Identification Of Key Parameters For Monitoring Changes In NOM Concentration In Response To Lake Recovery From Acidification

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Introduction

In response to acid rain control programs, there has been substantial reductions in SO_2 emissions; and SO_4 deposition in surface waters has also decreased. Some UK and Scandinavian countries have experienced signs of recovery from acidification, as evidenced by increasing surface water pH and a rise in DOC levels by up to 0.15 mg/L/year (Monteith et al., 2007).

Recently, lakes throughout Atlantic Canada have also shown signs of recovery from acidification (Anderson et al., 2017). Lake Major - a protected surface water supply located in Nova Scotia, Canada has experienced a 3.8x increase in color concentration over the past 16 years, corresponding with a similar increase in coagulant demand at the Lake Major Water Supply Plant (LMWSP) operated by Halifax Water (Anderson et al., 2017).

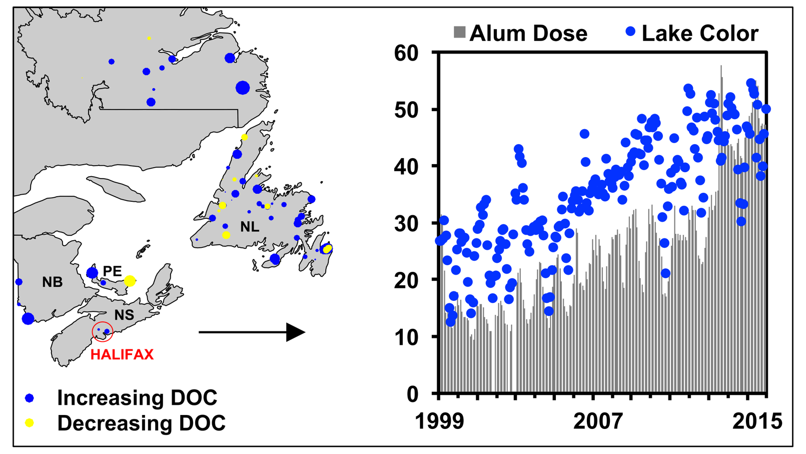

Figure 1. Treatment implications for increasing NOM concentration as a result of lake recovery from acidification (Anderson et al., 2017).

This phenomenon has highlighted the need for more detailed water quality monitoring programs, particularly with respect to natural organic matter (NOM) concentration and composition.

Accordingly, a NOM-focused water quality monitoring program was implemented at the LMWSP to help better understand the impact of lake recovery from acidification on subsequent water treatment processes (e.g. coagulation).

Objective

The overall objective of this study was to identify key water quality parameters for monitoring responses to recovery from acidification. Through extending our detection metrics, our aim will be to better understand the interaction between NOM tools as rapid monitoring tools for the water industry.

Methods

Study Location

Lake Major serves as the main water supply for Dartmouth, Nova Scotia, Canada. It is characterized by low alkalinity and low turbidity, with moderate to high levels of color and organic matter. The NOM in Lake Major is >90% dissolved. The LMWSP is a 45 MLD conventional filtration plant with upflow clarification.

Figure 2. A photo of the Lake Major watershed taken during monthly lake sampling.

Technical Approach

Traditional and emerging NOM surrogates (e.g. photoelectrochemical oxygen demand (peCOD)) were used to monitor the changes in NOM concentration. The peCOD analyzer enables rapid detection of COD without the use of hazardous chemicals. An at-line peCOD monitoring unit (Mantech-Inc.) was installed on the raw water intake at the LMWSP. It collected raw water samples at 2-hour intervals. The unit was commissioned in June 2016, however reliable data acquisition began July 2016. It was shut down at the end of November, 2016 until May 2017, as COD readings began to exceed the upper detection limit of 25 mg/L. Samples that did not meet calibration and QC specifications were removed from the dataset.

Grab samples were also collected throughout the Lake Major watershed (at depths of 0, 3, 6, and 9m), as well as from different locations in the treatment process at the LMWSP. These samples were analyzed for TOC and peCOD; and the mean oxidation state of carbon (MOSC) – a parameter that provides insight on the reactivity of organic compounds, was calculated following the method described by Li et al. (2017, not yet published) as follows:

$$\frac{\sum_1^i n_i OSC_i}{\sum_1^i n_i} = \frac{4(TOC\text{-}peCOD)}{TOC}$$

Where n_i is the molar concentration; OSC_i is the oxidation state of organic carbon for individual species; TOC is mol C/L; peCOD is mol O2/L.

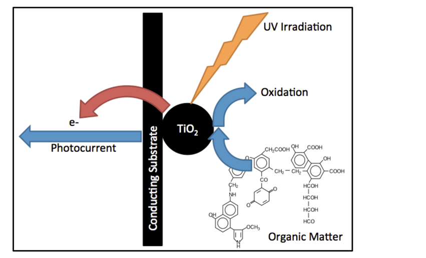

Figure 3. peCOD analyzer working principle (adapted from Mantech Inc., 2014).

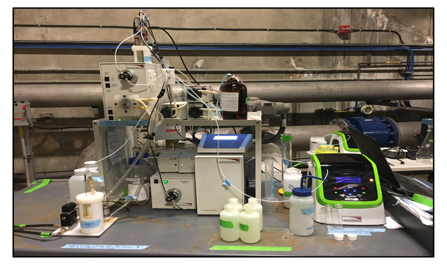

Figure 4. At-line peCOD analyzer at the Lake Major Water Supply Plant.

RESULTS AND DISCUSSION

SOURCE WATER MONITORING AT THE LMWSP

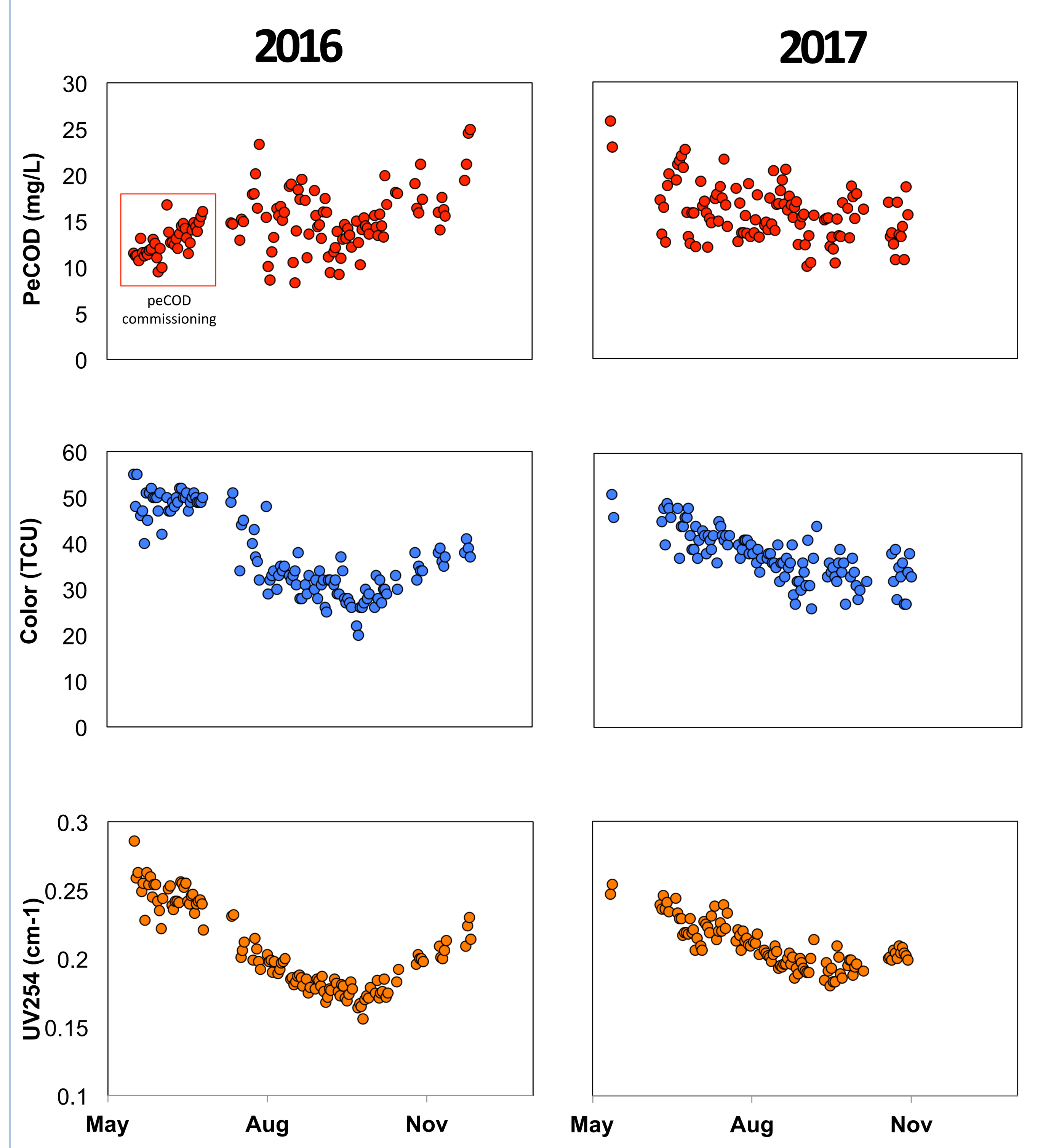

Figure 5. PeCOD, Color and UV254 trends in Lake Major during May to November 2016 and 2017. Each point represents a daily average.

PeCOD

- PeCOD values in Lake Major typically varied between ~10 and ~25 mg/L, depending on the season. Initial values during commissioning of the peCOD unit until June 2016 were lower than expected.
- Generally, peCOD values decrease throughout the summer and begin to increase in late fall during lake turnover.
- In September 2016, extreme drought conditions caused peCOD values to decrease to below 8 mg/L. PeCOD levels in 2017 are representative of typical NOM trends in Lake Major.
- It is expected that peCOD values will increase in late November (not yet captured).
- The peCOD technology provided a representative estimate of NOM concentration throughout Spring/Summer 2016 and 2017.
- On an hourly basis (not pictured), the peCOD was sensitive to changes in NOM concentration as a result of local climate (e.g. changes in temperature, wind speed/ direction, precipitation).

PeCOD vs. conventional NOM analytes

- Both color and UV254 followed similar trends; decreasing throughout summer and increasing during lake turnover in late fall.
- The peCOD generally followed the same trend as color and UV254. Previous work by Stoddart & Gagnon (2014) showed similar results.
- Color ranged between 20-55 TCU in 2016, and 26-51 TCU in 2017. In 2016, UV254 varied between 0.155 - 0.286 cm-1, and 0.180 -0.254 cm-1 in 2017.

IDENTIFICATION OF KEY PARAMETERS

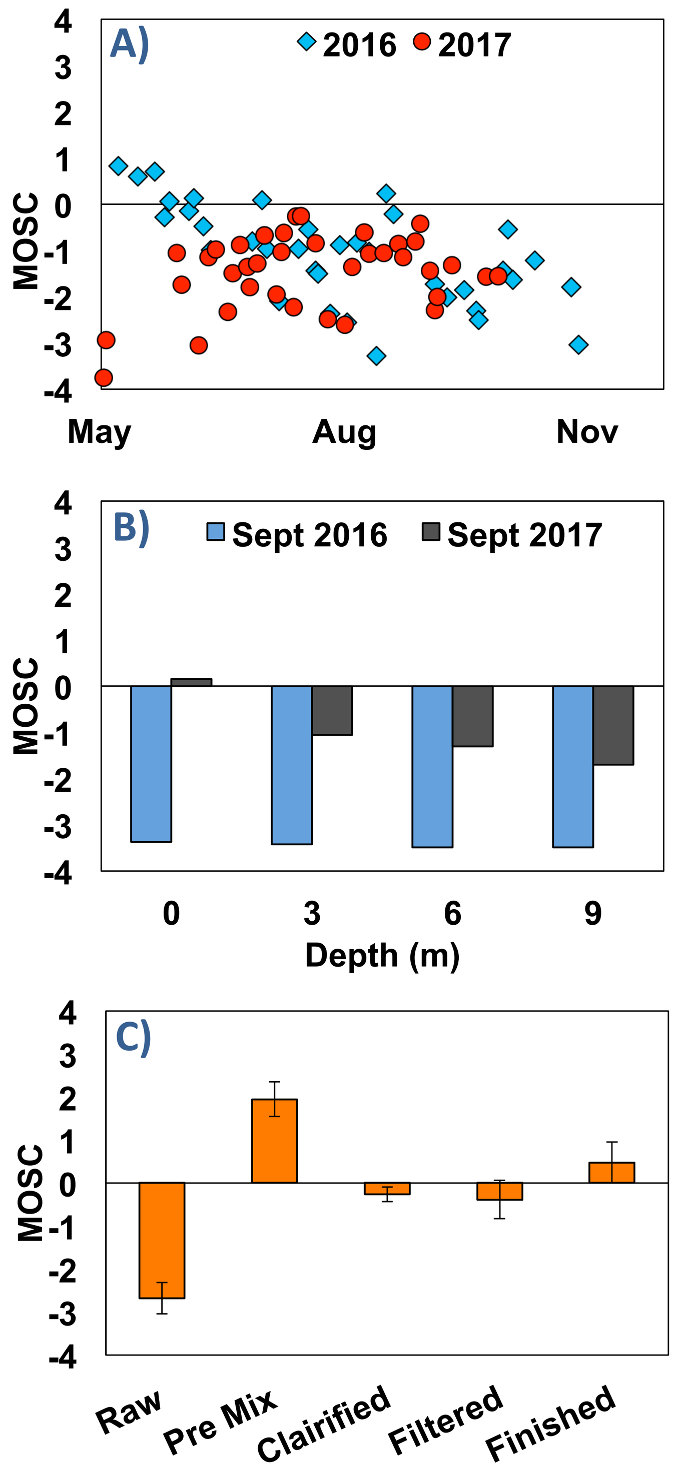

Figure 6a) MOSC trends in Lake Major during May-Nov 2016 and 2017; 6b) MOSC depth profiles in Lake Major; 6c) Average MOSC throughout the treatment train at the LMWSP - Oct, 2017.

Mean Oxidation State of Organic Carbon (MOSC)

The MOSC can be used to describe the oxidation state of organic compounds. It typically ranges between -4 and +4 (Mantzavinos et al., 1996) and can provide information on the reactivity of organic compounds (Riedel et al., 2012). A more positive MOSC indicates a higher level of oxidation. Thus, it can be used to understand the reactivity of NOM.

A) Temporal MOSC variations

The MOSC was evaluated on raw water samples during May-November 2016 and 2017.

- The decrease in MOSC throughout 2016 could be attributed to the extreme drought conditions. Drought is known to alter NOM (more hydrophilic), which ultimately affects NOM reactivity. More information on seasonal NOM composition is necessary to understand this relationship.
- Aside from May, the MOSC consistently ranged between -3 and -1 throughout the 2017 monitoring period.

B) MOSC depth profile

Samples from various depths in Lake Major were analyzed and MOSC was calculated.

- In 2016, the MOSC was relatively consistent at -3.5. This was likely due to drought and could be indicative of biological activity.
- Conversely, in 2017 the MOSC decreased from May (+0.15) to November (-1.7), when precipitation levels were normal.

C) MOSC during treatment

The MOSC was also evaluated for grab samples from full-scale treatment at the LMWSP.

- The MOSC shifted from negative (-2.7) to positive (+0.5) as treatment progressed. The positive MOSC in finished water is due to the addition of chlorine.
- The positive MOSC following pre-mix was high (+1.95). This was likely due to floc carryover in pre-mix TOC samples (compared to the peCOD, which did not quantify carryover – it does not digest particulate matter).
- Overall, this demonstrates the potential for using the MOSC in water treatment applications.

Conclusions

Lake recovery from acidification is causing increasing NOM concentrations throughout the Northern hemisphere. Therefore, more detailed, NOM-focused water quality monitoring programs are necessary. Accordingly, this work focused on the identification of key water quality parameters for monitoring responses to recovery from acidification. Preliminary results from this work indicate that:

- The at-line peCOD could detect fluctuations (on both daily and hourly basis) in NOM concentration in Lake Major and showed comparable trends to conventional NOM surrogates. Accordingly, this peCOD unit can be used as a reliable tool for near real time NOM monitoring.
- The various applications of MOSC showed that it can provide additional information on the reactivity of NOM. It allows for further insight on NOM compared to the use of TOC or peCOD individually. In the future, the MOSC could be used as a tool for providing information on oxidant addition, DBP formation, or biological aspects of raw/treated water.
- These tools will be particularly beneficial for water utilities drawing from surface waters that are experiencing elevated NOM concentrations as a result of recovery from acidification. Additional work will be necessary to understand the relationships between peCOD, MOSC, and NOM reactivity/characteristics.

Contact

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