Previously unaccounted atmospheric mercury deposition in a midlatitude deciduous forest

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Mercury is toxic to wildlife and humans, and forests are thought to be a globally important sink for gaseous elemental mercury (GEM) deposition from the atmosphere. Yet there are currently no annual GEM deposition measurements over rural forests. Here we present measurements of ecosystem–atmosphere GEM exchange using tower-based micrometeorological methods in a midlatitude hardwood forest. We measured an annual GEM deposition of 25.1 μg · m⁻² (95% CI: 23.2 to 26.7 1 μg · m⁻²), which is five times larger than wet deposition of mercury from the atmosphere. Our observed annual GEM deposition accounts for 76% of total atmospheric mercury deposition and also is three times greater than litterfall mercury deposition, which has previously been used as a proxy measure for GEM deposition in forests. Plant GEM uptake is the dominant driver for ecosystem GEM deposition based on seasonal and diel dynamics that show the forest GEM sink to be largest during active vegetation growing periods and middays, analogous to photosynthetic carbon dioxide assimilation. Soils and litter on the forest floor are additional GEM sinks throughout the year. Our study suggests that mercury loading to this forest was underestimated by a factor of about two and that global forests may constitute a much larger global GEM sink than currently proposed. The larger than anticipated forest GEM sink may explain the high mercury loads observed in soils across rural forests, which impair water quality and aquatic biota via watershed Hg export. Major uncertainties exist in regard to magnitude and seasonality of the dominant terrestrial GEM deposition and their controlling ecological and environmental controls. Data are particularly scarce from forests in which direct GEM exchange measurements are limited largely to summertime (12) or stem from Hg-contaminated sites (13, 14). Direct flux measurements are also required to partition GEM deposition into canopy and forest floor (litter and soil) contributions. In lieu of direct GEM flux measurements, GEM deposition across forests is often inferred from proxy measures such as mercury litterfall collected under canopies (8, 15). Litterfall mercury deposition, however, is not an ideal proxy for GEM dry deposition because it does not capture uptake by large woody tissues, nonvascular plants (i.e., lichen, mosses), and underlying soils, and it does not account for GEM re-emission back to the atmosphere after deposition (7). Here, we employed a micrometeorological flux-gradient method that directly quantifies GEM exchange at the ecosystem level over a 470-d record (May 2019 to August 2020) in a rural temperate forest in Massachusetts. The site is a second-growth forest that is actively accumulating biomass and is approaching standing biomass levels of old-growth stands in the region (16). The flux-gradient method we employed consists of GEM concentration measurements at two heights above the canopy in combination with quantification of atmospheric dry deposition | mass balance | mercury cycling


The authors declare no competing interest.

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Results and Discussion

Whole-Ecosystem GEM Exchange and Correlation to Vegetation Activity and CO2 Assimilation. Monthly averaged GEM fluxes showed atmospheric GEM deposition (negative exchange fluxes) during 12 of the 16 mo of measurements, with rates of deposition largest in summer and fall (August to November). We observed emissions to the atmosphere (positive fluxes) only during two winter and two spring months (May and December 2019 and January and April 2020), while small rates of deposition were observed during the rest of winter and springtime (Fig. 1A–C). GEM fluxes showed strong diel variability, particularly in summer with large GEM deposition during midday up to 28 ng · m⁻² · h⁻¹, compared to nighttime deposition maxima of 6 ng · m⁻² · h⁻¹ (Fig. 2 and SI Appendix, Table S1). Different diel patterns emerged in spring when deposition dominated during daytime, which reversed to emissions during daytime (e.g., in March and April 2020). In winter, there was smaller diel variability of GEM fluxes which remained relatively constant throughout the day. Wintertime snow cover quickly disappeared during the first 10 days of March 2020, but we did not observe a change in GEM flux dynamics before and after snow disappearance (Fig. 1C). Cumulative GEM exchange started with emissions in May 2019, which reversed quickly to deposition during the 2019 growing season and resulted in a substantial cumulative GEM deposition by end of November 2019. Winter months showed partial GEM emissions of about one-quarter of the previous summertime GEM deposition. In June 2020, GEM deposition resumed and strengthened throughout the second summer until the end of measurements in mid-August 2020. Cumulative net GEM deposition (i.e., all deposition minus emissions) between May 1, 2019, to August 12, 2020 (470 d), totaled 34.9 μg · m⁻² (Fig. 2C and Table 1), with a 95% CI of 33.0 to 37.2 9 μg · m⁻² (SI Appendix). Annual GEM deposition was 25.1 μg · m⁻² with a 95% CI of 23.2 to 26.7 μg · m⁻².

We attribute these seasonal and diel GEM exchange patterns to vegetation uptake of GEM. Both seasonal and diel GEM flux patterns are similar to those of CO2 fluxes, which generally exhibit large growing season and midday deposition due to photosynthetic CO2 assimilation by plants (18). As a result, seasonal and diurnal fluxes show a coupling between the exchanges of GEM and CO2. Seasonally, both GEM and CO2 fluxes showed pronounced growing-season deposition while winter and early spring showed either emissions or near-zero fluxes (Fig. 1C). The only notable discrepancy between seasonal GEM and CO2 flux patterns was observed in November 2019 (CO2 showing emissions while GEM fluxes showing strong deposition). It is notable that snow cover started on December 1, 2019, after which the active forest GEM sink ceased, suggesting that the forest floor also served as a GEM sink. Not including November, median monthly GEM fluxes linearly correlated with forest CO2 fluxes (r² = 0.52). During the active vegetation season between June and October, CO2 fluxes also explained 49% of the diel flux variability of GEM based on linear regressions between median monthly fluxes for each hour of the day. In support of an active role of vegetation for GEM deposition, GEM fluxes were correlated with forest leaf area index (LAI; r² of 0.61 not including November), and GEM fluxes were statistically different at LAI above 3 m² · m⁻² (average deposition of 2.3 ng · m⁻² · h⁻¹) compared to LAI below 3 m² · m⁻² (average emission of 2.6 ng · m⁻² · h⁻¹). In addition, monthly GEM fluxes linearly correlated with air temperatures (r² of 0.49) and soil temperatures (e.g., at 5-cm depth, r² of 0.57) showing increased deposition during the warmer growing seasons.

Fig. 1. (A) 30-min resolution GEM exchange fluxes measured over Harvard Forest. Negative fluxes denote deposition, and positive fluxes represent emissions. (B) Daily mean GEM fluxes and median monthly GEM fluxes (green lines). (C) Cumulative sums of daily fluxes of GEM and CO2 starting on May 1, 2019. Missing flux values were interpolated using median monthly values. Shaded lines represent 95% CIs based on random error analysis as described in SI Appendix. Corresponding patterns of LAI are shown together with the CO2 fluxes on the secondary y-axis.

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PNAS Obrist et al.

https://doi.org/10.1073/pnas.2105477118

2 of 7

Obrist et al.
GEM emission, however, largely ceased as the canopy began to leaf out and as emerging daytime GEM assimilation by plants dominated during active growing seasons and led to midday summertime deposition maxima.

**Forest-Floor GEM Exchange.** We quantified forest-floor GEM fluxes to assess their contributions to ecosystem-level GEM exchange using a second flux-gradient deployed above the forest floor (Fig. 3). Forest-floor GEM fluxes indicated consistent GEM deposition throughout the year (Fig. 3), suggesting that soil and litter served as additional ecosystem sinks of GEM. Forest-floor GEM uptake may include direct uptake and subsequent oxidation of GEM in soils (26) and GEM uptake in overlying litter layers (27). The observed deposition of atmospheric GEM to the forest floor could explain reported increases in Hg levels in litter during decomposition (27–29). Comparing cumulative flux patterns of the forest floor to that of ecosystem-level fluxes implies that limited periods of net GEM emissions at

![Fig. 2.](image)

**Table 1.** Summary of annual and seasonal GEM deposition and associated 95% CIs based on error propagation shown in SI Appendix

<table>
<thead>
<tr>
<th>Species/process</th>
<th>Time period</th>
<th>Source</th>
<th>Deposition (μg · m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GEM dry deposition</td>
<td>Study duration (470 d): May 1, 2019 to August 12, 2020</td>
<td>This study</td>
<td>34.9 (33.0 to 37.2)</td>
</tr>
<tr>
<td>GEM dry deposition</td>
<td>Annual (365 d)</td>
<td>This study</td>
<td>25.1 (23.2 to 26.7)</td>
</tr>
<tr>
<td>GEM dry deposition</td>
<td>Growing season: Jun 1 to Sep 30, 2019</td>
<td>This study</td>
<td>21.9 (20.9 to 23.1)</td>
</tr>
<tr>
<td>Litterfall deposition</td>
<td>Annual</td>
<td>This study: GOM @ conc. of 4.1 ± 5.6 pg · m⁻³ × v_d</td>
<td>1.9</td>
</tr>
<tr>
<td>GOM dry deposition</td>
<td>Annual</td>
<td>Average of North America (35)</td>
<td>1.1</td>
</tr>
<tr>
<td>PHg dry deposition</td>
<td>Annual</td>
<td>From NADP 2020, regional average</td>
<td>5.0</td>
</tr>
<tr>
<td>Wet Hg deposition</td>
<td>Annual</td>
<td>Dry (GEM + GOM + PHg) + wet deposition</td>
<td>33.1</td>
</tr>
<tr>
<td>Total Hg deposition</td>
<td>Annual</td>
<td></td>
<td></td>
</tr>
<tr>
<td>% GEM of total Hg deposition</td>
<td>Annual</td>
<td></td>
<td>76%</td>
</tr>
</tbody>
</table>

Additional estimates and constraints of wet and dry deposition of other major atmospheric mercury species are based on additional measurements and published literature data.
the ecosystem level in winter and spring are not caused by emissions from the underlying forest floor but may stem from above-ground tissues. Mixed forests maintain significant above-ground surface areas even during nonactive growing seasons due to woody biomass surfaces and coniferous needles, as evident by LAI which never dropped below 1.7 m² · m⁻² at this site (Fig. 1C). Forest-floor GEM deposition could also explain GEM deposition at the ecosystem level during nighttime and possibly the discrepancy between CO₂ and GEM fluxes in November 2019 when photosynthetic CO₂ uptake largely ceased while GEM continued to show GEM deposition. Accumulating forest litter in fall may further shield soil surface from incident solar radiation and reduce the potential for soil GEM emission. Full quantitative flux partitioning between canopy and forest floor contributions, however, was not feasible in this study because of different footprints of measurements (i.e., range of meters above the forest floor compared to a few hundred meters above the forest). In addition, magnitudes of forest-floor flux-gradient measurements may be unreliable when turbulence near the ground is weak and intermittent, and thus, the underlying assumptions for valid flux-gradient calculations are not met (30). We hence primarily use below-canopy GEM fluxes to indicate GEM flux direction from the underlying forest floor (i.e., emission or deposition) rather than full quantitative constraints.

GEM Deposition Studies over Other Terrestrial Ecosystems. The only previous ecosystem-level GEM flux study over a rural forest we know of was conducted over several months (June through October) in a deciduous maple forest in Connecticut. Using a relaxed eddy accumulation approach (12), the study provided evidence of GEM deposition in forests with an estimated growing season GEM deposition of 5.6 µg · m⁻², compared to a much larger deposition of 25.1 µg · m⁻² (range of 23.2 to 26.7 µg · m⁻²) from June 1 through October 31 in our study. The study suggests to possibly have underestimated growing season GEM uptake as they missed early leaf-out GEM deposition fluxes. In contrast to our study, the study reported GEM emissions in late summer and fall (August through October), and flux magnitudes were much higher and more variable than our measurements. Reasons for differences in GEM flux patterns include a different methodological approach, possible footprint contributions by surrounding open grassland in the Connecticut study, and proximity to more urban areas. Other studies reported forest GEM fluxes over mercury-contaminated forests in the United States (13) and China (14) and showed predominately GEM emissions to the atmosphere. The contrasting patterns of these studies are not surprising given that fluxes over mercury-contaminated areas strongly shift toward emissions (10, 25) and hence are not representative of GEM exchanges over rural ecosystems.

Only a few studies reported annual GEM fluxes over other ecosystem types. A total 2 y of GEM fluxes data over a tundra in northern Alaska (4) showed annual GEM deposition of 6.8 and 6.1 µg · m⁻² · yr⁻¹, respectively, compared to the annual deposition of 25.1 µg · m⁻² (range of 23.2 to 26.7 µg · m⁻²) in our forest. Annual GEM deposition over a temperate grassland in Switzerland was 25.4 µg · m⁻² · yr⁻¹ when using the flux-gradient method (31). Another grassland site dominated by grasses, brush, and dispersed trees after a recent forest clearing in Maryland reported a small annual GEM deposition of 3.3 µg · m⁻² · yr⁻¹ (32). Finally, an annual GEM flux study using relaxed eddy accumulation technique over a peatland in northern Sweden, a site with little vegetation growth, showed an annual net emission of GEM of 9.4 µg · m⁻² · yr⁻¹ (33). Most available GEM flux studies over terrestrial sites hence show an annual net GEM deposition, which in our deciduous forest was comparable to a productive grassland, higher than annual GEM deposition in an arctic tundra and a recently converted grassland, and in opposite direction to a reported GEM emission of a peatland.

Annual Deposition and Mass Balance Considerations. Cumulative GEM deposition shows that the mixed hardwood forest in Massachusetts served as a substantial GEM sink of 34.9 µg · m⁻² (range of 33.0 to 37.2 µg · m⁻²) over the duration of 470 d of measurements with an annual GEM deposition of 25.1 µg · m⁻² · yr⁻¹ (range of 23.2 to 26.7 µg · m⁻²). GEM deposition was by far the dominant source of mercury deposition (Table 1). It is important to note, however, that measuring small GEM fluxes against the relatively larger atmospheric background was challenging at the level of a forest ecosystem and resulted in substantial flux variability and uncertainty ranges (SI Appendix, Table S1 and Fig. S5). Detailed analyses of high-resolution data by means of frequency and autocorrelation analyses (SI Appendix, Figs. S2 and S3), consistent and repeatable seasonal and diel patterns (Figs. 1 and 2), and error propagation based on random error analysis of time-repeated measurements (SI Appendix, Fig. S5) provided high confidence in the reliability of our GEM flux measurements. Cumulative GEM exchange also showed similar seasonal flux patterns between the two years of measurements.

Mercury wet deposition by rain and snow is monitored across the United States by the National Atmospheric Deposition Program (34) and is about 5 µg · m⁻² · yr⁻¹ in this region based on interpolated deposition maps for the year 2017. We constrained dry deposition of gaseous oxidized mercury (GOM) based on limited measurements of GOM concentrations in late spring and early summer (SI Appendix, Fig. S6) which averaged 4.1 ± 5.6 µg · m⁻³ and yields a GOM deposition flux of 1.9 ± 2.6 µg · m⁻² · yr⁻¹ if extrapolated to a full year. This estimated GOM deposition at Harvard Forest is smaller than an average GOM deposition of 6.4 µg · m⁻² · yr⁻¹ estimated across North America (35), which is reasonable given that the North American average includes urban sites with higher GOM concentrations from anthropogenic emissions while our forest ecosystem is a rural site. We did not measure particulate mercury (PHg) deposition but assume an upper limit of 1.1 µg · m⁻² · yr⁻¹ of deposition, which is the average PHg deposition reported across North America (35). These comparisons strongly suggest that GEM dry deposition was by far the dominant deposition pathway in this forest accounting for 76% of a total annual mercury deposition of about 33.1 µg · m⁻² · yr⁻¹ (Table 1). The contributions of GEM to total

Fig. 3. Cumulative sum of ecosystem-level and forest-floor GEM exchanges. Forest-floor GEM fluxes are quantitatively uncertain due to application of the flux-gradient method below canopies and should be viewed as a measure of underlying flux direction. Shaded lines represent 95% CIs based on random error analysis as described in SI Appendix. Corresponding patterns of LAI (in meters² leaf area and meters² ground surface area) and daily air temperatures (in °Celsius; line represents smoothed data) are shown on the secondary y-axis.
deposition are surprisingly similar to an estimate of 71% GEM contributions in an Alaskan tundra (4) and agree with stable mercury isotope analyses that indicate atmospheric GEM-derived sources to account for 57 to 94% of mercury in forest soils across North America (2, 5).

Litterfall mercury deposition has been used as a proxy measure to estimate dry deposition fluxes in forests (36). Litterfall data across 23 forest sites in the United States have shown average litterfall mercury deposition of 12.3 μg · m⁻² · yr⁻¹ (range of 3.8 to 18.8 μg · m⁻² · yr⁻¹) notably exceeding corresponding wet deposition that averaged 9.6 μg · m⁻² · yr⁻¹ across the same region (37). We estimated litterfall mercury deposition at Harvard Forest using end-of-season foliage mercury concentration of four dominant tree species multiplied by a 10-yr record of litterfall biomass fluxes (Table 2). Our results show litterfall mercury deposition of 8.1 μg · m⁻² · yr⁻¹ that is about 3.1 times lower than measured annual GEM dry deposition. Using net daily CO₂ uptake to delineate periods of active vegetation growing periods (i.e., June 1 to October 1), the cumulative growing season dry deposition GEM sink amounted to 21.9 μg · m⁻² (range of 20.9 to 23.1 μg · m⁻²) (Tables 1 and 2), which is 2.7-fold the value of litterfall mercury deposition, providing evidence that forest-level GEM uptake strongly exceeds litterfall deposition. This finding supports previous reports that large additional deposition fluxes in addition to foliar litterfall and wet deposition are needed to explain observed mercury accumulation in soils along a glacier retreat chronosequence (38).

**Implications for Global and Regional Mercury Cycling.** Our measurements of annual GEM deposition suggest that GEM deposition in forests is strongly underestimated. Total global terrestrial GEM deposition currently is estimated at 1,500 to 1,800 Mg · yr⁻¹ (6). Global annual litterfall deposition, currently estimated in the range of 1,020 to 1,230 Mg · yr⁻¹ (8, 39) would amount to a global GEM deposition of 3,162 to 3,813 Mg · yr⁻¹ if GEM deposition exceeds litterfall deposition by a similar factor of 3.1 across other forests. The major reasons for higher deposition likely include unaccounted for GEM assimilation by vegetation and direct GEM uptake by the forest floor and soil. The forest GEM deposition sink at Harvard Forest may be enhanced by ongoing biomass growth and carbon sequestration driven by forest regrowth, climate warming, and increasing wetting and atmospheric CO₂ concentrations (16). Additional pathways of atmospheric GEM deposition include wash-off of GEM from plant surfaces and deposition via throughfall and stemflow deposition (38). A potentially larger and unaccounted for forest GEM sink will require major revision of other global pool sizes, atmospheric deposition and emission fluxes, and respective residence times in these environmental compartments. A larger than anticipated forest GEM sink also is consistent with strong mercury enhancements in soils across forests, which on average are 2.5 times higher than in barren soils (40, 41). High-soil mercury pools subsequently lead to water quality impairments via terrestrial runoff (42) and impact air quality when remobilized via wildfire emissions (43). Whole-ecosystem GEM fluxes across global forests and other ecosystems are needed to corroborate the strong GEM uptake observed in this midlatitute deciduous forest and constrain GEM sinks across global biomes.

**Materials and Methods**

**Study Site and Ecosystem Characteristics.** The measurement site is located in a temperate deciduous hardwood forest at Harvard Forest research station near Petersham, Massachusetts (42°32'N, 72°11'W), at an elevation of 340 m with an annual average precipitation of 1,071 mm and a mean annual temperature of 6.6 °C. Cold winter temperatures result in wintertime snow cover with a peak snow water equivalent of 82 mm in 2020 (February 19) and an average peak snow water equivalent of 98 mm since 2009. The site houses a 31-m-tall flux tower near a climate-controlled hut for instrumentation with power and network access. Average tree height is about 24 m with vegetation dominated by red oak (*Quercus rubra*) representing about 80% of the tree basal area and other major species including red maple (*Acer rubrum*) and hemlock (*Tsuga canadensis*). Forest ages at this site range from 85 to 125 y with few trees exceeding 200 y of age (16). Nearly all forests in the region are second-growth after large-scale forest clearing in the mid-1800, and a major hurricane damaged about 70% of the standing timber in 1938. Soils are Spodosols (suborder Orthods) formed over sandy loam glacial till. Near-continuous forest extends several kilometers in all directions with no occupied dwelling closer than 2 km distance, beyond which the area is also forests and sparsely populated. The nearest highway is about 5 km distant.

**Micrometeorological Measurements.** The site has been used for micrometeorological measurements since 1990 and is home to the longest available CO₂ flux Eddy Covariance (EC) dataset in the world (44). The site facilitates excellent micrometeorological flux measurements with local energy budget closures within 20% (45). The flux-gradient approach (30) consists of GEM gradient measurements at two heights above the canopy multiplied by a measure of atmospheric turbulence and provides an aerially integrated flux over a whole ecosystem. GEM fluxes (*F*<sub>GEM</sub>) are equal to gradients of a trace gas scaled by the rate of turbulent exchange according to the formula:

\[
F_{\text{GEM}} = -K \times \Delta C_{\text{GEM}}/\Delta z
\]

where *K* equals the vertical turbulent exchange coefficient (also termed eddy diffusivity; units of meters² · second⁻¹) and \(\Delta C_{\text{GEM}}/\Delta z\) is the concentration gradient of the trace gas (for GEM in units of nanogram · meter⁻²). Determination of *K* is performed by the aerodynamic method, whereby *K* parameterization involves Monin–Obukhov similarity theory and is calculated directly from sonic anemometer measurements (30) according to the following equation:

### Table 2. Calculation of annual litterfall at Harvard Forest based on a 10-yr record of litterfall mass measured at the site and end-of-season Hg analyses of foliar samples of four dominant tree species

<table>
<thead>
<tr>
<th>Species</th>
<th>Annual biomass litterfall (Mg · ha⁻¹)*</th>
<th>Litterfall mercury concentration (μg · kg⁻¹)†</th>
<th>Litterfall mercury deposition (μg · m⁻²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oak</td>
<td>234</td>
<td>16.9</td>
<td>3.9</td>
</tr>
<tr>
<td>Maple</td>
<td>112</td>
<td>23.3</td>
<td>2.6</td>
</tr>
<tr>
<td>Beech</td>
<td>32</td>
<td>34.1</td>
<td>1.1</td>
</tr>
<tr>
<td>Hemlock</td>
<td>20</td>
<td>22.2</td>
<td>0.4</td>
</tr>
<tr>
<td>Total</td>
<td>398</td>
<td>20.4*</td>
<td>8.1</td>
</tr>
</tbody>
</table>

*Based on measured annual litterfall from 2000 to 2007, averaging 1.99 Mg · C · ha⁻¹ (3.98 Mg · biomass · ha⁻¹). Annual litterfall was separated into four dominant species based on observed litterfall contributions and scaled up to 100% (Oak: 59%, Maple: 28%, Beech: 8%, and Hemlock: 5%).
†Foliage concentrations at the end of the growing season (September 2018).
‡Weighted average mean concentration.
where \( k \) is the Karman constant (0.4), \( u^* \) is the friction velocity, \( z \) and \( d \) are measurement height above ground and zero-plane displacement height, respectively, and \( \phi_m \) is the diabatic influence function for momentum. Trace gas flux footprints that contribute to the formation of the concentration profile at a sensor location are dependent on atmospheric stability and generally originate within 500 m distance to the measurement tower. Flux-gradient methods assume that no sources or sinks of the trace gas of interest exist between the two gradient inlets. For GEM, we consider this a valid assumption given that GEM has an atmospheric residence time of several months (47) and is highly stable within the short time of turbulent exchange within canopies (minutes to hours). It is unlikely that concentrations of GOM impact gradients given that concentrations are 300 times lower than GEM (SI Appendix, Fig. 56) and show low breakthrough with the inlet configuration used (48).

An EC system measured fluxes of \( \text{CO}_2, \text{H}_2\text{O} \) momentum, and sensible and latent heat at 29 m with a closed-path infrared gas analyzer (IRGA; Model 6261, LI-COR, Lincoln, Nebraska) sampling air to measure \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) at 4 Hz frequency. The IRGA was calibrated three times daily by standard ad.


