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ABSTRACT

Following decreases in acid deposition, some impacted surface waters in northern Europe and the northeastern USA are beginning to recover. The resultant increases in pH in these waters has coincided with increased dissolved organic carbon concentrations, which is also correlated with increases in both total mercury and methylmercury concentrations. Understanding how ecosystem mercury dynamics respond to recovery from acid deposition has important implications for fisheries and human exposure. Honnedaga Lake is one of seven lakes in the Adirondack Park of New York State with a heritage Brook trout (*Salvelinus fontinalis*) population, making the bioavailability and trophic transfer of mercury (Hg) a particular concern. Lime was applied to a tributary watershed of Honnedaga Lake in 2013 in an effort to accelerate biological recovery from acid deposition. Significant increases in DOC, THg and MeHg were evident in streamwater after treatment (maximum THg post-treatment=5.5 ng/L, maximum THg reference=2.15 ng/L). Six months after treatment, there was no significant difference in MeHg concentrations from reference values, while DOC and THg remained significantly higher than pre-treatment and reference values. This pattern suggests that Hg is leaching at elevated levels from the treated watershed, but that short-lived increases in MeHg could not be sustained due to limitations in either the net methylation rate or the transport of MeHg to the stream.

RESPONSE OF MERCURY IN A FOREST STREAM TO LIME APPLICATION: ACCELERATED WATERSHED RECOVERY

by

Geoffrey Dean Millard

B.S., St. Lawrence University, 2010

Thesis

Submitted in partial fulfillment of the requirements for the degree of

Master of Science in *Environmental Engineering Science*.

Syracuse University

July 2016

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Table of Contents

ABSTRACT I

INTRODUCTION 1

METHODS 5

RESULTS 8

DISCUSSION 14

CONCLUSIONS 18

FIGURES 20

TABLES 27

REFERENCES 27

VITA 39

INTRODUCTION

Acid deposition has been shown to cause a variety of adverse ecological effects since environmental concerns were first raised in the late 1960s and early 1970s (Oden 1968, Likens et al. 1972). Derived primarily from emissions of sulfur and nitrogen compounds (e.g., SO_2, NO_x), elevated inputs of strong acids have affected the structure and function of forested and aquatic ecosystems in North America, Europe and Asia (Driscoll et al. 2001). Leaching by elevated deposition of sulfate and nitrate removes exchangeable base cations from soil, mobilizes inorganic aluminum from soil to water, and decreases pH and acid neutralizing capacity (ANC) in surface waters, which may result in toxic conditions for terrestrial and aquatic biota (Baldigo et al. 2007, 2009; Lawrence et al. 2008).

In 1990, the United States Environmental Protection Agency (USEPA) established the Acid Rain Program (ARP) under the Clean Air Act, requiring major emissions reductions of the primary precursors of acid deposition from electric utilities (U.S. EPA 2009). Through the ARP, and subsequent rules, emissions have been significantly reduced resulting in marked decreases in acidic deposition (Burns et al. 2011, Greaver et al. 2012), and allowing acid impacted ecosystems in the northeastern United States to begin recovering (Driscoll et al. 2007a). However, this recovery process has been slow and delayed as decades of acidic deposition has removed available calcium (Ca) and other basic cations from soils (Warby et al. 2005). Improvements in surface water chemistry have been largely attributed to decreases in acid deposition (Driscoll et al. 2001, 2003a, 2007a; Chen and Driscoll 2005).

In addition to acid deposition, atmospheric Hg inputs impact remote forest ecosystems. Direct emissions from anthropogenic activities and legacy secondary re-emissions account for

the majority of global Hg emissions to the atmosphere at a rate 2-15 times greater than those from geogenic sources (Driscoll et al. 2013). In the northeastern United States, 60-80% of Hg deposition can be attributed to regional sources by deposition of gaseous or particulate ionic Hg (Selin 2009). Mercury can be deposited on trees and other plants, adsorbing to the surface of leaves and through stomata into leaves. This facilitates enrichment of foliar Hg which results in elevated deposition to soils via litterfall and throughfall (Hintelmann et al. 2002, Blackwell and Driscoll 2015). Soil Hg is largely bound to reduced sulfur groups associated with organic matter and is retained in the soil pool until the organic matter becomes water-soluble (Skyllberg et al. 2003). Once in the aquatic environment, Hg is transported largely by dissolved or particulate organic carbon (Dittman et al. 2010). Mercury can be converted to methylmercury (MeHg) by sulfate- or iron-reducing bacteria in reducing environments (Gilmour et al. 1998, Kerin et al. 2006).

In the methylated form, Hg is readily taken up at the base of aquatic food webs, and biomagnifies along the food chain. Resulting elevated concentrations can pose neurotoxicological risks, particularly to fish-eating birds and mammals, including humans (Driscoll et al. 2007b, 2013). Approximately 95% of MeHg consumed is absorbed through the gastrointestinal tract (Aberg et al. 1969). Once it enters the bloodstream, MeHg can cross barriers such as the blood-brain and blood-fetus barriers, causing neurological damage in humans and other top level predators (Burgess and Meyer 2008, Syversen and Kaur 2012, Schoch et al. 2014). One estimate indicates that the annual economic cost associated with health impacts from Hg will reach 3.7 billion USD globally by 2020 (Sundseth et al. 2010), while US economic benefits associated with reduced Hg emissions could reach $104 billion by 2050 (Giang and Selin 2016).

In New York State, the Department of Health has issued a statewide consumption advisory to eat no more than one meal of sport fish per week. More specific advisories for consumption of large predatory species and game fishes from individual lakes exist because of measured high levels of MeHg and other contaminants (New York State Department of Health 2015). In the Adirondack and Catskill Parks, an additional regional advisory is in place because the majority of surface waters in these regions have fish-Hg levels above consumption guidance values (New York State Department of Health 2015). In a 2008 survey of New York State, Yellow perch (*Perca flavescens*) in the Adirondack region had median Hg concentrations more than twice the values observed in the remainder of the state (382 ng/g vs. 162 ng/g respectively; Simonin, Loukmas, Skinner, & Roy, 2008).

In Northern Europe, the northeastern United States, and southeastern Canada, aquatic ecosystems are showing signs of recovery from acid deposition (Driscoll et al. 2001, Jeffries et al. 2003). There are important linkages between the effects of acid deposition and Hg deposition in remote acid-impacted watersheds, suggesting that decreases in acid deposition might have a co-benefit of decreasing fish Hg concentrations (U.S. EPA 2011). For example, bioaccumulation of MeHg increases with decreases in pH (Yu et al. 2011) and inputs of sulfate from acidic deposition can drive the formation of MeHg mediated by sulfate-reducing bacteria (Drevnick et al. 2007, Coleman Wasik et al. 2015). However, researchers have reported a coincident increase in Hg concentrations in fish with increases in dissolved organic carbon (DOC) associated with recovery from acid deposition (Hongve et al. 2012). Total Hg concentrations have a strong positive correlation with DOC concentrations (Dennis et al. 2005) and ultraviolet absorbance at 254nm (UV254) (Dittman et al. 2009). Despite decreases in U.S. Hg emissions (Zhang et

al.2016, Drevnick et al. 2012), Hg concentrations in recovering ecosystems remain elevated. This condition presents an ongoing risk of bioaccumulation of this potent neurotoxin.

Previous studies in both the Adirondacks and New Hampshire (Cirmo and Driscoll 1996, Cho et al. 2009) have shown that Ca additions in the form of lime ($CaCO_3$) and wollastonite ($CaSiO_3$), respectively, are viable options for accelerating recovery of watersheds impacted by acid deposition. These studies demonstrated that calcium base additions increase pH and ANC, while decreasing concentrations of inorganic monomeric aluminum. Base treatment to acidic forest soils may be an experimental analog to conditions occurring in response to decreases in acid deposition. The response of Hg dynamics in ecosystems recovering from acid deposition or following base treatment is not well understood. In this study, I examined the impact of a watershed lime application on Hg loss and speciation in a small tributary of Honnedaga Lake.

Honnedaga Lake, located in the southwestern Adirondacks, is one of seven Adirondack lakes with a heritage Brook trout (*Salvelinus fontinalis*) population. This genetically unique population has undergone a recovery in recent years (Josephson et al. 2014) in association with increasing lake pH and ANC (Josephson et al. 2014), but remains at risk from ongoing effects of acid deposition. The application of lime to the watershed of the Honnedaga Lake tributary was intended to improve and increase spawning habitat for Brook trout by improving tributary water quality, particularly by increasing ANC and reducing inorganic monomeric aluminum concentrations. This experiment provides an opportunity to examine changes in Hg dynamics after liming. I hypothesized that concentrations of both total mercury (THg) and MeHg would increase immediately following lime addition due to increases in the release of DOC from soil associated with increases in soil pH, but would decline within the first water year to pre-treatment/reference levels. By monitoring THg and MeHg concentrations in stream water

draining both a treatment and reference watershed, I investigated changes in Hg dynamics in response to lime application and with this information obtained insight on the response of watersheds recovering from elevated acid deposition.

METHODS

Study Site. Honnedaga Lake (3.1 km^2) is located in the southwestern Adirondacks (43°31'06"N and 74°48'31"W). The watershed (13.3 km^2) is completely forested, with 26 tributaries draining into the lake (Figure 1). The two tributaries examined in this study, T16 (T - treatment) and T24 (R - reference), were chronically acidic prior to treatment, with pH consistently below 4.8. These watersheds make up a small portion of the entire Honnedaga Lake watershed (T – 0.298km^2, R – 0.179km^2). The treatment and reference watersheds are characterized by steep topography (364m/km) and small wetland surface area (T – 4.3%, R ~ 0% of watershed area).

Each tributary has a gauging station installed just upstream of the outlet (T – 43°31'53"N 74°51'10"W, R – 43°32'02"N 74°51'42"W). Stream stage was measured by a submersible pressure transducer in a natural pool and recorded every 15 minutes on a data logger. Stage was converted to discharge through the use of a stage-discharge rating curve developed by making periodic discharge measurements with the use of a current meter under a range of flow conditions. Methods for measuring stream stage and discharge are described in Sauer and Turnipseed (2010), and Turnipseed and Sauer (2010).

The treatment watershed received 150 metric tons of limestone ($CaCO_3$), distributed in a pelletized form over the 30 hectare watershed. The lime was applied just after leaf fall on October 1, 2013 by helicopter, at a dose of 1.4 Mg of Ca/ha, which is comparable to application rates for other regional watershed liming studies (Driscoll et al. 1996, Peters et al. 2004).

Field Sampling of Streams. At each sampling location, an acid-washed 500-ml polyethylene bottle was rinsed three times with stream water and then filled with the sample for subsequent water chemistry analysis. Where possible, collection was done in a riffle reach to ensure swift velocity and well-mixed conditions. Water temperature was measured at the time of sampling and notes were made on weather conditions and estimated flow based on visual observation of water level relative to channel depth (high, medium, or low). Streamwater samples were collected approximately monthly using USEPA trace-metal clean techniques method 1669 (U.S. EPA 1995). During the first four weeks after lime addition, streamwater samples were collected weekly to evaluate the short-term response to treatment. Field blank and triplicate samples were collected for additional quality control. Streamwater samples were placed in a backpack for immediate transport to the field laboratory. The mercury water samples were filtered through 0.4 µm polycarbonate filters then acidified with concentrated hydrochloric acid. All streamwater samples were refrigerated at 4° C, and shipped on ice overnight to Syracuse University for Hg analysis and to USGS New York Water Science Center Laboratory in Troy, NY for ancillary chemical analysis.

Laboratory Processing and Chemical Analyses. Five aliquots of each stream sample were analyzed for different solutes. The first aliquot was separated in the field and analyzed for THg and MeHg. Total Hg was analyzed using an oxidation, purge and trap, desorption and cold-vapor atomic fluorescence spectrometry following U.S. EPA method 1631, revision E (U.S. EPA 2002). The detection limit for this method is 0.2 ng/L. Methylmercury was analyzed by distillation, ethylation, purge and trap, desorption and cold-vapor atomic fluorescence spectrometry according to U.S. EPA Method 1630 (U.S. EPA 2007). The detection limit for this method is 0.02 ng/L. The second aliquot was filtered with 0.4 µm polycarbonate filters and

stored at 4° C for analysis of SO_4^{2-} by ion chromatography. The third aliquot was passed through a 0.7 µm glass fiber filter (GFF) and stored at 4° C for analysis of UV254 and DOC by UV/persulfate oxidation in a total carbon analyzer. Specific ultraviolet absorbance (SUVA) was calculated from measured absorbance at 254 nm per DOC concentration. The fourth aliquot was filtered with 0.4 µm polycarbonate filters and acidifed with ultrapure nitric acid and analyzed for iron using an Inductively Coupled Plasma (ICP) spectrophotometer. The final aliquot remained unfiltered for measurement of pH electrometrically. Further details on USGS analytical methods can be found at http://ny.cf.er.usgs.gov/nyprojectsearch/projects/2457-A5Z-3.html (accessed 08/04/2015). Laboratory QA/QC procedures are described in Lincoln et al. (2009).

Determination of Fluxes. Flow data were obtained from USGS gauging stations on both the treatment and reference tributaries. Annual fluxes of sulfate, DOC, THg and MeHg were then determined using the software package Flux32 v 3.03. Data were stratified based on season and results for the concentration/discharge regression are reported, because this method returned the lowest variance across all sites and analytes.

Statistical Analysis. Data were summarized over a 13-month period from September 2013 through September 2014, with additional data from early sampling in June 2013 and September 2012. Three time periods were defined for the purpose of data analysis; pre-treatment (n=4), transitional post-treatment (Transitional, October 2013 through February 2014, n=7) and a longer term post-treatment (Post-Treatment, March through September 2014, n=5). Based on examination of water quality temporal patterns, the pre-treatment period was before lime application, the transitional period was the first five months following lime addition, while the post-treatment was the seven month period following the transition response. The reference watershed was monitored prior to and following the experimental treatment.

Statistical analysis was performed with the software package SASv9.4. Regression analysis was performed on concentration and log-transformed concentration data to ascertain correlations between DOC, sulfate, UV254 and SUVA with THg and MeHg at both the treatment and reference site. UV254 and SUVA were corrected for iron interference based on calculated absorbance (Poulin et al. 2014). Regressions between reference and treatment streams were then tested using ANOVA for significant differences.

Time series of THg, MeHg and DOC concentrations were used to observe any changes after lime addition. A Kruskal-Wallis test (robust ANOVA) was applied to examine statistical differences in the mean concentrations of sulfate, DOC, UV254, SUVA, THg, MeHg and %MeHg (MeHg/THg*100) over three time periods: pre-treatment, transition, and post-treatment. A p-value of less than or equal to 0.1 was considered significant.

RESULTS

Concentration Patterns

Stream pH for the pre-treatment period and reference watershed ranged from 4.41 in July 2012 to 4.91 in August 2011, with a mean of 4.57. The tributary pH at the treatment watershed abruptly increased to 7.46 immediately after the lime application, and decreased to an average of 5.46 during the post treatment period. Post-treatment observations were a marked departure from both reference stream and pre-liming values (Figure 2a).

Coincident with this increase in stream pH, DOC exhibited a marked increase after watershed liming (Figure 2b). Dissolved organic carbon concentrations at the reference site ranged from 2.8 mg C/L to 8.14 mg C/L, with a mean value of 4.7 mg C/L. At the treatment tributary, pre-treatment DOC concentrations ranged from 2.9 mg C/L to 10.5 mg C/L, with a mean of 5.5 mg

C/L and were significantly higher than reference stream observations over this period ($p=0.013$). Concentrations of DOC in the treatment tributary during the transitional period ranged from 3.9 mg C/L to 18.4 mg C/L, with a mean of 10.6 mg C/L. After this initial transitional period, DOC decreased to a range of 3.3 mg C/L to 15.0 mg C/L, with an average of 10.5 mg C/L. The difference in DOC concentrations between tributaries were significantly greater during the transitional and post-treatment periods than the pre-treatment period (Figure 3, $p<0.0001$).

Absorbance at UV254 had a similar response as DOC. The reference site observations ranged from 0.073 cm^{-1} to 0.292 cm^{-1}, with a mean of 0.164 cm^{-1}. These values were lower than pre-treatment observations at the treatment stream ($p=0.004$) which ranged from 0.113 cm^{-1} to 0.401 cm^{-1}, with a mean of 0.227 cm^{-1}. Stream UV254 increased in the treatment stream during the transitional period and was significantly higher than before the treatment, ranging from 0.147 cm^{-1} to 0.781 cm^{-1}, with a mean of 0.442 cm^{-1}. This increase was maintained through the post treatment period where observations ranged from 0.130 cm^{-1} to 0.658 cm^{-1}, with a mean of 0.385 cm^{-1}. The differences in UV254 between tributaries were significantly greater during the transitional and post-treatment periods than the pre-treatment period ($p<0.001$, Figure 2c).

Observations of SUVA indicate a shift in DOC quality after treatment with lime. Reference stream observations ranged from 2.4 L mg-C^{-1} m^{-1} to 3.9 L mg-C^{-1} m^{-1}, with a mean of 3.3 L mg-C^{-1} m^{-1}. These values were significantly lower than pre-treatment observations at the treatment stream ($p<0.001$) where values ranged from 3.3 L mg-C^{-1} m^{-1} to 4.4 L mg-C^{-1} m^{-1}, with a mean of 3.8 L mg-C^{-1} m^{-1}. Transitional observations at the treatment stream ranged from 3.7 L mg-C^{-1} m^{-1} to 4.5 L mg-C^{-1} m^{-1}, with a mean of 4.2 L mg-C^{-1} m^{-1}. These values were not significantly different from post-treatment ($p>0.5$) observations at the treatment stream which ranged from 3.9 L mg-C^{-1} m^{-1} to 4.7 L mg-C^{-1} m^{-1}, with a mean of 4.2 L mg-C^{-1} m^{-1}. The differences in SUVA

between tributaries were significantly greater during the transitional and post-treatment periods than the pre-treatment period ($p<0.001$, Figure 2d).

Total Hg concentrations over the pre-treatment period at the treatment stream and all reference stream observations were not significantly different and ranged from 0.33 ng/L to 3.33 ng/L, with an overall mean concentration of 1.32 ng/L. The treatment watershed stream exhibited marked increases in THg after application during the transition period, ranging from 1.07 ng/L to 5.50 ng/L, with a mean concentration of 3.26 ng/L. Treatment stream THg concentrations were significantly higher than reference stream observations over the same period ($p=0.037$). Post-treatment observations from the treatment stream ranged from a minimum of 0.69 ng/L to 3.40 ng/L, with a mean of 2.26 ng/L, which were also significantly higher than reference observations (Figure 4, $p=0.016$).

Methylmercury concentrations in the reference tributary ranged from 0.008 ng/L to 0.046 ng/L, with a mean of 0.019 ng/L. Immediately following treatment, MeHg showed a marked increase in the treatment tributary during the transition period when concentrations ranged from 0.004 ng/L to 0.194 ng/L, with a mean of 0.074 ng/L. Methylmercury concentrations in the treatment tributary over the transition period were significantly higher than the reference tributary ($p=0.078$). This difference did not persist in the post-treatment period ($p=0.114$), when treatment stream MeHg concentrations decreased, ranging from a minimum of 0.002 ng/L to a maximum of 0.0564 ng/L, with a mean of 0.027 ng/L. Post-treatment observations at the reference tributary ranged from 0.002 ng/L to 0.040 ng/L, with a mean value of 0.017 ng/L (Figure 5).

The percent MeHg of THg (%MeHg) displayed an interesting response to lime treatment. The reference stream ranged from 0.37% to 8.64%, and had a mean value of 1.72%. Pre- and post-treatment observations of the limed watershed were similar to reference watershed observations. Pre-treatment observations of the limed stream ranged from 0.24% to 2.68%, with a mean of 1.48%, while post-treatment observations ranged from 0.09% to 8.17%, with a mean of 2.15%. During the transition period, the treatment tributary had some higher values of %MeHg ranging from 0.08% to 18.15%, with a mean of 3.92%.

DOC and THg concentrations at the reference and treatment sites exhibited a strong positive correlation for the period of study (slope = 0.514 ng-Hg/mg-C and 0.517 ng-Hg/mg-C, adj-R^2 = 0.627 and 0.900, respectively). The slopes of these regressions were not statistically different using all available data (Figure 6A, $p>0.9$). There was a similar correlation between UV254 and THg concentrations at the reference and treatment sites over the period of study (slope = 11.1 ng-Hg/m and 11.5 ng-Hg/m, adj-R^2 = 0.508 and 0.896 respectively). Despite the similarity in these relationships, the slopes of the THg-UV254 regressions were statistically different using all available data (Figure 6C, $p<0.001$). The only other significant correlation was between SUVA and THg in the treatment stream (slope = 4.29 ng-Hg/L mg-C^{-1} m^{-1}, adj-R^2 = 0.378, Figure 6D). In contrast, MeHg was not significantly correlated with DOC, sulfate, UV254 or SUVA (Table 1). No significant relationships were found for log-transformed data.

Although the slopes from THg-DOC regression analysis were not significantly different, the THg:DOC ratio of treatment streamwater changed over the post-application period. In the reference tributary, there was a significant difference in THg:DOC between the transition and post-treatment periods (Figure 7, $p=0.008$). The THg:DOC ratio during the transition period in the reference stream ranged from 0.143 μg/g to 0.389 μg/g, with a mean value of 0.283 μg/g.

These values were higher than those observed for the post-treatment period, which ranged from 0.108 μg/g to 0.281 μg/g, with a mean of 0.176 μg/g. However, there was no significant difference for THg:DOC between the transition and post-treatment periods in the treatment stream. Observations during the transition period ranged from 0.208 μg/g to 0.476 μg/g, with a mean of 0.364 μg/g and were not significantly different from the same period at the reference tributary. There was no difference in MeHg:DOC between tributaries with values ranging from 0.369 ng/g to 49.7 ng/g, with a mean of 8.28 ng/g.

Concentrations of sulfate in the reference tributary ranged from 1.9 mg SO_4/L to 3.8 mg SO_4/L, with a mean of 2.9 mg SO_4/L during the pre-treatment period. Observations of SO_4 were not statistically different at the reference stream between the transitional and post-treatment periods. Over these time periods, SO_4 observations in the reference tributary ranged from 2.0 mg SO_4/L to 3.1 mg SO_4/L, with a mean of 2.5 mg SO_4/L and were significantly lower than pre-treatment reference observations ($p=0.001$). Pre-treatment observations from the limed stream were not significantly different from post-treatment observations. Sulfate during the pre-treatment and post-treatment periods ranged from 2.0 mg SO_4/L to 4.1 mg SO_4/L, with a mean of 3.2 mg/L. These SO_4 observations were significantly lower than observations during the transitional period in the treatment tributary ($p<0.001$). During the transition period, sulfate concentrations in the limed tributary ranged from 3.0 mg SO_4/L to 6.4 mg SO_4/L, with a mean of 3.6 mg SO_4/L (Figure 8, $p=0.813$). The differences in sulfate concentrations between tributaries were significantly greater during both the transitional ($p<0.001$) and post-treatment ($p=0.049$) time periods than the pre-treatment period. No statistically significant pattern was found between sulfate and DOC, MeHg or THg.

Fluxes

Calculated fluxes indicate an increase in yield after liming for all analytes except MeHg when compared with the reference watershed (Table 2). There is no significant difference in flow between the 2013 and 2014 water years (t-test, α=0.05). Annual DOC flux at the reference stream was 5693 g-C/m^2-y, with a standard deviation of 167 g-C/m^2-y. Pre-addition, the treatment stream annual DOC yields were 7748 g-C/m^2-y with a standard deviation of 142 g-C/m^2-y, somewhat higher than the DOC flux from the reference stream (5693±167 g-C/m^2-y). Post application there was an increase in DOC flux to 12,121 g-C/m^2-y, with a standard deviation of 178 g-C/m^2-y.

A similar comparison was difficult to perform for THg and MeHg fluxes because there were not enough observations to accurately calculate an annual pre-treatment flux. As a result, comparisons were made between reference and post-application observations only. The reference stream had an annual THg flux of 1.75 μg-THg/m^2-y, with a standard deviation of 2.79 μg-THg/m^2-y, which was lower than the post-application flux of 5.17 μg-THg/m^2-y, with a standard deviation of 3.4 μg-THg/m^2-y.

The MeHg flux was markedly different from the THg flux. Post-application MeHg flux from the treatment stream were slightly lower than the reference stream. The reference stream had an annual flux of 0.050 μg-Hg/m^2-y, with a standard deviation of 0.479 μg-Hg/m^2-y, while the treatment stream had a post-application flux of 0.034 μg-Hg/m^2-y, with a standard deviation of 0.389 μg-Hg/m^2-y.

Sulfate fluxes showed a somewhat different response than DOC fluxes. The reference site had an annual flux of 2905 g-SO_4/m^2-y, with a standard deviation of 119 g-SO_4/m^2-y, which is

approximately three quarters the pre-treatment value. Before lime addition, the treatment tributary had an annual flux of 4013 g-SO_4/m^2-y, with a standard deviation of 102 g-SO_4/m^2-y, which was not a large difference from the post-treatment flux of 4383 g-SO_4/m^2-y, with a standard deviation of 107 g-SO_4/m^2-y.

DISCUSSION

Lime addition to the treatment watershed markedly increased the pH of streamwater. For the first water year after the application, pH has remained above 5.0, which is protective of Brook trout health (Fost and Ferreri 2015). Many acid-impacted ecosystems like Honnedaga Lake are currently undergoing a natural recovery from acid deposition coincident with an increase in DOC (Monteith et al. 2007, Haaland et al. 2010). It might be anticipated that increases in pH associated with either decreases in acid deposition or base treatment would result in increased mobilization of DOC. While the drivers and mechanisms for increases in DOC can be complex (Clark et al. 2010), the mechanism in the treatment watershed is likely driven by a decrease in the partitioning of DOC to soil, with increases in soil pH (Ussiri and Johnson 2004). The shift towards higher SUVA values suggests more aromatic compounds were released from the treatment watershed following lime application coinciding with a decrease in DOC partitioning (Dittman et al. 2010).

These data suggest near-stream mercury pools were mobilized during the transitional period, while watershed mercury pools from soils further removed from the stream entered the tributary during the post-treatment period. MeHg is found at higher concentrations in soils and soil pore water in the hyporheic zone (Skyllberg et al. 2003). I hypothesize that limited near-stream Hg pool with elevated MeHg was mobilized immediately following lime application. Soil in more

upland areas of the watershed tend to be lower in MeHg and would take longer to reach the stream. This mechanism could explain the pattern of elevated THg and DOC concentrations through the post-treatment period while elevated MeHg concentrations decreased to reference levels within a short period after lime addition. The strong positive relation between THg and DOC provides increased opportunity for sulfate- and iron-reducing bacteria to co-metabolize THg, with the potential for increases in production of MeHg in downstream anaerobic lake sediments (Benoit et al. 2002, Podar et al. 2015).

Sulfate plays an integral role in MeHg formation (Benoit et al. 2002, Drevnick et al. 2007, Podar et al. 2015, Coleman Wasik et al. 2015). The treatment stream had higher sulfate concentrations before and after lime application. However, after application the difference in sulfate concentrations between the two streams increased. The SO4 annual flux increased by approximately 9%, while DOC increased by almost 60%. This difference in response between SO4 and DOC in the treatment stream coupled with a lower post-application MeHg flux relative to the reference stream suggests that methylation in these watersheds is not sulfate limited.

There is some evidence in the literature suggesting that high DOC concentrations can limit the bioavailablity of Hg. Using a series of Arctic lakes with a wide DOC gradient, French et al. (2014) showed that at DOC concentrations greater than approximately 8.5 mg/L, MeHg concentrations are diminished in biota. They suggest this effect is due to increased bonding of THg with larger molecular weight humic acids which are not easily degraded, limiting the release of ionic Hg and the formation of MeHg. While studies of riverine ecosystems in the Adirondacks have not observed this reduction in Hg bioaccumulation with elevated DOC (Riva-Murray et al. 2011), this has implications for downstream lakes.

Before lime addition, both the reference and treatment tributaries were contributing maximum DOC concentrations to Honnedaga Lake approaching or slightly above the value reported by French et al. (2014). Base treatment resulted in improvements in pH and mobilization of additional DOC to streamwater. This elevated DOC would have a larger humic fraction based on increased solubility of humic acids with increased pH (Ussiri and Johnson 2004) and evidenced by the increase in SUVA following lime treatment (Figure 2d). This pattern suggests a mobilization of humic organic matter in acid impacted soils when lime is applied. A higher humic acid DOC fraction entering could limit methylation of ionic Hg in downstream lakes.

Potential effects of liming on Hg cycling and bioaccumulation complicates assessment of liming as a management strategy (Lawrence et al. 2016). Lime can be applied in forested areas to protect against or reverse the impacts of acidic deposition and preserve or restore sensitive or impacted ecosystems. Concentrations of THg and DOC in the treatment stream have remained elevated for more than a year after treatment. Lime treatment is typically applied to drive a rapid increase in pH and ANC to pre-acidification levels and to mitigate the effects of acid deposition. At Honnedaga Lake, $CaCO_3$ was applied to improve spawning habitat for heritage Brook trout, increasing pH and decreasing concentrations of inorganic monomeric aluminum. These results suggest increases in DOC and THg are related to increases in pH. Higher concentrations and fluxes of THg in aquatic ecosystems are an unintended consequence of watershed liming. The effects of this management strategy on Hg bioaccumulation in riverine systems requires further investigation given the variety of interacting factors (Simonin et al. 2008a, Ward et al. 2010).

Increased mobilization of THg is a particular problem in forested areas as Hg accumulates in forest soils (Yu et al. 2011). In the northeastern United States, parks and conservation areas are typically forested. Applying lime to acid sensitive watersheds in the Adirondack Park would

drive improvements in pH and ANC, but simultaneously mobilize THg. Elevated transport of THg to downstream lakes would undoubtedly allow for deposition to anaerobic lake sediments, allowing for the formation of MeHg. Given that the treatment watershed is a relatively small tributary to Honnedaga Lake (2.7%), any change in flux would have minor impacts on the overall lake. However, if a complete liming of the Honnedaga Lake watershed were to be conducted, the response of the treatment tributary would suggest a 50% increase in load to Honnedaga Lake. This observed increase in Hg would likely persist beyond the first year after treatment with Hg dynamics different from those associated with natural recovery from acidic deposition.

The natural recovery of Honnedaga Lake from ongoing decreases in acid deposition further complicates assessment of this management strategy. Increases in DOC of approximately 1% per year have been reported in the northeastern United States following decreases in sulfate deposition (Monteith et al. 2007). The effect of observed DOC increases at Honnedaga Lake (Josephson et al. 2014) on Hg concentrations of lake-resident Brook trout, and tributary-resident macroinvertebrates is the subject of ongoing research.

These results have important implications for understanding the natural recovery of lake watersheds from acid deposition. This multi-decadal process (Driscoll et al. 2003b) will likely lead to continued increases in DOC and THg concentrations in recovering ecosystems. The increasing DOC and fish-Hg in aquatic ecosystems following decreases in sulfate deposition is indicative of this problem (Hongve et al. 2012; Josephson et al. 2014) Some studies have suggested that changes in the quality of DOC may occur coincident with increases in concentration of DOC (David and Vance 1991, Laudon et al. 2011, Vidon et al. 2014, Fakhraei

and Driscoll 2015), but it is unclear how changes in DOC quality would impact formation of MeHg in soils.

In the first water year after liming, the difference in THg and DOC concentrations between the treatment and reference tributaries were significantly greater than pre-liming. The strength of the THg:DOC relationship, the increase in DOC flux post-application, and the elevated THg flux from the treatment watershed, suggest a large mobilization of Hg following application. As the reference tributary recovers from acid deposition, a mass of Hg associated with soil organic matter (Demers et al. 2007, Burns et al. 2014) is available for future mobilization.

Additionally, the treatment watershed data indicate that available MeHg is removed from the watershed rapidly in response to altered chemical conditions. Post-application fluxes of MeHg from both watersheds are similar, despite the absence of any wetland area in the reference watershed. This would reduce exposure to the most biologically relevant species of Hg. Continued monitoring of the treatment tributary is required to determine how long these Hg dynamics are sustained.

CONCLUSIONS

Stream Hg concentrations and fluxes at a calcium carbonate treated and reference watersheds at Honnedaga Lake were examined for the first water year after lime addition. The response of Hg and DOC to base treatment can help inform our understanding of the natural recovery of watersheds impacted by acid deposition. These results also have implications for the downstream lake ecosystem where THg could be deposited to sediments and eventually converted to MeHg

The lime application resulted in a large increase in pH of the treatment tributary. This increase in pH mobilized organic carbon in treated soils, causing DOC and THg concentrations and fluxes to be elevated over reference and pre-treatment observations. In contrast, elevated MeHg concentrations were only observed during a five-month transitional period. After this transitional period, MeHg levels were not significantly different from reference values, suggesting that the enhanced concentrations of THg and DOC did not increase the supply of MeHg for an extended period following treatment. It is unclear what caused MeHg to return rapidly to pre-treatment levels while THg remained elevated, however it was speculated that MeHg was mobilized from near-stream pools. The relatively small quantity of these pools resulted in the limited duration of the MeHg treatment response. Further monitoring of these tributaries is required to evaluate the longer term impacts of using lime to accelerate recovery from acidification on Hg dynamics and Hg concentration in biota.

FIGURES

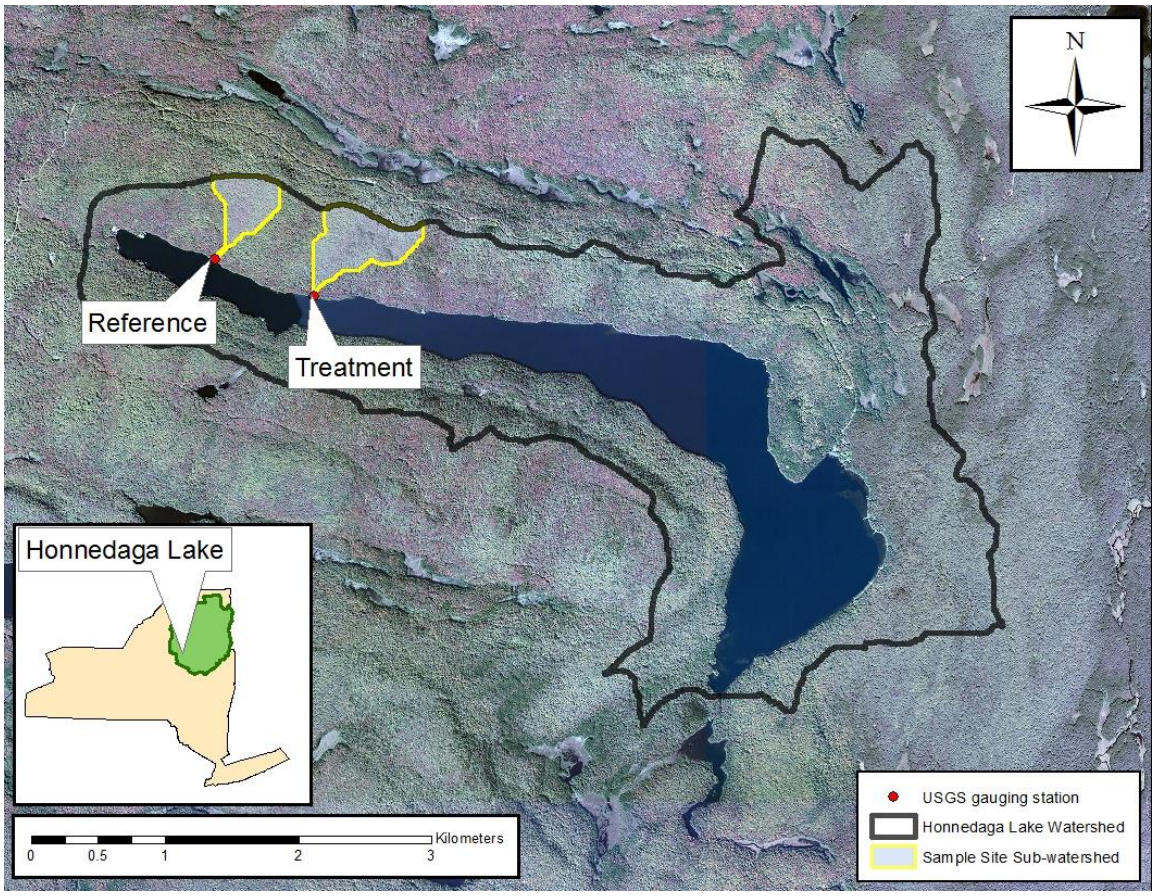

Figure 1: Map of Honnedaga Lake and the treatment and reference watersheds, located in the southwestern portion of the Adirondack Park (43º31'06"N and 74º48'31"W). This area of New York State is at a high elevation relative to the surrounding area (667m).

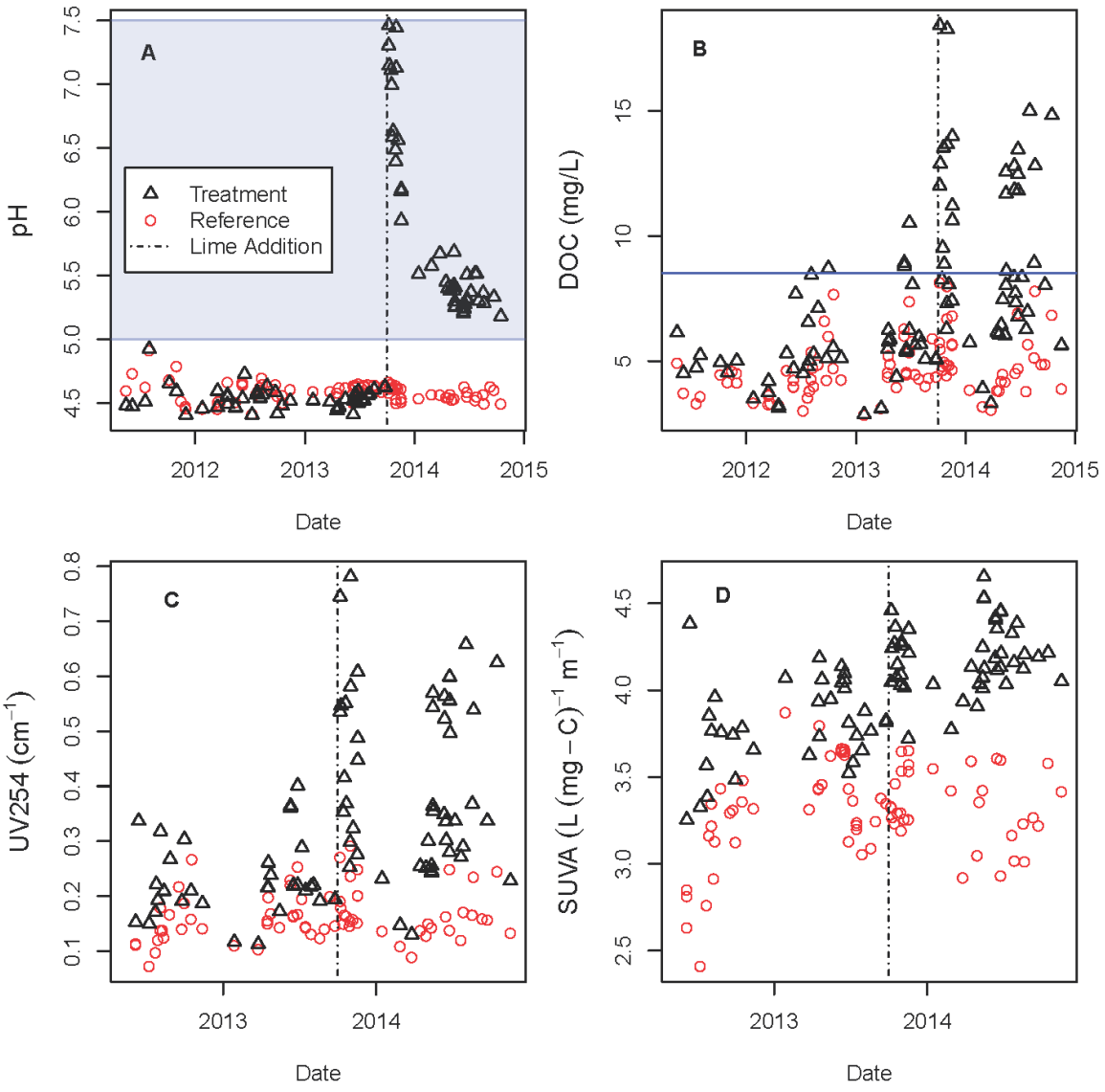

Figure 2: Time-series of pH (**A**), dissolved organic carbon (**B**), UV absorbance (**C**) and specific UV absorbance (**D**) of treatment and reference streams before and following lime application (1 October 2013 indicated by vertical line). For the first water year, pH values have remained above five in the treatment stream, while the reference stream remained chronically acidic. The blue box represents the pH range protective of brook trout. There was an increase in DOC following lime addition at the treatment stream. The horizontal blue line indicates DOC at 8.5mg-C/L. There was a marked increase in absorption in the treatment stream following treatment with lime. SUVA at the treatment stream started at a higher value prior to liming, and increased following lime application.

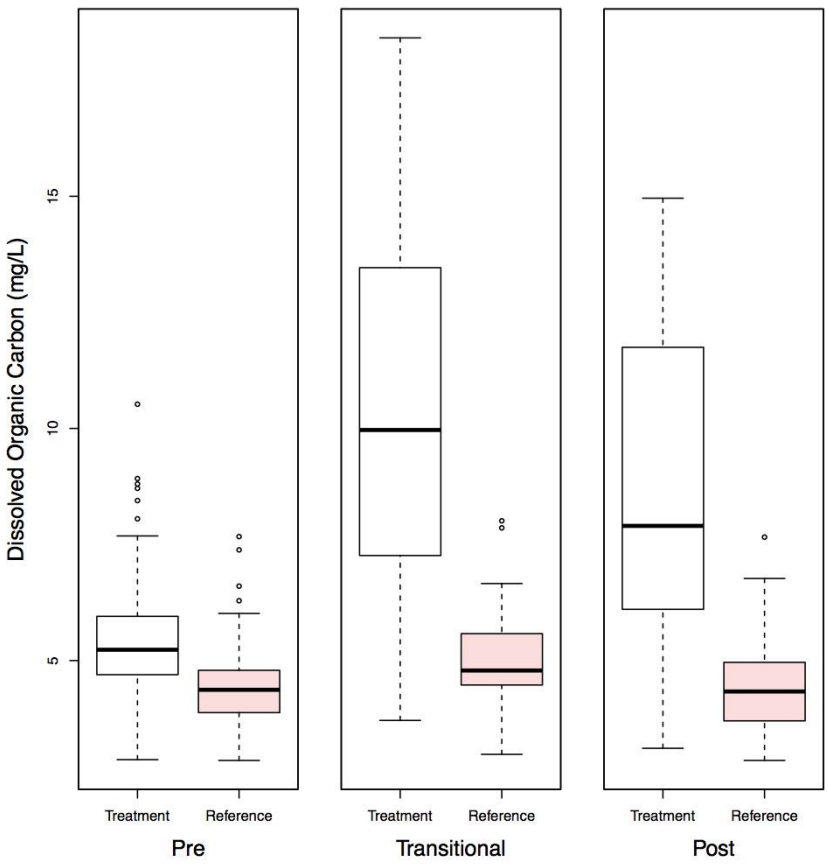

Figure 3: Dissolved organic carbon (DOC) concentrations before and following lime application in treatment and reference streams. There was no significant difference between the transitional and post treatment periods, but these were significantly higher than the pre-liming and reference observations ($p<0.0001$).

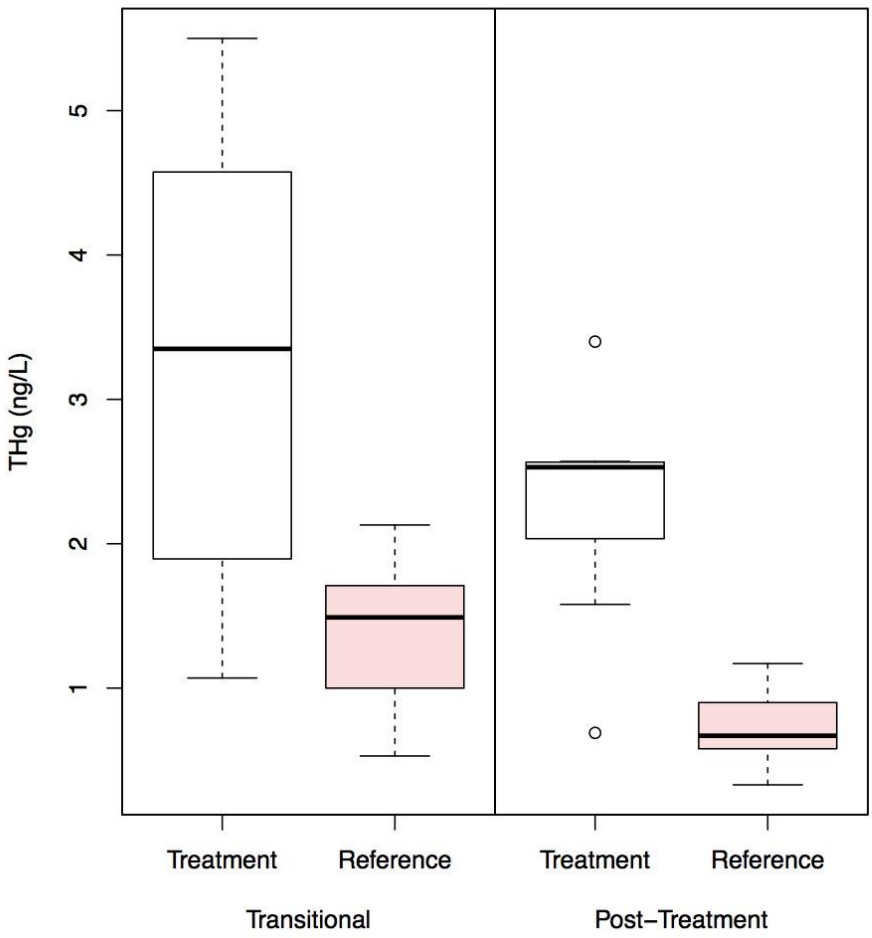

Figure 4: Total mercury (THg) concentrations following lime application in both the treatment and reference tributaries. Following application, the treatment stream has maintained THg concentrations significantly higher than the reference tributary (p=0.037 Transitional, p=0.016 post-treatment). Pre-treatment values were not shown because few samples were collected before the lime addition.

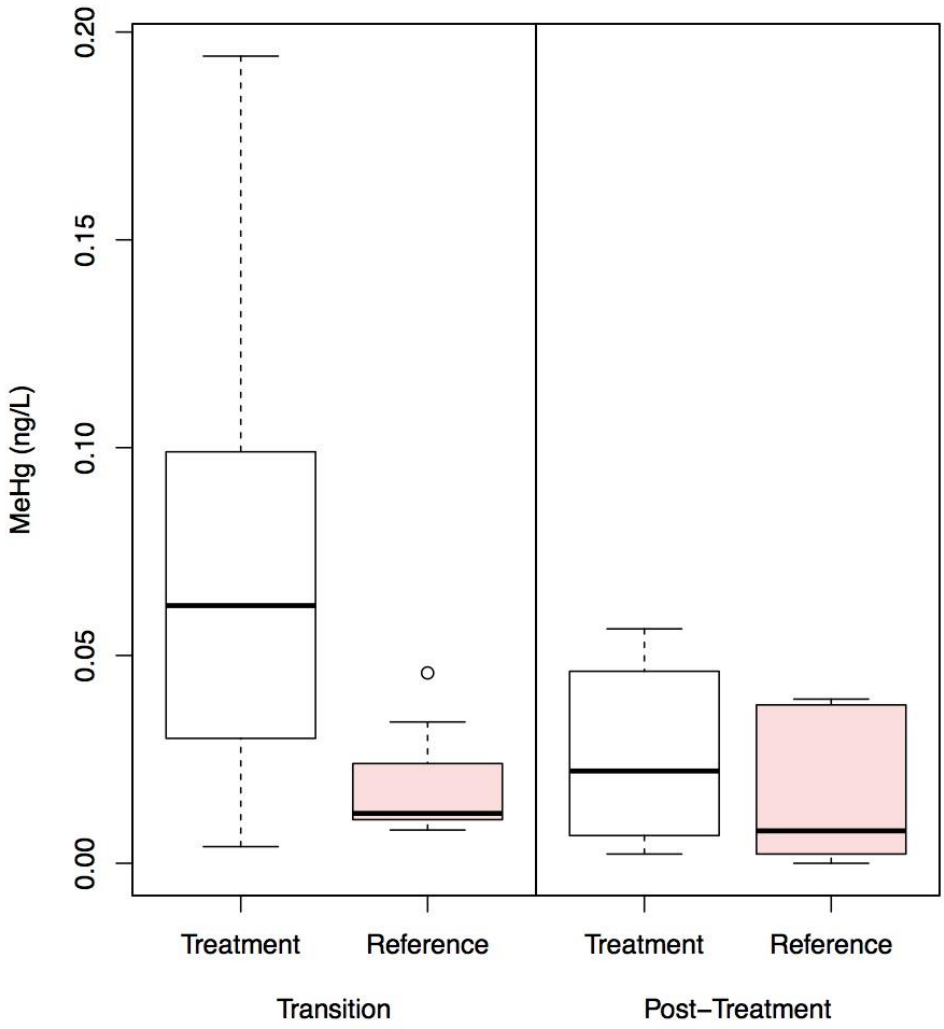

Figure 5: Concentrations of methylmercury (MeHg) in treatment and reference streams after lime application. MeHg was elevated over the transitional period (p=0.078). This statistical difference did not persist into the post-treatment period (p=0.114).

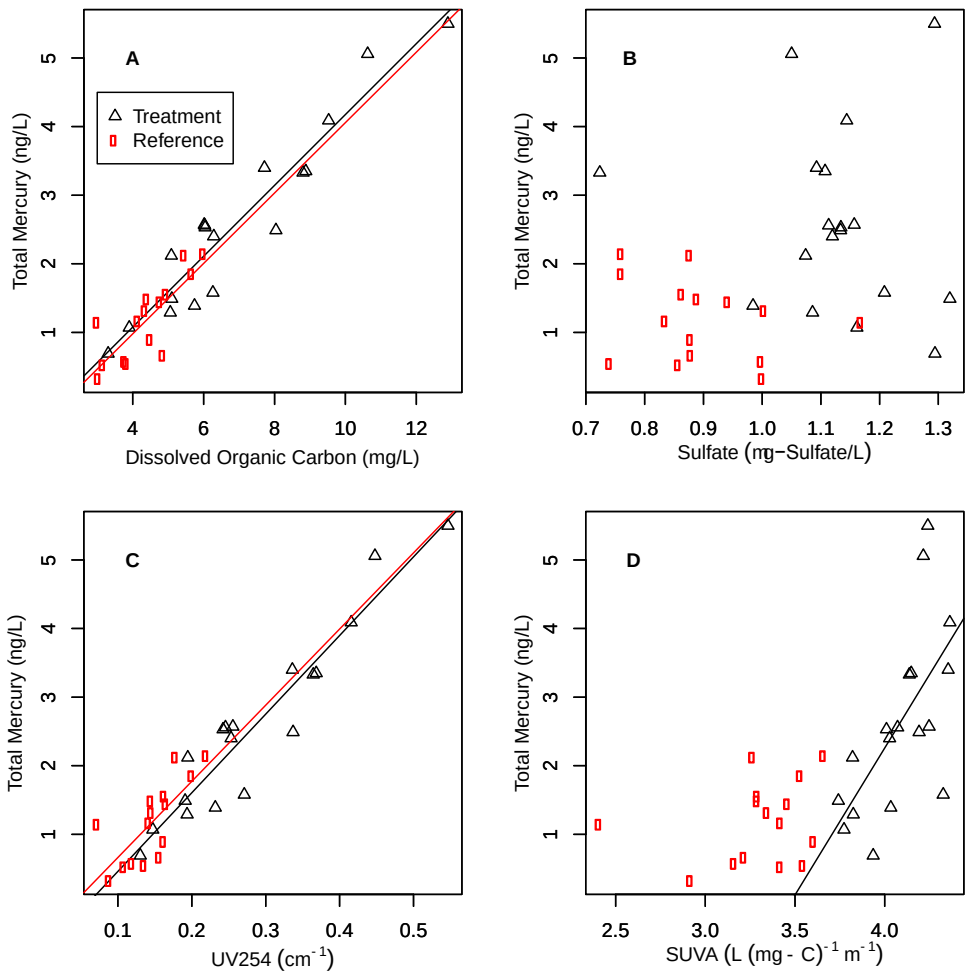

Figure 6: Relationship between concentrations of THg and DOC (**A**), sulfate (**B**), UV254 absorbance (**C**) and specific UV absorbance (**D**) in treatment and reference streams prior to and following lime treatment. The correlation between THg and DOC was stronger in the treatment stream than the reference stream (adj-R^2=0.900, 0.627 respectively) as was the relationship between THg and UV254 (adj-R^2=0.900, 0.528, treatment and reference stream respectively). There was no difference in slope observed at these sites for DOC ($p>0.9$, m=0.514ng-Hg/mg-C and 0.517ng-Hg/mg-C, for reference and treatment sites respectively), while the UV254 slopes were statistically different ($p<0.001$, m=11.12ng-Hg/m and 11.31ng-Hg/m, for reference and treatment sites respectively). The relationship between THg and SUVA in the treatment stream is the only other significant correlation ($p=0.004$, adj-R^2=0.377).

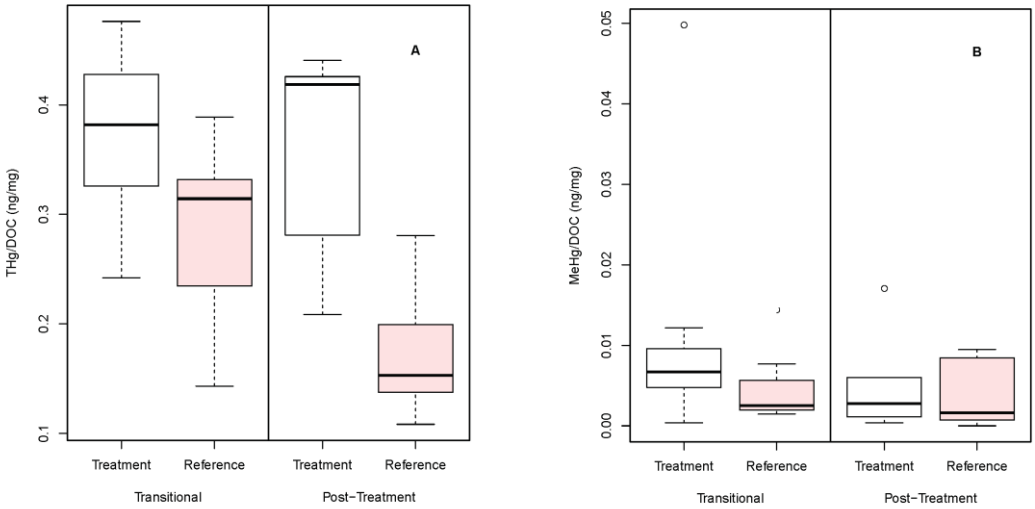

Figure 7: Ratio of **A**) THg:DOC and **B**) MeHg:DOC concentrations before and after lime application in treatment and reference streams. Greater THg per DOC was evident in the treatment stream compared to the reference stream during both the transitional and post-treatment periods. These two time periods were not different from each other in the treatment stream. There was no significant difference found in the MeHg:DOC ratio between the two tributaries.

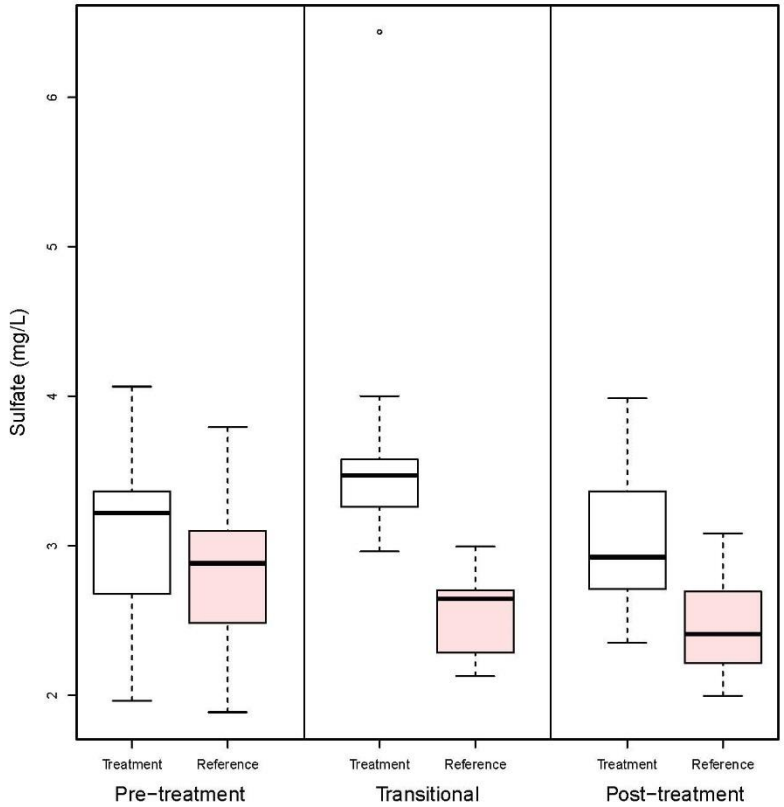

Figure 8: Concentrations of sulfate in treatment and reference stream water prior to and following lime addition. Treatment observations of

sulfate were not significantly different in the pre-treatment and post-treatment periods, but the transitional period was significantly higher than the other time periods (p<0.001). The treatment tributary was significantly higher, regardless of period. The seasonal variation of sulfate makes it difficult to determine if these differences were caused by the treatment.

TABLES

Table 1: Calculated p-values and adj-R2 for concentrations of THg and MeHg with DOC, sulfate, UV absorbance, and specific UV absorbance. Total Hg had significant relationships with DOC and UV absorbance at both reference and treatment streams, and specific absorbance at just the treatment stream. No significant relationships were found with MeHg.

	THg				MeHg			
	Reference		Treatment		Reference		Treatment	
	p-value	adj-R2	p-value	adj-R2	p-value	adj-R2	p-value	adj-R2
DOC	<0.001	0.627	<0.001	0.900	0.537	-0.44	0.813	-0.067
Sulfate	0.332	0.001	0.566	-0.040	0.231	0.040	0.189	0.056
UV254	0.001	0.528	<0.001	0.900	0.865	-0.074	0.848	-0.069
SUVA	0.321	0.004	0.002	0.412	0.136	0.098	0.662	-0.056

Table 2: Calculated fluxes and standard deviations from the reference and treatment tributaries. Not enough Hg data were collected prior to lime addition to calculate a MeHg or THg flux. Post-application values were calculated using data from the transitional and post-treatment time periods.

	MeHg (g-Hg/km2 y)		THg (g-Hg/km2 y)		DOC (kg-C/km2 y)		SO4 (kg-SO4/km2 y)	
	Flux	Std Dev.	Flux	Std Dev.	Flux	Std Dev.	Flux	Std Dev.
Pre-treatment	NA		NA		7748	142	4013	102
Post-application	0.034	0.389	5.17	3.4	12121	178	4383	107
Reference	0.050	0.479	1.75	2.79	5693	167	2905	119

REFERENCES

Aberg, B.; Ekman, L.; Falk, R.; Greitz, U.; Persson, G.; and Snihs, J. Metabolism of Methyl Mercury (203 Hg) Compounds in Man. *Archives of Environmental Health: An International Journal*. **1969**, *19* (4), 478–484. DOI: 10.1080/00039896.1969.10666872

Agency for Toxic Substances and Disease Registry (ATSDR). Toxicology Profile for Mercury. In U.S. Department of Health and Human Services, Public Health Service. Atlanta, GA.

Baldigo, B. P.; Lawrence, G. B.; Bode, R. W.; Simonin, H. A.; Roy, K. M.; and Smith, A. J. Impacts of acidification on macroinvertebrate communities in streams of the western Adirondack Mountains, New York, USA. *Ecological Indicators*. **2009**, *9* (2), 226–239. DOI: 10.1016/j.ecolind.2008.04.004

Baldigo, B. P.; Lawrence, G.; and Simonin, H. Persistent Mortality of Brook Trout in Episodically Acidified Streams of the Southwestern Adirondack Mountains, New York. *Transactions of the American Fisheries Society*. **2007**, *136* (1), 121–134. DOI: 10.1577/T06-043.1

Benoit, J. M.; Gilmour, C. C.; Heyes, A.; Mason, R. P.; and Miller, C. L. Geochemical and Biological Controls over Methylmercury Production and Degradation in Aquatic Ecosystems. In ACS symposium. pp. 262–297. DOI: 10.1021/bk-2003-0835.ch019

Blackwell, B. D.; and Driscoll, C. T. Using foliar and forest floor mercury concentrations to assess spatial patterns of mercury deposition. *Environmental Pollution*. **2015**, *202*, 126–134. DOI: 10.1016/j.envpol.2015.02.036

Burgess, N. M.; and Meyer, M. W. Methylmercury exposure associated with reduced productivity in common loons. *Ecotoxicology*. **2008**, *17* (2), 83–91. DOI: 10.1007/s10646-007-0167-8

Burns, D. A.; Lynch, J. A.; Cosby, B. J.; Fenn, M. E.; and Baron, J. S. National Acid Precipitation Assessment Program report to congress 2011: An integrated assessment. *Washington, DC: National Science and Technology Council*.

Burns, D. A.; Woodruff, L. G.; Bradley, P. M.; and Cannon, W. F. Mercury in the Soil of Two Contrasting Watersheds in the Eastern United States. *PLoS ONE*. **2014**, *9* (2), e86855. DOI: 10.1371/journal.pone.0086855

Chen, L.; and Driscoll, C. T. Regional Assessment of the Response of the Acid−Base Status of Lake Watersheds in the Adirondack Region of New York to Changes in Atmospheric Deposition Using PnET-BGC. *Environmental Science & Technology*. **2005**, *39* (3), 787–794. DOI: 10.1021/es049583t

Cho, Y.; Driscoll, C. T.; and Blum, J. D. The effects of a whole-watershed calcium addition on the chemistry of stream storm events at the Hubbard Brook Experimental Forest in NH, USA. *Science of The Total Environment*. **2009**, *407* (20), 5392–5401. DOI: 10.1016/j.scitotenv.2009.06.030

Cirmo, C. P.; and Driscoll, C. T. The impacts of a watershed CaCO3 treatment on stream and wetland biogeochemistry in the Adirondack Mountains. *Biogeochemistry*. **1996**, *32* (3), 265–297. DOI: 10.1007/BF02187142

Clark, J. M.; Bottrell, S. H.; Evans, C. D.; Monteith, D. T.; Bartlett, R.; Rose, R.; Newton, R. J.; and Chapman, P. J. The importance of the relationship between scale and process in understanding long-term DOC dynamics. *Science of The Total Environment*. **2010**, *408* (13), 2768–2775. DOI: 10.1016/j.scitotenv.2010.02.046

Coleman Wasik, J. K.; Engstrom, D. R.; Mitchell, C. P. J.; Swain, E. B.; Monson, B. A.; Balogh, S. J.; Jeremiason, J. D.; Branfireun, B. A.; Kolka, R. K.; and Almendinger, J. E. The effects of hydrologic fluctuation and sulfate regeneration on mercury cycling in an experimental peatland. *Journal of Geophysical Research: Biogeosciences*. **2015**, *120* (9), 1697–1715. DOI: 10.1002/2015JG002993

David, M. B.; and Vance, G. F. Chemical Character and Origin of Organic Acids in Streams and Seepage Lakes of Central Maine. *Biogeochemistry*. **1991**, *12* (1), 17–41.

Demers, J. D.; Driscoll, C. T.; Fahey, T. J.; and Yavitt, J. B. MERCURY CYCLING IN LITTER

AND SOIL IN DIFFERENT FOREST TYPES IN THE ADIRONDACK REGION, NEW YORK, USA. *Ecological Applications*. **2007**, *17* (5), 1341–1351. DOI: 10.1890/06-1697.1

Dennis, I. F.; Clair, T. A.; Driscoll, C. T.; Kamman, N.; Chalmers, A.; Shanley, J.; Norton, S. A.; and Kahl, S. Distribution Patterns of Mercury in Lakes and Rivers of Northeastern North America. *Ecotoxicology*. **2005**, *14* (1-2), 113–123. DOI: 10.1007/s10646-004-6263-0

Dittman, J. A.; Shanley, J. B.; Driscoll, C. T.; Aiken, G. R.; Chalmers, A. T.; and Towse, J. E. Ultraviolet absorbance as a proxy for total dissolved mercury in streams. *Environmental Pollution*. **2009**, *157* (6), 1953–1956. DOI: 10.1016/j.envpol.2009.01.031

Dittman, J. A.; Shanley, J. B.; Driscoll, C. T.; Aiken, G. R.; Chalmers, A. T.; Towse, J. E.; and Selvendiran, P. Mercury dynamics in relation to dissolved organic carbon concentration and quality during high flow events in three northeastern U.S. streams. *Water Resources Research*. **2010**, *46* (7). DOI: 10.1029/2009WR008351

Drevnick, P. E.; Canfield, D. E.; Gorski, P. R.; Shinneman, A. L. C.; Engstrom, D. R.; Muir, D. C. G.; Smith, G. R.; Garrison, P. J.; Cleckner, L. B.; Hurley, J. P.; Noble, R. B.; et al. Deposition and cycling of sulfur controls mercury accumulation in Isle Royale fish. *Environmental Science and Technology*. **2007**, *41* (21), 7266–7272. DOI: 10.1021/es0712322

Drevnick, P. E.; Engstrom, D. R.; Driscoll, C. T.; Swain, E. B.; Balogh, S. J.; Kamman, N. C.; Long, D. T.; Muir, D. G. C.; Parsons, M. J.; Rolfhus, K. R.; and Rossmann, R. Spatial and temporal patterns of mercury accumulation in lacustrine sediments across the Laurentian Great Lakes region. *Environmental Pollution*. **2012**, *161*, 252–260. DOI: 10.1016/j.envpol.2011.05.025

Driscoll, C. T.; Cirmo, C. P.; Fahey, T. J.; Blette, V. L.; Bukaveckas, P. A.; Burns, D. A.;

Gubala, C. P.; Leopold, D. J.; Newton, R. M.; Raynal, D. J.; Schofield, C. L.; et al. The experimental watershed liming study: Comparison of lake and watershed neutralization strategies. *Biogeochemistry*. **1996**, *32* (3), 143–174. DOI: 10.1007/BF02187137

Driscoll, C. T.; Driscoll, K. M.; Mitchell, M. J.; and Raynal, D. J. Effects of acidic deposition on forest and aquatic ecosystems in New York State. *Environmental Pollution*. **2003a**, *123* (3), 327–336. DOI: 10.1016/S0269-7491(03)00019-8

Driscoll, C. T.; Driscoll, K. M.; Roy, K. M.; and Dukett, J. Changes in the chemistry of lakes in the Adirondack region of New York following declines in acidic deposition. *Applied Geochemistry*. **2007a**, *22* (6), 1181–1188. DOI: 10.1016/j.apgeochem.2007.03.009

Driscoll, C. T.; Driscoll, K. M.; Roy, K. M.; and Mitchell, M. J. Chemical Response of Lakes in the Adirondack Region of New York to Declines in Acidic Deposition. *Environmental Science & Technology*. **2003b**, *37* (10), 2036–2042. DOI: 10.1021/es020924h

Driscoll, C. T.; Han, Y.Chen, C. Y.; Evers, D. C.; Lambert, K. F.; Holsen, T. M.; Kamman, N. C.; and Munson, R. K. Mercury Contamination in Forest and Freshwater Ecosystems in the Northeastern United States. *BioScience*. **2007b**, *57* (1), 17. DOI: 10.1641/B570106

Driscoll, C. T.; Lawrence, G. B.; Bulger, A. J.; Butler, T. J.; Cronan, C. S.; Eagar, C.; Lambert, K. F.; Likens, G. E.; Stoddard, J. L.; and Weathers, K. C. Acidic Deposition in the Northeastern United States: Sources and Inputs, Ecosystem Effects, and Management Strategies. *BioScience*. **2001**, *51* (3), 180. DOI: 10.1641/0006-3568(2001)051[0180:ADITNU]2.0.CO;2

Driscoll, C. T.; Mason, R. P.; Chan, H. M.; Jacob, D. J.; and Pirrone, N. Mercury as a global pollutant: Sources, pathways, and effects. *Environmental Science and Technology*. **2013**, *47* (10), 4967–4983. DOI: 10.1021/es305071v

Fakhraei, H.; and Driscoll, C. T. Proton and aluminum binding properties of organic acids in surface waters of the northeastern U.S. *Environmental Science and Technology*. **2015**, *49* (5), 2939–2947. DOI: 10.1021/es504024u

Fost, B. A.; and Ferreri, C. P. pH preference and avoidance responses of adult brook trout Salvelinus fontinalis and brown trout Salmo trutta. *Journal of Fish Biology*. **2015**, *86* (3), 952–966. DOI: 10.1111/jfb.12610

French, T. D.; Houben, A. J.; Desforges, J.-P. W.; Kimpe, L. E.; Kokelj, S. V; Poulain, A. J.; Smol, J. P.; Wang, X.; and Blais, J. M. Dissolved organic carbon thresholds affect mercury bioaccumulation in Arctic lakes. *Environmental Science and Technology*. **2014**, *48*, 3162–3168. DOI: 10.1021/es403849d

Giang, A.; and Selin, N. E. Benefits of mercury controls for the United States. *Proceedings of the National Academy of Sciences*. **2016**, *113* (2), 286–291. DOI: 10.1073/pnas.1514395113

Gilmour, C. C.; Riedel, G. S.; Ederington, M. C.; Bell, J. T.; Benoit, J. M.; Gill, G. a; and Stordal, M. C. Methylmercury concentrations and production rates across a trophic gradient in the northern Everglades. *Biogeochemistry*. **1998**, *40*, 327–345. DOI: 10.1023/A:1005972708616

Greaver, T. L.; Sullivan, T. J.; Herrick, J. D.; Barber, M. C.; Baron, J. S.; Cosby, B. J.; Deerhake, M. E.; Dennis, R. L.; Dubois, J. J. B.; Goodale, C. L.; Herlihy, A. T.; et al. Ecological effects of nitrogen and sulfur air pollution in the US: What do we know? *Frontiers in Ecology and the Environment*. **2012**, *10* (7), 365–372. DOI: 10.1890/110049

Haaland, S.; Hongve, D.; Laudon, H.; Riise, G.; and Vogt, R. D. Quantifying the Drivers of the Increasing Colored Organic Matter in Boreal Surface Waters. *Environmental Science & Technology*. **2010**, *44* (8), 2975–2980. DOI: 10.1021/es903179j

Hintelmann, H.; Harris, R.; Heyes, A.; Hurley, J. P.; Kelly, C. a.; Krabbenhoft, D. P.; Lindberg, S.; Rudd, J. W. M.; Scott, K. J.; and St. Louis, V. L. Reactivity and mobility of new and old mercury deposition in a boreal forest ecosystem during the first year of the METAALICUS study. *Environmental Science and Technology*. **2002**, *36* (23), 5034–5040. DOI: 10.1021/es025572t

Hongve, D.; Haaland, S.; Riise, G.; Blakar, I.; and Norton, S. Decline of acid rain enhances mercury concentrations in fish. *Environmental science & technology*. **2012**, *46* (5), 2490–1. DOI: 10.1021/es3002629

Jeffries, D. S.; Brydges, T. G.; Dillon, P. J.; and Keller, W. Monitoring the results of Canada/U.S.A. acid rain control programs: Some Lake responses. *Environmental Monitoring and Assessment*. **2003**, *88* (1-3), 3–19. DOI: 10.1023/A:1025563400336

Josephson, D. C.; Robinson, J. M.; Chiotti, J.; Jirka, K. J.; and Kraft, C. E. Chemical and biological recovery from acid deposition within the Honnedaga Lake watershed, New York, USA. *Environmental Monitoring and Assessment*. **2014**, *186* (7), 4391–4409. DOI: 10.1007/s10661-014-3706-9

Kerin, E. J.; Gilmour, C. C.; Roden, E.; Suzuki, M. T.; Coates, J. D.; and Mason, R. P. Mercury methylation by dissimilatory iron-reducing bacteria. *Applied and Environmental Microbiology*. **2006**, *72* (12), 7919–7921. DOI: 10.1128/AEM.01602-06

Laudon, H.; Berggren, M.; Ågren, A.; Buffam, I.; Bishop, K.; Grabs, T.; Jansson, M.; and Köhler, S. Patterns and Dynamics of Dissolved Organic Carbon (DOC) in Boreal Streams: The Role of Processes, Connectivity, and Scaling. *Ecosystems*. **2011**, *14* (6), 880–893. DOI: 10.1007/s10021-011-9452-8

Lawrence, G. B.; Burns, D. A.; and Riva-Murray, K. A new look at liming as an approach to

accelerate recovery from acidic deposition effects. *Science of The Total Environment*. **2016**, *562* (April), 35–46. DOI: 10.1016/j.scitotenv.2016.03.176

Lawrence, G. B.; Roy, K. M.; Baldigo, B. P.; Simonin, H. a; Capone, S. B.; Sutherland, J. W.; Nierzwicki-Bauer, S. a; and Boylen, C. W. Chronic and episodic acidification of Adirondack streams from acid rain in 2003-2005. *Journal of environmental quality*. **2008**, *37* (6), 2264–74. DOI: 10.2134/jeq2008.0061

Likens, G. E.; Bormann, F. H.; and Johnson, N. M. Acid Rain. *Environment: Science and Policy for Sustainable Development*. **1972**, *14* (2), 33–40. DOI: 10.1080/00139157.1972.9933001

Lincoln, T. A.; Horan-Ross, D. A.; McHale, M. R.; and Lawrence, G. . Quality-assurance data for routine water analyses by the U.S. Geological Survey laboratory in Troy, New York—July 2001 through June 2003: U.S. Geological Survey Open-File Report 2009–1232. [Online.] Available at http://pubs.usgs.gov/of/2009/1232/.

Monteith, D. T.; Stoddard, J. L.; Evans, C. D.; de Wit, H. a; Forsius, M.; Høgåsen, T.; Wilander, A.; Skjelkvåle, B. L.; Jeffries, D. S.; Vuorenmaa, J.; Keller, B.; et al. Dissolved organic carbon trends resulting from changes in atmospheric deposition chemistry. *Nature*. **2007**, *450* (7169), 537–540. DOI: 10.1038/nature06316

New York State Department of Health. Health Advice on Eating Sportfish and Game. [Online.] Available at http://www.health.ny.gov/publications/2800.pdf.

Oden, S. The acidification of air precipitation and its consequences in the natural environment. In Ecological Research Communications. Bulletin of NFR. Arlington (VA). p. Translation Consultants Parker.

Peters, S. C.; Blum, J. D.; Driscoll, C. T.; and Likens, G. E. Dissolution of wollastonite during the experimental manipulation of Hubbard Brook Watershed. *Biogeochemistry*. **2004**, *67*

(3), 309–329. DOI: 10.1023/B:BIOG.0000015787.44175.3f

Podar, M.; Gilmour, C. C.; Brandt, C. C.; Soren, A.; Brown, S. D.; Crable, B. R.; Palumbo, A. V; Somenahally, A. C.; and Elias, D. A. Global prevalence and distribution of genes and microorganisms involved in mercury methylation. *Science Advances*. **2015**, *1* (9), 1–13. DOI: 10.1126/sciadv.1500675

Poulin, B. A.; Ryan, J. N.; and Aiken, G. R. The effects of iron on optical properties of dissolved organic matter. *Environmental Science & Technologycience & technology*. **2014**, *48* (17), 10098–10106. DOI: 10.1021/es502670r

Riva-Murray, K.; Chasar, L. C.; Bradley, P. M.; Burns, D. A.; Brigham, M. E.; Smith, M. J.; and Abrahamsen, T. A. Spatial patterns of mercury in macroinvertebrates and fishes from streams of two contrasting forested landscapes in the eastern United States. *Ecotoxicology*. **2011**, *20* (7), 1530–1542. DOI: 10.1007/s10646-011-0719-9

Sauer, V. B.; and Turnipseed, D. P. Stage measurement at gaging stations: U.S. Geological Survey Techniques and Methods book 3, chap. A7,. [Online.] Available at http://pubs.usgs.gov/tm/tm3-a7/.

Schoch, N.; Glennon, M. J.; Evers, D. C.; Duron, M.; Jackson, A. K.; Driscoll, C. T.; Ozard, J. W.; and Sauer, A. K. The Impact of Mercury Exposure on the Common Loon (Gavia immer) Population in the Adirondack Park, New York, USA. *Waterbirds*. **2014**, *37* (sp1), 133–146. DOI: 10.1675/063.037.sp116

Selin, N. E. Global Biogeochemical Cycling of Mercury: A Review. *Annual Review of Environment and Resources*. **2009**, *34* (1), 43–63. DOI: 10.1146/annurev.environ.051308.084314

Simonin, H. a.; Loukmas, J. J.; Skinner, L. C.; and Roy, K. M. Lake variability: Key factors

controlling mercury concentrations in New York State fish. *Environmental Pollution*. **2008a**, *154*, 107–115. DOI: 10.1016/j.envpol.2007.12.032

Simonin, H.; Loukmas, J.; Skinner, L.; and Roy, K. Strategic Monitoring of Mercury in New York State Fish. [Online.] Available at http://www.dec.ny.gov/docs/wildlife_pdf/hgfish.pdf.

Skyllberg, U.; Qian, J.; Frech, W.; Xia, K.; and Bleam, W. F. Distribution of mercury, methyl mercury and organic sulphur species in soil, soil solution and stream of a boreal forest catchment. *Biogeochemistry*. **2003**, *64* (1), 53–76. DOI: 10.1023/A:1024904502633

Sundseth, K.; Pacyna, J. M.; Pacyna, E. G.; Munthe, J.; Belhaj, M.; and Astrom, S. Economic benefits from decreased mercury emissions: Projections for 2020. *Journal of Cleaner Production*. **2010**, *18* (4), 386–394. DOI: 10.1016/j.jclepro.2009.10.017

Syversen, T.; and Kaur, P. The toxicology of mercury and its compounds. *Journal of Trace Elements in Medicine and Biology*. **2012**, *26* (4), 215–226. DOI: 10.1016/j.jtemb.2012.02.004

Turnipseed, D. P.; and Sauer, V. B. Discharge measurement at gaging stations: U.S. Geological Survey Techniques and Methods book 3, chap. A8,. [Online.] Available at http://pubs.usgs.gov/tm/tm3-a8/.

U.S. EPA. Method 1669: Sampling Ambient Water for Trace Metals at EPA Water Quality Criteria Levels. *United States Environmental Protection Agency*. **1995**, 1–42.

U.S. EPA. Method 1631, revision E: mercury in water by oxidation, purge and trap, and cold vapor atomic fluorescence spectrometry. *United States Environmental Protection Agency*. **2002**, (August), 1–46.

U.S. EPA. Method 1630 Methyl Mercury in Water by Distillation, Aqueous Ethylation, Purge and Trap, and Cold Vapor Atomic Fluorescence Spectrometry. *United States Environmental*

Protection Agency. **2007**, 1–55.

U.S. EPA. Acid Rain and Related Programs: 2009 Highlights. *EPA reports*. [Online.] Available at http://nepis.epa.gov/Exe/ZyPDF.cgi/P1009I5K.PDF?Dockey=P1009I5K.PDF.

U.S. EPA. Risk and exposure assessment for review of the secondary National Ambient Air Quality Standards for oxides of nitrogen and oxides of sulfur. [Online.] Available at https://www3.epa.gov/ttn/naaqs/standards/no2so2sec/data/20110114pamain.pdf.

Ussiri, D. a. N.; and Johnson, C. E. Sorption of Organic Carbon Fractions by Spodosol Mineral Horizons. *Soil Science Society of America Journal*. **2004**, *68* (1), 253. DOI: 10.2136/sssaj2004.0253

Vidon, P.; Carleton, W.; and Mitchell, M. J. Spatial and temporal variability in stream dissolved organic carbon quantity and quality in an Adirondack forested catchment. *Applied Geochemistry*. **2014**, *46*, 10–18. DOI: 10.1016/j.apgeochem.2014.04.008

Warby, R. A. F.; Johnson, C. E.; and Driscoll, C. T. Chemical recovery of surface waters across the northeastern United States from reduced inputs of acidic deposition: 1984-2001. *Environmental Science and Technology*. **2005**, *39* (17), 6548–6554. DOI: 10.1021/es048553n

Ward, D. M.; Nislow, K. H.; and Folt, C. L. Bioaccumulation syndrome: Identifying factors that make some stream food webs prone to elevated mercury bioaccumulation. *Annals of the New York Academy of Sciences*. **2010**, *1195*, 62–83. DOI: 10.1111/j.1749-6632.2010.05456.x

Yu, X.; Driscoll, C. T.; Montesdeoca, M.; Evers, D.; Duron, M.; Williams, K.; Schoch, N.; and Kamman, N. C. Spatial patterns of mercury in biota of Adirondack, New York lakes. *Ecotoxicology*. **2011**, *20* (7), 1543–1554. DOI: 10.1007/s10646-011-0717-y

Zhang, Y.; Jacob, D. J.; Horowitz, H. M.; Chen, L.; Amos, H. M.; Krabbenhoft, D. P.; Slemr, F.; St. Louis, V. L.; and Sunderland, E. M. Observed decrease in atmospheric mercury explained by global decline in anthropogenic emissions. *Proceedings of the National Academy of Sciences*. **2016**, *113* (3), 526–531. DOI: 10.1073/pnas.1516312113

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