A Comparison of Photoelectrochemical Oxygen Demand to Traditional Methods for Monitoring Natural Organic Matter in Surface Water

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Introduction

Natural Organic Matter (NOM) refers to a group of carbon-based compounds found in natural water systems formed by decomposition of organic materials and associated metabolic reactions. While NOM itself does not pose a risk to human health, some NOM compounds are known to react with chlorine and chloramines in drinking water treatment to produce carcinogenic disinfection by-products (DBPs) such as Trihalomethanes (THMs) and Haloacetic Acids (HAAs).

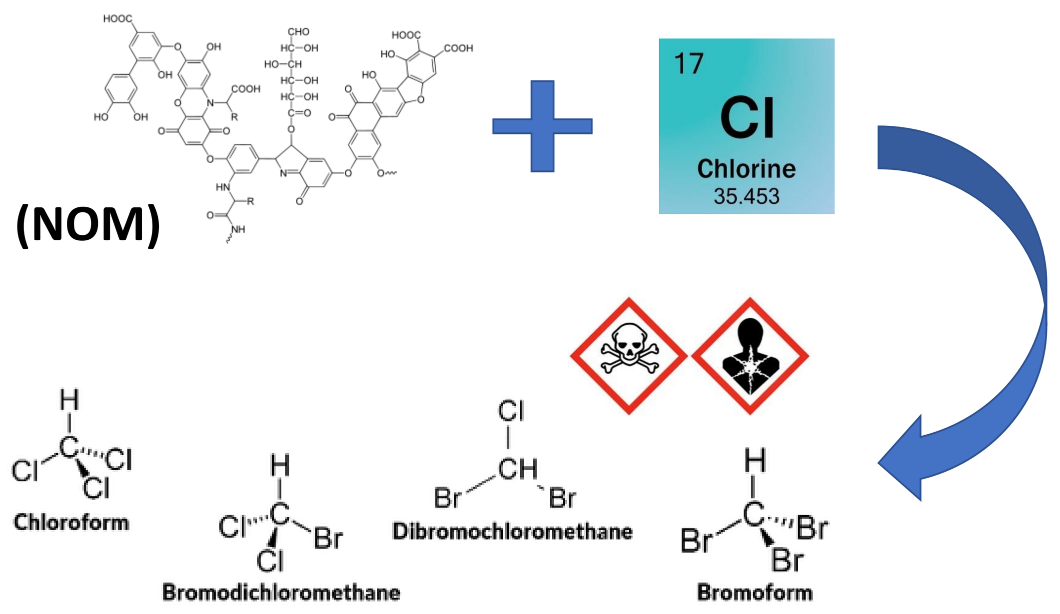

Figure 1: Disinfection By-Product (DBP) Formation Pathway

While it is possible to remove harmful DBPs post-treatment, this is very often not economically viable [1]. It is far more cost-effective to remove compounds that are known precursors to DBP formation, and effective removal requires a rapid method for accurately detecting and quantifying these precursor compounds. Drinking water utilities are being called upon across the world to address the growing concern over NOM and DBPs, leading to a demand for a monitoring solution that can detect, quantify, and characterize influent NOM to a treatment plant.

Existing Technology

Specific monitoring protocol differs between utilities based on source quality and expected temporal fluctuations. Some of the most common source monitoring parameters include Total Organic Carbon (TOC), Dissolved Organic Carbon (DOC), Ultraviolet Absorbance at 254nm (UV254), and Specific Ultraviolet Absorbance (SUVA). These may be monitored continuously online, or hourly/daily by grab sample. Each of these methods has limitations; TOC and DOC are only able to quantify carbon, shedding no light on oxidizability of the organics, and ultraviolet absorbance methods show a bias towards aromatic compounds.

Figure 2: Online TOC, UV254, and SUVA Analyzers at Massachusetts Utility.

1 – Reckhow, D., Singer, P. (2011) 19 - Formation and Control of Disinfection By-Products. In J. Edzwald (Ed.) *Water Quality and Treatment : a handbook on drinking water.* New York, New York: McGraw -Hill.

PeCOD® Technology

Photoelectrochemical Oxygen Demand (peCOD) is a new method for measurement of soluble organics, and has proven to be an effective parameter for quantification of NOM compounds in previous studies by Dalhousie University [2]. The working principle revolves around a 3-5 minute photo-catalyzed oxidation of organic species by immobilized Titanium Dioxide (TiO2).

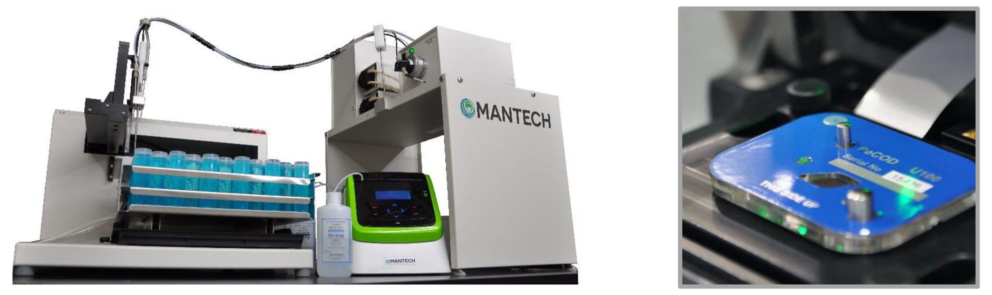

Figure 3: Automated PeCOD® Analyzer; TiO2 PeCOD® Sensor

The oxidation produces energy, which is captured in the form of electrons transferred to a working electrode. The total charge of transferred electrons is proportional to the Chemical Oxygen Demand (COD) of the sample.

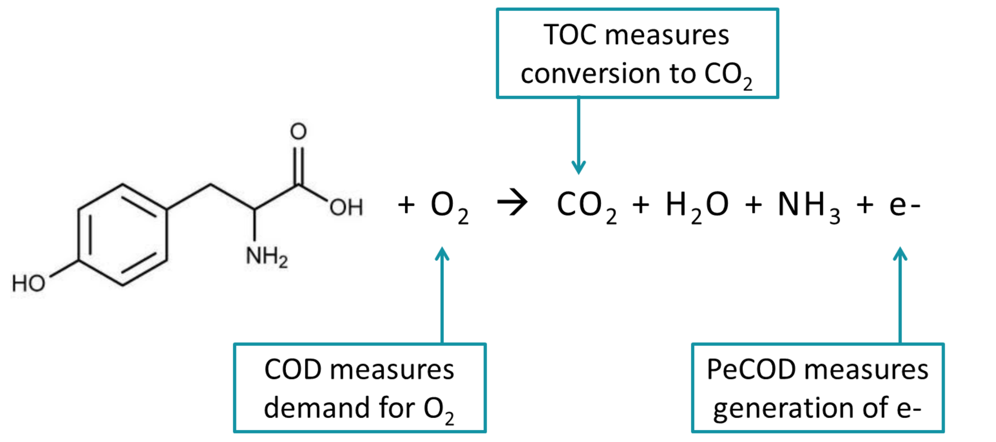

Figure 4: Oxidation Chemistry for COD, TOC, and peCOD

The PeCOD® Analyzer has a minimum detection limit of 0.7 mg/L, making it very suitable for monitoring both source and treated water. ASTM International released a standardized peCOD method in November 2017 based on the application of source and treated water. At an OWWA Treatment Seminar in March 2018, Health Canada presented that peCOD is included in the "NOM in Drinking Water Guidelines" alongside traditional parameters (TOC, DOC, UV254) [3]. It was also noted that peCOD gives indication of the **oxidizability** of the NOM, which relates to DBP formation potential, as well as taste, odour and colour issues.

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Standard Test Method for Photoelectrochemical Oxygen Demand of Freshwater Sources for Drinking Water Treatment Plants and Treated Drinking Water[1]

Objectives

The main objective of this study was to compare peCOD to traditional methods for monitoring NOM in an online monitoring scenario for one year; taking note of event detection capabilities, sensitivity to changes at high and low levels, ease of operation, and total uptime over the year.

2 – Stoddart, A., Gagnon, G. *Application of photoelectrochemical oxygen demand to drinking water*. Journal AWWA 106-9 (2014), E383-E390.

Materials and Methods

- Beginning in 2017, MANTECH worked with the University of Massachusetts-Amherst and a Massachusetts Water Utility to compare peCOD, TOC, and UV254 on the influent to a pilot-scale drinking water treatment plant.
- Influent to the plant was from a tributary stream to the Connecticut River, water supply for millions of people in Connecticut and New York.
- Online monitoring tools were set up in parallel, and sample stream was run through a coarse filter before running through analyzers.
- peCOD performed sampling once per hour, TOC performed a sample once every 3 minutes, and UV254 was measured every 30 seconds.
- Results for UV254 were multiplied by a factor of 20 to allow for easier numerical comparison to TOC and peCOD.

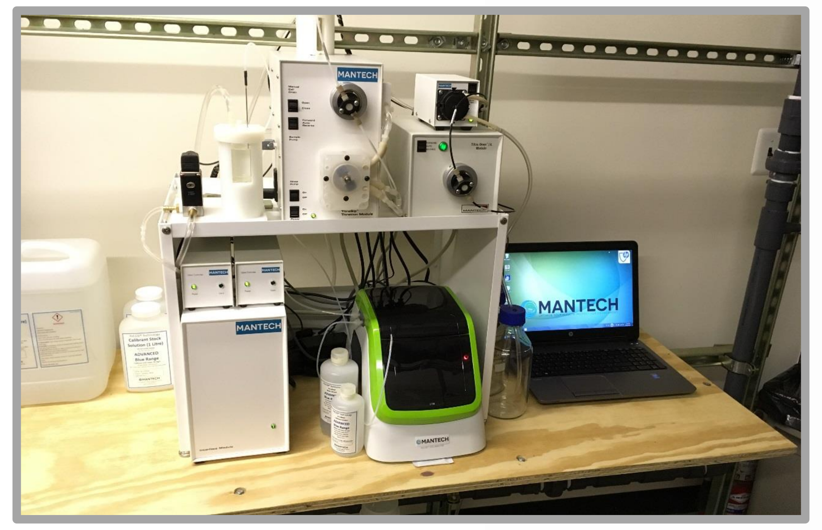

Figure 5: Online PeCOD® Analyzer at Massachusetts Utility

Data and Results

The first year of monitoring revealed a great deal about how peCOD, TOC, and UV254 respond to events affecting treatment conditions such as large storms producing runoff, large snowmelt events during the winter, and low-flow periods. Some interesting event responses and ambient conditions are highlighted in the following data graphs:

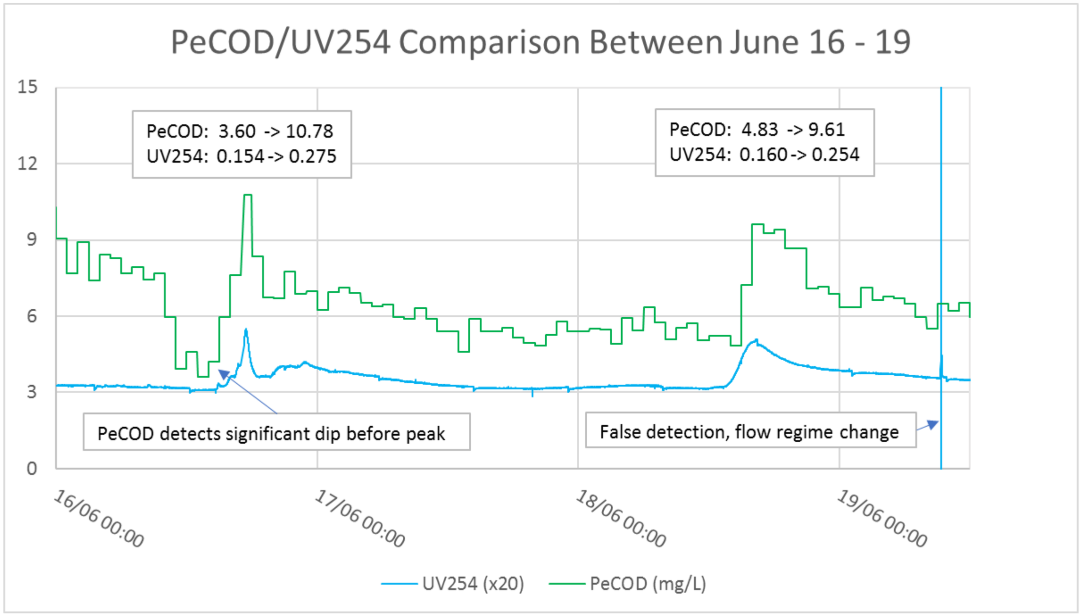

Figure 6: peCOD/UV254 Comparison Between June 16 – 19, 2017

3 – MacDonald, J. (2018, March) *Natural organic matter in drinking water*. Presentation at OWWA Water Treatment Seminar, Toronto.

Figure 6 shows a comparison between peCOD and UV254 over three days. The TOC analyzer was offline during these dates. The data shows that peCOD and UV254 picked up on the two spikes related to rain events. Interestingly, peCOD also picked up on a significant drop for 4-5 hours before the spike began, which was not registered on UV254. This behavior was seen multiple times, and it was hypothesized that it was picking up on a dilution of the river water by runoff, before organic material was stirred up, causing the spike. More data is necessary to confirm this.

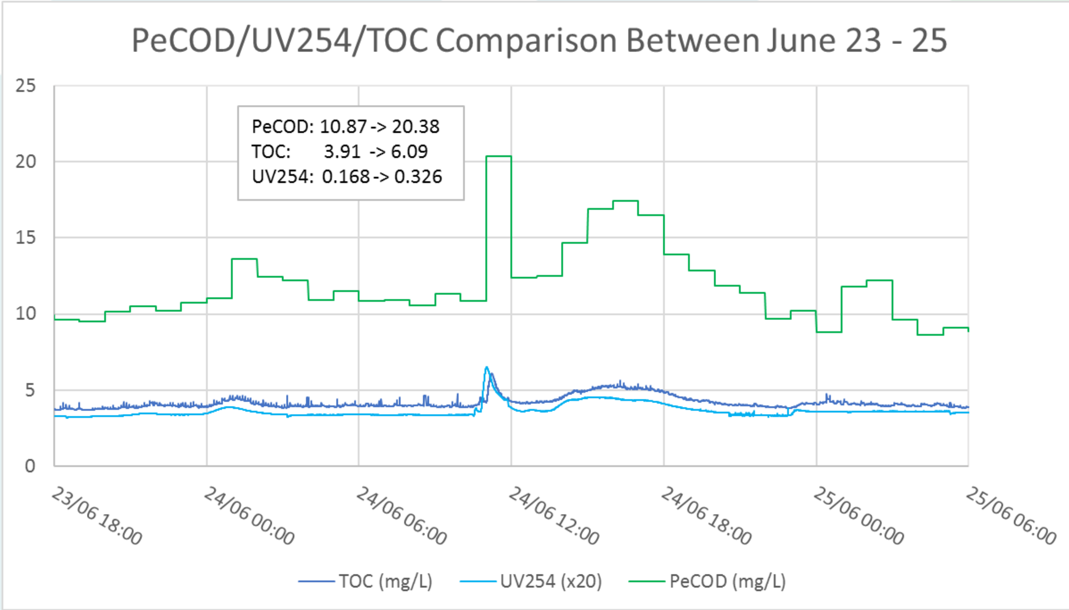

Figure 7: peCOD/UV254/TOC Comparison Between June 23 – 25, 2017

The comparison in Figure 7 shows a similar response to a short rainstorm, where peCOD values correlate fairly well with TOC and UV254 values. All three technologies picked up on a similar influx pattern due to the storm.

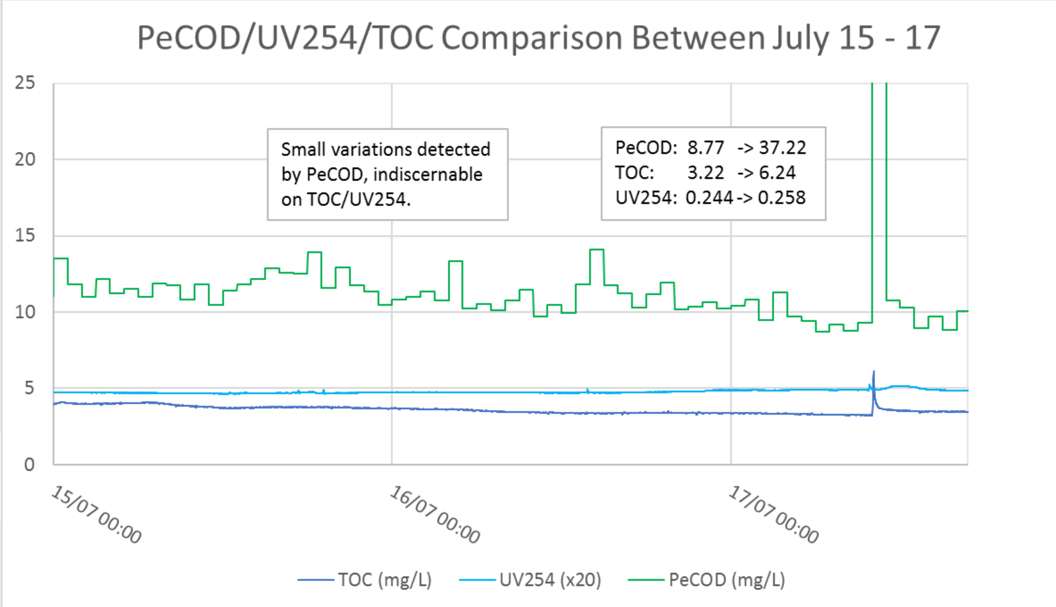

Figure 8: peCOD/UV254/TOC Comparison Between July 15 – 17, 2017

The comparison in Figure 8 shows a 3 day period with no weather related events, providing insight into the 3 technologies' responses to stable conditions. The data shows that peCOD continues to pick up on small variations of ± 2-3 mg/L, while TOC and UV254 barely change. It also shows that the peCOD and TOC follow a very slight downtrend over the period, but UV remained constant. On July 17th, it was suspected that a non-natural contaminant entered the pilot plant and was detected, and the response to this contaminant was quite different between the technologies. peCOD went up x4.2, TOC went up x1.9, and UV254 barely registered a change.

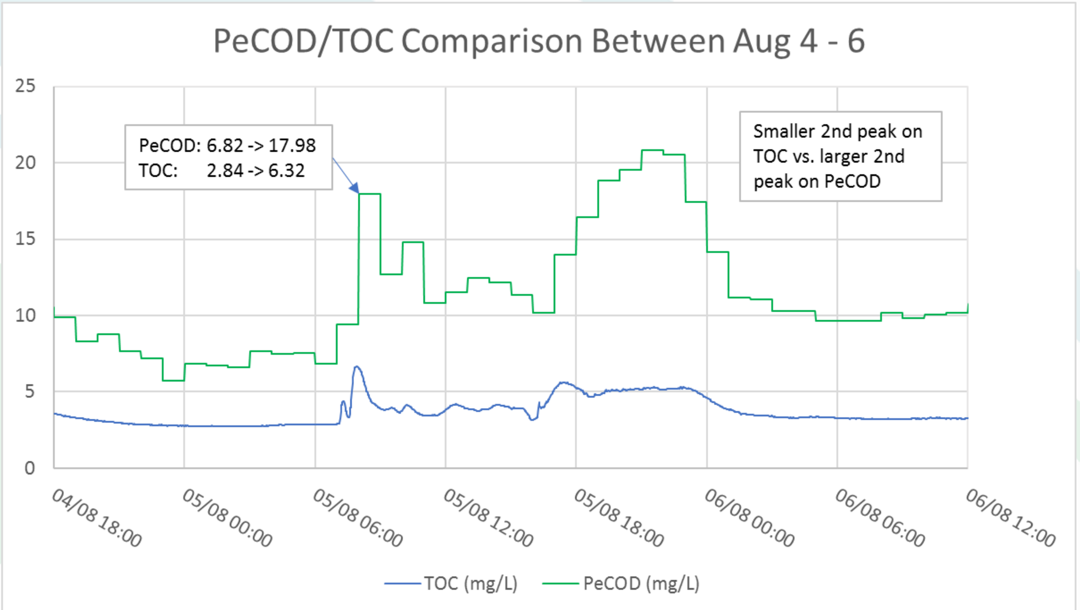

Figure 9: peCOD/TOC Comparison Between August 4 – 6, 2017

Figure 9 shows a comparison of peCOD and TOC, during a period that UV254 was offline. The data shows the responses to a large storm event, similar in pattern to the responses in Figure 7, with a short, high magnitude spike followed by a longer, lower magnitude rise above the baseline. Interestingly, peCOD showed a much greater second rise than TOC, hinting that this second spike in NOM consisted of compounds with higher reactivity per carbon than the first spike.

After the first year of running these monitoring tools side-by-side, the Massachusetts Utility operators gave the following feedback/rankings for each parameter:

Technology	Ease of Use	Uptime	Data Value
peCOD	Simple operation, reliable hardware	~85%	Sheds light on oxidizability, greatest magnitude of change
TOC	Hardware was difficult to troubleshoot	~60%	Common, easy to compare other utilities
UV254	Easy once running, difficult to get steady-state	~65%	Quickest results, but requires correlation for value outside detection

Figure 10: Massachusetts Utility Operator Feedback on peCOD, TOC, and UV254 Technologies for Source Water Monitoring

Conclusions

- peCOD is a complementary technology to TOC and UV254, providing insight on the **oxidizability** of NOM in source water.
- peCOD may show a greater magnitude response to detection of NOM with higher reactivity, which can be confirmed by speciated analysis of samples collected during a NOM spike.
- Operators were able to achieve the greatest uptime with the PeCOD® Analyzer due to simplicity of method and reliability of hardware.
- peCOD is a suitable parameter for source water monitoring for drinking water utilities.