Diminished mercury emission from waters with duckweed cover

Jennifer L. Wollenberg and Stephen C. Peters

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Duckweeds (Lemnaceae) are a widely distributed type of floating vegetation in freshwater systems. Under suitable conditions, duckweeds form a dense vegetative mat on the water surface, which reduces light penetration into the water column and limits gas exchange at the water-air interface by decreasing the area of open water surface. Experiments were conducted to determine whether duckweed decreases mercury emission by limiting gas diffusion across the water-air interface and attenuating light, or, conversely, enhances emission via transpiration of mercury vapor. Microcosm flux chamber experiments indicate that duckweed decreases mercury emission from the water surface compared to open water controls. Fluxes under duckweed were 17–67% lower than in controls, with lower fluxes occurring at higher percent cover. The decrease in mercury emission suggests that duckweed may limit emission through one of several mechanisms, including limited gas transport across the air-water interface, decreased photoreactions due to light attenuation, and plant-mercury interactions. The results of this experiment were applied to a model lake system to illustrate the magnitude of potential effects on mercury cycling. The mercury retained in the lake as a result of hindered emission may increase bioaccumulation potential in lakes with duckweed cover.


1. Introduction

The scientific community has actively studied the behavior of mercury in aquatic systems for several decades, in large part because of the potential for mercury to bioaccumulate in food webs and have toxic effects at higher trophic levels. One pathway that may remove mercury from the water column, thereby decreasing the amount available for methylation and bioaccumulation, is the emission of gaseous mercury from the water surface to the atmosphere. Elemental mercury (Hg$_0$) is only sparingly soluble in water [Sanemasa, 1975], so the reduction of dissolved Hg$^2+$ to gaseous Hg$_0$ often results in partitioning of mercury from terrestrial or aquatic reservoirs to the atmosphere [Lindberg et al., 1998; Morel et al., 1998].

Many natural waters are oversaturated with dissolved gaseous mercury with respect to the atmosphere [Vandal et al., 1991], generating a concentration gradient from the water to the air. The resultant flux of Hg$_0$ from the water surface, as measured using the dynamic flux chamber method described by Carpi and Lindberg [1998], can be calculated using the following equation:

$$ J_{Hg} = (C_i - C_o) \left( \frac{Q}{A} \right) $$ (1)

where $J_{Hg}$ is the calculated mercury flux, $Q$ is the sampling flow rate, $A$ is the measured surface area within the chamber, and $C_i$ and $C_o$ are the chamber and ambient mercury concentrations, respectively. Inherent in this equation is the emissive surface area; therefore, factors that decrease the effective surface area would be expected to inhibit mercury transport across the surface. Because they often occupy surface areas of ponds and wetlands, floating-leaved macrophytes may represent one such factor that influences Hg$_0$ flux across the air-water interface.

Aquatic plants of the family Lemnaceae (generally referred to as duckweeds) are a widely distributed type of floating vegetation in freshwater systems [Landolt, 1986]. The duckweeds have been extensively studied for their uses in toxicity testing and wastewater treatment [e.g., Wang, 1990]. Most toxicity studies of duckweed-mercury interactions have been conducted at concentrations far higher than normal environmental conditions (i.e., greater than 0.05 mg/L [Mo et al., 1989; Gebhard et al., 1990; Charlier et al., 2005]). One study found that duckweed accumulated up to 1,800 ug g$^{-1}$ mercury after 10 days when incubated in water with high dissolved mercury concentrations (10 mg/L), and did not appear to suffer from acute toxicity [Mo et al., 1989]. A more recent investigation also found significant mercury uptake by duckweed after 3 days (~18 ug/g wet wt.), accompanied by a reduction in growth of 10–30% [Charlier et al., 2005]. The tolerance of duckweed to mercury and other heavy metals has led to its consideration for phytoremediation of impacted aquatic systems [Mishra et al., 2008].

Duckweeds typically form a low-lying dense vegetative mat on the water surface, which affects the physico-
chemical properties of the underlying water by interfering with gas exchange across the water-air interface, and decreasing light penetration into the water column. Oxygen diffusion across the water-air interface has been shown to be significantly lower in the presence of duckweed cover [Pokorny and Rejmankova, 1983], and limitations on diffusion may similarly affect mercury emission. Floating mats of duckweed can also decrease penetration of photosynthetically active radiation (PAR) by 60% within the top 15 cm of the water column [Janes et al., 1996] and sometimes as much as 99% under particularly dense mats [Gunning and Wulff, 1970]. Solar radiation is an important parameter that governs mercury emission rates, with emission from the water surface generally increasing at greater light intensity [e.g., Krabbenhoff et al., 1998; Ferrara et al., 2000; Peters et al., 2007]. Direct photoreduction of mercury (Hg²⁺ → Hg⁰) may increase emission by increasing the concentration of Hg⁰ in solution [Amyot et al., 1997a]. Indirect photoreduction of mercury may also occur as part of a coupled reaction whereby dissolved organic carbon (DOC) is photooxidized and mercury is reduced [Amyot et al., 1997a; Tseng et al., 2004]. As a result, factors that decrease light penetration into the water column or decrease DOC photoreactivity would likely decrease mercury emission from aquatic systems. Direct photooxidation of mercury also can occur (Hg⁰ → Hg²⁺), and this reaction decreases emission rates by lowering the concentration of Hg⁰ in solution [Lalonde et al., 2001]. The modification of water surface properties by duckweed would therefore be expected to decrease mercury emission through a combination of decreasing (1) Hg⁰ diffusion across the water-air interface, (2) direct photoreduction of Hg²⁺, and (3) indirect reduction via coupled DOC photooxidation-Hg²⁺ reduction.

Conversely, previous studies have measured significant transpiration of Hg⁰ by plants, so it is possible that the floating vegetative mat could increase emission via transpiration of mercury vapor. Research on mercury emissions from plants has primarily focused on vegetation with significant aboveground biomass in both upland and wetland environments [Hanson et al., 1995; Leonard et al., 1998; Gustin et al., 2004; Lindberg et al., 2005; Fay and Gustin, 2007; Poissant et al., 2008]. Fluxes measured in terrestrial and aquatic vegetation range from deposition to significant emission. For example, measured fluxes in upland settings range from $-24.2$ ng m⁻² h⁻¹ (Abies balsamica) [Graydon et al., 2006] to $+92.6$ ng m⁻² h⁻¹ (Caulanthus sp.) [Leonard et al., 1998]. In wetland environments, reported fluxes from plants range from $-3.3$ ng m⁻² h⁻¹ (Spartina patens) [Lee et al., 2000] to $49$ ng m⁻² h⁻¹ (Typha sp.) [Lindberg et al., 2002].

Mercury emission from plants is dependent on both uptake of mercury from the sediment as well as the concentration gradient between the sediment and atmosphere [Lindberg et al., 2002; Ericksen and Gustin, 2004]. Duckweed has been shown to take up mercury from aqueous medium in numerous experiments [Mo et al., 1989; Wang, 1990; Charlier et al., 2005], thereby suggesting that transpiration of mercury vapor could be important. If mercury is assumed to be taken up from solution as Hg²⁺, then mercury reduction in the leaves would also be required in order for transpiration of mercury vapor to occur. Reduction of Hg²⁺ to Hg⁰ within leaves has been reported in barley plants grown in the laboratory [Battke et al., 2005], and Siegel et al. [1987] suggests that mercury reduction occurs in both terrestrial and aquatic plants.

Under eutrophic or stagnant water conditions, duckweed may cover almost the entire surface of ponds and waterways [Landolt, 1986], so it is possible that duckweed could affect the overall mercury budget of those systems if it significantly limits or enhances emission. In this research, we seek to determine whether duckweed limits mercury flux to the atmosphere by decreasing incoming light and interfering with air-water gas exchange, or whether it enhances emission from aquatic systems via transpiration of Hg⁰. We approach this question by varying the amount of duckweed cover in an experimental system and measuring the resulting mercury flux and formation of Hg⁰.

2. Experimental Design

2.1. Effect of Percent Duckweed Cover

Duckweed (Lemma minor, purchased from Carolina Biological Supply) was grown in an aquarium under ambient conditions in a greenhouse at Lehigh University in spring water supplemented with a small amount of commercially available fertilizer. Experiments were conducted in deionized water that was amended with Hg²⁺ (High Purity Standards, Charleston, SC) and allowed to equilibrate for >12 h prior to the start of the experiment. A mercury concentration of 22 ng/L was selected for the experiments in order to produce measurable emission from the small surface area in the experimental apparatus. In addition, this concentration has a low likelihood of toxicity to duckweed based on the results of studies conducted at much higher concentrations [Mo et al., 1989; Charlier et al., 2005], and is within the range of total mercury concentrations found at contaminated locations where duckweed has been observed (e.g., Kearny Freshwater Marsh, NJ [Kiviat and MacDonald, 2002; Bentivenga et al., 2004]).

Rectangular 10 L flux chambers were constructed of polystyrene, which transmits both visible and UV light. Average measured visible light transmittance was 88%, UV-A transmittance was 74%, and UV-B transmittance was 41% (spectral cutoff $\approx 290$ nm; Figure 1), as determined using a portable UV-Vis Spectrometer (Ocean Optics, Dunedin, FL, USA). Six holes, each approximately 3 mm in diameter, were drilled in the chambers approximately 2 cm above the water surface. Eight liters of the amended deionized water were transferred to two flux chambers and duckweed plants were transferred from the growth media to one of the flux chambers, in numbers sufficient to attain varying percent cover on the water surface (96%, 80%, 76%, 40%). The flux chamber without duckweed cover served as a control and was otherwise identical to the treatment, so that any observed differences could be attributable to the duckweed. Photographs of the water surface were digitized to calculate the percent of the water surface covered by duckweed. Perforated polypropylene (U.S. Plastics, Lima, OH) 0.4 cm thick with 0.2 cm diameter holes in rows with centers staggered 1.2 cm apart was also used for one experiment as an abiotic treatment (approximately 95% cover). The polypropylene sheet had average measured visible light transmittance of 68%, UV-A transmittance of 53%, and UV-B transmittance of 57%. During all experiments, light
was able to enter the flux chambers from the sides and the top of the flux chambers, minimizing the effect of shading by duckweed. A schematic diagram of the experimental apparatus, as well as the measured transmittance profile for the flux chamber material, is depicted in Figure 1.

[11] Chambers were sealed using clear plastic lids that had a similar transmittance profile to polystyrene, and were continuously pumped at a rate of 0.6 L min⁻¹ for the 6-h duration of the experiment. Mercury concentrations in the flux chamber headspace were measured at approximately 15-min intervals by gold amalgamation, thermal desorption, and absorbance detection using a field portable instrument (UT-3000, Mercury Instruments, Karlsfeld, Germany). Ambient mercury concentrations were measured at the inlets of the chambers, and mercury flux rates were calculated using equation (1). The mean chamber blank flux rate was 0.17 ± 0.04 ng Hg m⁻² h⁻¹, which is less than 15% of the smallest flux and less than 1% of the largest measured flux in the experimental treatments.

[12] Adsorption of mercury to the chamber and duckweed plants was measured in the dark to assess losses not accounted for in the emission measurements and to enable calculation of a mass balance. The adsorption measurement was conducted in both the presence and absence of duckweed plants to assess the contribution of each component. This calculation accounted for mercury emitted as well as beginning and ending dissolved mercury concentrations (measured in duplicate). The amount adsorbed onto the container and duckweed plants was determined starting with the initial dissolved concentration and subtracting the ending dissolved concentration and the mass emitted. Mass balance calculations indicated that approximately 12 to 15% of the mercury was lost due to adsorption to the chamber and duckweed plants. Approximately 7% more mercury was adsorbed in the presence of duckweed plants. It is also possible that some of the mercury was taken up by the duckweed plants, although previous studies have shown that mercury uptake in duckweed was ineffective below concentrations of 0.3 mg/L [Mo et al., 1989]. The short duration of the incubations (~6 h) also made significant uptake unlikely, and mercury concentrations were not measured in the plant tissue for this experiment.

[13] Emission experiments were conducted outside on cloudless days between approximately 9:30 A.M. and 3:30 P.M. to assess the effects of solar radiation on emission. The perforated plastic treatment was only run from approximately 12:00 P.M. to 3:30 P.M. due to equipment problems. Experiments were conducted in May, June, July, and August, 1 day for each percent cover and the perforated plastic treatment. It was not feasible to run all treatments on the same day, to allow for evaluation of data as it was collected, because suitable weather conditions were required.
and the availability of the mercury analyzer was limited. The duckweed used in each experimental exposure was discarded and new duckweed was used in each experiment. The flux chambers were emptied and cleaned between experiments. To account for differences in weather conditions between experiment days, solar radiation, temperature, and other weather measurements were obtained from a weather station (Davis Instruments, Hayward, CA) installed on Lehigh University’s campus. Water temperature inside the flux chambers was not controlled during initial experiments (96%, 80%, 76% cover), and water temperatures in the chambers increased during the experiment but were not significantly different between treatments and controls (Paired Student’s t test, \( t = -1.8 \) to 0.25, \( p > 0.05 \)). Although mercury flux measurements did not covary with water temperature \( (r^2 < 0.3, p > 0.05) \), this variable was controlled using a circulating water bath for subsequent 40% cover and perforated plastic treatments.

To measure the vitality of the duckweed during the experiments, \( CO_2 \) concentration inside the experimental chambers was measured using an instantaneous reading infrared gas analyzer (LI-840, LiCor, Omaha, NE) connected to the air outlet of the mercury analyzer. The \( CO_2 \) measurements were not affected by the mercury analyzer, as indicated by identical measurements made with and without the mercury analyzer inline (J. L. Wollenberg and S. C. Peters, unpublished data).

2.2. Aqueous Mercury Speciation

An additional experiment was conducted to evaluate changes in the speciation of mercury under duckweed cover over time. The intent of this experiment was to confirm that \( Hg^0 \) production occurred under duckweed despite the potentially diminished light penetration into the water column. Three identical flux chambers were established with a mercury concentration of approximately 22 ng/L in deionized water, and equal amounts of duckweed (19 g wet weight) were added to achieve approximately 60% duckweed cover. The experiment was conducted outside as described above, between the hours of 10 A.M. and 3 P.M. Two water samples were collected from each chamber at the start of the experiment \( (t = 0) \) for \( Hg^0 \) and total mercury determination, and then at 90, 180, and 270 min. Samples were filtered through 0.45 um polypropylene filters into acid-cleaned 40 mL glass vials with Teflon septa using clean techniques, with care taken to ensure that no headspace remained in the vial. Water samples for total mercury analysis were oxidized with approximately 1% (v/v) bromine monochloride at the time of collection and stored in the dark until analysis.

2.3. Sample Analysis

Water samples for \( Hg^0 \) determination were analyzed within 1 h of collection. Analysis was conducted by slowly pouring 40 mL of sample into an acid-cleaned 125 mL glass bubbler and purging samples with ultrapure argon gas for 20 min, at a rate of approximately 100 mL/min. The gas stream flowed through a gold trap, which was then thermally desorbed and measured using atomic fluorescence spectroscopy (Tekran Instruments, Knoxville, TN).

Total mercury samples were analyzed following the methods outlined by Gill and Fitzgerald [1987]. In summary, samples were sequentially reduced with hydroxylamine hydrochloride to destroy free halogens and stannous chloride to convert all \( Hg^{2+} \) to \( Hg^0 \), and then purified and analyzed as described for \( Hg^0 \) samples. System blanks were less than 1.3 pg Hg.

Samples for DOC analysis were collected at the start and end of the experiments and filtered using a prerinsed Whatman GF/F filter into glass vials with Teflon septa, with care taken to ensure that no headspace remained in the container. Water sample DOC concentration was measured on a Shimadzu TOC-V (Columbia, Maryland) considering the approach outlined by Sharp et al. [1993].

2.4. Data Analysis

Statistical analyses were performed using Statgraphics Centurion (StatPoint, Inc.). Paired Student’s t tests were used to compare \( J_{Hg} \) time series \( (n > 12) \) between duckweed and open water controls for each percent cover treatment, as well as the perforated plastic and open water control \( (n = 10) \). Correlation coefficients \( (r^2) \) were calculated to evaluate the relationship between \( J_{Hg} \) and environmental parameters (water and air temperature, total solar and UV radiation).

2.5. Estimation of Duckweed Effects on In-Lake Mercury Concentrations

The results of this experiment were applied to an idealized circular lake to generate a preliminary estimate of the potential effect of decreased mercury emission by duckweed cover on in-lake dissolved mercury concentrations. We designed the model lake to be a well mixed, perfect half-sphere with a surface area of 5000 m\(^2\) \( (volume = 1.3 \times 10^8 \text{ L}) \). Previous studies by others have measured a wide range of mercury emission rates in lakes, from 1 ng m\(^{-2}\) d\(^{-1}\) [Amyot et al., 1997a] to 130 ng m\(^{-2}\) d\(^{-1}\) [Boudala et al., 2000]. We assumed an emission rate of 30 ng m\(^{-2}\) d\(^{-1}\) throughout the year, similar to intermediate rates measured by others [Amyot et al., 1997b; Mason and Sullivan, 1998; Boudala et al., 2000; Tseng et al., 2004]. Although some studies have demonstrated that plant canopies can influence mercury deposition [Lee et al., 2000; Poissant et al., 2004], for the purpose of simplification the model was based on the assumption that atmospheric mercury deposition remained constant and was not affected by duckweed cover. Using these constraints, we calculated the range of potential effect of duckweed cover using the minimum (40%) and maximum (96%) percent covers measured in this study and a duckweed cover duration of 4 months.

3. Results

Mercury emission rates ranged from 1.8 to 15.7 ng m\(^{-2}\) h\(^{-1}\) in the open water controls, compared to 1.1 to 5.0 ng m\(^{-2}\) h\(^{-1}\) in the various duckweed treatments. Emission rates from duckweed treatments were significantly different from open water controls \( (t = -15.6 \text{ to } -5.6, \ p < 0.0001) \) for each value of percent cover, with emission from the treatments consistently lower than the open water controls (Figure 2). The \( CO_2 \) data confirmed that duckweed plants continued to transpire during the experimental exposures, as
Figure 2. Measured mercury fluxes from all treatments (solid symbols) and open water controls (open symbols). Differences in emission are due to changes in percent cover and differences in daily solar and UV radiation during the experimental period. Exposure dates are indicated.

Figure 3. Effect of duckweed cover on CO₂ concentrations in the flux chambers (open squares) as compared to the open water controls and ambient concentrations (gray markers). As expected, the CO₂ concentrations are significantly lower in the presence of duckweed (p < 0.05).
evidenced by CO₂ concentrations that were significantly lower in the duckweed flux chambers as compared to the open water controls (t = -25.6, p < 0.05; Figure 3). Measured emission rates in the abiotic experiment ranged from 2.0 to 3.4 ng m⁻² h⁻¹ in the open water control, compared to 1.9 to 2.7 ng m⁻² h⁻¹ in the perforated plastic treatment (Figure 2). Minimum, maximum, and mean observed fluxes for all treatments are summarized in Table 1.

**Table 1. Summary of Measured Mercury Emission Rates in All Treatments and Controls**

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Minimum Emission Rate</th>
<th>Maximum Emission Rate</th>
<th>Mean Emission Rate</th>
<th>Mean Percent Difference in Emission</th>
<th>Mean Emission per Joule UV Radiation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Treatment</td>
<td>Control</td>
<td>Treatment</td>
<td>Control</td>
<td>Treatment</td>
</tr>
<tr>
<td>96</td>
<td>3.2</td>
<td>8.5</td>
<td>4.9</td>
<td>15.7</td>
<td>3.9</td>
</tr>
<tr>
<td>80</td>
<td>1.0</td>
<td>1.9</td>
<td>2.6</td>
<td>3.2</td>
<td>1.3</td>
</tr>
<tr>
<td>76</td>
<td>1.2</td>
<td>2.4</td>
<td>3.0</td>
<td>5.1</td>
<td>2.3</td>
</tr>
<tr>
<td>40</td>
<td>1.9</td>
<td>2.2</td>
<td>5.0</td>
<td>6.5</td>
<td>3.3</td>
</tr>
<tr>
<td>PP</td>
<td>0.9</td>
<td>2.0</td>
<td>2.7</td>
<td>3.3</td>
<td>2.0</td>
</tr>
</tbody>
</table>

*Units are in ng m⁻² h⁻¹. The mean percent difference between mercury emission rates from duckweed treatments and open water controls is indicated. Mercury emission is significantly lower in the treatments than the controls (p < 0.0001). The mass of mercury (ng) emitted per Joule of UV radiation is also shown.*

To account for differences in solar radiation between treatments (Figure 4), the mass of mercury emitted per Joule of UV radiation was calculated for each measurement (Table 1). Differences in the mercury emitted per Joule of UV radiation for the duckweed treatments and open water controls from the same day were attributed to the effect of the duckweed on the emission of mercury.
The mean percent difference between emission from the duckweed treatment and the corresponding open water control on the same day was calculated for each value of percent cover. Mean emission from the treatment with 96% duckweed cover was 68% lower than emission from the corresponding open water control. Lower percent cover of duckweed resulted in smaller differences in emission between treatments and controls, with only 18% difference in emission for the 40% cover treatment. Emission in the perforated plastic treatment was 20% lower than the corresponding open water control (t = 3.8, p < 0.01). A crossplot of the percent duckweed cover versus the measured percent difference in mercury emission in the duckweed treatment with respect to the open water control suggests a consistent trend of diminished emission at greater duckweed coverage (Figure 5).

DOC concentrations in the experimental exposures are summarized in Table 2. DOC concentrations appeared slightly lower in postexposure duckweed treatments as compared to open water controls, though the difference was not significant (t = −3.8, p < 0.01). The postexposure DOC concentration in the abiotic control using a perforated plastic sheet was higher than the corresponding open water control as well as the starting solution, suggesting that the plastic may have leached organic matter into solution during the experiment.

### 3.1. Aqueous Mercury Speciation

The mean Hg0 concentration in the start solution for all replicates was 0.22 ng L⁻¹ ± 0.03 S.D., which is 1% of the total mercury in solution. Total Hg0 increased initially to a mean value of 2.4 ng L⁻¹ ± 0.07 SD (11.5% total Hg), and then declined to less than the starting Hg0 concentration during the remaining experimental period (Figure 6).

### 3.2. Estimation of Duckweed Effects on In-Lake Mercury Concentrations

The total mass of mercury emitted annually from the model system (surface area = 5000 m²) was calculated for 0% duckweed cover to be $5.5 \times 10^7$ ng a⁻¹ at an average emission rate of 30 ng m⁻² d⁻¹. Decreasing emissions by the 18% to 68% observed in this experiment resulted in approximate mean emissions of $4.5 \times 10^7$ and $1.8 \times 10^7$ ng a⁻¹, respectively, if duckweed covered the lake surface the entire year. However, since duckweed cover is seasonal, these numbers provide an overestimation of the effect. If corrected for limited emissions only a portion of the year (4 months cover assumed), the decreased emission rates resulted in the emission of $5.1 \times 10^7$ to $4.2 \times 10^7$ ng a⁻¹. If the lake were a well mixed, perfect half-sphere (volume = $1.3 \times 10^8$ L), retention of this amount of mercury corresponded to concentrations that are 0.03 to 0.09 ng L⁻¹ higher than they would be in the absence of duckweed cover.

### 4. Discussion

The results of this experiment indicate that the presence of duckweed inhibited mercury emission from the water surface rather than enhancing it via transpiration.

#### Table 2. DOC Concentrations for All Exposures

<table>
<thead>
<tr>
<th>Percent Cover</th>
<th>Treatment</th>
<th>DOC (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>start (all solutions)</td>
<td>1.1 ± 0.07</td>
</tr>
<tr>
<td>0</td>
<td>open water control (96%)</td>
<td>1.0</td>
</tr>
<tr>
<td>96</td>
<td>duckweed treatment</td>
<td>0.9</td>
</tr>
<tr>
<td>0</td>
<td>open water control (80%)</td>
<td>1.7</td>
</tr>
<tr>
<td>80</td>
<td>duckweed treatment</td>
<td>1.3</td>
</tr>
<tr>
<td>0</td>
<td>open water control (76%)</td>
<td>1.3</td>
</tr>
<tr>
<td>76</td>
<td>duckweed treatment</td>
<td>1.2</td>
</tr>
<tr>
<td>0</td>
<td>open water control (40%)</td>
<td>1.1</td>
</tr>
<tr>
<td>40</td>
<td>duckweed treatment</td>
<td>0.9</td>
</tr>
<tr>
<td>0</td>
<td>open water control (95%)</td>
<td>1.1</td>
</tr>
<tr>
<td>95</td>
<td>perforated plastic treatment</td>
<td>2.2</td>
</tr>
</tbody>
</table>

*The starting concentration is the mean and standard deviation for all solutions. All other values are single measurements of the ending solution. Open water controls are differentiated by the percent cover treatment to which they correspond in parenthesis.
Emission rates from the duckweed treatments were 18% to 68% lower than open water controls, depending on the degree of duckweed cover (Table 1 and Figure 5). Several possibilities could explain this result, including a decrease in light penetration under duckweed and resulting limits on photoproduction of Hg\textsuperscript{0}, a decrease in diffusion across a partially blocked surface, or interactions between the plants and dissolved mercury. Since light penetration into the water column was not manipulated in this experiment and the chambers were open to light on five sides, it is not likely that light attenuation by duckweed was the primary mechanism responsible for the decrease in emission observed in this experiment. Light may have been limited immediately under the duckweed mat, but the rest of the water column received the same irradiance as in the open water controls. A decrease in the effective water surface area across which mercury may be emitted, or plant-mercury interactions, are more likely to explain the decreased emission observed.

In aqueous systems, the relative rates of competing oxidation and reduction reactions control the distribution of mercury species between Hg\textsuperscript{0} and Hg\textsuperscript{2+}. In this experiment, the potentially decreased light penetration due to duckweed cover did not prevent the formation of Hg\textsuperscript{0} since light was able to penetrate the chamber from the sides. Hg\textsuperscript{0} concentrations in solution increased at the start of the experiment upon exposure of the flux chamber to sunlight (Figure 6), as reduction of Hg\textsuperscript{2+} occurred. For emission to occur, Hg\textsuperscript{0} must diffuse vertically through the water column and then cross the water-air interface. In the open water controls, this process proceeds unimpeded. However, in the duckweed treatments, transfer of Hg\textsuperscript{0} across the water-air interface may have been inhibited by duckweed plants by either decreasing the open water surface area or decreasing the effect of wind on the water surface [O’Driscoll et al., 2003]. The lower emission relative to the control observed in the treatment using the perforated polypropylene sheet provides some support for an abiotic process such as diminished diffusion.

It is also possible that mercury was adsorbed onto plant surfaces, thereby decreasing the pool of mercury available for photoreduction, or that the plants themselves play a role in mercury oxidation, as suggested by Garcia et al. [2006]. The Hg\textsuperscript{0} concentration in the water column decreased as the exposure progressed, which could be due to either reoxidation to Hg\textsuperscript{2+}, loss of mercury via adsorption onto the plants and flux chamber, or decreases in solar radiation toward the end of the experiment (Figure 6). As discussed in the methods section, adsorption of mercury onto the flux chambers and plants did occur during this experiment, but the ~7% loss due to adsorption on duckweed is not sufficient to account for the 18 to 68% difference in emission between treatments and controls. It is therefore likely that either enhanced reoxidation to Hg\textsuperscript{2+} or diminished diffusion across the water-air interface, or some combination of these mechanisms, played the most significant role in the observed decreases in emission from this experiment.

In natural systems where light must enter the water column solely from above, increased duckweed cover would also limit light penetration and further limit mercury reduction. The polypropylene sheet used in one of the
experiments transmitted some light in the visible and UV ranges, whereas individual duckweed leaves are likely to block most light transmission. Optical measurements of leaves from other plant species have demonstrated that leaf tissue absorbs an average of 83 to 87% of visible and most UV light [Krauss et al., 1997; Knapp and Carter, 1998]. Incident light measured in the water column under duckweed mats ranges from <1% to 40% of the surface irradiance [Ganning and Wulff, 1970; Janes et al., 1996]. Emission from the perforated plastic treatment was more similar to the open water control than to duckweed treatments with similar percent cover. This may have been the result of more light available for photo reactions under the perforated plastic, or differences in the size and shape of the holes in the polypropylene sheet compared to the size and shape of the open water between the duckweed plants that would influence the ability of lateral diffusion. In addition, higher postexposure DOC concentrations in the perforated plastic treatment suggest that the plastic may have leached some organic matter into solution. The ending DOC concentration was approximately double the starting concentration (Table 2), and this higher DOC concentration may have enhanced photo reduction of mercury in this treatment through coupled DOC photooxidation-Hg reduction [Allard and Arsenie, 1991].

[31] The decreases in mercury emission due to duckweed cover observed in this experiment represent a minimum effect, and it is likely that the effect in natural lakes and wetlands might be more significant due to shading of the water column and resultant decreases in photo reactions. This prediction is in contrast to the findings of a study that evaluated production of dissolved gaseous mercury in the presence and absence of submerged and floating aquatic macrophytes, and found no difference between vegetated and unvegetated waters [Garcia et al., 2006]. Although duckweeds have been shown to take up mercury from solution at high dissolved mercury concentrations [Mo et al., 1989], this is not expected to have a substantial effect on long-term lake mercury cycling. Any mercury taken up during the growing season is likely to be leached from the plant tissues during decomposition and reintroduced to the system.

[32] Mercury emission is an important mechanism for decreasing the overall dissolved mercury burden in aquatic systems [Fitzgerald et al., 1991; Watras et al., 1995]. We estimated the effect of limited mercury emission due to duckweed cover of 40% to 96% on a model lake system, and calculated that the dissolved concentration may be 0.03 to 0.09 ng L\(^{-1}\) higher, respectively, than it would be in the absence of duckweed cover. While this is not a large concentration increase, it may be important in low-mercury systems over the course of time. The limited emission under duckweed may result in higher concentrations of mercury available to methylators and thus increase the amount of mercury entering the food web. It is also possible that other species of floating aquatic vegetation (e.g., Salvinia, Eichhornia, Azolla species) may produce a similar effect on mercury emission.

5. Conclusions and Implications

[33] Emission of mercury from wetlands and water bodies may decrease in the presence of mats of floating vegetation. Using duckweed (Lemna minor) as a model organism, experiments showed that consistent decreases in emission occurred under these vegetative mats. The decreases in emission were likely due to diminished vapor transport across the water-air interface, decreased light penetration into the water column for photoreactions, and plant-mercury interactions such as adsorption or reoxidation of Hg\(^0\). The decreased emission of mercury from lakes and wetlands would be expected to result in higher mercury concentrations in the water column, which may then serve as a larger reactive pool for mercury methylation and accumulation into food webs.

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S. C. Peters and J. L. Wollenberg, Department of Earth and Environmental Sciences, Lehigh University, Bethlehem, PA 18015, USA. (scp2@lehigh.edu; jwollenberg@elmine.com)