluded in the mean) were clearly higher than those at any of the shaded forest sites, despite a generally lower Hg content (Tables I and III; Figure 3a). This field site was previously cleared for a building site, and the mean soil temperature at this site was the highest among all sites studied (Table III). The solar radiation effect could also contribute to higher fluxes (Carpi and Lindberg, 1997 and 1998), since this site obviously received more solar radiation than the forested sites (Table III). The TFC used for this study exhibited similar blanks in shade ($1.6 \text{ ng m}^{-2} \text{ hr}^{-1}$) and

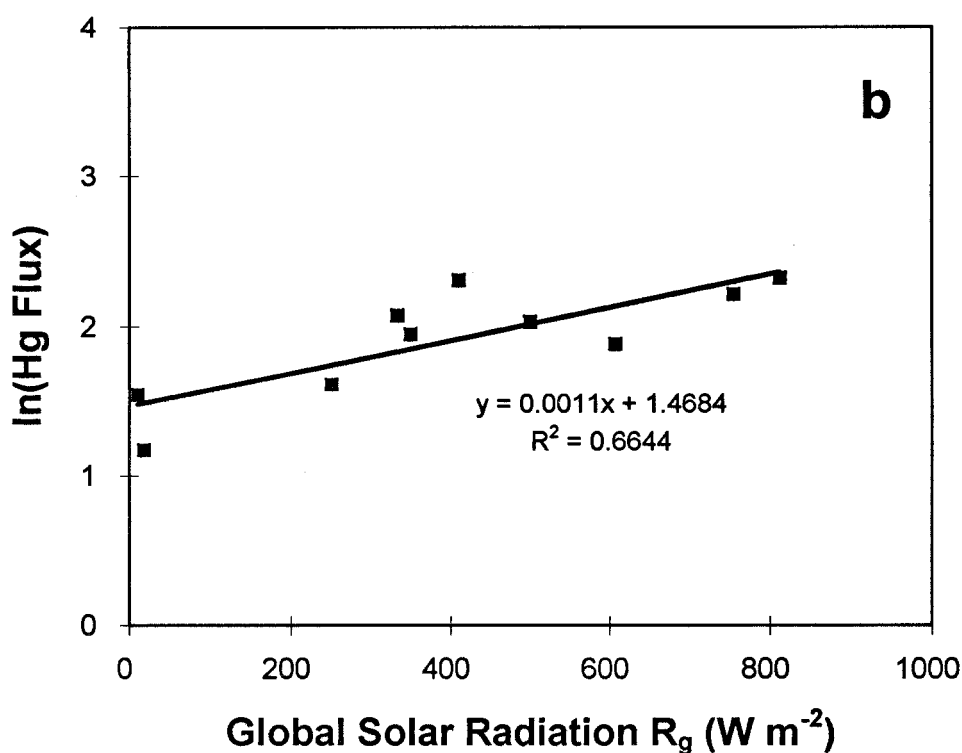


Figure 3b. Correlation between $\ln[\text{Hg flux}]$ and global solar radiation (R_g) at this site.

in the sun ($1.1 \text{ ng m}^{-2} \text{ hr}^{-1}$), suggesting that the chamber blank did not contribute significantly to this flux difference.

3.4. EFFECT OF SOIL TEMPERATURE ON Hg AIR/SURFACE EXCHANGE

Although a large range in Hg flux was observed at each of the five sites (Figures 2a–d and 3a), soil temperature generally varied very slightly at the shaded forest sites (RSD = 1.6–4.1%) (Table III, Figures 2b–d, and Figure 4) and only moderately at the open field site (RSD = 7.4%). Given soil Hg contents being similar at these sites, some other factor(s) (e.g., solar radiation) must be responsible for the observed trends in flux (discussed below). However, a significant correlation was found between mean Hg flux at each site and mean soil temperatures ($R^2 = 0.99$, Figure 4), indicating that soil temperature still appeared to affect the general magnitude of Hg fluxes over these background soils.

The air/surface exchange of mercury may be considered as a surface physico-chemical process comprising desorption (adsorption) of Hg from (to) soil particle surfaces and subsequent diffusion through soil pores:

$$F_{\text{Hg}} = r_{\text{Hg}} = d[\text{Hg}]_s/dt = k[\text{Hg}]_s^n \quad (2)$$

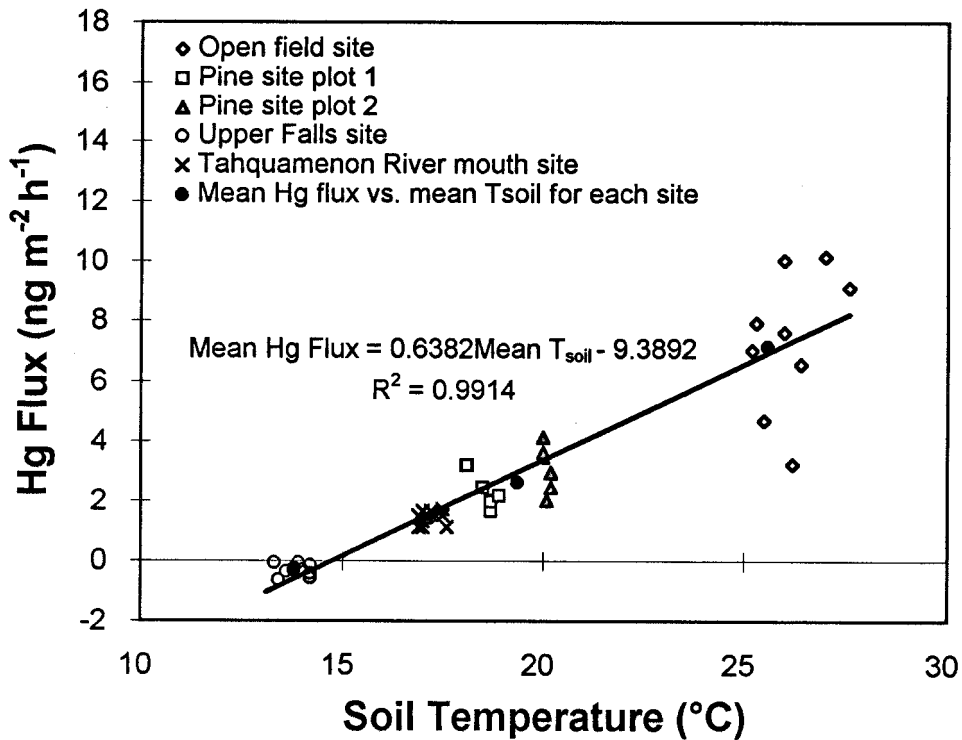


Figure 4. Correlation between Hg flux and soil temperature collectively for the data of different sites.

$$k' = k[\text{Hg}]_s^n, \text{ if } [\text{Hg}]_s = \text{constant} \quad (2-1)$$

where F_{Hg} is the Hg emission flux, r_{Hg} is the rate of Hg air/surface exchange ($\text{ng Hg m}^{-2} \text{hr}^{-1}$), $[\text{Hg}]_s$ is the surface Hg concentration (ng Hg m^{-2}) at soil particle surfaces, t is the time (h), k is the rate constant of the overall Hg air/surface exchange process, and n is the reaction order. Hence, the Arrhenius equation (Siegel and Siegel, 1988) can be applied to obtain the link between the kinetic rate constant of this process and the soil temperature:

$$\ln(k) = -E_a/RT_s + \text{constant} \quad (3)$$

where, E_a is the apparent activation energy required for the ongoing of the overall process, R is the gas constant ($1.9872 \text{ cal K}^{-1} \text{ mol}^{-1}$), and T_s is the soil temperature.

If $n = 0$, then $F_{\text{Hg}} = k$. Alternatively, $F_{\text{Hg}} = k'$ holds, if $[\text{Hg}]_s$ remains constant, which probably is a valid assumption in the case of continuous emission. In either case, substitution of F_{Hg} for the rate constant in Equation (3) leads to

$$\ln(F_{\text{Hg}}) = -E_a/RT_s + \text{constant} \quad (4)$$

Therefore, a linear relationship between $\ln(F_{\text{Hg}})$ and $1/T_s$ would suggest that the Hg air/surface exchange is a zero-order process, or that the surface Hg concentration ($[\text{Hg}]_s$) varies little during the overall Hg emission process, which would be expected at least for Hg-enriched soils. We found a linear correlation between $\ln(F_{\text{Hg}})$ and $1/T_s$ collectively for the data of the four sites which exhibited emission ($R^2 = 0.8190$, plot not shown), which suggests that the assumptions for Equation (4) probably also hold for background soils as long as Hg emission predominates (i.e. no negative Hg flux). The activation energy (E_a) was calculated to be 29.4 kcal mol⁻¹. This value is moderately higher than, yet still comparable to those obtained over other background soils (e.g., 17.3–25.8 kcal mol⁻¹ over Tennessee forest soils by Kim *et al.*, 1995; 18.0–24.9 kcal mol⁻¹ over Tennessee soils by Carpi and Lindberg, 1998; 20.5 kcal mol⁻¹ over a southern Quebec soil by Poissant and Casimir, 1998).

3.5. EFFECT OF SOLAR RADIATION ON Hg AIR/SURFACE EXCHANGE

Enhancement of Hg emission by solar radiation has been observed previously both over naturally enriched or contaminated soils (Carpi and Lindberg, 1997; Gustin *et al.*, 1998 and 1999b) and over background soils (Carpi and Lindberg, 1998; Poissant and Casimir, 1998). Figure 2b shows a typical example, where the Hg flux over the pine site shared the same trend as solar radiation (R_g). Although canopy shading restrained solar radiation fluctuations at the forest sites, on the whole in this study, the higher the mean R_g values, the higher the mean Hg fluxes (Figure 5).

To further demonstrate this solar effect at background soils, we conducted a few tests at the open field site by shading the TFC for a short period of time (e.g., 20 min) with aluminum foil or by a plastic UV filter (high density polycarbonate, 40% and <0.3% UV transmission at 380 nm and below 340 nm, respectively; transmission in PAR = ~98%). As shown in Figure 3a, completely shading the TFC with aluminum foil led to an immediate, large decrease in Hg flux (from 9.1 to 3.2 ng m⁻² hr⁻¹ in 20-min average, a decrease of ~65%), while the soil temperature remained unchanged. In another test, shading with the UV filter also induced an immediate, significant decrease in Hg flux (from 10.0 to 7.6 ng m⁻² hr⁻¹, a decrease of 24%) while the soil temperature changed little. These tests suggest that both UV and visible light can strongly enhance Hg emission from background soils. Moreover, this solar effect was independent of soil temperature, which remained nearly unchanged during our tests (Figures 2a–d and 3a). This suggests that the increase of Hg fluxes in the sun was induced solely by photo energy (Gustin *et al.*, 1998 and 1999b). These observations are in good agreement with some indoor simulation observations that Hg flux increased immediately after visible light was shed on soil samples (Gustin *et al.*, 1998; Gustin *et al.*, 1999b).

We also found a good linear correlation between $\ln[F_{\text{Hg}}]$ and R_g (global solar radiation) for the open field site (Figure 3b), which experienced no canopy shading, as previously shown by Carpi and Lindberg for Tennessee background soils

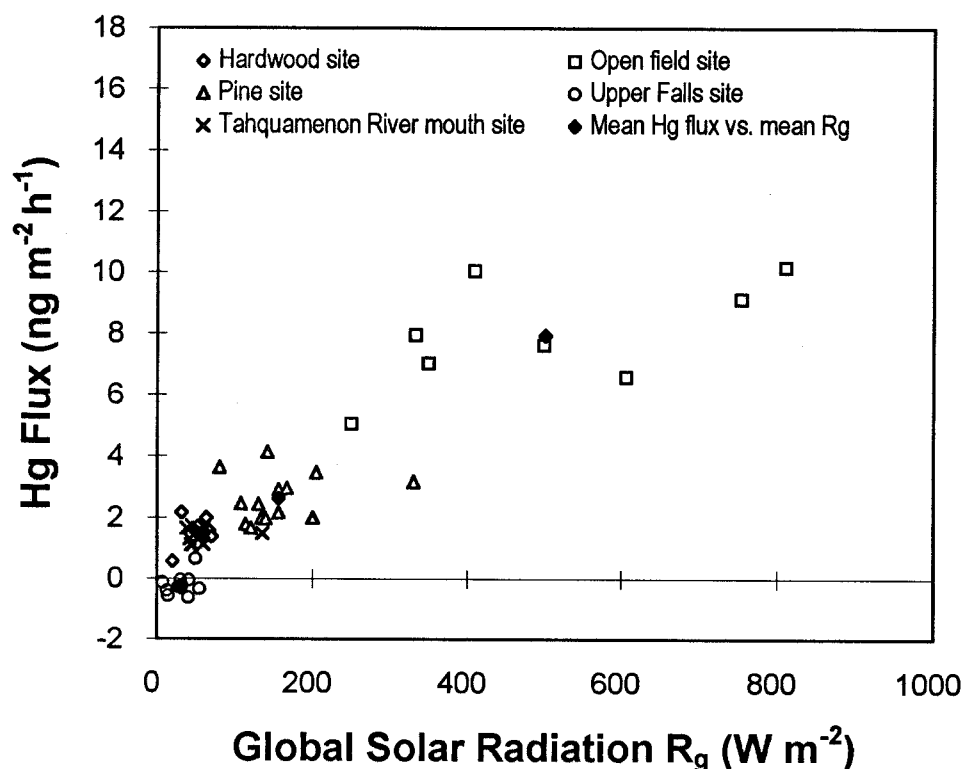


Figure 5. Correlation between Hg flux and solar radiation (R_g) collectively for the data of different sites.

(1998). Hypothetically, absorption of photo(solar) energy by gaseous Hg^0 atoms could decrease the apparent activation energy (E_a in Equations (3) and (5)) for Hg^0 desorption and emission from soils as a result of excitation of the Hg^0 atoms. Hence,

$$E'_a = E_a - E_{\text{solar}} \quad (5)$$

where E_{solar} is the photo energy absorbed by gaseous Hg atoms, and

$$E_{\text{solar}} = \Sigma(mh\nu \times 6.023 \times 10^{23}) \quad (6)$$

where m is the molar fraction of the Hg atoms absorbing the photo energy at a certain wavelength (λ), h is the Planck constant, and ν is the frequency ($= 1/\lambda$). Substitution of Equation (5) in Equation (4) leads to

$$\ln(F_{\text{Hg}}) = -(E_a - E_{\text{solar}})/RT_s + \text{constant} = E_{\text{solar}}/RT_s + \text{constant}' \quad (7)$$

Thus, the linear correlation between $\ln(F_{\text{Hg}})$ and R_g ($\propto E_{\text{solar}}$) can be explained well by Equation (7).

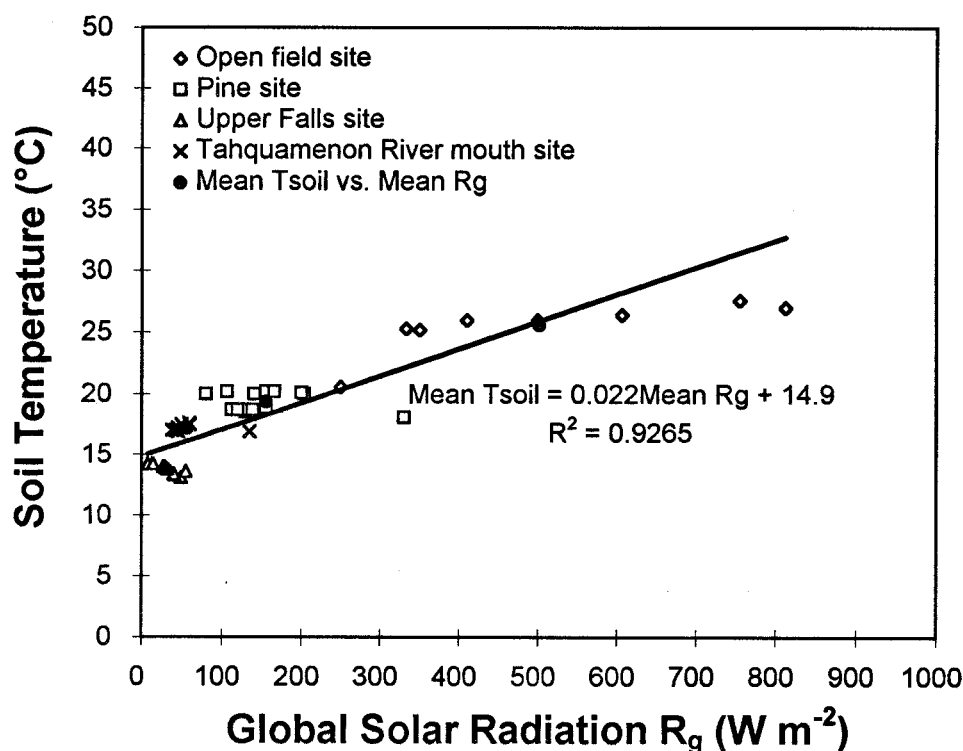


Figure 6. Correlation between soil temperature and solar radiation (R_g) collectively for the data of different sites.

Solar radiation not only directly enhanced Hg emission from these soils on short time scales (min) hypothetically through direct transfer of the photoenergy to Hg atoms, but also indirectly affected the general magnitude of Hg fluxes over longer periods (hr) by increasing soil temperature (Figure 6) through conversion of solar energy to thermal energy. However, which wavelength(s) of solar radiation is involved in these processes remains unknown.

3.6. EFFECT OF ARTIFICIAL IRRIGATION ON Hg AIR/SURFACE EXCHANGE

The enhancing effect of precipitation (or artificial irrigation) on Hg emission has been observed over naturally enriched soils (Lindberg *et al.*, 1999, and our unpublished data) and forest soils (Advokaat and Lindberg, 1996). We further tested this effect over background soils. Figure 2b shows a typical example of this effect over the soil at the pine site. We found that artificial irrigation of ~ 1.1 cm rain equivalent (~ 1.3 L high purity deionized water) induced a rapid increase in Hg flux from 3.0 to 5.6 $\text{ng m}^{-2} \text{hr}^{-1}$, $\sim 87\%$ of increase within ~ 15 min. Similar response was also observed at the open field site (Figure 3a). This effect was most probably caused by the release of gaseous Hg atoms adsorbed on soil particle surfaces by the

incoming water molecules, which have a higher physical affinity for soil particle surfaces than Hg^0 (Lindberg *et al.*, 1999; Zhang and Lindberg, 1999). Increasing evidence for the influence of rainfall on Hg emissions over soils warrants appropriate consideration of this effect in Hg modeling. Over a wet soil around or above field capacity, however, Hg emission can be substantially inhibited resulting from significantly decreased diffusion of Hg^0 in water covering soil particle surfaces and flooded soil pores (Zhang and Lindberg, unpublished) as observed over the wet soil at the Upper Falls site.

3.7. COMPARISON WITH Hg AIR/SURFACE EXCHANGE RATES OF OTHER BACKGROUND SOILS

The Hg emission fluxes observed over the background soils in the Tahquamenon River watershed are comparable to those measured at other northern background sites (Table IV). The mean flux at the four forest sites ($1.4 \text{ ng m}^{-2} \text{ hr}^{-1}$) is very close to the overall mean flux in a deciduous forest of Sweden ($1.4 \text{ ng m}^{-2} \text{ hr}^{-1}$) (Shroeder *et al.*, 1989) and also to the mean flux in a coniferous forest of Sweden ($0.8 \text{ ng m}^{-2} \text{ hr}^{-1}$) (Xiao *et al.*, 1991). It is also close to the mean flux for a southern Quebec soil ($3.0 \text{ ng m}^{-2} \text{ hr}^{-1}$) (Poissant and Casimir, 1998). These similarities show that Hg emissions from forest soils of the northern regions over the world seem to share the same magnitude. The overall mean flux at the four forest sites is, however, lower than mean fluxes measured over several temperate forest soils in Tennessee (range in means for four sites = $2.7\text{--}12.5 \text{ ng m}^{-2} \text{ hr}^{-1}$) (Table IV). It must be kept in mind that the Tennessee sites were subject to elevated Hg deposition in the past as a result of local emissions (Lindberg *et al.*, 1995). There are few other published data available reporting Hg emission fluxes over background soils in the southern US.

4. Conclusions

This study showed that Hg emission fluxes over background soils in the Tahquamenon River watershed in the Michigan Upper Peninsula were generally very low (mean $<3 \pm 1.0 \text{ ng m}^{-2} \text{ hr}^{-1}$ over shaded forest soils), which may be due to a rather low load of historical Hg deposition in this region or due to various losses of the deposited Hg, such as desorption and leaching in these sandy soils. Dry deposition of Hg^0 does occur over the soils in some pristine forests as shown by five hours of measurements at the Upper Falls site ($-0.2 \pm 0.3 \text{ ng m}^{-2} \text{ hr}^{-1}$). The magnitudes of Hg fluxes measured over these forest soils agree well with those over other northern forest soils worldwide. However, the mean Hg flux at the open field site ($7.6 \pm 1.7 \text{ ng m}^{-2} \text{ hr}^{-1}$) was significantly higher than at all the forest sites.

Among the environmental factors, solar radiation and irrigation were found to be most influential to Hg air/surface exchange over the shaded background soils.

TABLE IV
Summary of emission fluxes over soils and comparison to fluxes of other background soils

| Soil | Site description | Time | T _{soil} (°C) | Mean flux (ng m ⁻² hr ⁻¹) | Reference |
|--------------------------------------|------------------|------------------|------------------------|--|-------------------------------|
| Tahquamenon River watershed soils | | | | | |
| Overall forest sites | Forest | June 1998 | 13.8–19.4 | 1.4±1.4 | This study |
| Open filed site | Field | June 1998 | 20.6–27.6 | 7.6±1.7 | This study |
| Comparison to other background soils | | | | | |
| St. Anicet, S. Quebec | Field | July 1995 | ~26 | 3.0±2.2 | Poisant and Casimir, 1998 |
| Deciduous, Sweden | Forest | August 1987 | 10 | 1.4±0.5 | Shroeder <i>et al.</i> , 1989 |
| Coniferous, Sweden | Forest | Dec. 1987 | -5 | 1.4±0.2 | Xiao <i>et al.</i> , 1991 |
| Conifeous, Sweden | Forest | May 1988 | 10–12 | 0.8±1.1 | Xiao <i>et al.</i> , 1991 |
| | | June 1989 | 7–12 | | |
| Conifeous, Sweden | Forest | August 1987 | 10–11 | 0.8±0.3 | Shroeder <i>et al.</i> , 1989 |
| Conifeous, Sweden | Forest | June 1994 | 11.3–16.6 | -0.017±2.8 | Lindberg <i>et al.</i> , 1998 |
| WBW ^a , East TN | Forest | May.-Aug. 1993 | 13.7–36.2 | 7.6 | Kim <i>et al.</i> , 1995 |
| | | Oct.-Nov.1993 | 12.1–17.6 | 7.1 | |
| WBW ^a East TN | Forest | April, June 1995 | 12–25 | 7.0±1.9 | Capri and Lindberg, 1998 |
| Watson Forest, E. TN | Forest | May, Juny 1995 | 15–22 | 2.7±0.48 | Capri and Lindberg, 1998 |
| Nelson Field, E. TN | Field | June-Aug. 1995 | 25–50 | 12.5±5.4 | Capri and Lindberg, 1998 |
| Florida | Field | April 1997 | 23–26 | 5.0±5.0 | Lindberg and Price, 1998 |

^a WBW: Walker Branch Watershed.

Soil temperature fluctuated only slightly under the forest canopy in the daytime even during the summer season, and thus played a less controlling role. The variation in mean Hg flux at different sites is strongly influenced by the variation in soil temperature, which was controlled by solar radiation as suggested by the positive correlation between solar radiation and soil temperature at these sites.

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References

- Advokaat, E. M. and Lindberg, S. E.: 1996, Presented at the Fourth International Conference on Mercury as a Global Pollutant, Hamburg, August.
- Anoshin, G. N., Malikova, I. N. and Kovalev, S. I.: 1996, in Baeyens, W. *et al.* (eds), *Global and Regional Mercury Cycles: Sources, Fluxes, and Mass Balances*, Kluwer Academic Publishers, pp. 475–489.
- Carpi, A. and Lindberg, S. L.: 1997, *Environ. Sci. Technol.* **31**, 2085.
- Carpi, A. and Lindberg, S. L.: 1998, *Atmos. Environ.* **32**, 873.
- Gustin, M. S., Lindberg, S. E., Marsik, F., Casimir, A., Ebinghaus, R., Edwards, G., Fitzgerald-Hubble, C., Kemp, R., Kock, H., Leonard, T., London, J., Majewski, M., Owens, J., Pilote, M., Poissant, L., Rasmussen, P., Schaedlich, F., Schneeberger, D., Schroeder, W., Sommar, J., Turner, R., Vette, A., Wallschlaeger, D., Xiao, Z. F. and Zhang, H.: 1999a, *J. Geophys. Res.* **104**, 21831.
- Gustin, M., Maxey, R., Rasmussen, P. and Beister, H.: 1998, *Proceedings of Air and Waste Management Association Specialty Conference, Measurement of Toxics and Related Airpollutants*. Cary, NC, September, pp. 224–235.
- Gustin, M., Rasmussen, P., Edwards, G., Schroeder W. and Kemp, J.: 1999b, *J. Geophys. Res.* **104**, 21873.
- Gustin, M. S., Tayler Jr., G. E., Leonard, T. L. and Keislar, R. E.: 1996, *Environ. Sci. Technol.* **30**, 2572.
- Kim, K. H., Hanson, P. J., Barnett, M. O. and Lindberg, S. E.: 1997, *Metal Ions in Biological Systems* **34**, 185.
- Kim, K. H. and Lindberg, S. E.: 1995, *Water, Air, and Soil Pollut.* **80**, 1059.
- Kim, K. H., Lindberg, S. E. and Meyers, T. P.: 1995, *Atmos. Environ.* **29**, 267.
- Lindberg, S. E.: 1996, in Baeyens, W., Ebinghaus, R. and Vasiliev, O. (eds), *Global and Regional Mercury Cycles: Sources, Fluxes, and Mass Balances*, Elsevier Amsterdam, The Netherlands, pp. 359–380.

- Lindberg, S. E., Kim, K. H., Meyers, T. P. and Owens, J. G.: 1995, *Environ. Sci. Technol.* **29**, 126.
- Lindberg, S. E., Hanson, P. J., Meyers, T. P. and Kim, K. H.: 1998, *Atmos. Environ.* **32**, 895.
- Lindberg, S. E. and Harriss, R. C.: 1974, *Environ. Sci. Technol.* **8**, 459.
- Lindberg, S. E. and Price, J.: 1999, *J. Air and Waste Manage. Assoc.* **49**, 520.
- Lindberg, S. E., Zhang, H., Gustin, M., Vette, A., Marsik, F., Owens, J., Casimir, A., Ebinghaus, R., Edwards, G., Fitzgerald, C., Kemp, J., Kock, H. H., London, J., Majewski, M., Poissant, L., Pilote, M., Rasmussen, P., Schaedlich, F., Schneeberger, D., Sommar, J., Turner, R., Walshlager, D. and Xiao, Z.: 1999, *J. Geophys. Res.* **104**, 21879.
- Lindqvist, O., Johansson, K., Aastrup, M., Andersson, A., Bringmark, L., Hovsenius, G., Hakanson, G., Iverfeldt, A., Meili, M. and Timm, B.: 1991, *Water, Air, and Soil Pollut.* **55**, 73–100.
- Poissant, L. and Casimir, A.: 1998, *Atmos. Environ.* **32**, 883.
- Rasmussen, P. E.: 1994, *Environ. Sci. Technol.* **28**, 2233.
- Rea, A.: 1998, *The Processing of Mercury in Forested Ecosystem*, Ph. D. thesis. University of Michigan, Ann Arbor.
- Rea, A. and Keeler, G. J.: 1998, *Biogeochemistry* **40**, 115.
- Schroeder, W. H., Munthe, J. and Lindqvist, O.: 1989, *Water, Air, and Soil Pollut.* **48**, 337.
- SCS USDA: 1990, *Soil Survey of Chippewa County*, Michigan.
- Siegel, S. M. and Siegel, B. Z.: 1988, *Water, Air, and Soil Pollut.* **40**, 443.
- Xiao, Z. F., Munthe, J., Schroeder, W. H. and Lindqvist, O.: 1991, *Tellus* **43B**, 267.
- Zhang, H. and Lindberg, S. E.: 1999, *J. Geophys. Res.* **104**, 21889.