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Lake Recovery Through Reduced Sulfate Deposition: A New Paradigm for Drinking Water Treatment

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Supporting Information

ABSTRACT: This study examined sulfate deposition in Nova Scotia from 1999 to 2015, and its association with increased pH and organic matter in two protected surface water supplies (Pockwock Lake and Lake Major) located in Halifax, Nova Scotia. The study also examined the effect of lake water chemistry on drinking water treatment processes. Sulfate deposition in the region decreased by 68%, whereas pH increased by 0.1-0.4 units over the 16-year period. Average monthly color concentrations in Pockwock Lake and Lake Major increased by 1.7 and 3.8×, respectively. Accordingly, the coagulant demand increased by 1.5 and 3.8× for the water treatment plants supplied by Pockwock Lake and Lake Major. Not only was this coagulant increase costly for the utility, it also



resulted in compromised filter performance, particularly for the direct-biofiltration plant supplied by Pockwock Lake that was found to already be operating at the upper limit of the recommended direct filtration thresholds for color, total organic carbon and coagulant dose. Additionally, in 2012-2013 geosmin occurred in Pockwock Lake, which could have been attributed to reduced sulfate deposition as increases in pH favor more diverse cyanobacteria populations. Overall, this study demonstrated the impact that ambient air quality can have on drinking water supplies.

INTRODUCTION

As a result of successful air emissions control, a number of studies have shown evidence of lake recovery from acidification.¹⁻³ Lake recovery is defined by increasing acid neutralization capacity (ANC), alkalinity and/or pH,⁴ and is often associated with increasing natural organic matter (NOM) as measured by dissolved organic carbon (DOC). Increasing concentrations of DOC in surface waters in the Northern hemisphere have been reported in areas that were previously exposed to chronic sulfate (SO₄) deposition through acid rain,⁵⁻⁸ and therefore increasing DOC is often viewed as evidence for recovery from acidification. For example, Monteith et al.8 studied the spatial distribution of DOC trends in data collected in six North European and North American countries between 1990 and 2004 and found widespread significant upward trends in DOC in the northeastern portion of the United States, southern Nordic regions, and in the United Kingdom (UK), which Monteith and co-workers related to reductions in atmospheric deposition of SO₄ across large areas. Garmo et al.³ analyzed trends in surface water chemistry for 12 sites in Europe and North America and found that during the period between 1990 and 2008, sulfate deposition declined at 87% of study sites, corresponding with increasing DOC concentrations. Other instances of increasing DOC, pH and

diversity have occurred in lakes without associated increases in nutrient levels,⁹ leading to the concept that Nova Scotia lakes are undergoing some form of change, observed through increased NOM, which may be associated with lake recovery.

In drinking water, NOM may contribute to taste, color, and odor issues that can be problematic from a consumer standpoint. As well, NOM from source water similar to the lakes studied have shown to contribute to the formation of chlorinated disinfection byproducts (DBPs) following chlorination.^{10–12} Accordingly, coagulation processes are widely used to destabilize negatively charged particulate matter¹³ and through enhanced coagulation, conventional treatment processes can be adapted to remove NOM.¹⁴ It has been suggested that surface waters recovering from acidification produce NOM with a greater hydrophobic fraction as the solubility of NOM increases,^{15–17} which will have potential to increase coagulant demand. Such changes in influent water quality will also have implications for energy use and carbon emissions associated with water treatment processes. The operational embodied

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energy for a water treatment facility represents the energy needed to produce a unit volume of drinking water, and consists of direct and indirect energy. Direct energy is comprised of electricity and fuel consumption, and indirect energy is from the production and transport of water treatment chemicals. Santana et al.¹⁸ showed that increases in chemical dosing at a water treatment plant in Florida was responsible for 14.5% of the total operational embodied energy for the facility. Accordingly, increases in NOM concentration and changes in composition associated with recovery from acidification are anticipated to have significant impact on water treatment, though there are limited, if any data reported in the literature.

In addition to abiotic water quality indicators for recovery (e.g., increasing NOM concentration), changes in biotic water quality in terms of species richness and taxonomic composition are among the best-known indicators of biological recovery from acidification.¹⁹ Experimental acidification of lakes has demonstrated loss of algal species,^{20,21} reduced species richness, and changes in algal community structure as the phytoplankton community shifts from cyanobacteria to large dinoflagellates.²¹⁻²⁴ Anthropogenic acidification has also caused longterm changes in algal community abundance, spatial distribution, and taxonomic composition.²¹⁻²⁴ Findlay et al.²¹ showed that experimental and anthropogenic acidification had an impact on the species diversity of phytoplankton, which was positively correlated with pH. Findlay et al.²¹ also noted that cyanobacteria were significantly reduced below pH 5.1, and increased during recovery at a pH between 5.5 and 5.8. In the northeastern U.S., decreased sulfate deposition throughout the 1980s-2000s and subsequent increases in ANC corresponded with increased phytoplankton species richness.²⁵ It has been widely reported that some cyanobacteria produce taste and odor compounds in surface waters.²⁶⁻²⁸ For example, one of the most prevalent taste and odor compounds-geosmin (trans-1,10-dimethyl-trans-9-decalol) is produced by a subset of filamentous cyanobacteria and is a common challenge for drinking water utilities. In Fall 2012, previously unreported incidents of geosmin were identified in Pockwock Lake.²⁴ ⁹ Prior to 2012, geosmin was not a water quality concern for Halifax Water. Consumer complaints regarding the earthy, musty smell of geosmin in treated tap water began in 2012, which initialized Halifax Water's geosmin monitoring routine.

The objective of this study is to examine the impact of decreased sulfate deposition and its effect on lake water quality and water treatment practices over the period 1999–2015. This study focuses on two lakes that are used as drinking water supplies in Nova Scotia, Canada. It also contributes to understanding the impact of decreased sulfate deposition on water treatment practices and has implications to water utilities in regions with surface waters that have been impacted by anthropogenic emissions of sulfur dioxide (SO_2) to the atmosphere.

EXPERIMENTAL SECTION

Study Sites. Lake Major and Pockwock Lake are protected watershed areas and are not impacted by wastewater discharges. Both lakes are used for drinking water supply and are operated by Halifax Water located in the Halifax Regional Municipality of Nova Scotia, Canada. Pockwock Lake is characterized as a low-pH (pH < 6), low-turbidity (<0.5 nephelometric turbidity units (NTU)) and low-alkalinity (<5 mg CaCO₃/L) source water.^{30,31} Pockwock Lake is the water supply for the J.D. Kline Water Supply Plant (JDKWSP), which has an average daily

flow of 85 million liters per day (MLD). The JDKWSP, commissioned in 1973, underwent conversion from direct filtration (i.e., no clarification step before filtration) to direct biofiltration through removal of prechlorination in 2013.³² Lake Major also has a low pH (pH < 6), low alkalinity (<5 mg CaCO₃/L) and low turbidity (<0.5 NTU) and is the water supply for the Lake Major Water Supply Plant (LMWSP) which is a 45 MLD (average daily production) conventional filtration plant (commissioned in 1999) with upflow clarification.

Water Quality Analysis and Data Acquisition. Historical raw water quality data for both Lake Major and Pockwock Lake were obtained from records provided by Halifax Water staff. Reported raw water pH and turbidity data were measured by Halifax Water operations staff using a benchtop probe and turbidimeter, respectively, unless otherwise specified. Raw water color was determined by Halifax Water operations staff using a benchtop spectrophotometer (Hach Company, Loveland CO). Color data are presented in True Color Units (TCU). Water quality data for both lakes were obtained from an online data historian for the period January 1, 1999 to December 31, 2015. However, pH was recorded on a limited basis during the period 1999-2003 for Pockwock Lake and was not reported in this study. Additional pH data for Pockwock Lake was obtained from Environment Canada's Freshwater Quality Monitoring and Surveillance Program³³ during the period beginning in May 2000 to November 2012, when samples were collected from Pockwock Lake approximately once per month. DOC data for surface water bodies in Atlantic Canada (New Brunswick (NB), Prince Edward Island (PE), Newfoundland (NL)) was also obtained from Environment Canada's Freshwater Quality Monitoring and Surveillance Program for the period between 1990 and 2013. The Environment Canada Freshwater Quality Monitoring and Surveillance Program database did not contain sufficient DOC data for Nova Scotia surface waters during this period.

Compliance samples collected by Halifax Water staff were analyzed for sulfate by an independent laboratory and entered into Halifax Water's compliance software (WaterTrax). Sulfate data (annual averages) for this work were obtained from the WaterTrax database from the period 2004-2015. For the period between 1999 and 2003, sulfate data were obtained from Annual Water Quality Reports³⁴ published by Halifax Water. Annual mean total organic carbon (TOC) data were obtained from Annual Water Quality Reports and unpublished data from a NOM data set developed by the Centre for Water Resources Studies (CWRS) at Dalhousie University in Halifax, Nova Scotia, which contains several years of TOC data acquired from various projects. Samples for TOC were collected headspacefree, acidified to pH < 2 with phosphoric acid, and were analyzed with a TOC-V CPH analyzer (Shimadzu Corporation, Kyoto, Japan).

Chemical dosages for the period 1999–2015 were obtained from Halifax Water's operational reports completed by operations staff. Mean monthly dosages were computed from daily values. Geosmin data for Pockwock Lake were also obtained from Halifax Water. Geosmin was measured in raw water from Pockwock Lake and in treated water from the JDKWSP between 2 and 4 times per month beginning in 2012. Samples collected by Halifax Water staff were sent to an independent external laboratory (SGS Lakefield Research Ltd., Lakefield, Ontario) that used gas chromatography with mass spectrometer detection (GC/MS) for geosmin analysis. Indirect embodied energy estimates for chemical use at the LMWSP were calculated using the procedure outlined by Santana et al. 18

Atmospheric Deposition and Climate Data. Sulfate deposition data were obtained from Environment Canada's Canadian Air and Precipitation Monitoring (CAPMoN) program collected at Kejimkujik Lake.³⁵ Sulfate deposition data were not available for Lake Major and Pockwock Lake; therefore Kejimkujik Lake (44°24'11.020" N, 65°12'11.070" W) was chosen to approximate wet deposition in Halifax due to data completeness at this site, and proximity to the study area (141 km from Lake Major, 117 km from Pockwock Lake). Sulfate deposition data were obtained from the CAPMoN database at Kejimkujik for the period January 1984 to September 2015. Data were sea salt corrected (e.g., marine aerosol contribution was subtracted) by Environment Canada. Daily sea salt corrected sulfate deposition data (mg/L) and daily total precipitation (mm) were used to calculate total annual sea salt corrected sulfate deposition (kg/ha/year). Others^{36,37} have also used the Kejimkujik CAPMoN site to represent deposition in Nova Scotia.

Mean monthly temperature and precipitation levels for Halifax (1999–2015) were obtained from Environment Canada's National Climate Archives.³⁸

Statistical Methods. For each water quality parameter, the annual and monthly arithmetic mean was calculated to minimize the effect of variable sampling frequency on the ability to detect trends. The Mann Kendall Test (MKT)³⁹ was applied to annual means and the Seasonal Mann Kendall Test (SMKT) was applied to monthly arithmetic means (when available) to statistically evaluate temporal trends in historical water quality parameters and atmospheric sulfate deposition data. The MKT, a form of nonparametric monotonic trend regression analysis for data with serial dependence, analyzes the sign of the difference between later-measured and earlier measured data, and is used to determine the statistical significance of the identified trend ($\alpha = 0.05$). Sen's slope estimation (m)⁴⁰ was used to calculate the magnitude of significant trends identified using MKT and SMKT. Sen's slope estimate represents the median of all pairwise slopes in the data set. Kendall's tau correlations (τ) were applied to monthly means to understand the relationship between various water quality parameters. All statistical analyses were computed using MATLAB R2015b (The Mathworks, Inc.).

RESULTS AND DISCUSSION

Sulfate Deposition and Sulfate Concentration in Study Lakes. Figure 1 depicts trend in total annual wet deposition of sulfate (sea salt corrected) at the Kejimkujik Lake CAPMoN site for the period 1985–2015. It is likely that sulfate deposition at the Lake Major and Pockwock Lake study sites were higher due to proximity to localized sources of sulfate such as the Tufts Cove Generating Station which burned coal from 1965 to 2004. Wet deposition sulfate data at the Kejimkujik CAPMoN site showed a significant decreasing trend (p < 0.05) at a rate of 0.3 kg/ha/year (Sen's slope estimate) from 1984 to 2015. The overall decrease in sulfate deposition was approximately 83%. The reductions of sulfate deposition were consistent with the decrease in SO_x emissions over a similar period (1990-2014) published by Environment Canada⁴¹ as the total annual SO_x emissions were reduced by 63% for the period between 1990 and 2014.⁴¹



Figure 1. Total sea salt corrected wet deposition sulfate trends from the CAPMoN site at Kejimkujik, Nova Scotia. Dashed line represents approximation of linear trend (p < 0.05, m = -0.3 kg/ha/year).

Date-Years

Sulfate is typically the dominant anion in acidified lakes of eastern North America, northwestern Europe, and Scandinavia⁴² and hence has been widely used as a measure of the intensity of lake acidification.⁴³ Although chloride ions primarily dominate Nova Scotia lakes as a result of proximity to the Atlantic Ocean, data corrected for marine contributions generally show that Nova Scotia lakes were also dominated by sulfate.⁴⁴ Thompson and Hutton⁴⁵ demonstrated a correlation between annual sulfate deposition and sulfate concentration in watersheds of eastern Canada.

Significant decreasing trends in sulfate concentrations were observed in Lake Major (p < 0.05, m = -0.2 kg/ha/year) (Table S1, Supporting Information (SI)) and to a lesser extent in Pockwock Lake (p < 0.10, m = -0.1 kg/ha/year) (Table S2, SI) over the study duration. In 2015 sulfate concentrations in Pockwock Lake and Lake Major were reduced by 38% and 52%, respectively, from 1999 levels. These findings were consistent with other studies investigating the effects of acidic deposition on surface water quality in Atlantic Canada.^{36,37,46}

The decrease in atmospheric deposition of sulfate was higher compared to the reductions in lake sulfate concentration for both Pockwock Lake and Lake Major. This difference can be explained by several factors including the release of sulfate retained in catchment soils during previous periods of high sulfate deposition.^{45,47}

Abiotic Indicators of Lake Recovery. There have been several reports of increasing pH as a result of reduced sulfate deposition in the northeastern U.S., ^{3,7,8,48-50} the UK^{3,4,8} and Scandinavian countries.^{3,5,8} Figure S1 (SI) depicts average monthly raw water pH for Pockwock Lake. Data from plant records prior to 2004 were omitted, as they were deemed to be incomplete due to missing pH data during this time period. As described previously, additional pH data was obtained from Environment Canada's Freshwater Quality Monitoring and Surveillance Program³³ in order to capture seasonal trends in pH for Pockwock Lake before 2004. Statistical analysis with SMKT confirmed that Pockwock Lake pH increased significantly (p < 0.05, m = 0.06 pH units/year) over the time period studied. The average annual pH in Pockwock Lake increased from 5.2 in 2004 to 5.6 in 2015. Average monthly raw water pH for Lake Major is provided in Figure S2 (SI). The average annual pH increased from 5.3 in 1999 to 5.4 in 2015 for Lake Major. Because of the size of the data set, the increase in annual pH was also significant over the time period studied (p< 0.05, m = 0.01 pH units/year). A cyclic trend in the mean monthly pH was observed throughout the study period for

both Lake Major and Pockwock Lake. For most years, pH was lower from November through to May, and increased from June through October during biologically productive months.⁵¹

The frequency of days where pH was below 5 was evaluated for both lakes (Figure 2). The pH of 5 was selected as a



Figure 2. Frequency of low pH (days where pH < 5) in Lake Major and Pockwock Lake. Diamonds denote Lake Major, whereas circles denote Pockwock Lake.

reference point for sustaining fish habitat in Atlantic Canadian lakes.⁵² In 2002 there were 153 days where pH was less than 5 in Lake Major; whereas for the period between 2010 and 2015, there were less than 10 days in total when the pH was lower than 5. Similarly, in Pockwock Lake there were 162 days in 2005 where pH was less than 5, and from 2010 to 2015 there were only 7 days in total that had a pH < 5.

Many surface waters in the Northern hemisphere have experienced increases in color concentration along with corresponding decreases in sulfate deposition and increases in pH.^{53,54} Figure S3 (SI) and Figure 3 depict average monthly



Figure 3. Monthly mean color in Lake Major and corresponding alum consumption at the Lake Major Water Supply Plant since commissioned in 1999. Circles denote lake water color (TCU), columns denote alum dose (mg/L). Solid line represents approximation of linear trend for color (p < 0.05, m = 1.6 TCU/year), dashed line represents approximation of linear trend for alum dose (p < 0.05, m = 1.7 mg/L/year).

color concentrations for both Pockwock Lake and Lake Major, respectively. Color was selected as an indicator for NOM, as daily TOC and/or DOC data were not available for the entire study duration. Table S1 (SI) and Table S2 (SI) show average annual TOC concentrations for Lake Major and Pockwock Lake, during a limited time period. For lakes in Atlantic Canada, color has been shown to correlate strongly with

TOC.^{55,56} Statistical analysis with SMKT confirmed that mean color in both Lake Major (m = 1.6 TCU/year) and Pockwock Lake (m = 0.55 TCU/year) increased significantly (p < 0.05) over the time period studied. In particular, average color doubled in Lake Major from 1999 to 2015. Additionally, average annual TOC concentrations in Pockwock Lake (Table S2, SI) and Lake Major (Table S1, SI) increased by approximately 1 mg/L since 1999. This trend is not localized to the Halifax area. Analysis of data from Environment Canada's Freshwater Quality Monitoring and Surveillance Program (Figure 4) shows that during the period ranging



Figure 4. Change in dissolved organic matter concentration for Atlantic Canadian surface water bodies. Data for NB, PE, and NL interpreted from Environment Canada's Freshwater Quality Monitoring and Surveillance Program. Data for Halifax, NS (Pockwock Lake and Lake Major) interpreted from Tables S1 and S2. Point size is proportional to the magnitude of the linear trend between 1990 and 2013.

between 1990 and 2013, many other surface water bodies throughout Atlantic Canada have also been experiencing an increasing trend in organic matter concentrations measured as DOC. Additionally, there are more instances of increasing DOC in Atlantic Canadian surface waters than there are decreasing.

Both drinking water supplies studied were considered to have low color and had water treatment plants that were designed based on this concept. For example, in 1999 the year the LMWSP was commissioned there were 70 days when color concentration in Lake Major was <15 TCU (the aesthetic objective for color in the Guidelines for Canadian Drinking Water Quality), and in 2015 there was only 1 day where color was <15. Similarly, for Pockwock Lake, there were 179 days in 1999 and 43 days in 2015 where color was <15. Tropea et al.⁵⁷ also noted low color levels in Pockwock Lake during the period from 1990–2000.

During the period between 1990 and 2000, Hongve et al.⁵³ found that color and organic acid concentrations increased by as much as 50% in Norwegian lakes, which also showed

decreased sulfate concentrations during the same period. Vogt et al.⁵⁸ also reported a strong correlation between sulfate deposition and the characteristics of dissolved NOM, where NOM with high molecular weight, aromaticity and color was observed at locations that received low sulfate deposition.

Several researchers have explained the mechanism for increased NOM concentration in surface water. The solubility and mobility of organic matter has been shown to increase with decreased ionic strength, which would be the case with decreasing inputs of sulfate ion.^{8,16,54} For example, Vogt⁵⁹ noted that declining ionic strength would increase the repulsion forces between organic molecules, decreasing the ability to precipitate out of water, resulting in highly colored water. Worrall and Burt¹⁷ noted that reductions in the ionic strength of soil pore water would lead to increases in DOC solubility that in turn could cause more hydrophobic compounds to become mobile. Others^{15,16} have also shown that such increases in DOC solubility correspond with a shift of NOM quality toward more hydrophobic, aromatic, and colored NOM with higher molecular weights.

In addition to reduced acidic deposition, others have attributed increasing NOM concentrations to climatic factors including increasing precipitation levels and/or temperature. For example, de Wit et al. 60 noted that the current increasing trend in surface water NOM concentration will be further impacted by a wetter climate. Specifically, de Wit et al.⁶⁰ projected a 30 to 50% increase in organic carbon concentrations in regions of Scandinavia that had a 10% increase in precipitation level. This was related to an increase in mobilization of NOM to freshwaters through lateral flows across catchment soils.⁶⁰ NOM concentrations have also been known to increase with temperature as NOM decomposition and solubilization rates are more rapid at higher temperatures.⁶ Increased greenhouse gas emissions have also been implicated as a possible cause of increased NOM concentrations in surface waters.^{62,6}

For this work, precipitation and temperature data for Halifax were analyzed to consider whether changes in local climate contributed significantly to the color increases observed in Pockwock Lake and Lake Major. First, the correlations between mean monthly lake color with average air temperature and precipitation levels (both on a monthly time scale) were considered. Results showed that color in Lake Major was weakly correlated with precipitation levels ($\tau = 0.07$) and air temperature ($\tau = -0.08$), while mean color in Pockwock Lake showed similar results ($\tau = 0.02$ and $\tau = -0.17$ for precipitation and air temperature, respectively). Analysis with SMKT revealed that both monthly precipitation levels and average air temperature in Halifax did not show any significant (p =0.22 and 0.38, respectively) increase throughout the period 1999-2015. In fact, temperature and precipitation levels remained relatively consistent throughout the study period. Based on these weak correlations and the lack of significant change in local climate, it was determined that neither temperature nor precipitation levels were primarily responsible for the increase in color levels in Pockwock Lake and Lake Major.

Previous studies^{64,65} have found that increased DOC concentration can sometimes retard the recovery of pH caused by decreasing sulfate deposition. Erlandsson et al.⁶⁴ noted that increased DOC in recent decades has slowed the recovery from acidification by up to 1 pH unit for some lakes. Many other studies have examined the impact of buffering by organic acids

on retarding the recovery in pH.^{48,64,66,67} This study demonstrated that reduced acid deposition may in fact be contributing to recovering pH, even in lakes with poorly buffered soils and low alkalinity such as those throughout Atlantic Canada. Kent et al.¹² studied six lakes in Atlantic Canada that were dominated by hydrophilic neutrals (53% of NOM in Pockwock Lake) and hydrophobic acid (28% of NOM in Pockwock Lake) fractions, which are the weakest in carboxyl acidic strength compared to hydrophilic acids (12% of NOM in Pockwock Lake).¹² Therefore, it is possible that pH in Pockwock Lake was able to recover because the NOM fractions present are predominately comprised of neutral and weak acids as opposed to the stronger hydrophilic acid fraction that would have more of an effect on pH.¹²

Impacts on Plant Operations. In the following section the authors present operational data to quantify and assess the impacts of reduced acid deposition and corresponding increases in pH and organic matter concentration in Pockwock Lake and Lake Major on the direct-biofiltration (JDKWSP – Pockwock Lake) and conventional coagulation (LMWSP - Lake Major) treatment facilities drawing from these lakes. It is probable that water utilities in Scandinavia, the UK, in the northeastern U.S., and more recently in Atlantic Canada, will experience similar operational challenges as lake recovery and increasing NOM concentrations are well documented in these regions.

Recently, the JDKWSP has experienced reduced filter run times, as well as the need to increase their alum $(Al_2(SO_4)_2)$ dose to 12 mg alum/L after consistently dosing at 8 mg alum/L for the last 35 years. Direct filtration treatment plants are commonly used to treat high quality surface waters with moderate to low color (<20 TCU), and low TOC (<4 mg/ L).⁶⁸ Waller et al.⁵⁵ described median color and TOC concentrations for Pockwock Lake in 1992-1993 at 9 TCU and 2.6 mg/L, respectively. Since the JDKWSP was built in the 1970s, the Pockwock Lake water supply as described by Waller et al.55 in the 1990s remained well suited for direct filtration based the thresholds described by Crittenden et al.⁶⁸ As shown in Table S2 (SI), TOC concentrations in Pockwock Lake have increased from 2.4 mg/L in 1999 to 3.4 \pm 0.2 mg/L in 2015, whereas color concentrations have increased from 12 ± 6 to 21 \pm 5 TCU over the same period. Consequently, the treatment system at the JDKWSP is approaching the upper thresholds (i.e., ≤ 20 TCU, < 4 mg/L) for direct filtration in terms of both color and TOC, which has been shown by the need for increased aluminum sulfate (alum) dosage and shorter filter run times. Hutchinson⁶⁹ and others⁷⁰ have suggested an upper limit of 15 mg/L for alum dosing in direct-filtration plants. Accordingly, the JDKWSP is also approaching the suggested upper limit for alum dosing in direct filtration plants.

As mentioned previously, researchers have suggested that not only the quantity, but the composition of NOM is changing as more hydrophobic fractions are becoming prevalent in surface waters recovering from acidification.^{15–17} Kent et al.¹² showed that Pockwock Lake was dominated by hydrophilic neutrals (53% of NOM in Pockwock Lake), and hydrophobic acid (28% of NOM in Pockwock Lake). It is widely reported that coagulant demand is predominately generated by hydrophobic NOM fractions^{71–73} and therefore a shift toward more hydrophobic NOM in Pockwock Lake would create an increase in coagulant demand. Further NOM characterization studies (e.g., fractionation) are necessary to fully understand the impacts on treatment at the JDKWSP. It is probable that water utilities in Atlantic Canada and in other regions currently experiencing recovery from acidification and subsequent increases in NOM concentration will face similar operational challenges as direct-filtration plants were generally well suited for highly acidified surface waters with low NOM concentrations.

In addition to the process issues associated with elevated NOM concentrations, Pockwock Lake has also experienced geosmin occurrences. Figure 5 depicts geosmin concentrations



Figure 5. Geosmin concentrations in Pockwock Lake throughout the period 2012 to 2015. Filled diamonds denote raw water geosmin concentration, white diamonds denote treated water geosmin concentration, and dashed line represents minimum detection limit for geosmin.

measured in Pockwock Lake from 2012 to 2015. The first indication of geosmin in Pockwock Lake was in October 2012. Prior to 2012, Halifax Water had not experienced water quality issues associated with geosmin (e.g., earthy and musty taste/ odor) in Pockwock Lake and therefore had not routinely tested for it. Consequently, the presence or absence of geosmin in Pockwock Lake before 2012 cannot be confirmed. It generally persisted throughout the winter of both 2012 and 2013 reaching maximum concentrations of 12 and 21 ng/L in October 2012 and November 2013, respectively. In 2014 and 2015, the period of geosmin occurrence was shorter, as it only reemerged in August and September at maximum concentrations of 11 and 14 ng/L for 2014 and 2015, respectively. The maximum concentrations of geosmin experienced in Pockwock Lake were generally above the odor threshold concentration for humans ranging between 4^{74} to 10^{75} ng/L.

The main source of geosmin in freshwater systems are cyanobacteria (e.g., blue green algae).^{76,77} Accordingly, the occurrence of geosmin in Pockwock Lake may be linked to biological responses to chemical recovery as it is well documented that increases in pH generally favor more rich/ diverse cyanobacteria populations. The main genera of cyanobacteria that are known to contain geosmin-producing species are Anabaena, Aphanizomenon, Lyngba, Oscillatoria, Planktothrix, and Symploca.⁷⁸⁻⁸⁰ Although the preferred growth conditions vary by species and are dependent upon several environmental factors, it is generally known that cyanobacterial production of geosmin occurs at a pH between 6 and 9 at temperatures ranging between 15 and 30 °C.81 Anabaena has been identified as the dominant geosmin producing species in the Pockwock watershed (Halifax Water, unpublished data). Anabaena has been reported to grow at pH 682,83 although lower pH values (i.e., pH < 6) can be deleterious to the growth of *Anabaena* cyanobacteria.⁸⁴ In 2013, the pH in Pockwock Lake began seasonally approaching pH 6 (Figure S1 in SI)

which coincided with the most prevalent occurrence of geosmin and the detection of *Anabaena*.

Reductions in sulfate deposition have been connected to changes in phytoplankton species richness and community structure elsewhere.^{24,25,85} For example, geosmin has been abundant in the Great Lakes,⁷⁷ a region that has been undergoing recovery from acidification.⁸⁶ Findlay et al.²⁴ studied the response of phytoplankton communities to recovery from acidification in several Ontario lakes and found that changes in phytoplankton community assemblages were observed in species richness and diversity, both of which were significantly correlated with pH. Rönicke et al.85 studied the effects of chemical neutralization of a highly acidified lake on changes in the phytoplankton community and found that with increasing pH, the community became more diverse as diatoms, chrysophyceans, and blue green algae contributed significantly to biomass. Finally, Sutherland et al.25 documented biotic recovery in Brooktrout Lake as a response to reductions of sulfate deposition throughout the 1980s-2000s and observed increased phytoplankton species richness corresponding with decreased sulfate deposition.

The LMWSP has also faced serious treatment challenges associated with increasing NOM (i.e., color and TOC) in Lake Major (Figure 3; Table S1 in SI). Mean color concentrations in Lake Major have more than doubled, and TOC concentrations have increased by 1.1 mg/L since the plant was commissioned in 1999. To assess the impact of increasing NOM on coagulant demand, daily historical coagulant (alum) dosages at the LMWSP were consulted (Figure 3).

Average coagulant dosages at the LMWSP showed significant (p < 0.05) increase during the period between 1999–2015. Between 2000 (the first full year postcommissioning) and 2015, the average alum dose at the LMWSP increased by nearly $4\times$ (12.9-49.5 mg/L). Other factors affecting coagulant dosing such as raw water temperature and turbidity were also investigated (Table S1 in SI). During the period of 1999-2015, monthly mean turbidity in Lake Major was poorly correlated with monthly mean alum dose ($\tau = 0.01$) at the LMWSP, whereas temperature showed an inverse correlation with alum dose ($\tau = -0.23$) as expected, since seasonal cold water conditions often warrant increases in coagulant dose. Based on these weak correlations, it was determined that changes in turbidity and temperature were not the primary cause for increasing coagulant dose at the LMWSP. In contrast, mean monthly color had the strongest correlation with alum dose ($\tau = 0.63$). Furthermore, the alum dose at the LMWSP was increasing at a similar rate to color concentration in Lake Major (Sen's slope estimates for color and alum dose at 1.6 TCU/year and 1.7 mg/L/year, respectively), and therefore it is likely that increasing color concentrations were the main driver for coagulant increase at the LMWSP. There is also potential for shifts in NOM composition in Lake Major causing increases in NOM solubility that in turn could cause more hydrophobic, aromatic and colored NOM compounds to become mobile.^{15–17} This would create an even greater coagulant demand at the LMWSP, as hydrophobic NOM generally controls coagulant requirements.

In addition to increased alum consumption, further analysis of chemical use at the LMWSP revealed that lime (a chemical used to adjust pH/alkalinity during coagulation) consumption has also increased by $1.75 \times$ since 2000, while average water production rates decreased by approximately 26% (51.5 MLD in 2000 to 38 MLD in 2015). This increase in lime

consumption was attributed to the significant increase in alum dosing, as adding more coagulant requires further addition of lime to maintain target coagulation pH. As described previously, significant amounts of energy are required to produce and transport the chemicals used in water treatment facilities. This energy is commonly referred to as indirect embodied energy or production and transport energy, and it represents a fraction of the total embodied energy for a water treatment facility (the remaining fraction is associated with fuel and electricity). The production and transport embodied energy for alum and lime have been estimated by Santana et al.¹⁸ as 10.8 and 8.12 MJ/kg, respectively. Based on these estimates, the transport and production energy associated with alum and lime consumption at the LMWSP was approximately 4×10^6 MJ in the year 2000 and 9.7×10^6 MJ in the year 2015, an overall increase in indirect embodied energy of 58.5% which is substantial considering the decrease in average water production rates. Ultimately, utilities with surface water supplies experiencing increased NOM concentrations will not only be faced with increasing costs associated with chemical consumption, but environmental costs associated with increased energy and carbon emissions from the use of greater quantities of water treatment chemicals that are extremely energy intensive to produce and transport. In addition to Atlantic Canada, this will be of significance for eastern U.S., northwestern Europe, and Scandinavia, which were regions heavily impacted by acidic deposition. The described lake recovery processes will ultimately pose a challenge for affected drinking water utilities; however, these challenges do not diminish the benefit of improved fish stock^{87°} and other ecosystem services associated with less impacted freshwater systems.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b04889.

Supplementary tables (Table S1 and Table S2) and figures (Figures S1–S3) (PDF)

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