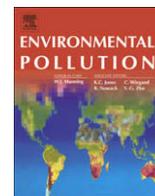




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Short Communication

Ultraviolet absorbance as a proxy for total dissolved mercury in streams

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Ultraviolet absorbance measurements are a cost-effective proxy to estimate dissolved mercury concentration in stream water.

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ABSTRACT

Stream water samples were collected over a range of hydrologic and seasonal conditions at three forested watersheds in the northeastern USA. Samples were analyzed for dissolved total mercury (THg_d), DOC concentration and DOC composition, and UV₂₅₄ absorbance across the three sites over different seasons and flow conditions. Pooling data from all sites, we found a strong positive correlation of THg_d to DOC ($r^2 = 0.87$), but progressively stronger correlations of THg_d with the hydrophobic acid fraction (HPOA) of DOC ($r^2 = 0.91$) and with UV₂₅₄ absorbance ($r^2 = 0.92$). The strength of the UV₂₅₄ absorbance–THg_d relationship suggests that optical properties associated with dissolved organic matter may be excellent proxies for THg_d concentration in these streams. Ease of sample collection and analysis, the potential application of *in-situ* optical sensors, and the possibility for intensive monitoring over the hydrograph make this an effective, inexpensive approach to estimate THg_d flux in drainage waters.

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1. Introduction

The northeastern U.S. exhibits widespread mercury (Hg) contamination because of moderate levels of atmospheric Hg deposition coupled with sensitive landscape characteristics (Driscoll et al., 2007). Environmental Hg contamination is a natural resource management concern because Hg is a bioaccumulating neurotoxin that poses a health risk to both humans and wildlife. Elevated concentrations of Hg in fish have led to consumption advisories in all 50 states (<http://www.epa.gov/mercury/>) which encompass more than 53,000 km² of lakes and 1,230,000 km of rivers (Driscoll et al., 2007).

A large pool of Hg present in upland soils of the northeastern US is the legacy of elevated Hg emissions associated with human activities since the late 1800s (Lorey and Driscoll, 1999). Up to 90% of the Hg deposited on the terrestrial landscape is thought to be retained (Krabbenhoft et al., 1995; Scherbatskoy et al., 1998; Kamman and Engstrom, 2002) making this a potentially important source of Hg to downstream ecosystems. The potential fate and bioavailability of this Hg is controlled, to a large extent, by its

interactions with natural organic matter (NOM). It is well established that Hg has a strong affinity for organic matter, and Hg retention in soils primarily occurs by the interactions of ionic Hg (Hg II) with NOM associated with reduced S groups (Haitzer et al., 2002; Skyllberg et al., 2003). In turn, the export of Hg and dissolved organic carbon (DOC) in drainage waters from watersheds is controlled by water flux and hydrologic flowpaths. Riparian areas and wetlands represent areas of high NOM accumulation and high water tables, and are likely zones where Hg–organic complexes are mobilized to streamwater, especially during high flow events (Grigal, 2002).

Better estimates of stream Hg flux are needed to improve understanding of the fate of Hg deposited within a watershed, and to quantify the response of ecosystems to decreases in Hg emissions. However, obtaining accurate Hg flux estimates for rivers and streams is difficult due to sampling limitations and the expense of low-level Hg analysis. Typical Hg budgets for small catchments are developed using measured continuous discharge and interpolated or modeled Hg concentrations based on relatively coarse fixed interval sampling to estimate stream Hg flux. Obtaining Hg measurements during high flow events can be difficult; however, most of the annual Hg flux occurs during spring snowmelt and other high flow periods (Aastrup et al., 1991; Bishop et al., 1995; Scherbatskoy et al., 1998). Weekly or monthly grab samples for Hg

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determination typically fail to capture high flow events, and thereby may underestimate Hg export from watersheds. Here we propose to use ultraviolet (UV) absorbance an effective, inexpensive approach for improving estimates of dissolved total mercury (THg_d) concentration and flux in drainage waters.

2. Methods

This study was conducted at three northern forested watersheds in New Hampshire, Vermont, and New York, U.S.A. The Hubbard Brook Experimental Forest (HBEF) (43°56'N, 71°45'W), located in the southern White Mountain region of New Hampshire, was sampled at Watershed 6, the biogeochemical reference watershed (Likens and Bormann, 1995). The HBEF has well-drained soils, and is low in DOC¹ (1–2 mg C L⁻¹). The Sleepers River watershed (44°30'N, 72°10'W) in northeastern Vermont was sampled at Watershed 9. Sleepers River has areas of poor drainage supporting small wetlands, peat, and mucky riparian soils, and a range of DOC concentrations from 1 to 4 mg C L⁻¹ (Shanley et al., 2004). Arbutus Lake Watershed (ALW) is in the central Adirondack Mountains of New York (43°59'N, 74°14'W). Samples were collected at two locations on Archer Creek (Beaver Meadow site and Lake Inlet site). The ALW is intermediate in drainage class and has higher range of DOC concentration (3–6 mg C L⁻¹) compared to our other sites (Selvendiran et al., 2008). All three systems are long-term watershed study sites, with supporting hydrologic and biogeochemical measurements.

Stream water samples were collected at each of the sites during base flow and high flow periods (spring snowmelt and summer storms) from September 2005 to July 2007. Stream water samples (total $n = 127$) were collected for THg_d analyses according to established USGS protocols using clean techniques for low concentration analytes (Horowitz et al., 1994; Wilde et al., 1998). Samples were filtered using a polyethersulfone (PES) filter (0.45 μm) prior to acid preservation for the analysis of THg_d. Three liters of sample were collected and filtered in the field through Gelman AquaPrep 600 capsule filters™ (0.45 μm) for DOC and UV absorbance measurements. Samples were shipped overnight in coolers with ice packs to Syracuse University (Syracuse, NY) for THg_d analysis and the USGS laboratory (Boulder, CO) for DOC and UV absorbance analyses. Prior to analysis, samples were stored at both laboratories in a dark cold room at 4 °C.

Dissolved organic carbon samples were fractionated using XAD-8 and XAD-4 extraction methods (Aiken et al., 1992). Samples were analyzed for DOC concentration using the Pt catalyzed persulfate wet oxidation method (O.I. Corporation Analytical Model 700 TOC Analyzer™). Quality assurance (QA) procedures for analysis of DOC concentration were maintained through method blanks, daily calibration with potassium hydrogen phthalate (KHP), and calibration check standards prepared from sodium benzoate. UV absorbance was measured on aliquots of stream water samples at λ = 254 nm, a wavelength at which humic rich matter strongly absorbs (Weishaar et al., 2003). Filtered UV samples were measured at room temperature (25 °C) between 200 nm and 800 nm in a 1 cm quartz cell with distilled water as the blank. Samples were analyzed in duplicate for DOC concentration and UV absorbance and for DOC fractionation when volume sample permitted. Samples were analyzed within 2 weeks after collection for DOC concentration and UV absorbance and within 3 weeks after collection for DOC fractions.

Water samples were analyzed for total mercury THg_d utilizing automated oxidation, purge and trap, desorption, and cold-vapor atomic fluorescence spectrometry (CVAFS) (Tekran 2600; Tekran, Toronto, ON) following US EPA method 1631, revision E (US EPA, 2002). QA procedures for THg_d analysis were maintained through blanks (field, method and filter blanks), duplicates (field and method duplicates), and matrix spikes. Instrument performance and stability were evaluated with initial and ongoing precision recovery, instrument detection limit standards, and verification of independent primary and secondary source standards. QA procedures and instrument performance and stability standards were analyzed in every batch of 20 samples. The accuracy and precision of the spikes and standards were maintained within 10% and method blanks were below the reporting limit (<0.5 ng L⁻¹).

3. Results and discussion

Stream water THg_d concentrations increased with DOC concentrations at all three study sites (Fig. 1). There is strong evidence supporting Hg transport through watersheds in association with dissolved and particulate organic matter (Mierle and Ingram, 1991; Driscoll et al., 1995; Hurley et al., 1998). While DOC facilitates the transport of Hg, DOC also plays a complex role in Hg

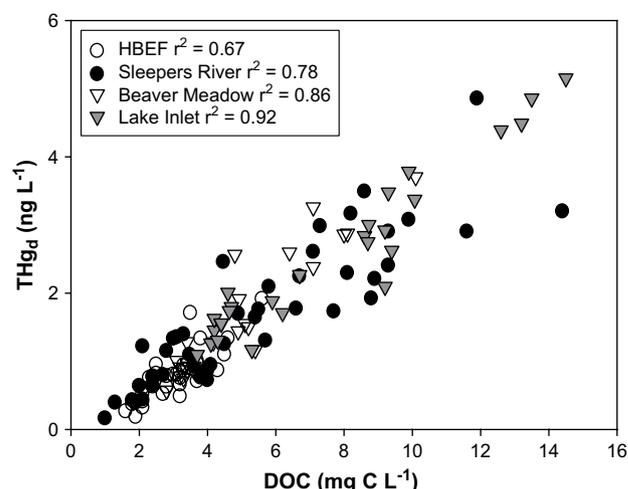


Fig. 1. Stream water dissolved total mercury (THg_d) concentration (ng L⁻¹) as a function of dissolved organic carbon (DOC) concentration (mg C L⁻¹). There was no statistical difference ($p > 0.05$) between the slope and intercept for the four linear regression equations, indicating that the four lines were coincident. (Linear regression equation for overall dissolved THg_d-DOC correlation: $y = 0.338x - 0.1303$ $r^2 = 0.87$, $p < 0.001$).

biogeochemistry by strongly binding Hg thereby controlling the availability of Hg for methylation and bioavailability to fish and other aquatic organisms (Driscoll et al., 1994, 1995; Hudson et al., 1994).

Dissolved organic carbon is a complex heterogeneous mixture of low to high molecular weight species (Aiken et al., 1992); therefore the “quality” (i.e., aromatic carbon content) and the composition of DOC (i.e., hydrophilic versus hydrophobic) can have important influences on the transport and fate of Hg (Schuster et al., 2008). For example, stream water export of THg_d is strongly correlated to the export of humic material associated with hydrophobic organic matter (Mierle and Ingram, 1991; Grigal, 2002). At each of our sites, we found the relationship between the hydrophobic organic acid (HPOA) fraction (the largest component of DOC) and THg_d (Fig. 2) to be stronger than the relationship between total DOC and THg_d

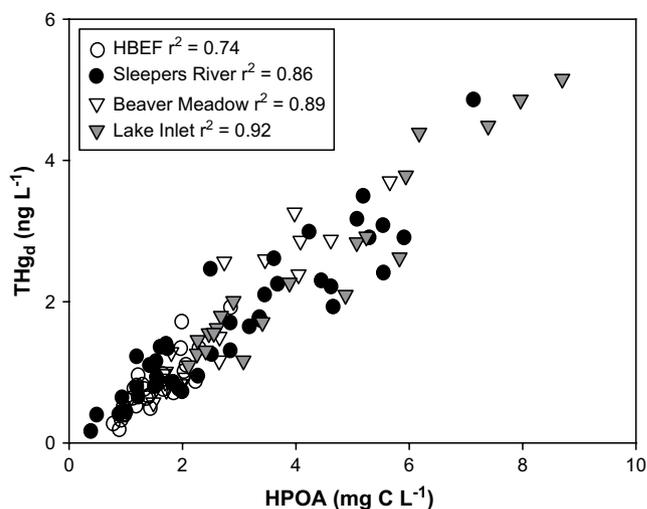


Fig. 2. Stream water dissolved total mercury (THg_d) concentration (ng L⁻¹) as a function of hydrophobic organic acid concentration (mg C L⁻¹). There was no statistical difference ($p > 0.05$) between the slope and intercept for the four linear regression equations, indicating that the four lines were coincident. (Linear regression equation for overall dissolved THg_d-HPOA correlation: $y = 0.5995x - 0.057$ $r^2 = 0.91$, $p < 0.001$).

¹ Estimates for DOC for each of the three watersheds are given for base flow conditions.

(Fig. 1). The HPOA fraction may have chemical qualities such as more reduced sulfur sites that make HPOA a stronger ligand for Hg (Schuster et al., 2008). The HPOA fraction comprised from 40–60% of DOC at each of the watersheds. As DOC concentration increased during high flow events, the percentage of HPOA remained constant or increased slightly. Thus the stream transport of HPOA and in turn THg_d , increased dramatically during events.

A key finding of this study was that UV_{254} absorbance associated with DOC was a stronger predictor of THg_d concentrations (Fig. 3) than either DOC (Fig. 1) or HPOA (Fig. 2). The correlation between UV_{254} absorbance and THg_d concentration ranged from $r^2 = 0.80$ at the HBEF up to $r^2 = 0.94$ at the Lake Inlet site in the Archer Creek watershed (Fig. 3). Also note that THg_d - UV_{254} relationships were coincident (i.e., no statistical difference ($p > 0.05$) between the slope and intercept for the four regressions) across these three sites with variable DOC and THg_d over different seasons. UV_{254} absorbance is an extensive property that depends on the concentration of absorbing compounds. We contend that nearly all of the THg_d is bound in this UV-absorbing DOC fraction, making UV absorption a potentially useful proxy for THg_d concentration.

The UV_{254} absorbance was strongly correlated to the HPOA concentration across the sites (HBEF $r^2 = 0.96$, $p < 0.001$; Sleepers $r^2 = 0.99$, $p < 0.001$; Beaver Meadow $r^2 = 0.98$, $p < 0.001$; Lake Inlet $r^2 = 0.97$, $p < 0.001$). As soils become saturated, particularly during snowmelt, interflow mobilizes hydrophobic organic matter which is rich in humic complexes (Aiken and Cotsaris, 1995). Mierle and Ingram (1991) reported that the export of Hg was closely related to color, a measure of the humic matter in water. However, we are not aware of any study since that time that has demonstrated these linkages through concurrent measurements of THg_d , DOC, HPOA content, and UV_{254} absorbance.

There are several key benefits of using UV_{254} measurements as a surrogate for predicting THg_d concentrations. Sample collection for UV_{254} measurements is simple and does not require trace-clean protocols which can be difficult to achieve during storm events. Samples for UV_{254} absorbance can be easily obtained with automated sampling devices that can be programmed to collect samples over high flow hydrographs. The proxy approach lends itself to the use of new-generation *in-situ* optical measurements of UV_{254} absorbance and NOM fluorescence that can provide high-resolution times series and thus enables accurate THg_d flux calculation.

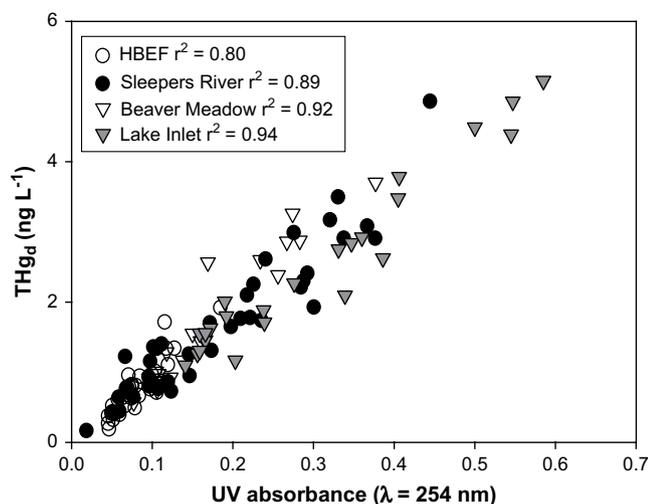


Fig. 3. Stream water dissolved total mercury (THg_d) concentration (ng L^{-1}) as a function of UV absorbance ($\lambda = 254 \text{ nm}$). There was no statistical difference ($p > 0.05$) between the slope and intercept for the four linear regression equations, indicating that the four lines were coincident. (Linear regression equation for overall dissolved THg_d - UV_{254} absorbance correlation: $y = 8.627x + 0.063$ $r^2 = 0.92$, $p < 0.001$).

Laboratory analysis for UV_{254} absorbance is simpler, faster, and less expensive than Hg or HPOA analysis. The UV_{254} measurement itself is nondestructive and requires small sample volumes with no need for hazardous reagents. Using UV_{254} measurements as a surrogate for THg_d allows for increased sample frequency of observations. By increasing the number of samples, particularly during high flow events, we can improve Hg flux estimates in stream water allowing for overall better Hg budget estimates to enhance understanding of Hg transport and fate.

The strong correlation between UV_{254} absorbance and THg_d concentration holds promise for improving estimates of Hg flux from watersheds. However, there are some considerations for using UV_{254} absorbance measurements. Discrete sampling is required to establish the empirical relationship for sites of interest. High particulate loads in unfiltered stream water samples can absorb and/or scatter light in the near UV causing interference with the UV absorbance of DOC. Inorganic species such as iron and nitrate that absorb light in the near UV absorbance of DOC can also potentially cause interference (Weishaar et al., 2003).

4. Conclusions

We observed consistent patterns between THg_d and both DOC concentration and the amount of HPOA fraction in water samples from three diverse forest watersheds, demonstrating that THg_d concentrations are highly dependent on flow and DOC concentration and quality in these northern forest watersheds. The strong correlations between DOC and HPOA concentration and UV_{254} absorbance suggest that these relationships could be exploited to improve understanding of fluvial THg_d transport. Indeed, UV_{254} absorbance was found to be an excellent predictor of THg_d concentrations in our study. Given the strong correlations between THg_d and UV_{254} absorbance, determination of UV_{254} absorbance may be a useful surrogate for THg_d in stream water and an effective way to improve estimates of THg_d flux in rivers and streams. Sample collection and analysis for determination of DOM optical properties is simpler, less expensive and subject to fewer complications than for determination of THg_d concentrations. Upon establishing the relationship between THg_d concentration and UV_{254} absorbance (or another optical parameter) for a given system, the optical data can be a powerful proxy for estimating THg_d concentration and unraveling the fine-scale dynamics of THg_d -DOC behavior in drainage waters. These data can subsequently be used to provide better overall estimates of THg_d flux, to tighten Hg budgets within watersheds and to improve our understanding of ecosystem response to changes in atmospheric Hg deposition.

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