Chapter 11

Mean oxidation state of organic carbon: A novel application to evaluate the extent of oxidation of natural organic matter in drinking water biological treatment

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11.1 INTRODUCTION

Understanding of the oxidation of organic matter by chemical and biological reactions is crucial in water treatment. Much of the literature published on drinking water utilizes total organic carbon (TOC), dissolved organic carbon (DOC) or related parameters to quantify natural organic matter (NOM). In practice, TOC and DOC are used as key indicators of bulk NOM concentration. However, measurement of NOM by TOC/DOC overlooks a key feature of biological stability: organic carbon is an electron donor (Rittmann & Huck, 1989). For example, the same TOC concentration of formic acid (HCOOH) and methanol (CH_3OH) would not represent the same amount of electrons because the oxidation state of carbon in methanol is –2 while that in formic acid is +2 (Rittmann & Huck, 1989). Theoretically, a highly reduced organic carbon would contribute more electrons than a relatively oxidized organic carbon. Therefore, TOC and DOC cannot always provide sufficient information on the transformation of NOM from various drinking water treatment processes, due to the incomplete oxidation of organic carbon. Incomplete oxidation widely exists in biochemical reactions. In incomplete oxidation, NOM cannot be completely converted to the final oxidation product (e.g., carbon dioxide) (Rieger

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et al., 1983). The intermediates of incomplete oxidation would be quantified as TOC/DOC. This disadvantage limits further understanding about the transformation of NOM, especially during biological treatment of drinking water (e.g., biofiltration).

In both complete oxidation and incomplete oxidation, the formation of bonds between oxygen and carbon and the deformation of bonds between hydrogen and carbon increase the oxidation state of organic carbon (Kroll et al., 2011). Combining chemical oxygen demand (COD) with TOC/DOC measurement can provide valuable information on the oxidation state of organic carbon during drinking water treatment. However, the conventional dichromate COD method is not sensitive enough to measure COD in surface water (Rittman & Huck, 1989; Stoddart & Gagnon, 2014). Advancements in sensor development for the determination of COD in water (Zhang *et al.*, 2004) have allowed researchers to rapidly quantify COD during drinking water treatment using photoelectrochemical chemical oxygen demand (peCOD) (Stoddart & Gagnon, 2014). When applied in a full-scale biofiltration drinking water treatment plant, peCOD removal was greater than TOC/DOC removal (Stoddart & Gagnon, 2014), which indicated peCOD might be more sensitive than TOC/DOC analysis for understanding biological treatment performance. Even though peCOD indicated a promising application in drinking water treatment performance monitoring, the lack of understanding of the relationship between peCOD and TOC/DOC in drinking water limits its application. This is due in part to many years of TOC/DOC data which supports our understanding of NOM in drinking water. There is a need to construct a "bridge" to connect the conventional TOC/DOC evaluation system and novel approaches such as the peCOD evaluation system.

Therefore, a concept of mean oxidation state (MOS) of organic carbon ($\overline{Cos}$), combining TOC/DOC and peCOD, is introduced in this study. The major advantages of this method are: (i) $\overline{Cos}$ could provide more information about the transformation of NOM than TOC/DOC, especially when incomplete oxidation dominates the biochemical reactions of treatment; (ii) theoretically, $\overline{Cos}$ only responds to oxidation-reduction reactions, which means that physical removal (e.g., filtration, precipitation and adsorption) does not change the value of $\overline{Cos}$; (iii) $\overline{Cos}$ is a dimensionless number that is not affected by the concentration fluctuation of NOM and only represents the oxidation potentials of organic carbon. In addition, it may be possible to correlate $\overline{Cos}$ with biomass concentration, as determined by measurements such as adenosine triphosphate (ATP), to further understand NOM removal mechanisms during biological drinking water treatment processes, such as biofiltration.

11.2 BACKGROUND

11.2.1 Quantifying natural organic matter by Photoelectrochemical Chemical Oxygen Demand (peCOD)

Photoelectrochemical chemical oxygen demand (peCOD) is a rapid and environmentally friendly COD measurement method that holds promise for the

drinking water industry (Stoddart & Gagnon, 2014). The determination of peCOD involves the mineralization of organic matter by titanium dioxide (TiO_2) under ultraviolet (UV) irradiation.

Photo-generated holes, formed by the illumination of TiO_2 with photons, have a powerful oxidation capacity for almost all organic matter in water (Qiu *et al.*, 2012). However, oxygen concentration (e.g., less than 10 ppm at 25°C, 1 atm) could inhibit the reaction rate of mineralization process (Equation (1)) in a conventional TiO_2 photocatalysis system.

$$C_xH_yO_zX_q + \left(x + \frac{y - 2z - q}{4}\right)O_2 \rightarrow xCO_2 + xH^+ + qX^- + \left(\frac{y - x}{2}\right)H_2O \quad (1)$$

The peCOD method utilizes immobilized nanostructured TiO_2 and an electric field to improve the oxidation efficiency. In a peCOD system, the nanostructured TiO_2 is immobilized on conducting materials which functions as the working electrode. A force generated by the electric field separates the photoelectron from TiO_2 particles (Zhang *et al.*, 2004). Therefore, the reduction reactions on the auxiliary electrode replace the function of adsorbed O_2 (Qiu *et al.*, 2012). The generated electron can be quantified and converted to COD concentration by Faraday's law.

11.2.2 Mean Oxidation State (MOS) of organic carbon (Cos)

During the biological oxidation of NOM in drinking water treatment, not all organic carbon is converted to carbon dioxide (CO_2) or other inorganic carbon (e.g., CO_3^{2-} and HCO_3^{1-}). Accordingly, TOC/DOC measurements cannot quantify intermediate compounds that are formed during oxidation. Previous studies indicated that Cos could be used to investigate the oxidation potential of carbon in advanced oxidation processes (AOPs) (Vogel *et al.*, 2000; Mantzavinos *et al.*, 1996). The following assumptions were used to derive the concept of Cos in drinking water:

(i) NOM is the most abundant organic compound in treated drinking water.
(ii) The value of peCOD can represent the amount of NOM.
(iii) In treated drinking water, the number of organically bound heteroatoms (i.e., S, P, and Cl) is negligible compared to C, H, O, and N. In other words, Cos is determined mostly by the ratios among C, H, O, and N.
(iv) H has an oxidation state of +1, O has an oxidation state of –2, and N has an oxidation state of –3.

Zhao *et al.* (2004) described the stoichiometric photoelectrochemical oxidation of organic compounds by Equation (2).

$$C_yH_mO_jN_kX_q + (2y - j)H_2O \rightarrow yCO_2 + qX^- + kNH_3 + (4y - 2j + m - 3k)H^+ + (4y - 2j + m - 3k - q)e^- \quad (2)$$

where *X* represents a halogen atom; the numbers of C, H, O, N and halogen atoms are represented by *y*, *m*, *j*, *k* and *q*.

Therefore, peCOD is expressed by Equation (3). $\overline{\text{Cos}}$ can be expressed by TOC (or DOC) and total peCOD (or dissolved peCOD) as shown in Equation (4) (Mantzavinos *et al.*, 1996).

$$\text{peCOD (mol O}_2\text{)} = \frac{(4y - 2j + m - 3k - q)}{4} \tag{3}$$

$$\overline{\text{Cos}} = \frac{\sum_1^i n_i \text{OSC}_i}{\sum_1^i n_i} = \frac{2j - m + 3k + q}{y} = \frac{4(\text{TOC} - \text{total peCOD})}{\text{TOC}} \tag{4}$$

where n_i is the molar concentration; OSC_i is the oxidation state of organic carbon for individual species i; TOC is in mol C/L; total peCOD is in mol O_2/L.

11.2.3 Biomass Adenosine Triphosphate (ATP)

Adenosine triphosphate (ATP) carries the energy in cellular metabolism and is the primary compound for most biochemical enzymatic reactions (Tifft & Spiegel, 1976). In general, ATP is regarded as a key indicator of biochemical reactions and can be used to indicate the presence and abundance of active/viable biomass (Berney *et al.*, 2008). ATP concentration is quantified by the light produced from luciferin/luciferase enzyme with Mn^{2+} and O_2. The reactions between ATP, adenosine 5′-monophosphate (AMP) and the luciferin/luciferase enzyme are shown in Equations (5) and (6) (Marques & Esteves da Silva, 2009).

$$\text{Luciferin} + \text{Luciferase} + \text{ATP} - \text{Mg}^{2+} \leftrightarrow \text{Luciferase} \cdot \text{Luciferin} - \text{AMP} + \text{Pyrophosphate} - \text{Mg}^{2+} \tag{5}$$

$$\text{Luciferase} \cdot \text{Luciferin} - \text{AMP} + \text{O}_2 \rightarrow \text{Luciferase} + \text{AMP} + \text{CO}_2 + \text{Oxyluciferin} + \text{Photon} \tag{6}$$

Reaction with luciferase enzyme and quantification of the photon emitted in relative light units (RLU) using a luminometer enable ATP measurements using rapid test procedures (i.e., approximately 5 min per sample). Commercial ATP test kits with favourable precision, accuracy, span, representativeness and selectivity/specificity (Evans *et al.*, 2013b) are now available for the water industry. The ability to rapidly measure ATP has notable applications in the water industry where conventional biomass quantification techniques require hours – if not days – to complete (i.e., heterotrophic plate counts [HPC]).

Many studies have found correlations between ATP and conventional biomass analysis methods in drinking water treatment. Delahaye *et al.* (2003) found that ATP concentration was correlated with HPC by investigating a drinking water distribution system in Paris. Dowdell (2012) reported a correlation coefficient of

0.91 between biomass ATP and phospholipid content in drinking water biofilters. Furthermore, ATP measurements on granular activated carbon (GAC) have been shown to correlate with total direct bacterial cell counts (Magic-Knezev & van der Kooij, 2004).

Currently, there is a specific need for monitoring tools for drinking water biofiltration that can provide insight on biofilter biomass to improve filter operation and ensure process optimization (Evans *et al.*, 2013a). ATP measurements have been used to assess when GAC (Velten *et al.*, 2011) and anthracite-sand (Stoddart & Gagnon, 2015; Stoddart *et al.*, 2016) filters have become biologically active. An evaluation of several full-scale drinking water biofilters conducted by Evans *et al.* (2013a) found that order of magnitude changes in ATP concentration over time is considered significant. For example, Stoddart *et al.* (2016) converted a full-scale conventional filter to biofiltration and demonstrated that biomass ATP had an initial concentration of 60 ng ATP/cm^3 media and matured to 270 ng ATP/cm^3 media once steady-state was achieved (approximately 220 days after conversion to biofiltration).

11.3 MATERIALS AND METHODS

11.3.1 Full-scale drinking water biofilters

The investigation of full-scale drinking water biofilters was conducted in J. D. Kline Water Supply Plant, Halifax, Nova Scotia, Canada. J. D. Kline Water Supply Plant is a direct filtration water treatment plant with a designed capacity of 227 ML/day (Figure 11.1). The source water comes from Pockwock Lake, which is characterized as low-turbidity (~0.4 NTU), low-alkalinity (<1mg/L), low-pH (~5.5), and low-organic carbon (~2.5 mg DOC/L; ~2.5 mg TOC/L) (Stoddart *et al.*, 2016; Stoddart & Gagnon, 2015; Vadasarukkai *et al.*, 2011).

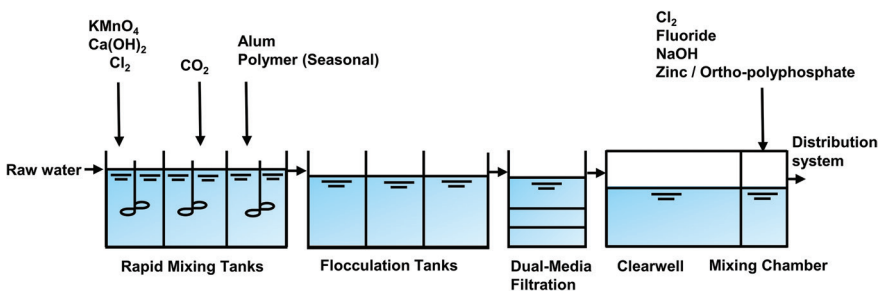

Figure 11.1 Schematic of J.D. Kline Water Supply Plant, Halifax, Nova Scotia, Canada.

In the J. D. Kline Water Supply Plant, the pre-mix process involves the addition of calcium hydroxide and potassium permanganate for the oxidation of

metal, pH adjustment by carbon dioxide, and coagulation with aluminium sulfate. Flocculation is conducted using three-stage hydraulic mixing. Eight dual media anthracite-sand filters (600 cm of anthracite, 300 cm of sand) are used as biofilters. Detailed information concerning the biofiltration performance for this facility is described elsewhere (Stoddart *et al*., 2016; Stoddart & Gagnon, 2015).

Two biofilters (biofilter A and biofilter B) were operated in parallel for the duration of the study. Biofilter influent water (common to both biofilters), biofilter A effluent, biofilter B effluent and filter media from the tops (0–10 cm) of both filters were sampled at various points during a 53 h filter cycle.

11.3.2 Analytical methods

11.3.2.1 Total organic carbon (TOC)/dissolved organic carbon (DOC)

TOC and DOC were monitored on influent and effluent of biofilters. DOC samples were filtered through preconditioned 0.45 µm polyethersulfone filter membranes and stored in headspace-free 40 mL vials, preserved at 4°C to pH < 2 by phosphoric acid addition. TOC and DOC samples were analyzed with a TOC-V CPH analyzer (Shimadzu Corp, Kyoto, Japan).

11.3.2.2 Photoelectronchemical chemical oxygen demand (peCOD)

Total peCOD and dissolved peCOD (0.45 µm polyethersulfone filter membrane) were monitored on influent and effluent of biofilters. All samples were preserved at 4°C to pH < 2 by addition of sulfuric acid. Samples were measured using a PeCOD® L100 AssayPlus™ analyser (Mantech Inc., Guelph, Canada) after neutralizing to pH 7.0 with sodium hydroxide. The water samples were analysed as described by Stoddart and Gagnon (2014).

11.3.2.3 Adenosine triphosphate (ATP) of biomass

Filter media samples from two paired biofilters were taken from the top of each filter bed using a sampling pole fitted with a wide mouth polypropylene bottle. Biomass ATP was measured immediately using 1 g (wet weight) subsamples. The biological activity of biomass was measured by ATP using surface analysis test kits (Deposit Surface Analysis test kit, LuminUltra Technologies Ltd., Fredericton, Canada) and a luminometer (PhotonMaster™ Luminometer, LuminUltra Technologies Ltd., Fredericton, Canada). In short, this method involved biomass extraction from filter media using chemical removal, followed by a dilution of the extracted biofilm suspension. Luciferin/luciferase enzyme was used to react with the ATP of diluted biofilm suspension to emit light. The biomass ATP concentration was quantified by the intensity of light using a luminometer.

11.3.2.4 Data analysis

The growth phase of biomass was analysed as described by Baranyi & Roberts (1994) and Stoddart *et al.* (2016). Statistical summary and local polynomial regression were performed using the R programming language (version 3.3.3).

11.4 RESULTS AND DISCUSSION

11.4.1 Mean oxidation state of organic carbon before/after biofiltration

The evolution of $\overline{Cos}$ was investigated in two paired full-scale drinking water biofilters. After biofiltration, average TOC decreased from 3.2 mg/L (biofilter influent) to 2.2 mg/L (effluent of biofilter A) and 2.2 mg/L (effluent of biofilter B) (Table 11.1). Average TOC concentrations of both biofilter effluents were almost the same as the biofilter effluent DOC of 2.1 mg/L (biofilter A) and 2.1 mg/L (biofilter B). No significant decrease in DOC occurred from biofiltration. This indicated that primarily particulate TOC (e.g., the floc formed from coagulation and flocculation) had been removed by filtration and that DOC represented the vast majority of residual organic carbon in the biofilter effluent.

Table 11.1 Summary of water qualities in influent and effluents of biofilters.

	Avg. TOC (mg/L)	Avg. DOC (mg/L)	Avg. Total peCOD (mg/L)	Avg. Dissolved peCOD (mg/L)
Influent ($n = 7$)	3.2 ± 0.1	2.2 ± 0.1	8.3 ± 0.6	7.3 ± 0.5
Biofilter A ($n = 11$)	2.2 ± 0.2	2.1 ± 0.1	5.1 ± 1.0	4.4 ± 0.6
Biofilter B ($n = 11$)	2.2 ± 0.2	2.1 ± 0.1	5.1 ± 0.9	4.4 ± 0.8

Significant removal of peCOD was observed after biofiltration; total peCOD and dissolved peCOD decreased 39% and 40%, respectively. Total and dissolved $\overline{Cos}$ increased after biofiltration (Figure 11.2). Total $\overline{Cos}$ increased from 0.12 to 0.46 (biofilter A) and 0.49 (biofilter B). Dissolved $\overline{Cos}$ increased from –1.2 to 0.79 (biofilter A) and 0.83 (biofilter B). The increased dissolved $\overline{Cos}$ and relatively consistent DOC before/after biofiltration suggests that the majority of dissolved organic carbon underwent incomplete oxidation and still existed in water as DOC, while a small amount of DOC (0.08 to 0.09 mg/L) was completely oxidized to inorganic carbon. The difference of total $\overline{Cos}$ before/after biofiltration was lower than that of dissolved $\overline{Cos}$ which may be because the particle TOC cannot be completely oxidized by the peCOD system without digestion.

The increase in $\overline{Cos}$ indicated the incomplete oxidation of NOM provided electrons for biomass growth in both biofilters. It proved suggested that, during

biofiltration, biomass utilized NOM as substrate to support metabolism. Some NOM was completely oxidized as inorganic carbon, which represents the removal of DOC. On the other hand, the increased $\overline{Cos}$ means the source of electrons comes not only from complete oxidation of NOM but also from incomplete oxidation of NOM. The application of $\overline{Cos}$ provides another method to evaluate the performance of biofiltration, because TOC/DOC overlooks the electrons that come from the incomplete oxidation of organic carbon. The combination of TOC/DOC and $\overline{Cos}$ would provide a comprehensive understanding of the transformation of NOM during the biofiltration.

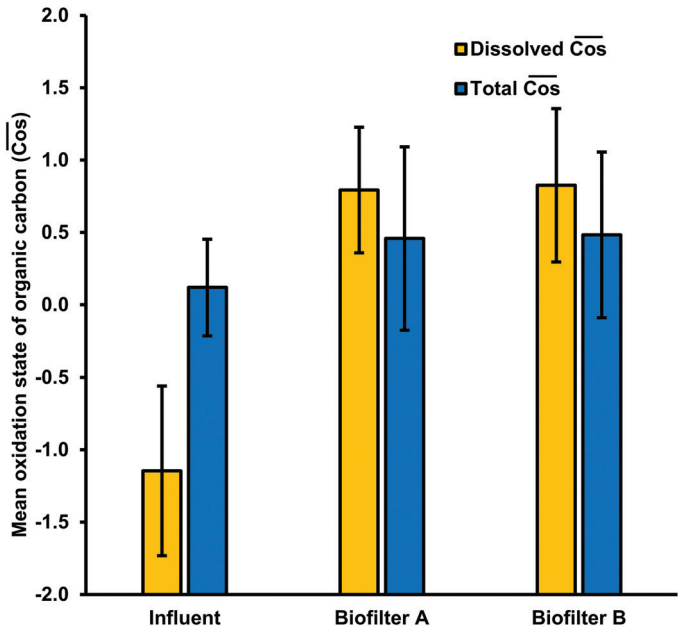

Figure 11.2 Mean oxidation state of dissolved organic carbon (dissolved $\overline{Cos}$) and total organic carbon (total $\overline{Cos}$) in influent and effluents of biofilter A and biofilter B.

11.4.2 Evolution of biomass ATP and mean oxidation state of organic carbon

In both biofilters, evolutions of $\overline{Cos}$ and biomass ATP concentration demonstrated a similar trend (Figure 11.3). In biofilter A, the increased biomass ATP concentration at 24 to 47 h corresponded to the increased $\overline{Cos}$. In biofilter B, the rapid increase of biomass ATP concentration at 3 to 22 h and 29 to 53 h corresponded to the increased $\overline{Cos}$ at 5 to 22 h and 29 to 53 h. In addition, the rapid decrease of $\overline{Cos}$ seems to have followed the decrease of biomass ATP. The decrease of $\overline{Cos}$ at 2 to 5 h and at 22

to 24 h in biofilter A, and that at 22 to 29 h in biofilter B also corresponded to the rapid decrease in biomass ATP. The local polynomial regression of the biomass ATP and $\overline{Cos}$ (Figure 11.4) indicated that the extent of oxidation increased with the maturation of biomass. Based on the biomass growth model described by Baranyi and Roberts (1994) and Stoddart *et al.* (2016), the exponential phase was regarded as the first few hours of biofilter operation. This corresponded to ATP ≤ 370 ng/g during the exponential phase and ATP > 370 ng/g during the steady phase. $\overline{Cos}$ increased gradually during the exponential phase. Then, total $\overline{Cos}$ of the fitting curve increased from 0 to 1.5 and dissolved $\overline{Cos}$ of the fitting curve increased from 0.5 to 1.5, when the biomass ATP was greater than approximately 380 ng/g during the steady growth phase.

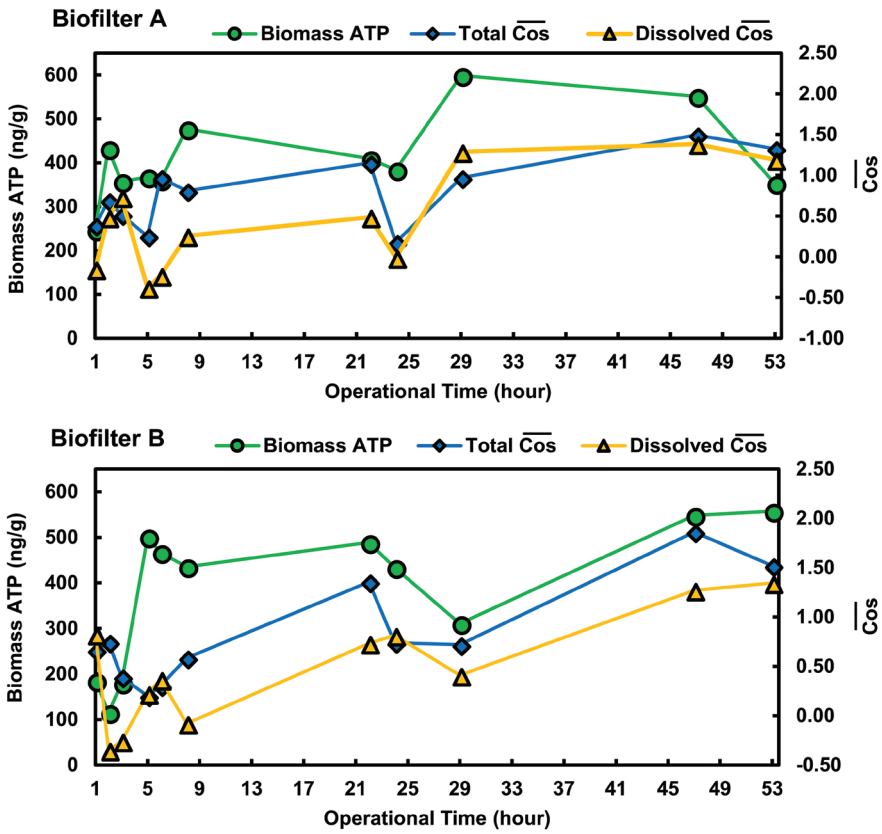

Figure 11.3 Biomass ATP and mean oxidation state of dissolved organic carbon (dissolved $\overline{Cos}$) and total organic carbon (total $\overline{Cos}$) in effluent of biofilter A (top) and biofilter B (bottom) within one filter cycle.

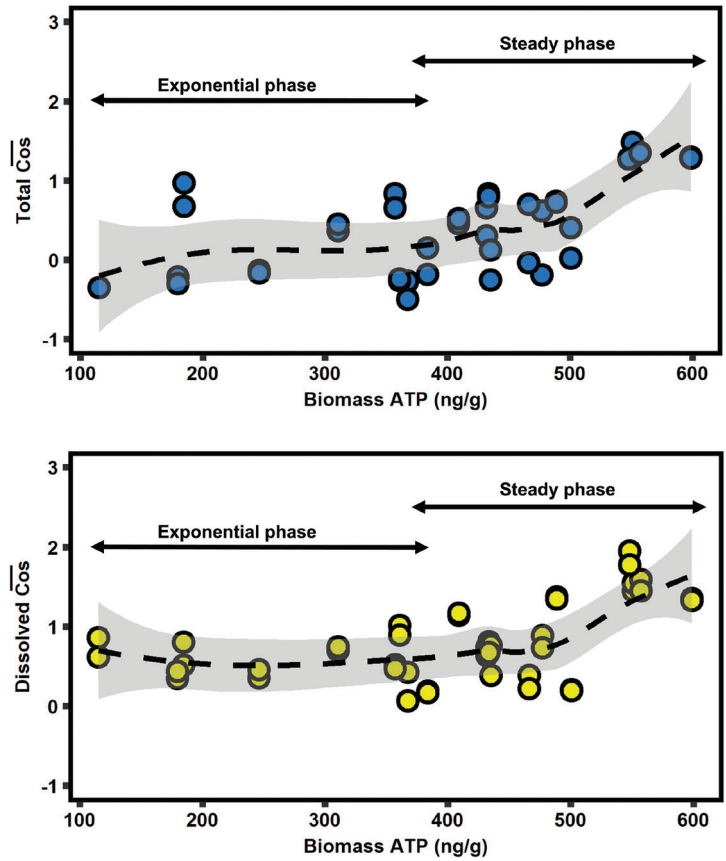

Figure 11.4 Local polynomial regression of biomass ATP and mean oxidation state of organic carbon (total $\overline{Cos}$ and dissolved $\overline{Cos}$). The grey background is the 99% confidential interval. The exponential phase and steady phase were determined by the growth model described by Baranyi and Roberts (1994) and Stoddart *et al.* (2016).

The same trend between $\overline{Cos}$ and biomass ATP indicated the possible relationship between food substrate and biomass growth. Both complete oxidation and incomplete oxidation of NOM contribute electrons to biomass growth, which results in the increase/decrease in biological activity (i.e., biomass ATP). Due to the limitation of TOC/DOC analysis, biomass ATP is not necessarily related to TOC or DOC removal (Pharand *et al.*, 2014). The possible relationship between $\overline{Cos}$ and biomass ATP was shown in this study. It is noted that not all data points were fitted within the 99% confidence interval, especially when the biomass ATP was in the range of 350 to 400 ng/g. The ATP growth model derived from Stoddart *et al.* (2016) in the same biofilters indicated that the biomass growth shifted from exponential phase to steady

phase when biomass ATP was around 370 ng/g. The change in biomass concentration during this period provides a possible explanation for the fluctuation in effluent water quality. These data point to the need for a greater dataset and use of rapid test procedures such as ATP and peCOD. Although the data set presented in this Chapter was small in size, the relationships point to an opportunity for integrating rapid tests procedures to improve decision making in biological treatment processes.

11.4.3 Implications for drinking water utilities

The present work demonstrates that $\overline{Cos}$ can be used an indicator to evaluate the transformation of NOM in drinking water treatment processes with low oxidation efficiency (e.g., biofiltration). The results of full-scale biofilters provide insights that $\overline{Cos}$ could be useful for monitoring the performance of drinking water biofilters when coupled with other measurements (e.g., biomass ATP). In drinking water treatment, conventional TOC/DOC only provides information about physical removal and complete oxidation of organic carbon. Except for physical removal (e.g., filtration or adsorption), in a low-oxidation efficiency system (e.g., biofiltration), incomplete oxidation of organic carbon may play a major role which would not result in the significant removal of TOC/DOC. If NOM transformation is not detected, TOC/DOC measurement might not provide information about the performance of biological treatment in biofilters. For example, TOC/DOC removal results may not correlate to water quality objectives (e.g., reduction of disinfection byproduct formation). However, $\overline{Cos}$, combining peCOD and TOC/DOC analyses, is an easily accomplished method to evaluate the incomplete oxidation of organic carbon in biological treatment. Through the monitoring of $\overline{Cos}$, drinking water utilities would obtain more information about the reactivity of NOM and performance of biological treatment.

In addition, the mass balance between substrate and biomass is the foundation of biological treatment. However, in drinking water biofiltration, the relationship between substrate (i.e., TOC/DOC) and biomass (i.e., ATP) is still unclear. The possible reason is, besides the complete oxidation of organic carbon, the incomplete oxidation of organic carbon also contributes electrons to the metabolism of microorganisms. In this study, a possible relationship between $\overline{Cos}$ and biomass ATP has been observed in full-scale biofilters. Therefore, $\overline{Cos}$ could close the gap in the relationship between substrate and biomass in drinking water treatment. Finally, many years TOC/DOC built our understanding of NOM in drinking water treatment; however peCOD is gradually being applied in more and more research studies and industrial projects (e.g., pulp and paper, and breweries). TOC/DOC and peCOD are two different methods to quantify NOM in drinking water, which result in different measurement results (e.g., percentage removal). $\overline{Cos}$ is a connection between these two parameters, which would help us to have a better understanding of the conventional TOC/DOC and unconventional peCOD measurements.

11.5 CONCLUSION

Mean oxidation state (MOS) of organic carbon ($\overline{Cos}$) is a promising indicator to evaluate the extent of oxidation of NOM in drinking water treatment. The application of $\overline{Cos}$ provided additional valuable information about the transformation of NOM during drinking water biofiltration, which solved the limitation of conventional TOC/DOC analysis in relation to incomplete oxidation. In a low-energy/oxidant consuming treatment scenario (i.e., biofiltration), TOC/DOC could not quantify the incomplete oxidation of NOM. Incomplete oxidation of organic carbon increases the oxidation state of carbon and does not improve the removal of TOC/DOC. $\overline{Cos}$ could represent the incomplete oxidation NOM to give a more comprehensive evaluation of the performance of biofiltration. In this case study, the increased $\overline{Cos}$ and relatively consistent DOC concentration indicated that incomplete oxidation was the dominant biochemical function in the studied biofilters. Notably, $\overline{Cos}$ was correlated with biomass ATP; $\overline{Cos}$ and biomass ATP indicated the same trend within a filter cycle, which has not been observed before.

Since this study only investigated two full-scale biofilters within one filter cycle, further studies and long-term investigations are required to validate the relationship between biomass ATP concentration and $\overline{Cos}$ in full-scale drinking water biofilters identified in this case study.

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