# Application of photoelectrochemical chemical oxygen demand to drinking water

AMINA K. STODDART[1] AND GRAHAM A. GAGNON[1]

[1]Department of Civil & Resource Engineering, Dalhousie University, Halifax, N.S., Canada

This study investigated the use of a photoelectrochemical chemical oxygen demand (peCOD) analyzer for the detection of model organic compounds and natural organic matter (NOM) from four drinking water treatment plants in Nova Scotia, Canada. Most model organic compounds showed reasonable correlation between peCOD and theoretical oxygen demand (ThOD), indicating that peCOD was a reasonable predictor of chemical oxygen demand (COD). Results also showed that peCOD/TOC (total organic carbon) ratios followed predicted values from stoichiometry, when peCOD was a good predictor of ThOD. peCOD determination for surface water showed that peCOD was measurable in the raw and treated drinking water range and trended with other organic matter surrogates. Finally, pooling of raw water, finished drinking water, and water sampled throughout the treatment process at these four utilities showed that peCOD was correlated with specific ultraviolet absorbance at 254 nm (SUVA).

**Keywords:** *photoelectrochemical, chemical oxygen demand, surface water, drinking water*

Natural organic matter (NOM) in surface waters can be produced through many pedogenic and aquagenic processes (Krasner et al, 1996). NOM in drinking water source water is of specific concern because it has been identified as a precursor to regulated and unregulated disinfection by-products (DBPs) with both known and unknown health effects (Nieuwenhuijsen et al, 2000; Villanueva et al, 2000; Krasner et al, 2006; Krasner et al, 1989). As summarized in the literature by Matilainen et al (2011), NOM can be characterized using several spectroscopic, chromatographic, and mass spectrometric methods to provide very specialized information on NOM character. Of these methods, high-performance size exclusion chromatography, ultraviolet (UV) absorption at different wavelengths, and resin fractionation are common (Cabaniss et al, 2000; Krasner et al, 1996; Edzwald et al, 1985). For nonselective and efficient NOM monitoring, tools such as total organic carbon (TOC), dissolved organic carbon (DOC), and UV absorption at a wavelength of 254 nm ($UV_{254}$) are often used to provide rapid assessment of NOM in water. Although these are widely used tools, there are continuing needs to develop new monitoring tools to better understand and efficiently manage NOM in drinking water processes.

Chemical oxygen demand (COD) is the amount of oxygen required to fully oxidize organic matter, as determined by using a strong oxidant (Droste, 1997). COD is often measured using method 5220 of *Standard Methods*, which involves oxidation of organic matter at high temperatures with sulfuric acid, dichromate, and a catalyst for 2 to 3 hours, followed by indirect determination of COD through unreacted dichromate. This method involves the use of hazardous chemicals (i.e., mercury, hexavalent chromium, sulfuric acid, and silver) and is suitable for COD concentrations > 50 mg/L with alterations to allow for COD detection from 5 to 50 mg/L. Adjustments to the COD procedure for the lower detection range are at the expense of accuracy and precision (APHA, 2012). The method can also be altered to reduce wastes, but again at the expense of accuracy (APHA, 2012). Although these alterations can allow for the detection of COD in surface waters, the dichromate method is typically not sensitive enough for treated drinking waters (Rittman and Huck, 1989).

COD also can be measured using a photoelectrochemical method (Zhao et al, 2004). Recently, a commercial COD analyzer using this photoelectrochemical method has been developed. With a calculated method detection limit of 0.5 mg/L, it was anticipated that this tool could be a useful surrogate parameter (much like TOC, DOC, and specific ultraviolet absorbance at 254 nm [SUVA]) for assessing NOM in raw and treated drinking water that could overcome challenges with traditional COD methods through improved detection limit and reduction in hazardous wastes.

The hypothesis of this study was that photoelectrochemical chemical oxygen demand, or peCOD, could provide analysis of NOM removal that would be applicable to the drinking water industry. To address this hypothesis, the study was structured into the following research tasks: (1) evaluate the ability to detect and quantify COD from model organic compounds (e.g., amino acids and carboxylic acids) in a concentration range relevant for drinking water; (2) compare peCOD analysis to traditional NOM detection techniques (e.g., TOC analysis); and (3) evaluate peCOD concentration range in source water and during subsequent treatment from surface water treatment plants in Nova Scotia, Canada. Because COD is a measure of oxidizable organic matter, relationships between peCOD and traditional NOM surrogates were also studied.

## MATERIALS AND METHODS

**Model compound preparation.** Three amino acids (tyrosine, tryptophan, phenylalanine), three carboxylic acids (sodium acetate, sodium oxalate, and sodium formate), and two reference standards (potassium hydrogen phthalate [KHP] and caffeine) were used as model organic compounds. These model organic compounds are summarized in Table 1.

Carboxylic acids and amino acids are found in natural waters and can make up 8% and 2–3% of COD in natural waters, respectively (Langlais et al, 1991). Relative proportions of amino acids to organic matter surrogates such as DOC can vary considerably from source to source. In a survey of 16 utilities across the United States, Dotson and Westerhoff (2009) found that raw water total amino acid concentration accounted for between 0.19 and 11.6%, or 3.5%, on average, of raw water DOC. As summarized by Dotson and Westerhoff (2009), amino acids are precursors to regulated and unregulated DBPs, and amino acids with aromatic side chains, such as tryptophan and tyrosine, can have the highest DBP yields on a carbon basis. KHP was chosen because it is commonly used as a reference standard for TOC determination. Finally, caffeine was chosen as it is commonly used as a marker for human contamination.

Model compound stock solutions (100 mg C/L) were prepared by diluting chemical in deionized (DI) water (Millipore). Stock solutions were then further diluted with DI water to 0.25, 0.5, 1, 3, and 5 mg C/L as TOC in the range of 1.5–5 mg/L represents common raw and treated water TOC content in surface water in Nova Scotia. Model compounds were prepared for TOC and COD.

**Surface water collection.** Samples were collected from four surface water treatment plants in Nova Scotia. Treatment trains included one biofiltration plant (Pockwock Lake), one ultrafiltration/nanofiltration membrane plant (Fletcher Lake), and two conventional filtration plants (Lake Major and Bennery Lake). Details of the treatment process for each plant are described in Table 2.

Samples included raw water, prefiltered water, filtered water, and finished water from each location, with the exception of prefiltered water and finished water from Fletcher Lake. Raw water samples were taken from the plant's raw water intake at all locations. Prefiltered water was taken from the final flocculation tank for the Pockwock and Bennery Lake samples, and from the top of the clarifier, prior to prechlorine addition, for the Lake Major sample. A prefiltered sample was not taken at Fletcher Lake because no additional chemicals were added between the raw water intake and ultrafiltration step. Filtered samples were taken immediately following filtration and before the addition of any finish chemicals at all locations. For Fletcher Lake, this included a sample immediately after ultrafiltration and another sample immediately after nanofiltration. Finished water samples were taken from finished water compliance taps in all locations, with the exception of Fletcher Lake where no finished water sample was taken. Samples were collected in clean, 1-L plastic bottles. Samples were stored on ice during transport to the laboratory and stored at 4°C in the laboratory. Samples were analyzed for TOC, DOC, $UV_{254}$, and peCOD.

**TABLE 1** Model organic compound descriptions

| Compound | Chemical Formula | Description | Molecular Weight *g/mol* |
|---|---|---|---|
| Potassium hydrogen phthalate | $C_8H_5KO_4$ | Reference standard | 204.22 |
| Caffeine | $C_8H_{10}N_4O_2$ | Reference standard | 194.19 |
| Phenylalanine | $C_9H_{11}NO_2$ | Amino acid | 165.19 |
| Tyrosine | $C_9H_{11}NO_3$ | Amino acid | 181.19 |
| Tryptophan | $C_{11}H_{12}N_2O_2$ | Amino acid | 204.23 |
| Sodium formate | HCOONa | Carboxylic acid | 68.01 |
| Sodium acetate | $C_2H_3O_2Na$ | Carboxylic acid | 82.03 |
| Sodium oxalate | $Na_2C_2O_4$ | Carboxylic acid | 134.00 |

**Determination of organic carbon and UV absorbance.** TOC and DOC samples were prepared, headspace-free, in baked (100°C for 24 h) 40 mL borosilicate glass vials, preserved with three drops of phosphoric acid to pH < 2, and analyzed using a TOC analyzer.[1] Samples for DOC were filtered through a 0.45-mm filter paper that was rinsed with 500 mL deionized water prior to preparation. Samples were analyzed for $UV_{254}$ using a spectrophotometer.[2] Specific SUVA was determined by dividing the $UV_{254}$ ($cm^{-1}$) by the DOC (mg/L) and multiplying by 100. Model compound TOC and peCOD samples were prepared immediately after the compounds were diluted. Surface water sample preparation was completed within eight hours of sample collection.

**peCOD analysis.** Samples were analyzed for peCOD using a commercial COD analyzer[3] with an autosampler[4] and associated

**TABLE 2** Treatment train descriptions for four surface water treatment plants in Halifax, N.S., Canada

| Source | Treatment |
|---|---|
| Pockwock Lake | Lime, potassium permanganate, carbon dioxide, aluminum sulfate coagulation, seasonal polymer,* three-stage hydraulic flocculation, direct anthracite-sand biofiltration, chlorination, sodium hydroxide, zinc orthopolyphosphate, fluoride |
| Bennery Lake | Lime, potassium permanganate, carbon dioxide, aluminum sulfate coagulation, three-stage hydraulic flocculation, sedimentation, anthracite-sand filtration, chlorination, sodium hydroxide, zinc orthopolyphosphate |
| Fletcher Lake | Ultrafiltration, nanofiltration, ultraviolet, chlorination |
| Lake Major | Lime, carbon dioxide, aluminum sulfate coagulation, polymer, flocculation, up-flow clarification, prechlorination, anthracite–sand filtration, chlorination, sodium hydroxide, zinc orthopolyphosphate, fluoride |

*The treatment plant at Pockwock Lake was not using seasonal polymer when sampling was conducted.

automation software.[5] This method has a manufacturer-reported calculated method detection limit of 0.5 mg/L and sample analysis time ranging from 5 to 10 min. To measure COD, the analyzer measures the current generated from the photocatalytic oxidation of organic matter using a titanium dioxide catalyst irradiated with UV light from a light-emitting diode. The analyzer performs a direct count of the electrons transferred during the oxidation of the sample. This method of COD determination does not include a digestion step and is therefore considered a measure of soluble COD.

Samples were measured after a single-point calibration with 20 mg/L COD calibrant[6] and calibration verification with calibrant standards of 20, 15, 10, 5, 3, 1, 0.5, and 0.25 mg/L for model organic compounds and of 20, 15, 10, 5, 3, and 1 mg/L for surface waters. The system was operated with a sample-to-electrolyte ratio of 3:1, in which the electrolyte is used to determine the background photocurrent generated by the oxidation of water. Calibration was accepted when the COD-to-charge-generated ratio was between 0.02 and 0.06 COD/µC, the terminal photocurrent generated was > 90% of the 20 µA baseline, and the $R^2$ of the calibration verification was ≥ 0.99. A COD-to-charge-generated ratio in this range ensured that the charge generated from the oxidation reaction was adequate for the expected calibrant concentration (20 mg/L). A terminal photocurrent near the baseline photocurrent ensured that the calibrant was oxidized completely.

**Determination of theoretical oxygen demand (ThOD).** ThOD is the amount of oxygen required to oxidize a given compound based on stoichiometry (Droste, 1997). ThOD was determined according to the equation described by Baker et al (1999):

$$\mathrm{C_nH_mO_eX_kN_jS_iP_h} + b\mathrm{O_2} \rightarrow$$

$$n\,\mathrm{CO_2} + \frac{m-k-3j-2i-3h}{2}\,\mathrm{H_2O} + k\mathrm{HX} + j\mathrm{NH_3} + i\mathrm{H_2SO_4} + h\mathrm{H_3PO_4} \quad (1)$$

in which $X$ is the sum of halogens and

$$b = n + \frac{m-k-3j-2i-3h}{4} - \frac{e}{2} + 2i + 2h \quad (2)$$

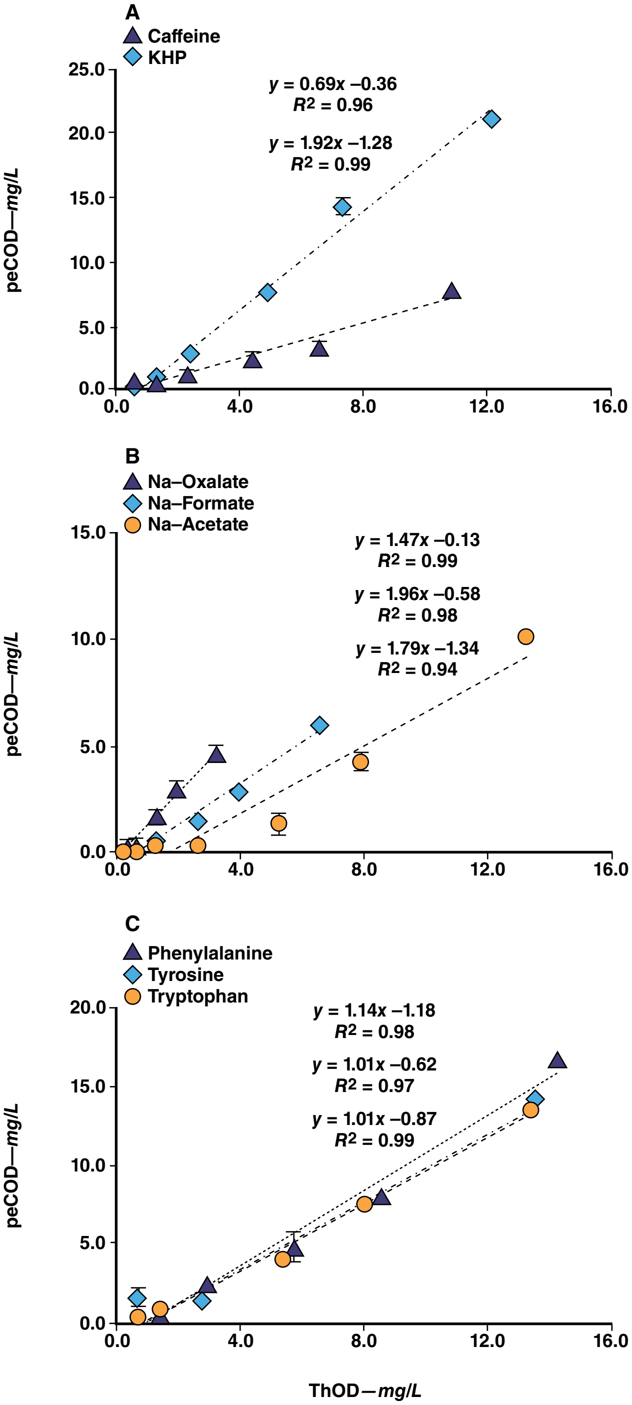
ThOD for sodium acetate, sodium oxalate, and sodium formate dilutions was calculated on the basis of the acid form for each—acetic acid, oxalic acid, and formic acid.

## RESULTS AND DISCUSSION

**Correlation between peCOD and ThOD.** The model organic compounds were used to determine peCOD correlation to ThOD. In this case, a value of unity demonstrated that peCOD was a complete predictor of ThOD. Overall, model compound peCOD measurements showed reasonable correlation with ThOD, with the exception of the reference standards.

The reference standards, caffeine and KHP, had slopes of 0.69 ($R^2$ = 0.96) and 1.92 ($R^2$ = 0.99), respectively (Figure 1, part A). The value of unity was not contained in the 95% confidence interval of the regression slope for either reference compound, indicating peCOD was not a good predictor of ThOD for these compounds.

**FIGURE 1** Relationship between ThOD and peCOD for reference (A), carboxylic acid (B), and amino acid (C) model organic compounds



KHP—potassium hydrogen phthalate, Na—sodium, peCOD—photoelectrochemical chemical oxygen demand, ThOD—theoretical oxygen demand

Error bars represent 95% confidence intervals with *n* = 3.

Oxalate, formate, and acetate had slopes of 1.47 ($R^2$ = 0.99), 0.96 ($R^2$ = 0.98) and 0.79 ($R^2$ = 0.94), respectively (Figure 1, part B). Formate and acetate peCOD correlated well with ThOD as the 95% confidence intervals of both regression slopes contained the expected value of unity. Oxalate gave a statistically higher peCOD/ThOD response than expected. Esler et al (2010) found a similar result in which the COD/ThOD ratio for oxalic acid was greater with peCOD than dichromate COD. Esler et al (2010) attributed this to current doubling (one UV photon yielding two photocurrent electrons) during the photocatalytic reaction. This photocatalytic reaction behavior was unique to oxalic acid among the 34 compounds investigated by Esler et al (2010).

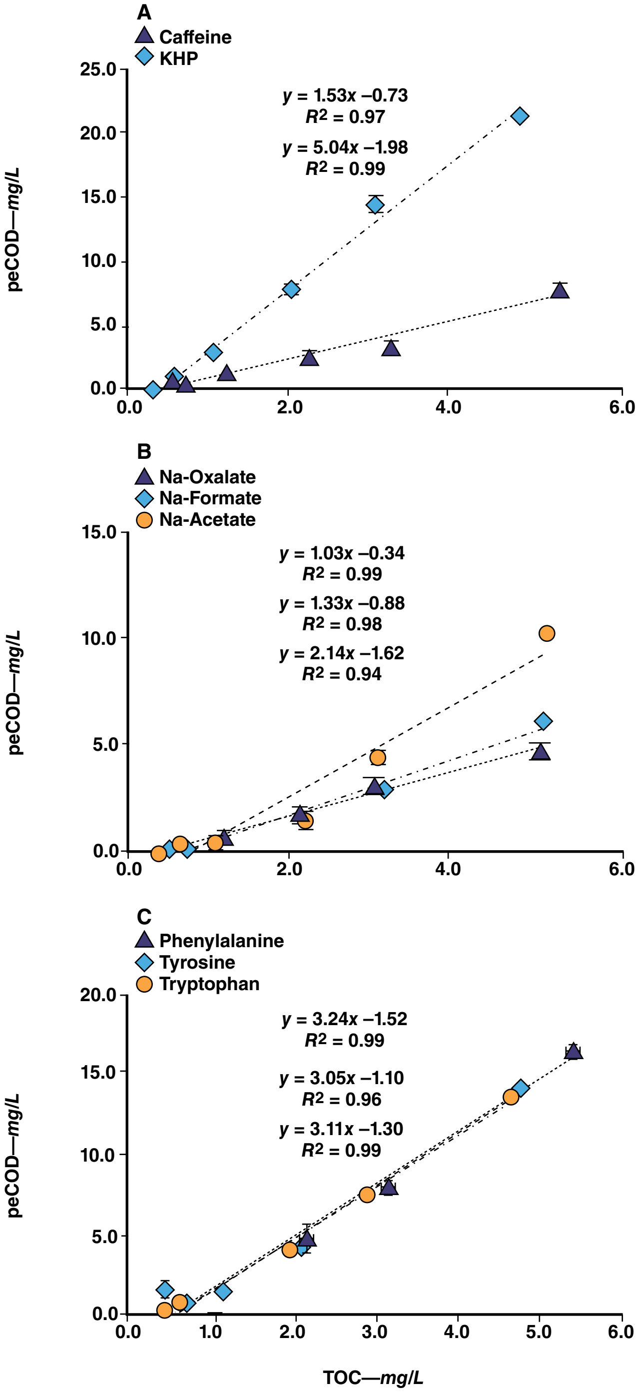
Phenylalanine, tyrosine, and tryptophan had slopes of 1.14 ($R^2$ = 0.98), 1.01 ($R^2$ = 0.97), and 1.01 ($R^2$ = 0.99), respectively (Figure 1, part C). Regressions for all three amino acids had slopes with 95% confidence intervals containing the expected value of unity, demonstrating excellent correlation between amino acid peCOD and ThOD.

**Model compounds.** peCOD-to-TOC relationships were observed for model compounds. On the basis of the stoichiometry of the oxidation reactions, the theoretical COD-to-TOC ratios (molecular ratio of oxygen to carbon) for caffeine and KHP are 2.17 and 2.5, respectively. Measured slopes for caffeine and KHP were 1.53 ($R^2$ = 0.97) and 5.04 ($R^2$ = 0.99), respectively (Figure 2, part A). Theoretical COD-to-TOC ratios were not contained in the 95% confidence interval of the regression slope for either reference compound. This is likely a result of poor correlation of peCOD to ThOD for these compounds as noted earlier.

The theoretical COD/TOC values for oxalate, formate, and acetate are 0.67, 1.33 and 2.67, respectively. The carboxylic acid group had measured slopes of 1.03 ($R^2$ = 0.99), 1.33 ($R^2$ = 0.98) and 2.14 ($R^2$ = 0.94) for oxalate, formate, and acetate, respectively (Figure 2, part B). The intercepts were not statistically different from zero ($p > 0.05$) for two of the three carboxylic acids with formate being the exception ($p = 0.019$). Regressions for formate and acetate had slopes with 95% confidence intervals containing the theoretical COD-to-TOC ratio. The 95% confidence interval for the COD-to-TOC ratio for oxalate did not contain the theoretical COD/TOC value of 0.67. This difference is likely a result of the peCOD overestimation of oxalate ThOD.

Theoretical COD/TOC relationships for phenylalanine, tyrosine, and tryptophan are 2.96, 2.81 and 2.79, respectively. The amino acid group had measured slopes of 3.24 ($R^2$ = 0.99), 3.05 ($R^2$ = 0.96), and 3.11 ($R^2$ = 0.99) for phenylalanine, tyrosine, and tryptophan, respectively (Figure 2, part C). The intercepts were statistically different from zero ($p < 0.05$) for phenylalanine and tryptophan but not for tyrosine ($p = 0.219$). Regressions for all three amino acids had slopes with 95% confidence intervals containing the theoretical COD-to-TOC ratio.

**FIGURE 2** Relationship between TOC and peCOD for reference (A), carboxylic acid (B), and amino acid (C) model organic compounds



KHP—potassium hydrogen phthalate, Na—sodium, peCOD—photoelectrochemical chemical oxygen demand, TOC—total organic carbon

Error bars represent 95% confidence intervals with $n = 3$.

**Surface and treated waters.** Recognizing the potential for peCOD to evaluate NOM in water, four surface waters were analyzed during the course of treatment. peCOD, TOC, DOC, $UV_{254}$, and peCOD/TOC ratio results are provided in Table 3. Results show that raw water peCOD for all locations was < 50 mg/L, preventing use of COD methods 5220Ba, 5220C, and 5220D. Method 5220B can be altered (5220Bb) at the expense of precision and accuracy

**TABLE 3** peCOD, TOC, DOC, $UV_{254}$, and peCOD/TOC ratio for four surface water treatment trains

| Surface Water | Sample Location | peCOD—*mg/L* | TOC—*mg/L* | DOC—*mg/L* | $UV_{254}$—*/cm*$^3$ | peCOD/TOC |
|---|---|---|---|---|---|---|
| Fletcher Lake | Raw | 15.1 | 4.60 | 4.37 | 0.19 | 3.3 |
| | Ultrafilter | 14.4 | 4.29 | 4.25 | 0.17 | 3.4 |
| | Nanofilter | 0.1 | 0.26 | 0.38 | 0.00 | 0.5 |
| Lake Major | Raw | 17.6 | 5.30 | 5.25 | 0.25 | 3.3 |
| | Clarifer | 4.7 | 2.11 | 2.05 | 0.04 | 2.2 |
| | Filter | 4.0 | 1.93 | 1.88 | 0.03 | 2.1 |
| | Finish | 4.0 | 2.05 | 2.00 | 0.03 | 1.9 |
| Bennery Lake | Raw | 20.5 | 5.91 | 5.92 | 0.23 | 3.5 |
| | Floc | 6.5 | 6.48 | 2.87 | 0.05 | 1.0 |
| | Filter | 6.2 | 2.83 | 2.81 | 0.05 | 2.2 |
| | Finish | 6.2 | 2.75 | 2.74 | 0.04 | 2.3 |
| Pockwock Lake | Raw | 7.4 | 2.73 | 2.71 | 0.09 | 2.7 |
| | Floc | 5.6 | 2.83 | 1.97 | 0.04 | 2.0 |
| | Filter | 4.1 | 1.68 | 1.71 | 0.03 | 2.4 |
| | Finish | 3.8 | 1.70 | 1.66 | 0.03 | 2.2 |

DOC—dissolved organic carbon, peCOD—photoelectrochemical chemical oxygen demand, peCOD/TOC—peCOD-to-TOC ratio, TOC—total organic carbon, $UV_{254}$—ultraviolet absorbance at 254 nm

All values are average with *n* = 3.

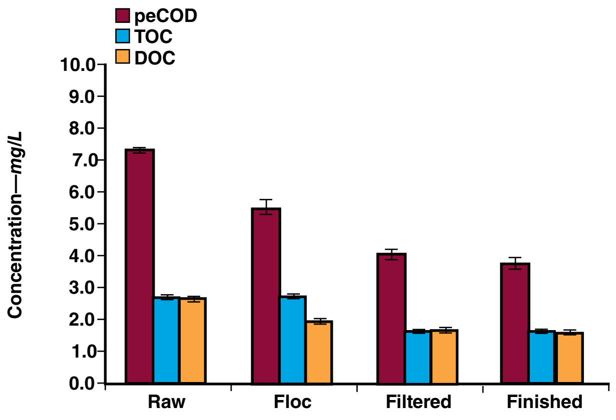
to allow COD determination from 5 to 50 mg/L. The use of this method would allow for COD determination of raw water from the four locations. However, peCOD decreased with treatment progression for all treatment trains, resulting in filtered water peCOD concentrations less than 5 mg/L for three of the four treatment systems investigated.

As with model compounds, peCOD/TOC ratios were calculated for each surface water sample location (Table 3). Measured and compared on a regular basis, these ratios could provide utilities with insight into the relative proportions of oxidizable organic matter, as increases in COD/TOC ratios over reaction times have been attributed to the formation of degradation products and subsequent increase in easily oxidizable organic matter (Balcioglu and Arslan, 1998). Additionally, previous studies with Nova Scotia surface water have shown that TOC was strongly correlated with DBP formation (Waller et al, 1996).

Overall, reductions in peCOD during the course of treatment at all utilities mirrored reductions in TOC and DOC, demonstrating the ability of peCOD to function as a treatment-performance indicator similar to TOC and DOC.

As shown in Table 3, the DOC in Pockwock Lake was reduced from 2.71 mg/L to 1.66 mg/L, or a total of 1.05 mg/L, from raw to finished water. Comparatively, the peCOD reduction from raw to finished water was much greater at 3.6 mg/L. This expanded scale of resolution noted with peCOD could allow for easier detection of subtle changes in treatment performance and subsequent water quality. This expanded scale could be especially important for biofiltration monitoring because the biodegradable fraction of DOC typically represents between 10 and 30% of the total DOC (Joret et al, 1991), often putting DOC reductions across biofilters in the micrograms-per-litre range. For example, reduction in DOC across the filter was similar to values reported elsewhere (Lauderdale et al, 2012) but, as illustrated in Figure 3, Pockwock Lake had a much larger

**FIGURE 3** Comparison of Pockwock Lake peCOD, TOC, and DOC during treatment



DOC—dissolved organic carbon, floc—flocculated water, peCOD—photoelectrochemical chemical oxygen demand, TOC—total organic carbon

Error bars represent 95% confidence intervals with *n* = 3.

peCOD reduction (1.5 mg/L) than DOC reduction (0.26 mg/L) across the biofilter.

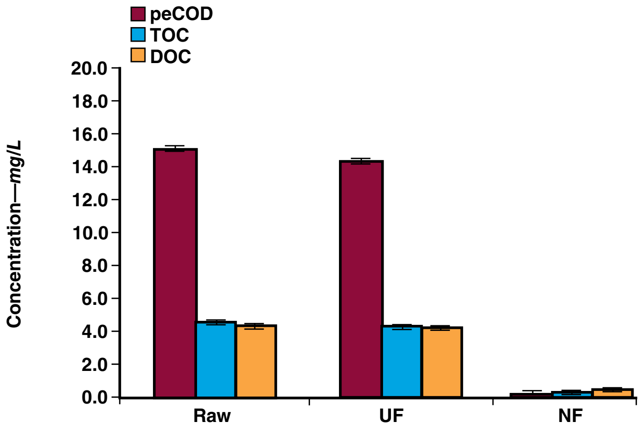
COD is common in monitoring wastewater treatment processes; it has not been used frequently for drinking water because method detection limitations have prevented application in drinking water treatment. The use of TOC to replace COD in the wastewater treatment industry has been cautioned because TOC does not represent the electron-donating capacity of a compound (Mara and Horan, 2003). When assessing the performance of drinking water biological treatment, this has led to the use of slower, more labor-intensive measurement techniques such as assimilable organic carbon and biodegradable DOC (Huck, 1990). With biological treatment gaining popularity in the drinking water industry, rapid assessment tools are required, and determination of COD in the treated drinking water range is increasingly important. Measurable reductions in peCOD across the biofilter at Pockwock Lake show the potential for peCOD use as a biofiltration performance indicator. Measurement of COD at drinking water concentrations would also be beneficial for monitoring oxidation processes preceding biofiltration because COD can distinguish between compounds with the same number of carbon atoms at different oxidation states.

In the Fletcher Lake raw water sample, 95% of TOC was in the dissolved form and, therefore, there was very little reduction of TOC and DOC with ultrafiltration (UF) at this facility. As a result, the majority of TOC and DOC removal at this facility is through nanofiltration causing significant NOM loading to the nanofilter and increasing fouling rates. The difficulties with the membrane process at this treatment facility have been documented elsewhere (Lamsal et al, 2012). As shown in Figure 4, similar to TOC and DOC removal, reduction in peCOD with UF was also limited, with the majority of peCOD removed with nanofiltration demonstrating the ability of peCOD to provide similar treatment performance information to TOC and DOC.

The analysis of surface waters showed that peCOD was correlated with TOC and DOC in four raw and treated surface waters, which is consistent with the model organic compounds studied in this article. The correlations peCOD = 2.69TOC + 0.49 ($R^2$ = 0.64) and peCOD = 3.91DOC – 3.08 ($R^2$ = 0.97) were identified. The slopes of both correlations were significant at $p < 0.01$. The intercept was only significant for the DOC relationship ($p < 0.01$). It was anticipated that peCOD would be better correlated with DOC than TOC because, as previously mentioned, peCOD does not include a digestion step and thus is a measure of soluble COD.

SUVA was also determined during the course of treatment for the four surface waters. SUVA is considered an indicator of aromaticity (Weishaar et al, 2003), which is often associated with reactivity of NOM. The relationship peCOD = 4.27SUVA – 2.26 ($R^2$ = 0.84) was identified for pooled data for samples taken at the source, during treatment and after treatment at the four locations (Figure 5). The slope of the correlation was significant at $p < 0.01$, and the intercept was not statistically different from zero with $p = 0.131$. This relationship shows that peCOD has a relationship with SUVA for the waters tested and could provide additional insight into reactivity of organic matter for these sites.

**FIGURE 4** **Comparison of Fletcher Lake peCOD, TOC, and DOC during treatment**



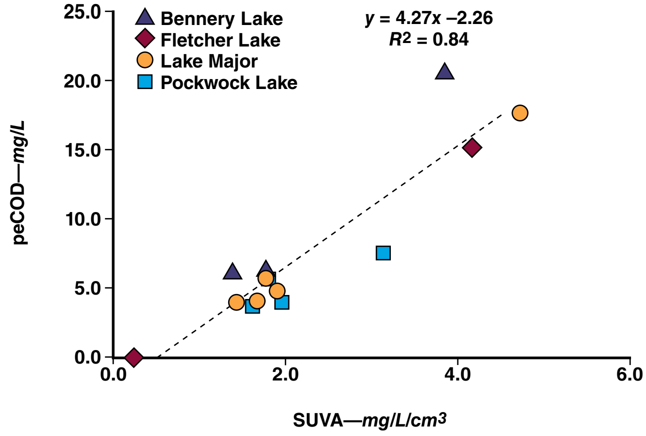
DOC—dissolved organic carbon, NF—nanofiltration, peCOD—photoelectrochemical chemical oxygen demand, TOC—total organic carbon, UF—ultrafiltration

Error bars represent 95% confidence intervals with *n* = 3.

A relationship could be useful in a practical sense because SUVA determination typically involves the use of two analytical tools (spectrophotometer for $UV_{254}$ determination and TOC analyzer for DOC determination), whereas peCOD can be determined rapidly with a single analytical tool.

Overall, it is noteworthy that this work was conducted in oligotrophic Canadian waters, and further work would be required for its suitability to other water matrixes. Although not an issue for the waters investigated in this study, Zhang

**FIGURE 5** **Relationship between SUVA and peCOD for four surface water sources pre-, during, and post-treatment**



peCOD—photoelectrochemical chemical oxygen demand, SUVA—specific UV absorbance at 254 nm and Zhao (2008) found that peCOD was sensitive to chloride concentrations above 26.6 mg/L. To address conductivity concerns, the authors reported that measurement error could be reduced to acceptable levels (i.e., < 5%) with a chloride-to-organics ratio smaller than 5:1. Similarly, the current study provides evidence for the development of peCOD as a useful drinking water NOM surrogate.

## CONCLUSIONS

This article demonstrates the potential for photoelectrochemical determination of COD in the drinking water industry. Analysis with eight reference compounds was reproducible and followed a predictable trend with ThOD and TOC for most compounds. peCOD was also used to monitor NOM at four surface water treatment plants. It was found that the removal of peCOD followed a trend that was similar to other NOM surrogate parameters, such as TOC and DOC. When compared with other surrogate parameters, peCOD had an expanded scale of resolution, highlighting its ability to provide information on treatment performance even when NOM removal is small (e.g., in the micrograms-of-carbon-per-litre range across a biofilter). Given the need for rapid response time in treatment plant analysis, it is conceivable that this tool could be accepted for inline analysis or for analysis of water treatment processes that require more understanding of NOM removal such as biofiltration and advanced oxidation.

## ACKNOWLEDGMENT

The authors acknowledge the support of the Natural Sciences Engineering Research Council(NSERC) and Mantech Inc. through an NSERC Engage Grant, as well as the support of both NSERC and Halifax Water through the NSERC/Halifax Water Industrial Research Chair program. The authors also acknowledge NSERC for funding for Amina Stoddart's PhD work through an NSERC Alexander Graham Bell Post-Graduate Scholarship. In addition, the authors thank Lindsay Peddle from Mantech Inc. for training and technical assistance, and Jordan Schmidt, Dallys Serracin-Pitti, Maggie Grierson, Heather Daurie, and Elliott Wright for laboratory and analysis assistance, and Halifax Water plant staff for surface water sample-collection assistance.

## ABOUT THE AUTHORS

***Amina K. Stoddart** is a PhD candidate in the Department of Civil and Resource Engineering at Dalhousie University where she is studying civil engineering. In 2010, she received a bachelor's degree in biological engineering from the same university, 1360 Barrington St., Halifax, NS B3H 4R2, Canada. She may be contacted at amina.stoddart@dal.ca. Graham A. Gagnon is a professor and the Natural Sciences and Engineering Research Council of Canada/Halifax Water Industrial Research Chair in Water Quality and Treatment at Dalhousie University, Sexton Campus. He may be contacted at graham.gagnon@dal.ca.*

## PEER REVIEW

Date of submission: 01/16/2013
Date of acceptance: 04/22/2014

## FOOTNOTES

[1] TOC-V CPH analyzer, Shimadzu Corp., Kyoto, Japan
[2] DR/4000 U Spectrophotometer and DR 5000™ UV-Vis Laboratory Spectrophotometer, Hach Co., Mississauga, Ont., Canada
[3] PeCOD® L100 AssayPlus™ analyzer, Mantech Inc., Guelph, Ont., Canada
[4] AutoMax™ 73 autosampler, Mantech Inc., Guelph, Ont., Canada
[5] PC-Titrate™ software, Mantech Inc., Guelph, Ont. Canada
[6] Blue range (< 25 mg/L) calibrant, Mantech Inc., Guelph, Ont., Canada

## REFERENCES

Baker, J.R.; Milke, M.W.; & Mihelcic, J.R., 1999. Relationship Between Chemical and Theoretical Oxygen Demand for Specific Classes of Organic Chemicals. *Water Research,* 33:2:327.

Balcioglu, I.A. & Arslan, I., 1998. Application of Photocatalytic Oxidation Treatment to Pretreated and Raw Effluents from the Kraft Bleaching Process and Textile Industry. *Environmental Pollution,* 103:2:261.

Cabaniss, S.E.; Zhou, Q.; Maurice, P.A.; Chin, Y.P.; & Aiken, G.R., 2000. A Log-Normal Distribution Model for the Molecular Weight of Aquatic Fulvic Acids. *Environmental Science & Technology,* 34:6:1103.

Dotson, A. & Westerhoff, P., 2009. Occurrence and Removal of Amino Acids During Drinking Water Treatment. *Journal AWWA,* 101:9:101.

Edzwald, J.K.; Becker, W.C.; & Wattier, K.L., 1985. Surrogate Parameters for Monitoring Organic Matter and THM Precursors. *Journal AWWA,* 77:4:122.

Esler, M.; Chinen, K.; Higginbotham, H.; & Reddy, P., 2010. Systematic Comparison of PeCOD® and Dichromate Methods of COD Measurement for a Suite of 34 Organic Species. Application Note 005 v02, Aqua Diagnostic, Melbourne, Australia.

Huck, P.M., 1990. Measurement of Biodegradable Organic Matter and Bacterial Growth Potential in Drinking Water. *Journal AWWA,* 82:7:78.

Joret, J.C.; Levi, Y.; & Volk, C., 1991. Biodegradable Dissolved Organic Carbon (BDOC) Content of Drinking Water and Potential Regrowth of Bacteria. *Water Science & Technology,* 24:2:95.

Krasner, S.W.; McGuire, M.J.; Jacangelo, J.G.; Patania, N.L.; Reagan, K.M.; & Aieta, E.M., 1989. The Occurrence of Disinfection By-Products in US Drinking Water. *Journal AWWA,* 81:8:41.

Krasner, S.W.; Croué, J.P.; Buffle, J.; & Perdue, E.M., 1996. Three Approaches for Characterizing NOM. *Journal AWWA,* 88:6:66.

Krasner, S.W.; Weinberg, H.S.; Richardson, S.D.; Pastor, S.J.; Chinn, R.; Sclimenti, M.J.; Onstad, G.D.; & Thruston, A.D., 2006. Occurrence of a New Generation of Disinfection Byproducts. *Environmental Science & Technology,* 40:23:7175.

Lamsal, R.; Chaulk, M.; Zevenhuizen, E.; Walsh, M.E.; & Gagnon, G.A., 2012. Integrating Bench- and Full-Scale Nanofiltration Testing for Two Surface Waters. *Journal of Water Supply: Research and Technology—AQUA,* 61:5:291.

Langlais, B.; Reckhow, D.A.; & Brink, D.R. (editors), 1991. *Ozone in Water Treatment: Application and Engineering.* CRC Press LLC, Boca Raton, Florida.

Lauderdale, C.; Chadik, P.; Kirisits, M.J.; & Brown, J., 2012. Engineered Biofiltration: Enhanced Biofilter Performance Through Nutrient and Peroxide Addition. *Journal AWWA,* 104:5:298.

Mara, D. & Horan, N.J. (editors), 2003. *Handbook of Water and Wastewater Microbiology.* Academic Press.

Nieuwenhuijsen, M.J.; Toledano, M.B.; Eaton, N.E.; Fawell, J.; & Elliott, P., 2000. Chlorination Disinfection Byproducts in Water and Their Association with Adverse Reproductive Outcomes: A Review. *Occupational and Environmental Medicine,* 57:2:73-85.

*Standard Methods for the Examination of Water and Wastewater,* 2012 (22nd ed.). APHA, AWWA, and WEF, Washington.

Villanueva, C.M.; Cantor, K.P.; Cordier, S.; Jaakkola, J.J.; King, W.D.; Lynch, C.F.; Porru, S; & Kogevinas, M., 2004. Disinfection Byproducts and Bladder Cancer: A Pooled Analysis. *Epidemiology,* 15:3:357.

Waller, D.H.; MacPhee, M.J.; Prendiville, P.W.; McCurdy, R.F.; Gates, A.W.; & D'Eon, W.J., 1996. Characterization of Nova Scotia Surface Waters and Treatment Options for Removal of Colour and Trihalomethane Precursors. *Canadian Journal of Civil Engineering,* 23:6:1316.

Weishaar, J.L.; Aiken, G.R.; Bergamaschi, B.A.; Fram, M.S.; Fujii, R.; & Mopper, K., 2003. Evaluation of Specific Ultraviolet Absorbance as an Indicator of the Chemical Composition and Reactivity of Dissolved Organic Carbon. *Environmental Science & Technology,* 37:20:4702.

Zhang, S. & Zhao, H. 2008. A New Approach Prevailing Over Chloride Interference in the Photoelectrochemical Determination of Chemical Oxygen Demand. *Analyst,* 12:1684.

Zhao, H.; Jiang, D.; Zhang, S.; Catterall, K.; & John, R., 2004. Development of a Direct Photoelectrochemical Method for Determination of Chemical Oxygen Demand. *Analytical Chemistry,* 76:1:155.