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ORIGINAL RESEARCH

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Monitoring natural organic matter in drinking water treatment with photoelectrochemical oxygen demand

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Abstract

Conventional metrics such as total organic carbon (TOC) and ultraviolet absorbance at 254 nm (UV_{254}) may oversee aspects of natural organic matter (NOM) reactivity in drinking water treatment. The novel photoelectrochemical oxygen demand (peCOD) analyzer indirectly measures the oxygen consumed during NOM oxidation with photo- and electrochemical methods, quantifying NOM reactivity. peCOD was valuable for tracking NOM degradation in nine drinking water treatment facilities, particularly in processes where conventional metrics failed to capture changes in NOM from partial oxidation (e.g., biofiltration and oxidation). However, peCOD exhibited moderate correlations with TOC ($R^2 = 0.67$) and UV_{254} ($R^2 = 0.48$), indicating the need for its concurrent use with conventional methods. While peCOD was not a significant predictor of disinfection by-product formation potential ($R^2 < 0.20$), its inclusion alongside standard NOM metrics improved the performance of multivariable regression models. Thus, peCOD provided a rapid, standardized, operator-friendly, environmentally conscious, concentration-based approach for evaluating NOM characteristics in drinking water samples.

KEYWORDS

advanced treatment processes, drinking water treatment, natural organic matter, photoelectrochemical oxygen demand

1 | INTRODUCTION

Wide-spread accounts of brownification—increasing concentration of natural organic matter (NOM)—and shifts in the NOM character have been reported in surface waters across the Northern Hemisphere (Anderson et al., 2017; Anderson, DeMont et al., 2023; Clair et al., 2011; DeMont et al., 2021; Garmo et al., 2020; Monteith et al., 2007; Redden et al., 2021; Ritson et al., 2014). These changes are frequently linked to climate change, reversal of acidification (e.g., acid rain), or land-use changes (Anderson, DeMont et al., 2023; Kritzberg et al., 2020). Although NOM is inherently nontoxic, it is a precursor for disinfection by-products (DBPs), a primary source of color, taste, and odor compounds, a vector for heavy metals (e.g., iron, lead, and

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manganese), and it interferes with corrosion control in drinking water distribution systems (Anderson et al., 2021; Locsin et al., 2023; Sillanpää et al., 2015; Trueman et al., 2017).

These shifts in NOM concentration and character have presented major challenges for drinking water treatment (Anderson, DeMont et al., 2023). For example, shifts in NOM character in UK source waters resulted in decreased dissolved organic carbon (DOC) removal and increased coagulant doses (Worrall & Burt, 2010). Similarly, increased DOC concentrations have also necessitated consideration of retrofitting existing treatment trains with additional technologies, such as granular activated carbon (Anderson, Tchonlla et al., 2023). As optimization of these adaptations is dependent on the ability to evaluate the intended performance of specific technologies, appropriate, frequent, and rapid monitoring tools, that consider both NOM character (quality) and concentration (quantity) are critical for responsive treatment operational decisions, particularly in browning source waters.

Traditionally, NOM monitoring strategies employ metrics such as total organic carbon (TOC), DOC, and ultraviolet absorbance at 254 nm (UV_{254}). These metrics, however, may be poorly suited for identification of some changes to source water quality and evaluation of treatment performance (i.e., removal or degradation of NOM) via advanced processes (e.g., oxidation-based technologies). TOC and DOC are bulk parameters that indicate NOM concentration in the raw and treated water but fail to capture any information on its elemental nature, structure, or reactivity (Pan et al., 2016; Sillanpää et al., 2015). Further, the efficacy of treatment technologies that partially oxidize NOM are not always reflected in organic carbon concentration measurements. Advanced oxidation processes (AOPs) in drinking water treatment applications typically do not result in NOM mineralization and thus show minimal changes to TOC concentrations (Li et al., 2023; Liu et al., 2012: Wang et al., 2017). Conversely, UV_{254} can give some insight into the reactivity of NOM, as double bonds, and aromatic rings, which are reactive sites with chemical oxidants such as chlorine, often absorb UV light at 254 nm (AWWA & Edzwald, 2011; Chang et al., 2001). As such, UV_{254} is often linked to DBP formation potential (Chen & Westerhoff, 2010; Sadiq & Rodriguez, 2004); however, some DBP precursors do not absorb UV light at 254 nm (Chen & Westerhoff, 2010; Yang et al., 2008), and therefore, the metric may not adequately capture all variations of NOM. The specific ultraviolet absorbance (SUVA), or the ratio of UV_{254} absorbance to DOC, is often used to estimate the hydrophobicity of DOC, with values >4 L/mg C/m indicating a mainly hydrophobic DOC composition and values <2 L/mg C/m indicating mainly hydrophilic DOC (Edzwald, 1993). SUVA has also been used to estimate DOC removal via coagulation/flocculation (AWWA & Edzwald, 2011), and DBP formation (Chen & Westerhoff, 2010). However, SUVA does not accurately represent the true character of NOM in the water sample and may further be impacted by interfering constituents (e.g., hydrophobic bases and neutral organic compounds, iron and nitrate) (Edzwald, 1993; Roccaro et al., 2009; Weishaar et al., 2003).

Article Impact Statement
Photoelectrochemical oxygen demand measurements were more sensitive to changes in natural organic matter than conventional metrics and well suited for monitoring advanced oxidation processes.

Other tools that consider NOM character include fluorescence spectroscopy, which measures the intensity of fluorophores associated with various NOM components, providing information on NOM through excitation emission matrices (EEMs) (Anderson, DeMont et al., 2023; Bridgeman et al., 2011; Matilainen et al., 2011). EEMs can track changes at low NOM concentrations and offer immediate insight into the composition of fluorescent NOM with minimal sample preparation (Bridgeman et al., 2011; Li et al., 2020). Past work has correlated EEM components to the hydrophobicity of NOM, DBP prediction models, SUVA, UV_{254}, and molecular weight (Li et al., 2020). However, <1% of NOM in natural water samples is typically fluorescent and complete understanding of how these fluorescent compounds is representative of the bulk NOM is outstanding (Chen & Yu, 2021). Further, EEMs require sophisticated and complex data processing for quantitative analysis, which is often oversimplified (Rosario-Ortiz & Korak, 2017) and may limit its uptake (Carstea et al., 2020). Electron donating capacity (EDC) is a novel surrogate that measures the electrons transferred from NOM during oxidation, typically via 2, 2′-azino-bis (3-ethylbenzothiazoline-6-sulfonic acid) radicals ($ABTS^{\bullet+}$) (Ji et al., 2024; Önnby et al., 2018; Rougé et al., 2020; Walpen et al., 2016). The technology has been applied in conjunction with UV_{254} to study oxidation-based treatment mechanisms (Chon et al., 2015; Önnby et al., 2018; Rougé et al., 2020) and optimize oxidant dosing via grab samples (Yuan et al., 2019) and in-line measurements (Walpen et al., 2022). However, EDC analysis is highly dependent on the reaction conditions (e.g., oxidant type and initial concentration, reaction time, solution pH) and thus results may vary depending on the chosen method, which is not yet standardized (Ji et al., 2024).

Like EDC, chemical oxygen demand (COD) is an indication of the reactivity of constituents in a water matrix. COD is commonly used in wastewater treatment and measures the oxygen consumed by the chemical oxidation of the organic and inorganic species in a solution, although the organic reactions are most often dominant (APHA et al., 2017). As COD informs on the reactivity of compounds in a water sample, it is also well suited for quantifying changes in NOM characteristics and evaluating the performance of oxidation-based treatment processes in degrading organic compounds. The conventionally used potassium dichromate method for COD measurement (Standard Method 5220), however, is not appropriate for frequent analysis of treated drinking water samples as it uses expensive, corrosive, and toxic reagents, and has a detection limit of 50 mg/L, or 5 mg/L with lesser accuracy (APHA et al., 2017; Zhao et al., 2004). Health Canada has proposed a COD guideline of 5 mg O_2/L in treated drinking water (Health Canada, 2019) and some European countries have already implemented regulations at this same threshold (Government of France, 2007). Thus, the dichromate method is not suited to detect COD levels below expected regulatory guidelines in drinking water.

Photoelectrochemical oxygen demand (peCOD) technology measures the COD of a water sample via photoelectrocatalytic oxidation. The technology completely oxidizes all organic material in the water sample within 5–15 min, enabling rapid detection of COD at concentrations suitable for drinking water treatment applications (i.e., as low as 0.7 mg/L O_2/L) (ASTM, 2017; Stoddart & Gagnon, 2014). In peCOD analysis, water samples are mixed with an electrolyte and passed through a microcell that houses a TiO_2 thin film sensor. The sensor is subject to irradiation by UV light from light emitting diodes and an applied voltage, resulting in photoelectrocatalytic oxidation of compounds in the sample and generation of a photocurrent. The electrical signal is then converted to a chemical oxygen demand measurement (ASTM, 2017; Zhao et al., 2004). Providing results in minutes, the peCOD method is a more environmentally friendly and accessible NOM detection method for near real-time monitoring of COD in drinking water treatment plants.

While peCOD analysis does depend on the concentration of NOM present in the water matrix, it is also largely dependent on the reactivity of present NOM components. A highly reactive source water with a low TOC concentration may have equivalent peCOD readings to a less reactive source water with a high TOC concentration (Health Canada, 2019). The additional information provided on NOM character by peCOD has been beneficial in drinking water treatment applications; Li et al. (2018) found peCOD readings effective for monitoring the partial oxidation of NOM in a biofiltration plant. Stoddart and Gagnon (2014) first demonstrated the potential for peCOD technology in four drinking water treatment plants in Atlantic Canada. They found that peCOD values correlated well with SUVA ($R^2 = 0.84$, $n = 13$), which is often used to estimate the reactivity of NOM in a water sample with chemical coagulants, and thus could be potentially be used to replace two analytical tools (UV_{254} spectrophotometer and TOC/DOC analyzer). These limited applications of peCOD have proven to enhance drinking water treatment monitoring; however, the existing work is restricted both geographically (i.e., Atlantic Canada) and in treatment technology (i.e., conventional and biofiltration treatment only).

Additionally, given peCOD is dependent on both NOM oxidizability and concentration, it was hypothesized that peCOD measurements would be good predictors of DBP formation potential (DBPfp), an indicator of NOM reactivity with chlorine, and improve DBPfp model performance. Existing work has focused on developing empirical relationships between DBP concentrations (or DBPfp) and water quality parameters such as pH, water temperature, chlorine dose, reaction time, and NOM surrogates (Chen & Westerhoff, 2010; Chowdhury et al., 2009; Sadiq & Rodriguez, 2004). Some models have further considered the quality of NOM by including chlorophyl-a and fluorescence (Chowdhury et al., 2009; Trueman et al., 2016); however, none have included peCOD to date.

Therefore, the objective of this work was to further consider the utility of peCOD measurement in drinking water treatment by (a) investigating relationships between peCOD and conventionally used NOM metrics and indicators, (b) evaluating peCOD as an indicator of treatment performance (i.e., removal or degradation of NOM) through various drinking water treatment processes, and (c) assessing peCOD as an indicator of precursor material that may form DBPs. Nine drinking water treatment plants across Atlantic Canada and the United Kingdom were sampled over a three-month period and one Atlantic Canada plant was studied for one year. It was hypothesized that peCOD would capture changes in the reactivity (i.e., character) of NOM that would not be recognized by conventional NOM metrics, and thus, inform on DBP formation potential (DBPfp). Monitoring the changes in NOM character in both drinking water sources and through unit treatment processes will help inform treatment practices and efficiency of operations.

2 | METHODS

2.1 | Full-scale water treatment plant descriptions

Three drinking water treatment plants in the United Kingdom and six in Atlantic Canada were considered for this study. Both regions have previously been exposed to chronic acidification and are now

experiencing changes in water chemistry due to recovery from acidification and climatic pressures (Anderson et al., 2017; Anderson, DeMont et al., 2023; Clair et al., 2011; Garmo et al., 2020; Monteith et al., 2007; Redden et al., 2021). The three plants in the United Kingdom were in the east of England. Of the Atlantic Canada sites, three (ATL_A, ATL_B, ATL_C) were operated by a utility in Halifax, NS, one (ATL_D) was operated by a municipality in New Brunswick, and two (ATL_E, ATL_F) were operated by municipalities in Cape Breton, NS. Table 1 outlines the water source and unit operations in each of the studied drinking water treatment plants, which included conventional, direct filtration, ozonation, and UV-based AOPs treatment plants. The treatment facilities ranged in capacity from 8 MLD to 200 MLD and were chosen to include two types of source waters (lakes and reservoirs) (Table 1).

2.2 | Sample collection and analysis

2.2.1 | Monthly samples of full-scale treatment plants

For each of the described sites, water samples were collected from the raw water intake ("Raw") and various points throughout the treatment processes. The Atlantic Canadian plants were sampled after the flocculation process ("Floc"), after the filtration process ("Filter"), and as the water exits the plant after disinfection ("Finish"). At the UK sites, raw, post floc, post filter, and finished water samples were also collected, along with additional samples from post-GAC filtration ("GAC") and post-advanced oxidation processes ("AOP"). Depending on the plant configuration, "GAC" samples sometimes replaced "Filter".

Samples were collected at minimum monthly, from June to August 2019. Each sample was analyzed using conventional NOM metrics (i.e., TOC, UV_{254}) and peCOD at research laboratories in close proximity to the treatment facilities (i.e., samples were not shipped between the United Kingdom and Atlantic Canada). Unquenched samples were immediately analyzed for NOM metrics. Similarly, peCOD analysis was also performed immediately after sample collection and did not require quenching (i.e., chlorine was found to not interfere with peCOD analysis; Figure SI.1) or sample preservation. TOC samples were preserved on-site with phosphoric acid to pH <2.

2.2.2 | High-resolution sampling of ATL-A

In addition to monthly sampling, weekly grab samples were collected at ATL_A from October 2018 to October 2019. Grab samples were collected from raw and filtered water (unchlorinated) and were analyzed for peCOD, UV_{254}, and TOC. TOC was used in replacement of DOC as the two metrics were statistically equivalent at this site (95% confidence interval of the true mean difference: −0.053 to 0.050; $n = 49$). Online peCOD data were collected on the raw intake and finished water stream from May 2019 to February 2020. Additionally, weekly grab samples were collected from the raw water influent and

TABLE 1 Description of unit operations for the nine drinking water treatment plants studied.

Plant ID	Source	Capacity (MLD)	Type of plant	Plant description
ATL_A	Lake	85	Direct biofiltration (BIOFILT)	Aluminum sulphate (alum) coagulation, biofiltration, chlorine gas disinfection
ATL_B	Lake	45	Conventional (CONV)	Alum coagulation, up-flow clarification, multi-media filtration, chlorination
ATL_C	Lake	8	Conventional	Alum coagulation, sedimentation, biofiltration, chlorination
ATL_D	Reservoir	35	Conventional	Alum coagulation, up-flow clarification, multi-media filtration, chlorination
ATL_E	Lake	10	Dissolved air flotation (DAF)	Alum coagulation, DAF clarification, rapid filtration, chlorination
ATL_F	Lake	9.5	Ultrafiltration (UF)	Polyaluminum chloride coagulation, ultrafiltration, chlorine disinfection
UK_A	Lake	200	Conventional with ozonation	Pre-ozonation, alum coagulation, sedimentation, rapid filtration, ozonation, granular activated carbon (GAC) adsorption, chloramination
UK_B	Reservoir	20	Ultrafiltration/ advanced oxidation	GAC roughing filter, ultrafiltration, advanced oxidation (UV/H_2O_2), GAC contactor, UV disinfection, chlorination
UK_C	Reservoir	27	DAF with ozonation	Pre-ozonation, coagulation, DAF clarification, rapid filtration, post-ozonation, GAC contactor, chlorine gas disinfection

filter effluents of the ATL_A pilot plant from April to July 2019. The pilot-plant, which replicates the treatment train of the full-scale ATL_A plant (as described in Table 1), operated at an average flow of 10 L/min and the same operational conditions (e.g., coagulant dose, pH, flocculation times) as the full-scale plant. Further information on the layout of the pilot-plant train is described in DeMont et al. (2021). The pilot-plant samples were analyzed for UV_{254}, and peCOD on-site. Samples were prepped for DBP formation potential (trihalomethane formation potential; THMfp, and haloacetic acid; HAAfp) on-site.

2.3 | Analytical and laboratory methods

UV_{254} samples were filtered through a 0.45-μm polysulfone filter membrane (GE Water and Process Technologies) that was primed with 500 mL Milli-Q water to prevent leaching of organics from filter papers into the sample. Filtered samples with were then analyzed for UV_{254} with a HACH DR5000 UV/VIS spectrophotometer (Hach Company, Loveland, CO). TOC samples were collected head-space free in 40 mL pre-cleaned glass vials and preserved with concentrated phosphoric acid to pH <2. TOC measurements were performed using a TOC-V CPH analyzer with a Shimadzu ASI0-V autosampler and a catalytically aided combustion oxidation nondispersive infrared detector having a method detection limit of 0.08 mg/L (Shimadzu Corporation, Kyoto Japan). Units for UV_{254} and organic carbon are reported cm^{-1} and mg C/L, respectively. peCOD samples were mixed (3:1 ratio) with electrolyte (Mantech Inc., Ontario, CA) which is used to determine the background photocurrent generated by the oxidation of water (Stoddart & Gagnon, 2014). Samples were analyzed using a commercial COD analyzer and associated automation software (Mantech Inc., Ontario, CA). This method has a manufacturer reported detection limit of 0.7 mg/L (ASTM, 2017) and upper analysis limit of 25 mg/L. Samples with measurements below the detection limit were reported at 0 mg O_2/L. Instrument calibration was performed as per ASTM D8084 (ASTM, 2017), and the instrument was recalibrated whenever quality control samples deviated ±20% from expected values. For online peCOD analysis, the same methods were used; however, operating chemicals (e.g., calibrant, electrolyte) were automatically pumped into a cup to be mixed with the appropriate sample (e.g., milli-Q or water sample) using the manufacturer provided equipment. Online samples were alternated from raw and filtered water streams, and calibrations were performed twice a day or as needed as per ASTM D8084 (ASTM, 2017). The sensor for the online system was changed approximately once per week, or when calibrations failed consistently.

Samples were prepared for DBPfp measurements following uniform formation conditions (Summers et al., 1996), which included buffering the sample to pH 8 with borate buffer, chlorine dosing with a combined chlorine-pH 8 buffer solution, and a 24-hr dark incubation at room temperature (20°C). The residual free chlorine after 24 hours was 1.0 ± 0.4 mg/L (Summers et al., 1996). The incubated sample was then prepped for THM and HAA analysis via preservation with ammonium chloride, sodium thiosulfate, and hydrochloric acid, and ammonium chloride, respectively. THM and HAA analyses were performed using modified versions of Standard Methods 5710 (APHA et al., 2017). Gas chromatography electron capture (GC-ECD) measurement was performed with a Hewlett Packard 5890 Series II-Plus GC equipped with a DB-5 column for primary analysis of THMs and a DB-5 column for primary analysis of HAAs. A DB-1701 column was used for confirmation for both types of DBPs. A Fisons mass spectrometer (Trio 1000) was used for compound identification. THMs were extracted following liquid–liquid extraction with pentane and HAAs were extracted with methyl tert-butyl. THMs quantified in the described analysis were chloroform, bromodichloromethane (BDCM), dibromochloromethane (DBCM), and bromoform. The THM minimum detection limit (MDLs) were 2 μg/L, except chloroform, which was 4 μg/L. The corresponding limit of quantifications (LOQs) was at most 3 μg/L. Nine HAAs were monitored: chloroacetic acid (CAA), bromoacetic acid (BAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), bromochloroacetic acid (BCAA), dibromoacetic acid (DBAA), bromodichloroacetic acid (BDCAA), chlorodibromoacetic acid (CDBAA), and tribromoacetic acid (TBAA). The HAA MDLs and LOQs were at most 3 μg/L and 5 μg/L. NOM indicator calculations and statistical analysis.

Additional NOM indicators were used throughout the analysis. In SUVA calculations, DOC was replaced with TOC as they were deemed statistically equivalent in the source waters considered.

The SUVA calculation is shown in Equation (1) (Edzwald, 1993).

$$\mathrm{SUVA} = \frac{\mathrm{UV_{254}}}{\mathrm{TOC}} \times 100 \tag{1}$$

The mean oxidative state of carbon (Cos) was calculated with Equation (1) (Li et al., 2018).

$$\mathrm{Cos} = \frac{4(\mathrm{TOC} - \mathrm{peCOD})}{\mathrm{TOC}} \tag{2}$$

Statistical analyses were conducted with R (R Core Team, 2020; Wickham et al., 2019). Normality of data sets were tested with the Shapiro–Wilk test. The level of

significance for all statistical tests was $\alpha = 0.05$. Single- and multivariable linear regressions were performed to assess the relationships between peCOD and conventional NOM metrics, and NOM metrics to DBPfp. Single-variable linear regression models (i.e., peCOD = A × NOM metric + B) were fit to correlate TOC, UV_{254}, and SUVA (inputs) to peCOD readings (output). Further, linear regression and power models with either THMfp and HAAfp as the independent variables were fit to correlate DBP formation potential with peCOD, UV_{254}, and TOC as singular and multivariable inputs. The models are further described in Tables SI.1–SI.4. Models were compared using the coefficient of determination (R^2) and Akaike's Information Criterion (AIC).

3 | RESULTS & DISCUSSION

3.1 | Comparison of peCOD to conventional NOM metrics in drinking water treatment applications

3.1.1 | peCOD measurements had higher variance than conventional NOM metrics

Results from the three-month sampling program indicated substantial variations in peCOD values for source waters in Atlantic Canada and the United Kingdom, although both regions had similar ranges in magnitudes (Figure 1). In Atlantic Canada, raw water peCOD values ranged between 4.0 and 23.9 mg/L, while those in the United Kingdom were between 5.5 and 22.0 mg/L. Similarly, raw water UV_{254} absorbance had a wide range in both regions—0.050 to 0.249 cm^{-1} and 0.048 to 0.212 cm^{-1}, respectively. Measurements of TOC were less variable than peCOD and UV_{254}; raw water samples recorded TOC concentration between 2.1 and 6.1 mg/L in Atlantic Canada, and 5.8 and 8.7 mg/L in the United Kingdom. Greater variation in peCOD measurements compared with TOC was also reported in high-resolution grab sampling that occurred over a longer time frame (Oct 2018 to Oct 2019) at ATL_A (Figure 2). Fluctuations in raw water peCOD measurements over the high-resolution study period ranged from 5 mg/L to 16 mg/L; other NOM metrics were less variable (TOC: 2.7 to 4.1 mg/L; UV_{254}: 0.071to 0.154 cm^{-1}). Similarly, long-term online measurements of peCOD at ATL_A (Figure 3) varied from 0 to 24.9 mg/L over the period of study. Paired online TOC and UV_{254} data were not available.

The wider ranges of peCOD measurements as compared with TOC in raw water samples were further demonstrated by the mean percent standard deviations of each metric in the United Kingdom, Atlantic Canada, ATL_A grab sampling, and ATL_A online measurements (Table 2). These results demonstrated that peCOD often displayed a wider range in measurements, normalized by the measurement value, as compared with TOC or

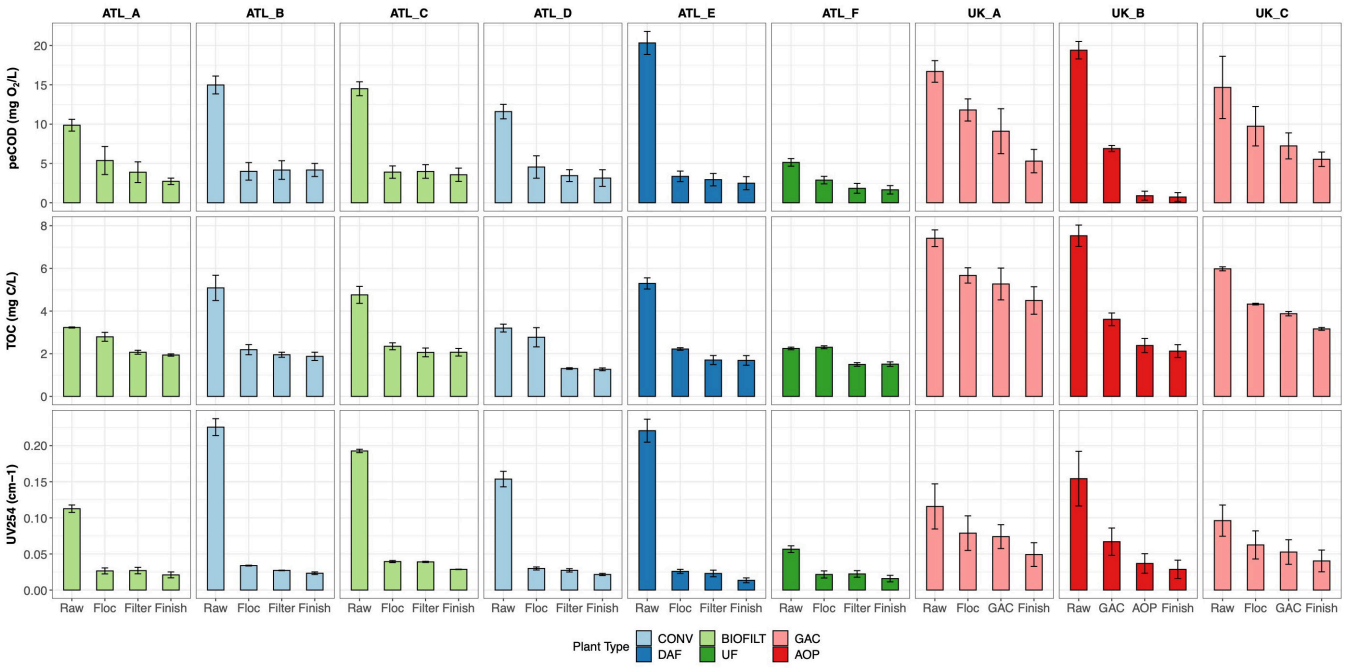

FIGURE 1 Mean peCOD, TOC, and UV_{254} values in raw waters and after progressive treatment processes in nine drinking water plants in Atlantic Canada and the United Kingdom. Error bars are representative of the 95% confidence interval ($n = 3$).

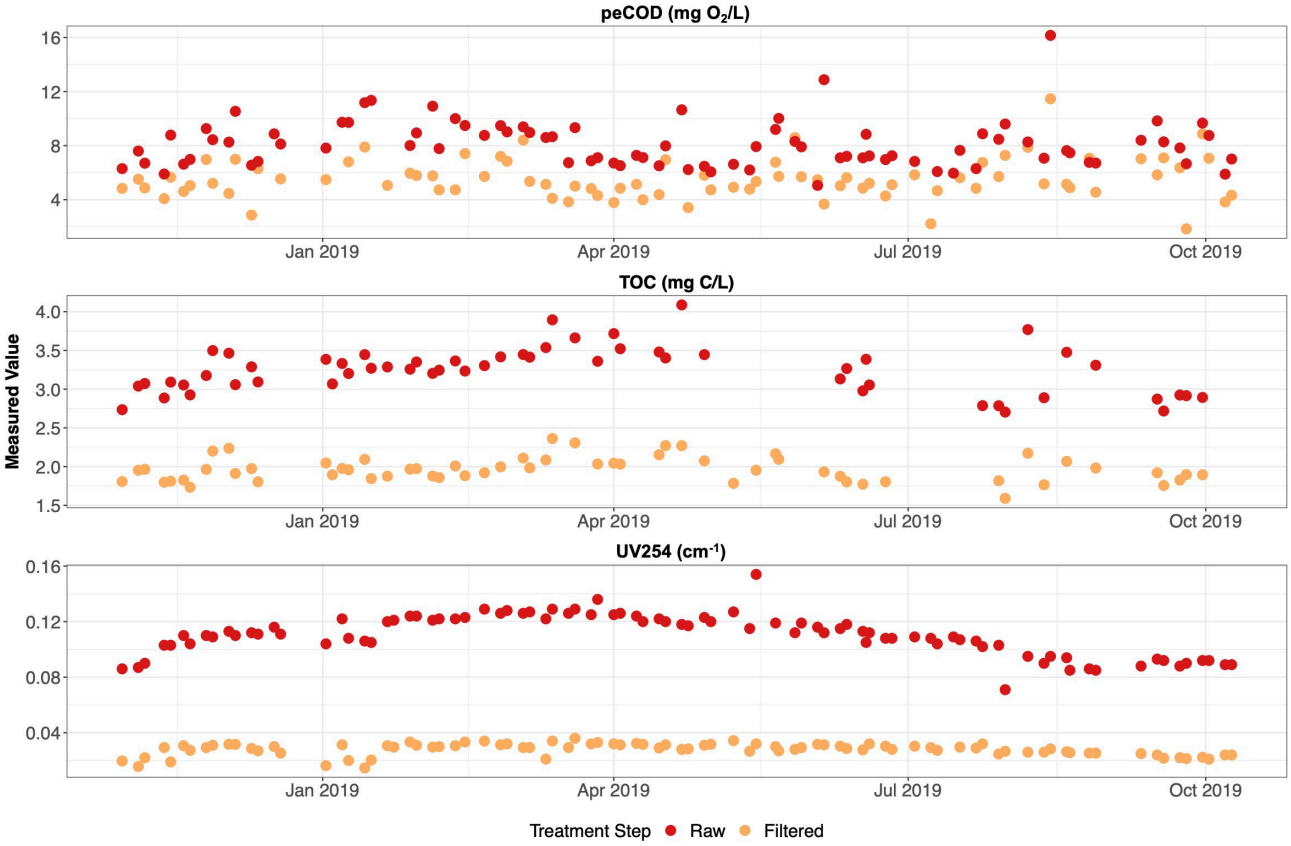

FIGURE 2 Long-term peCOD, TOC, and UV_{254} results from raw and filtered water grab samples at ATL_A from October 2018 to October 2019.

FIGURE 3 In-line peCOD values reported in raw and filtered water streams at ATL_A from May 2019 to February 2020.

UV_{254}. To ensure that the greater variability was respect to the sensitivity of the instrument, and not its inaccuracy, the percent standard deviations of COD standards with concentrations expected in drinking water samples (i.e., 5, 10 and, 20 mg O_2/L) were analyzed in triplicate (Figure SI.2). The average percent standard deviation was

Region	Mean percent standard deviation (%)			Sample size
	peCOD	TOC	UV_{254}	
UK	29	10	52	3 plants
ATL	16	12	12	6 plants
Atlantic Canada (grab)	21	9	13	89 samples
Atlantic Canada (in-line)	27	NA	NA	1565 samples

TABLE 2 Mean percent standard deviations of raw water peCOD sampling programs in Atlantic Canada and the United Kingdom.

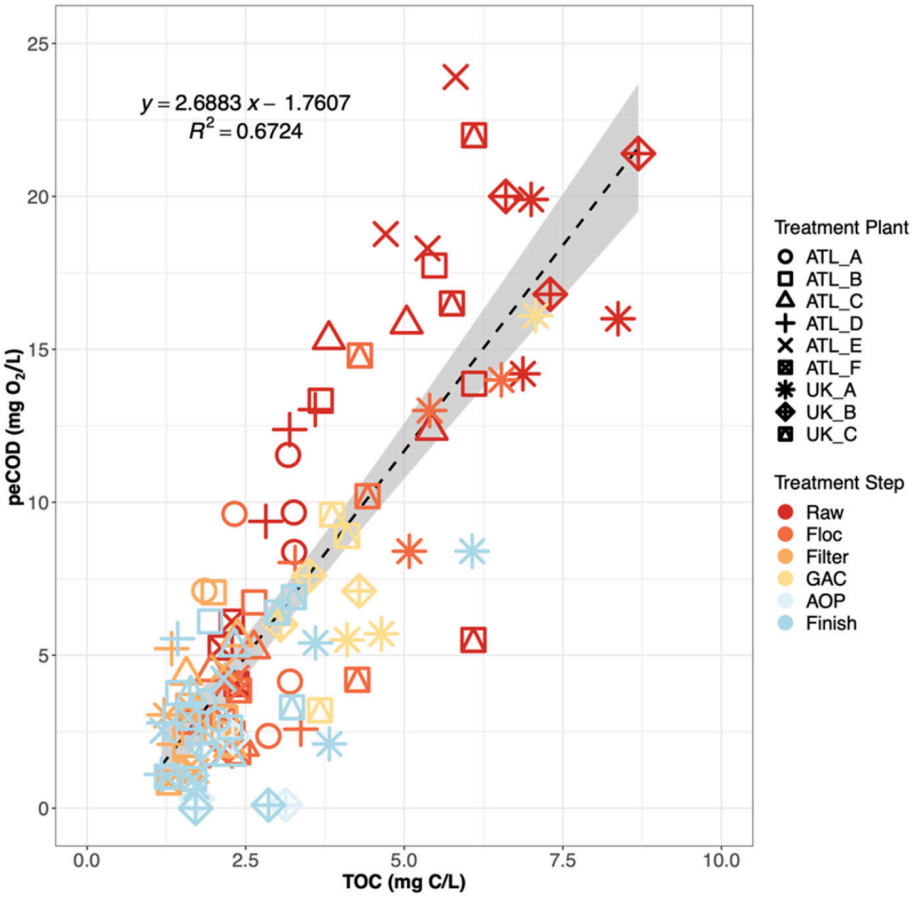

FIGURE 4 Paired TOC and peCOD values of samples collected after various treatment steps in nine drinking water treatment plants across Atlantic Canada and the United Kingdom from June to July 2019. The dashed line indicates the line of best fit for all data.

4.5% (95% CI: 3.24%–5.77%) and the maximum percent standard deviation measured on triplicate readings of known standards was 8.46% on a 10 mg O_2/L standard (Figure SI.2); that is, measurements of a unique sample varied up to ~6% of the mean of triplicate readings, which was well below the minimum 16% percent standard deviation reported in the monitoring data (Table 2). While some variability in measurement can be attributed to the instrument, the variability in sample measurements exceeds the instrument variability, and thus, the peCOD shows a higher sensitivity compared with conventional metrics. Comparatively, the deviations in the UV_{254} and TOC readings were also only partially due to the instrument error. UV_{254} readings were never greater than 0.001 cm^{-1}, which was <1% of mean source water UV_{254} reading on triplicate readings. Further, the percent standard deviation associated with the TOC analyzer on 0.2-mg/L standards was 6.6%. This additional sensitivity with peCOD analysis could improve monitoring programs by identifying subtle changes in source water quality and NOM reactivity that may go unnoticed by conventional metrics due to their lower sensitivity. If the treatment processes are impacted by the NOM character (i.e., reactivity with chemical oxidants), then capturing these subtle changes may improve treatment optimization.

3.1.2 | Weak relationships found between peCOD and conventional NOM metrics and indicators

In the three-month sampling program, higher peCOD values corresponded with higher TOC measurements; peCOD increased between 2.33 to 3.05 mg O_2/L per 1 mg/L

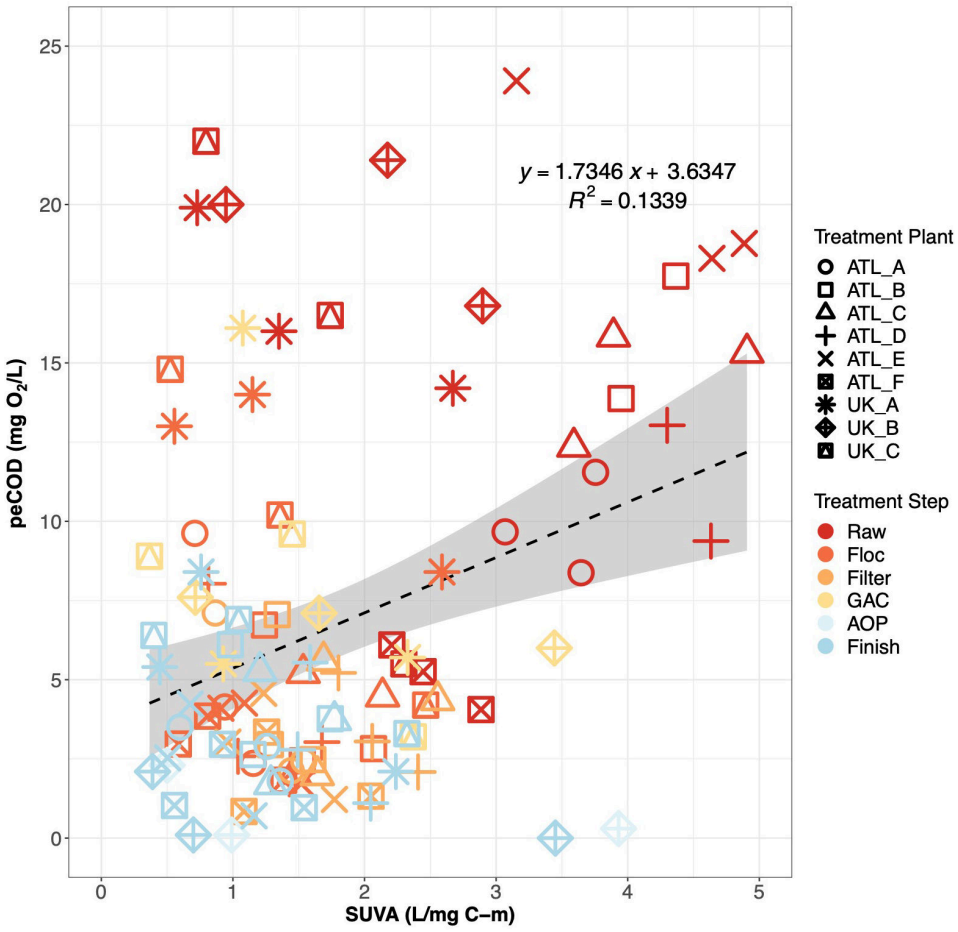

FIGURE 5 PeCOD measurements and corresponding SUVA values of samples collected after various treatment steps in nine drinking water treatment plants across Atlantic Canada and the United Kingdom from June to July 2019. The dashed line indicates the line of best fit for all data.

increase in TOC concentration (95% confidence interval) (Figure 4). The linear model (i.e., $peCOD = A*TOC + B$) residuals demonstrated that as the TOC increased (i.e., samples earlier in the treatment train containing more organic material), the relationship between peCOD and TOC weakened (Figure SI.3). This is suggestive that peCOD is more correlated to TOC in treated water samples. However, when analyzing the long-term sampling of ATL_A, the relationships between TOC and peCOD of raw and filtered (treated) samples were poorly represented by a linear model (Figure SI.4), suggesting that TOC and peCOD may not be well correlated even when considering a single source water or sampling location. Past work has shown strong linear relationships ($R^2 > 0.9$) between peCOD and TOC, with comparable slopes with the present work (Stoddart & Gagnon, 2014). However, data were limited to model compounds (e.g., caffeine, tyrosine, and tryptophan) in ultrapure water and thus were not representative of natural drinking water, where the complex and varying nature of NOM within a given source water, and between source waters, may cause the relationship between peCOD and conventional NOM metrics to deviate from a linear model matrices (Stoddart & Gagnon, 2014). Others have also observed a similar positive relationship between TOC and COD (Johansson et al., 2010; Kortelainen, 1993), though no universal relation to convert one metric to the other has been established (Kritzberg & Ekström, 2012; Wang et al., 2021).

When comparing peCOD and UV_{254}, similar results were observed. peCOD measurements increased significantly as UV_{254} increased (Figure SI.5). However, a weaker relationship was observed between peCOD and UV_{254} ($R^2 = 0.48$) compared with peCOD and TOC ($R^2 = 0.67$). Similarly, a weak relationship between SUVA and peCOD was determined from the data collected in the three-month sampling program ($R^2 = 0.13$) (Figure 5) and in the long-term ATL_A sampling program ($R^2 < 0.03$ for both Raw and Filtered samples) (Figure SI.6). This was contrary to past work done in Atlantic Canada, where SUVA correlated well with peCOD readings taken through conventional drinking water treatment plants (Stoddart & Gagnon, 2014). However, the sample size for this study was limited ($n = 13$), and over 50% of the data were clustered around 1.75–2.0 mg/L/m and 4–5 mg O_2/L (Stoddart & Gagnon, 2014). As such, it was not representative of a wide range of water qualities, as displayed in this work.

The lack of relationship between peCOD and UV_{254}-based metrics highlights that peCOD can provide additional insight into the chemical reactivity of NOM in a water sample. As previously discussed, SUVA is reflective only of organic material that absorbs UV light at 254 nm, mainly aromatic or unsaturated aliphatic compounds. Considering many known organic compounds do not absorb at this wavelength (Ritson et al., 2014; Weishaar et al., 2003), it is likely that some were not captured by SUVA/UV_{254} readings due to the wavelength limitation. If the oxidizable NOM in a given source water is well correlated with UV_{254}, a relationship between peCOD and UV_{254}/SUVA may be observed. However, the lack of established relationship between conventional NOM metrics and peCOD in this case further emphasize that peCOD can provide additional information of NOM quality not quantified by TOC or UV_{254} and could be used to complement conventional bulk NOM metrics.

3.2 | Assessment of treatment performance

Overall percent removals of organic matter (i.e., from raw to finished samples) through each of the nine plant samples in the three-month program are shown in Figure 6. PeCOD and UV_{254} removals were equivalent, however, both showed significantly higher overall removal than TOC. Similar results were observed by Stoddart and Gagnon (2014), who found peCOD removals ranging between 49% and 99% in four Atlantic Canada drinking water treatment plants. Most peCOD values of finished water samples were below 5 mg/L (Figure 1)—a regulatory guideline in place in some European jurisdictions (European Union, 2014). In France, for example, the guidelines for treated water include 2-mg/L TOC as well as an oxidizability limit of 5 mg O_2/L (Government of France, 2007). Health Canada has proposed the same 5-mg/L threshold for treated water in their guidance document on NOM in drinking water, advising peCOD as the prescribed measurement tool (Health Canada, 2019).

3.2.1 | PeCOD is effective for monitoring partial oxidation of NOM

The value of peCOD as a treatment monitoring tool was further illustrated when comparing the individual steps of various treatment plants (Figure 7). ATL_A is a direct biofiltration plant, where NOM was partially oxidized by the biological activity on filter media and physically removed via filtration of formed flocs. The mean peCOD removal across the biofilter ('Filter) was 24%, and the mean TOC removal was 25%. These removals, along with a reduction in mean peCOD:TOC ratio (discussed further in the following section) from 1.97 to 1.41 mg O_2/mg DOC, indicate both physical removal and oxidation of organic material. However, in comparison, the mean UV_{254} removal across the biofilter was 1%. As such,

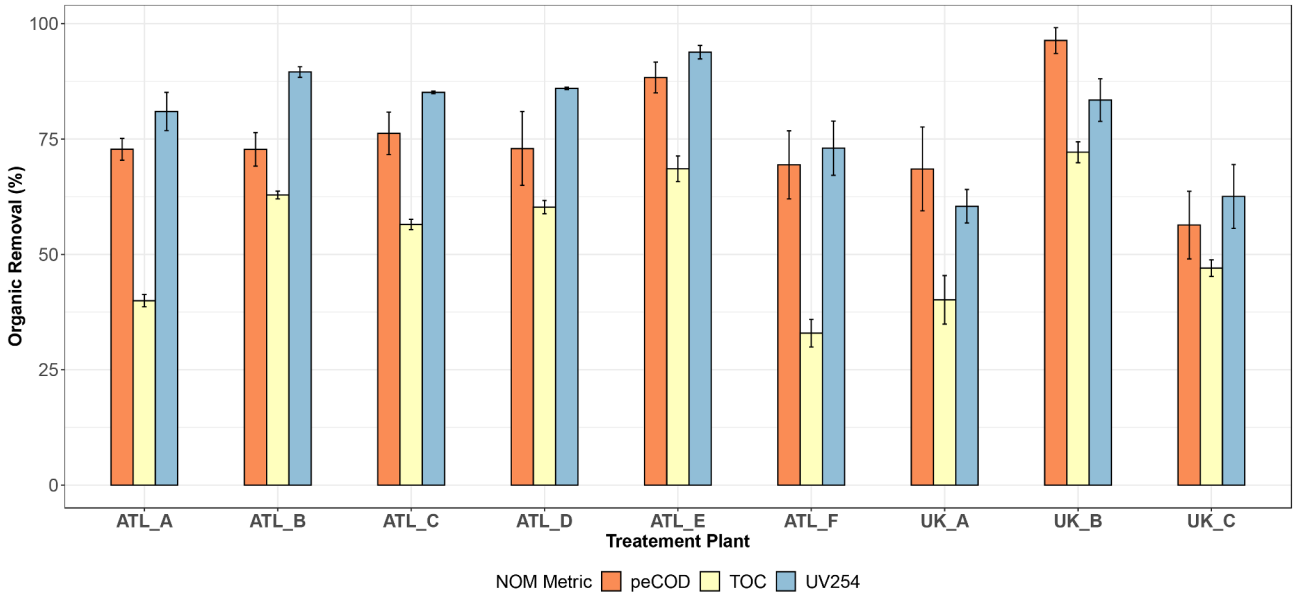

FIGURE 6 Treatment performance in nine plants in Atlantic Canada and the United Kingdom as indicated by the mean overall removal of organic matter (i.e., percentage of raw water NOM concentration removed through entire treatment plant) measured by peCOD, TOC, and UV_{254}. Error bars are representative of the 95% confidence interval ($n = 3$).

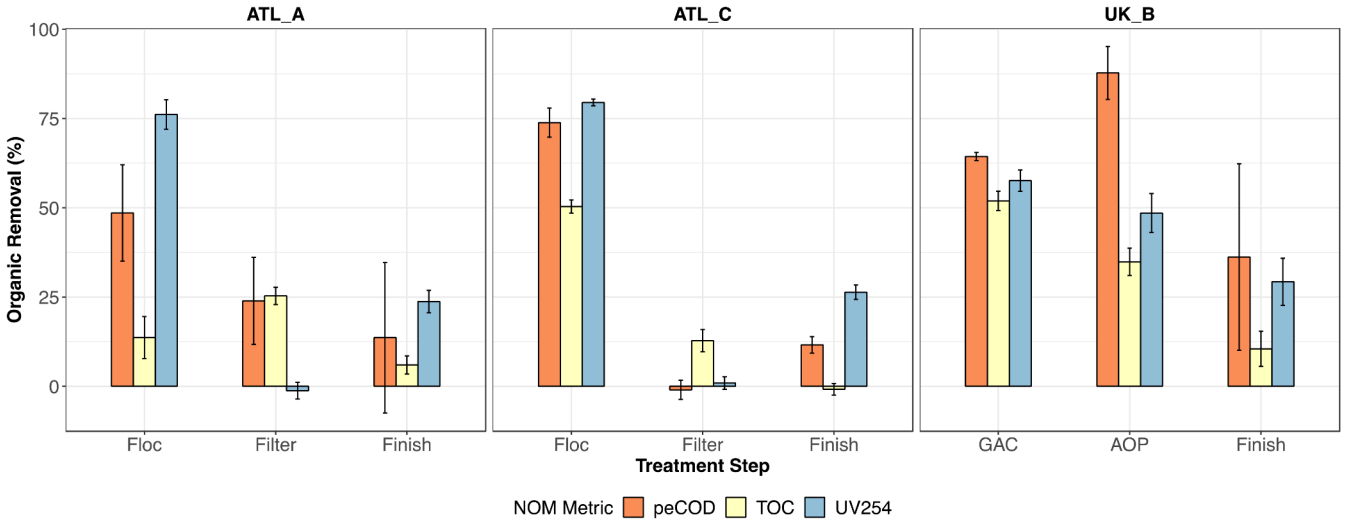

FIGURE 7 Mean organic matter removal determined by percent removal of peCOD, TOC, and UV_{254} through subsequent treatment steps (i.e., percent of influent NOM to unit process removed during said process) in ATL_A (direct biofiltration), ATL_C (conventional), and UK_B (GAC and AOP). Error bars are representative of the 95% confidence interval ($n = 3$).

reliance on UV_{254} as a monitoring tool in ATL_A illuded that biofiltration did not degrade organic material. peCOD measurements, combined with TOC removal, suggested adequate treatment of reactive organic material via biodegradation or filtration, as the average peCOD in the filter effluent was below the proposed Health Canada 5-mg O_2/L guideline.

The benefit of peCOD for treatment performance evaluation was also evident when considering treatment via chemical oxidation. For example, mean peCOD removal during oxidation with chlorine ('Finish' step, Figure 7) in ATL_C was 11.6%, where TOC removal was −0.8%. Similar observations were identified in chlorine disinfection in ATL_A and UK_B as well, where mean peCOD removal was greater than the mean TOC removals. Further, the 'AOP' step at UK_B (Figure 7) reduced the average peCOD value by 6.0 mg/L (88%), compared with a 1.29 mg/L (36%) reduction in average TOC concentrations. While some oxidizable organic material would be filtered by the ultrafiltration step prior to UV/H_2O_2 and adsorbed by the GAC contactor following UV/H_2O_2 that were merged with the 'AOP' in the UK_B plant, the high decrease in peCOD value compared with moderate TOC removals in oxidation-based treatment steps implied both physical removal and oxidation of NOM. Reliance on TOC removal alone would not have accurately reflected chemical degradation of NOM in these cases. As such, peCOD may be useful for optimization of oxidation-based processes, where conventional metrics fail to accurately capture the changes in NOM during treatment. However, additional work is required to establish performance objectives which will likely be source water and treatment plant dependent.

3.2.2 | PeCOD-based indicators reflect changes, or lack thereof, in chemical reactivity through drinking water treatment

Additional peCOD-based metrics have been established to monitor the oxidation of organic carbon in drinking water treatment (Li et al., 2018; Stoddart & Gagnon, 2014). The peCOD:TOC ratio is a measure of the chemical oxygen demand normalized per mg of total organic carbon. Cos estimates the oxidation state of organic carbon; a change in Cos approximates the number of electrons lost (increase in Cos due to oxidation) or gained (reduction in Cos due to reduction) during reduction–oxidation reactions (Li et al., 2018). Comparison of SUVA and peCOD-based NOM indicators (i.e., peCOD:TOC ratio and Cos) through subsequent treatment steps in a conventional treatment plant (ATL_B) and AOP plant (UK_B), further highlighted the additional insight provided by peCOD measurement, especially in advanced treatment processes (Figure 8).

In ATL_B, the mean SUVA value decreased from 4.55 L/mg C/m in the raw water to 1.29 L/mg C/m in the finished water (72% removal). The peCOD:TOC ratio decreased from 3.04 to 2.31 mg O_2/mg C (24% removal). Based on the SUVA results, hydrophobic and aromatic (e.g., more reactive) NOM were effectively removed during treatment, as the treated water SUVA was, on average, <2 mg/L, indicating mainly the hydrophilic, less reactive NOM fraction remained (Edwards, 1997). Conversely, the smaller change to the paired peCOD:TOC ratio after treatment at ATL_B demonstrated that residual TOC was of similar reactivity toward chemical

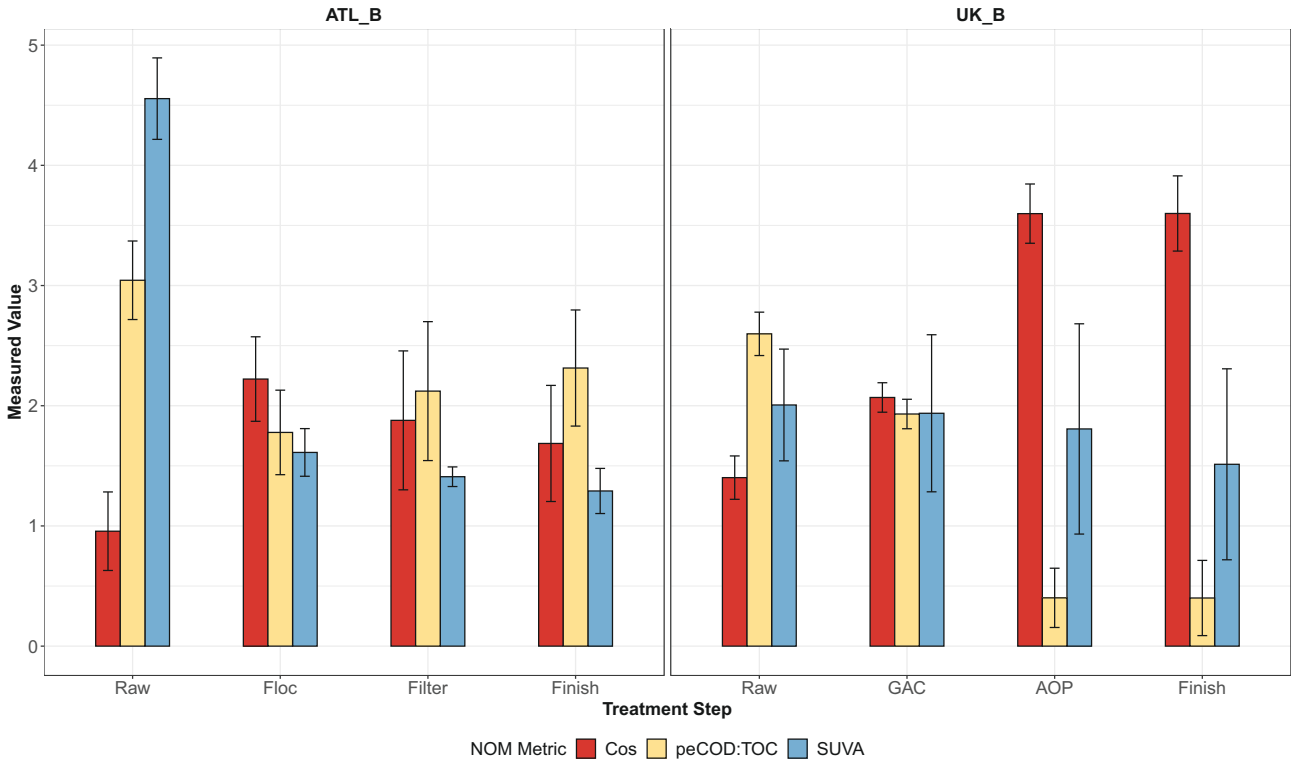

FIGURE 8 Mean values of Cos, peCOD:TOC, and SUVA values through subsequent treatment steps in ATL_B (conventional sedimentation) and UK_B (GAC and AOP). Error bars are representative of the 95% confidence interval ($n = 3$).

TABLE 3 Comparison of peCOD-based NOM indicators and UV_{254}-based indicator in ATL_A grab sampling program ($n = 55$).

	Avg peCOD:TOC ratio ± SD	Avg SUVA ± SD
Raw	2.57 ± 0.46	3.39 ± 0.35
Filtered	2.84 ± 0.72	1.41 ± 0.26

oxidants, on a per mass-basis, as in the raw influent stream. An analogous observation was noted in the long-term sampling of ATL_A, where SUVA decreased below 2 m-L/mg after direct filtration treatment but the peCOD:TOC ratio remained unchanged from the raw water stream to filter effluent (Table 3).

In the advanced oxidation plant (UK_B), the most notable changes in peCOD-based NOM indicators were after the AOP treatment step ('GAC' to 'AOP') (Figure 8). The mean peCOD:TOC ratios decreased from 1.80 to 0.4 mg O_2/mg C (78%); the Cos increased from 2.07 to 3.60 (174% increase). The substantial decrease in peCOD:TOC ratio and increase in Cos reflected the oxidation of organic material through AOP treatment. The residual organic material was thus at a higher oxidation state and less chemically reactive, indicating effective treatment. Conversely, there were no significant changes in mean SUVA values over the course of treatment at UK_B, which only decreased 7% (1.94 to 1.80 L/mg C/m) after the nanofiltration, advanced oxidation treatment, and GAC treatment step ('AOP' on Figure 8). Eliminating the oversight of chemical reactivity with SUVA by incorporating peCOD-based indicators will enhance performance monitoring and treatment decision-making for advanced drinking water treatment operations.

3.3 | Estimating disinfection by-product formation potential

3.3.1 | PeCOD and conventional NOM metrics were weak indicators of DBP formation potential

Linear regression ($\text{DBPfp} = A \times \text{NOM metric} + B$) and power models ($\text{DBPfp} = A \times \text{NOM metric}^b$) demonstrated that peCOD was typically not a significant predictor of THMfp nor HAAfp in both the raw and filtered (treated) water samples (Table SI.1–SI.4). The exception to this finding was found in modeling HAAfp of filtered water samples (Table SI.4), where peCOD was a significant predictor in both the linear and power models. However, the coefficients of determination still indicated weak

relationships between peCOD and HAAfp ($R^2 < 0.20$), and UV_{254} was a better predictor of HAAfp compared with peCOD. The limited relationship between DBPfp and peCOD measurements may be explained by the strong oxidizing ability of peCOD technology, which generates highly reactive hydroxyl radicals, compared with the weaker oxidation potential of chlorine (Stefan, 2018). PeCOD fully oxidizes most organic compounds in a solution, some of which are not able to be oxidized by chlorine, and thus peCOD is likely to overestimate the reactivity toward chlorine.

Conventional metrics (i.e., TOC and UV_{254}) were also very weak predictors of both THMfp and HAAfp in filtered and raw water samples with R^2 values not exceeding 0.20. Further, relationships between DBPfp and NOM surrogates were stronger in filtered water samples as compared with raw water matrices. These findings contrast existing work that has shown strong, positive relationships between DBPfp (i.e., HAAfp and THMfp) and conventional NOM surrogates (Golea et al., 2017; Uyak et al., 2007; van Leeuwen et al., 2005). For example, van Leeuwen et al. (2005) reported R^2 values exceeding 0.68 when relating DOC concentrations and THM formation potential in coagulated water samples. Further, Golea et al. (2017) found strong relationships ($R^2 > 0.74$) between DBPfp and conventional NOM metrics (UV_{254}, DOC) in raw water samples. The relationships were weaker for treated water, where coefficients of determination were between 0.21 and 0.63 for UV_{254} and DOC. Additional work has also shown negative correlations between HAA concentrations and NOM surrogates (Uyak et al., 2007). Uyak et al. (2007) found increasing HAAfp with decreasing SUVA values, which contradicts most findings in this field (Sadiq & Rodriguez, 2004). The discrepancies found in this work and in literature demonstrate the complexities in the relationships between NOM surrogates and DBP formation, as well as the difficulties in generating universally applicable DBP predictive models.

3.3.2 | Addition of peCOD to multivariable DBP predictive models can improve model performance

Despite poorly fit models with peCOD and conventional NOM metrics as the sole predictor of DBPfp, the inclusion of peCOD analysis did, at times, improve estimation of DBPfp. Evaluation of multivariable linear and power functions using AIC, which accounts for the number of variables included in the model, show that HAAfp power models are improved with the inclusion of peCOD, for both raw and filtered water matrices.

Nonetheless, the use of alternative NOM monitoring techniques may better inform on DBPfp. For example, prediction of DBPfp using FEEMs has shown positive results (Trueman et al., 2016; Xu et al., 2021). The combination of peCOD and FEEMs may provide a more holistic approach to predicting DBPs in water treatment applications and should be considered in future work. Additionally, the study considered the formation of only regulated DBPs; however, there are many known chlorinated by-products that were not considered in this study (Allen et al., 2022; Richardson & Plewa, 2020). For example, EDC abatement has been well correlated to unregulated DBPs (i.e., haloacetonitriles) (Rougé et al., 2020). More encompassing indicators of DBP formation may better correlate with peCOD measurements because they are not limited to only regulated compounds (Andersson et al., 2020; Yao et al., 2019).

4 | CONCLUSIONS

As source water quality changes due to climate change, recovery from acidification, and changing land use, drinking water treatment facilities must adapt. Consequently, both NOM source water monitoring strategies and treatment performance evaluation must also advance to reflect the given changes in water quality and to ensure consistent treatment outcomes. The peCOD method was a reliable concentration-based NOM monitoring metric in drinking water sources, providing more sensitive analysis compared conventional metrics and insight into the reactivity of organic compounds. The increased sensitivity of peCOD may improve detection of subtle changes to water quality in drinking water treatment operations and help more accurately inform treatment decisions. Further, peCOD can quantify the reactivity of all organic material in a water sample, compared to UV_{254} or SUVA, which are limited to organic material that absorb at a single wavelength. Nonetheless, the weak relationships between peCOD and UV_{254}, TOC, and SUVA identified in this work indicate that peCOD should be used to complement existing NOM metrics (e.g., UV_{254}, TOC) that offer additional information such as aromaticity and total mass organic carbon concentration.

The application of peCOD in evaluating treatment of NOM was most beneficial in oxidation-based unit processes, where partial mineralization of NOM was not always recorded by UV_{254} or TOC. In biofiltration, UV_{254} measurements failed to capture shifts in NOM that were reported by a reduction in both TOC concentration and the peCOD:TOC ratio—indicating physical removal and biological oxidation of NOM. Further, in AOP

treatment processes, peCOD identified shifts in NOM character (i.e., less reactive) due to advanced oxidation while there were no changes to TOC concentrations. PeCOD-based NOM indicators (i.e., Cos, peCOD:TOC ratio) also complemented performance monitoring, as trends in SUVA and peCOD-based indicators did not always align. In nanofiltration/AOP treatment, SUVA indicated no change in NOM character due to treatment, but peCOD-based indicators suggested effective oxidation of NOM. The contrary was true for conventional treatment processes, where SUVA suggested a significant decrease in reactive NOM, but peCOD-based indicators showed no significant change. The ability to quantify shifts in NOM reactivity on a concentration-basis with peCOD will become increasingly important as the drinking water treatment industry shifts toward biofiltration and advanced oxidation processes for control of emerging contaminants that are resistant to conventional treatment processes, such as cyanotoxins, taste, and odor compounds, and hydrophilic DBP precursors (Anderson, DeMont et al., 2023). If treatment of NOM, which competes with the emerging contaminants, can be effectively monitored, treatment strategies can be optimized for effective removal of the micropollutant (Ji et al., 2024). The addition of peCOD to performance monitoring in drinking water treatment plants may facilitate this fine-tuning of treatment operations and offers a benefit over other advanced NOM tools, such as EEMs or EDC, through concentration-based measurements that capture the entire NOM profile and is repeatably and reliable via a standard method (ASTM, 2017).

Further, inclusion of peCOD monitoring may lead to reduced impact on water quality outside of the treatment plant (e.g., DBP formation) if reactive NOM can effectively be monitored and removed within the plant. However, peCOD-based parameters were found to be weak predictors of DBPfp. Other NOM metrics (e.g., FEEMs, EDC) have proven to be good predictors of DBPfp in previous work and should be considered in conjunction with peCOD in the future.

AUTHOR CONTRIBUTIONS

Isobel DeMont: Conceptualization; formal analysis; investigation; methodology; writing – original draft; writing – review and editing. **Lindsay E. Anderson:** Conceptualization; data curation; investigation; methodology; writing – original draft; project administration; writing – review and editing. **Jessica L. Bennett:** Writing – original draft; writing – review and editing. **Chrissa Sfynia:** Investigation; methodology. **Paul Bjorndahl:** Formal analysis; writing – review and editing. **Peter Jarvis:** Writing – review and editing. **Amina K. Stoddart:** Supervision; funding acquisition; writing – review and editing. **Graham A. Gagnon:** Supervision; funding acquisition; project administration; writing – review and editing.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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