Corrigendum


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The authors regret that,

Abstract:

"Filtered (0.2 μm) and unfiltered samples were analyzed for gross photoreduction, gross photooxidation, and net reduction rates of mercury using pseudo first-order curves. Unfiltered samples had higher concentrations (p=0.04) of photoreducible divalent mercury (Hg(II)RED) (mean of 754±253 pg/L) than filtered samples (mean of 482±206 pg/L); however, gross photoreduction and photooxidation rate constants were not significantly different in filtered or unfiltered samples in early summer. DOC was not significantly related to gross photoreduction rate constants in filtered (R²=0.43; p=0.08) and unfiltered (R²=0.02; p=0.71) samples; DOC was also not significantly related to gross photooxidation rate constants in filtered or unfiltered samples. However, DOC was significantly negatively related with Hg(II)RED in unfiltered (R²=0.53; p=0.04), but not in filtered samples (R²=0.04; p=0.60)."

Should be revised to

"Filtered (0.2 μm) and unfiltered samples were analyzed for gross photoreduction, gross photooxidation, and net reduction rates of mercury using pseudo first-order curves. Unfiltered samples had higher concentrations (p=0.037) of photoreducible divalent mercury (Hg(II)RED) (mean of 801±260 pg/L) than filtered samples (mean of 502±225 pg/L); however, gross photoreduction and photooxidation rate constants were not significantly different in filtered or unfiltered samples in early summer. DOC was weakly related to gross photoreduction rate constants in filtered (R²=0.41; p=0.08) and unfiltered (R²=0.45; p=0.07) samples; DOC was also not significantly related to gross photooxidation rate constants in filtered or unfiltered samples. However, DOC was weakly and negatively related with Hg(II)RED in unfiltered (R²=0.53; p=0.07), but not in filtered samples (R²=0.03; p>0.10)."

Section 1.2:

\[ \text{Hg}(0)_k = [\text{Hg(II)}]_{\text{RED}} - e^{kt} [\text{Hg(II)}]_{\text{RED}} \]

This can be rewritten as:

\[ \text{Hg}(0)_k = [\text{Hg(II)}]_{\text{RED}} (1 - e^{kt}) \]

Should be revised to

\[ \text{Hg}(0)_k = [\text{Hg(II)}]_{\text{RED}} - e^{-kt} [\text{Hg(II)}]_{\text{RED}} \]

This can be rewritten as:

\[ \text{Hg}(0)_k = [\text{Hg(II)}]_{\text{RED}} (1 - e^{-kt}) \]

Section 1.3:

"Once the gross reduction and net reduction rate constants were determined, gross photooxidation rate constants were derived by subtracting net photoreduction data points from gross photoreduction data, and a pseudo first order reaction
equation was fitted to the resulting curve using Sigma-Plot 12.0 (Fig. 2)."

Should be revised to

"Once the gross reduction and net reduction rate constants were determined, gross photooxidation rate constants were derived by subtracting net photoreduction rate constants from gross photoreduction rate constants. Curves of gross photooxidation can then be derived using the resulting equation for a pseudo first order reaction (Fig. 2)."

Section 2.1:

"In all lakes, unfiltered samples had significantly higher concentrations of photoreducible mercury, Hg(II)\textsubscript{RED} (mean = 754 ± 253 pg/L) than 0.2 μm filtered samples (mean = 482 ± 206 pg/L) (t-test; p = 0.04; Shapiro Wilk normality P = 0.63)."

Should be revised to

"In all lakes, unfiltered samples had significantly higher concentrations of photoreducible mercury, Hg(II)\textsubscript{RED} (mean = 801 ± 260 pg/L) than 0.2 μm filtered samples (mean = 502 ± 225 pg/L) (t-test; p = 0.04; Shapiro Wilk normality P = 0.61).

Section 2.2

"In this work, gross photoreduction rate constants ranged from 1.63 × 10^{-3} hr\textsuperscript{-1} to 3.42 × 10^{-3} hr\textsuperscript{-1} in filtered samples, and 1.29 × 10^{-3} hr\textsuperscript{-1} to 2.93 × 10^{-3} hr\textsuperscript{-1} in unfiltered samples, for lakes sampled in May of 2008 and 2009 (Table 1). Similar results were found for the gross photooxidation rate constants, which ranged between 1.42 × 10^{-3} hr\textsuperscript{-1} and 3.04 × 10^{-3} hr\textsuperscript{-1} for filtered samples, and 1.21 × 10^{-3} hr\textsuperscript{-1} to 2.78 × 10^{-3} hr\textsuperscript{-1} for unfiltered samples (Table 1). It can be seen in Table 1 that the lakes sampled late in the summer season (August of 2010; Pebblelodge, Peskowes, and Beaverskins lakes) have significantly larger gross photoreduction and gross photooxidation rate constants than the lakes sampled in early summer (Table 1). It is interesting to note, however, that the net photoreduction rate constants are in a similar range for all lakes; this suggests that while the rate of both photooxidation and photoreduction reactions has increased, the overall effect on the net mercury reduction rate constant did not change substantially, due to the close balance of photoreduction and photooxidation reactions occurring in these lakes. The near-balance of mercury photooxidation and photoreduction observed in these lakes may suggest a common linking component between lakes, such as the atmospheric deposition of reactive mercury being the dominant mercury pool undergoing these photoreactions (Orihel et al., 2007).

Our data show that gross photoreduction (mean = 2.46 × 10^{-3} hr\textsuperscript{-1}, SD = 6.72 × 10^{-4} hr\textsuperscript{-1} for filtered; mean = 2.07 × 10^{-3} hr\textsuperscript{-1}, SD = 5.08 × 10^{-4} hr\textsuperscript{-1} for unfiltered) and photooxidation rate constants (mean = 2.04 × 10^{-3} hr\textsuperscript{-1}, SD = 5.57 × 10^{-4} hr\textsuperscript{-1} for filtered; mean = 2.00 × 10^{-3} hr\textsuperscript{-1}, SD = 4.76 × 10^{-4} hr\textsuperscript{-1} for unfiltered) are not significantly different between filtered and unfiltered lake waters, sampled in early summer (respective t-tests; p = 0.2; p = 0.8); this demonstrates that the rate constants of these mercury photoreactions are not significantly affected by the presence of particles or particle-bound mercury species in solution. This result is in contrast to the results for photoreducible mercury amounts (Hg(II)\textsubscript{RED}) presented above, which do show significant differences between filtered and unfiltered samples. This lack of an effect on rate constants by the presence or absence of 0.2 μm filterable material supports the conclusions of Qureshi et al. (2010) and Beucher et al. (2002), who observed no substantial influence of filtration (or biotic activity) on mercury reduction rate constants in ocean water. Relative standard error associated with the derivation of the rate constant for gross photoreduction was <1% in all cases and was substantially higher for net photoreduction and gross
photooxidation (ranging 34%-1747 %). The high error on the gross photooxidation results are a result of the high error on curve fitting associated with net photoreduction experiments due to the low masses of mercury being quantified. There is also some indication of declines in Hg(0) concentrations in the net photoreduction experiments after 12 hr such that a pseudo first order reaction equation was not always a good fit (Appendix A Fig. SI-5). There is very limited data available in the literature for mercury photoreduction rate constants. Lalonde et al. (2001) found the net mercury photoreduction rate constant for a freshwater river was 0.26 hr⁻¹ which is lower but not a good point of comparison for the gross photoreduction rates measured here. Our results are more comparable to the work of Garcia et al. (2005b) who calculated gross mercury photoreduction rate constants for freshwaters ranging from 0.02 to 0.07 hr⁻¹."

Section 2.3

"The mean concentration of net Hg(0) (i.e. DGM) measured in water from all lakes was approximately 8.5% of the total Hg(II)RED for the gross photoreduction experiments (ranging 15 to 80 pg/L; mean = 41 ± 17.5 pg/L). This result indicates that there is a much larger capacity for mercury photoreduction and volatilisation from these lakes that might be released with decreases in gross photooxidation kinetics. The net mercury reduction rate constants derived from the data for filtered samples (ranging 1.28 × 10⁻⁵ to 8.30 × 10¹ hr⁻¹; mean = 1.15 × 10² hr⁻¹; SD = 2.71 × 10¹ hr⁻¹) and for unfiltered samples (ranging 3.20 × 10⁻¹ to 1.93 × 10³ hr⁻¹; mean = 8.77 × 10¹ hr⁻¹; SD = 4.96 × 10¹ hr⁻¹) were more variable than those derived from the gross photoreduction experiments (Table 2). Many studies have focussed on the in situ net photoreduction of mercury in aquatic systems; for example, Poulain et al. (2004) determined that the DGM formation rate constant ranged from 0.76 – 1.4 h⁻¹ in a wetland area, and 0.21 – 0.47 h⁻¹ for a pelagic area. Another study by Amyot et al. (1994) determined the mean net mercury reduction rate constant to be 0.10 h⁻¹. A review by Vost et al. (2011) found that net mercury reduction rate constants ranged between 0.1 and 2.2 h⁻¹ for freshwater samples, which are within the range of net mercury photoreduction constants measured in this study for unfiltered water samples. However, the unfiltered water samples show slower rates possibly due to slow release of reducible mercury from solid particles in unfiltered samples similar to what has been proposed between soil particles and soil solution (Pannu et al., 2014)."

Should be revised to

"In addition, the decline of Hg(0) after 12 hr in some experiments suggest a pseudo first order may not be best fit for these data (Appendix A Fig. SI-5). The mean concentration of net Hg(0) (i.e. DGM) measured at the end of each 24 h experiment in water from all lakes ranged from 1.6% to 22.7% of the total Hg(II)RED for the gross photoreduction experiments (ranging 7 to 119 pg/L; mean = 30 ± 24 pg/L). This result indicates that there is a much larger capacity for mercury photoreduction and volatilisation from these lakes that might be released with decreases in gross photooxidation kinetics. The net mercury reduction rate constants derived from the data for filtered samples (ranging 2.49 × 10⁻¹ to 4.6 × 10⁰ hr⁻¹; mean = 1.24 × 10⁰ hr⁻¹; SD = 1.32 × 10⁰ hr⁻¹) and for unfiltered samples (ranging 3.18 × 10⁻¹ to 1.99 × 10⁰ hr⁻¹; mean = 8.87 × 10⁻¹ hr⁻¹; SD = 5.07 × 10⁻¹ hr⁻¹) were more variable than those derived from the gross photoreduction experiments (Table 2). Many studies have focussed on the in situ net photoreduction of mercury in aquatic systems; for example, Poulain et al. (2004) determined that the DGM formation rate constant ranged from 0.76 – 1.4 h⁻¹ in a wetland area, and 0.21 – 0.47 h⁻¹ for a pelagic area. Another study by Amyot et al. (1994) determined the mean net mercury reduction rate constant to be 0.10 h⁻¹. A review by Vost et al. (2011) found that net mercury reduction rate constants ranged between 0.1 and 2.2 h⁻¹ for freshwater samples, which are within the range of net mercury photoreduction constants measured in this study.

Figure 3 – DOC (mg/L⁻¹) plotted against (A) the gross photoreduction rate constant (hr⁻¹); filtered R²=0.16, p>0.10 and unfiltered R²<0.36, p>0.10 (B) the gross photoreduction rate constant (hr⁻¹); filtered R²=0.42, p=0.08 and unfiltered R²=0.06, p<0.10, and (C) photoreducible Hg(II) (pg/L); filtered R²=0.03, p>0.10 and unfiltered R²=0.45, p=0.07 for both filtered (open circles) and unfiltered samples (shaded circles), respectively, from 7 lakes in KNP (lakes sampled in 2008 and 2009). No significant relationship was observed with photooxidation rate constants. Lakes sampled in August 2010 have substantially larger gross photoreduction rate constants (see Table 1) and are excluded from this graph."
for both filtered and unfiltered water samples. The unfiltered water samples show slower rates possibly due to slow release of reducible mercury from solid particles in unfiltered samples similar to what has been proposed between soil particles and solid solution (Pannu et al., 2014)."

Section 2.4

"Gross photooxidation rate constants were not significantly related to DOC in filtered ($R^2=0.20$, $p > 0.10$) or unfiltered samples ($R^2=0.0007$, $p > 0.10$). There was no significant linear relationship between DOC and the gross photooxidation rate constants in either filtered ($R^2=0.43$, $p = 0.08$) or unfiltered ($R^2=0.02$, $p = 0.71$) samples (Fig. 3B). While not statistically significant, the trend suggests that in filtered water samples, as DOC increases, the rate at which photoreducible mercury is converted to Hg(0) may slow; this slowing of mercury photoreduction with increasing DOC water agrees with findings of a study done by Garcia et al. (2005a), who examined DOC fluorescence and DGM, finding that DGM was negatively correlated with DOC. However more data is required to determine if this trend is significant in larger numbers of samples. In the unfiltered samples it is also possible that particulate-bound Hg(II) and Hg(0) that are variable with respect to biological transformations and photoactivity interfere with this relationship and so a much weaker interaction is observed.

In contrast to the lack of significant relationships between DOC and photoreduction rate constants, there is a significant negative linear relationship ($R^2=0.53$, $p=0.04$) between DOC and Hg(II)RED observed in unfiltered samples, and no relationship ($R^2=0.04$, $p=0.64$) observed in filtered samples (Fig. 4C)."

Table 1 and Figure 3 should be revised to the following.

Table 1: Rate constants (k; hr$^{-1}$) derived for gross photoreduction, net photoreduction, and gross photooxidation of mercury with standard error from curve fitting technique and total reducible (Hg(II)RED; pg/L). Note that lakes sampled in August 2010 are highlighted in grey, lakes sampled in May of 2008 and 2009 are not highlighted.

The authors would like to apologise for any inconvenience caused.