Rapid Source and Treated Water Quality Testing using Chemical Oxygen Demand

Justin Dickerman, MANTECH

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Introduction: Water Quality Monitoring

- Drinking water treatment is one of the main safeguards of public health, utilities are under constant pressure to improve
- Movement towards online monitoring systems for event detection
- Focus on Natural Organic Matter (NOM)
- Traditional technologies are not providing the full picture
  - Total Organic Carbon (TOC)
  - Dissolved Organic Carbon (DOC)
  - UV Absorbance at 254nm (UV254)
  - Specific UV Absorbance (SUVA)

Natural Organic Matter (NOM)

- Wide variety of organic compounds originating from terrestrial, aquatic and anthropogenic sources within a watershed
- Characteristics heavily influenced by site-specific conditions:
  - Watershed size, hydrology, retention time
  - Presence of wetlands, forest, ponds/lakes
  - Human impact, both direct and indirect
- Potentially high temporal variation
  - Seasonal variation
  - Storm events
  - Drought events

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Natural Organic Matter (NOM)

- NOM is a critical target for drinking water treatment
- The presence of NOM causes many challenges in drinking water treatment processes
    - Taste, colour, and odor issues
    - Increased coagulation and disinfection dose
    - Increased fouling, requiring more frequent backwashing
    - Increased sludge production
    - Promotes biological growth in distribution systems
- NOM compounds are known to react with common disinfectants to produce harmful and potentially carcinogenic disinfection by products (DBPs) such as trihalomethanes (THMs) and haloacetic acids (HAAs)

Challenge:

Utilities require a parameter that provides them with information on treatment efficiency, NOM removal, and potential for DBP formation. Existing NOM surrogates may not be well suited.

TOC and DOC

- Do not quantify reactive organic species
- Does not represent the electron-donating capacity of a compound
- Can be difficult to implement and reliably operate

UV254 and SUVA

- Rely on aromaticity, which is not a chemical feature of all organic compounds
- Surrogate measure requiring matrix-specific calibration, difficult to compare between locations.

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Chemical Oxygen Demand (COD)

- COD is the amount of oxygen required to fully oxidize organic matter
  - It is used as a measurement of the oxygen-depletion capacity of a sample contaminated with organic waste
- COD measures reactivity/oxidizability of organic contamination
  - NOM that are potential precursors for DBPs (Reckhow et. Al citation)
- Not typically a parameter used in drinking water treatment
  - Had been investigated in the past, but standard method (Dichromate digestion) was found to be unsuitable
  - Not accurate at low levels, long test time, hazardous chemicals (potassium dichromate, mercuric compounds) not wanted in DW plants

PeCOD® COD Method

- Photoelectrochemical Oxygen Demand (PeCOD)
- Safe for both the environment and the analyst
- Simple method, easy to learn and operate
- Results in <10 minutes
- Accurate method, capable of direct online measurement identical to lab method
- Patented nanotechnology, consisting of UV-activated TiO_2 to perform advanced oxidation on organics
  - Liberated electrons pass through external circuit
  - Charge from electron transfer is measured

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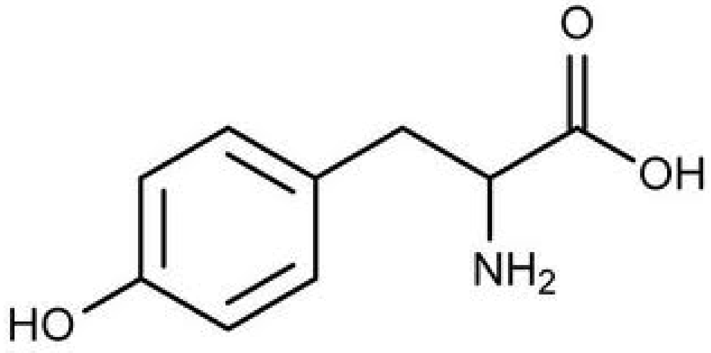
What is COD?

TOC measures conversion to CO_2



$$+ O_2 \rightarrow CO_2 + H_2O + NH_3 + e^-$$

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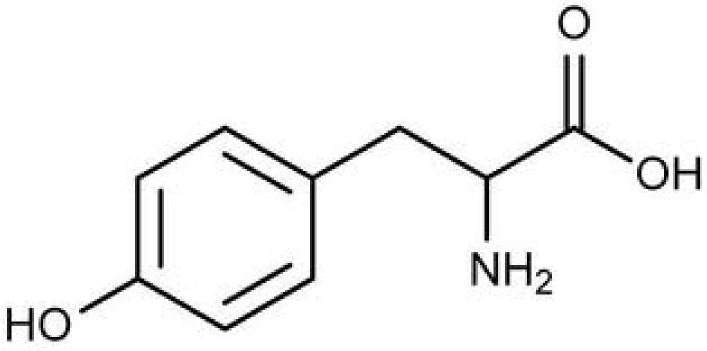

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COD measures demand for O_2

What is COD?

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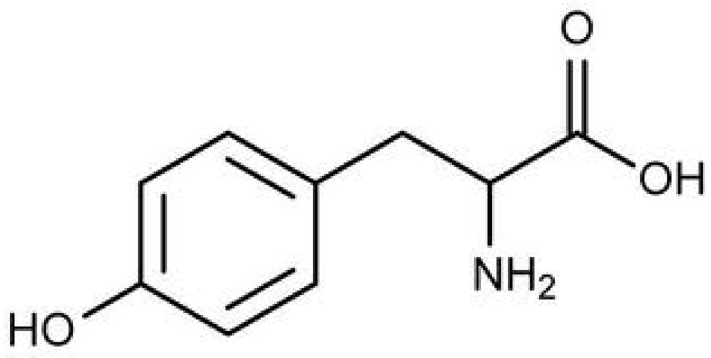
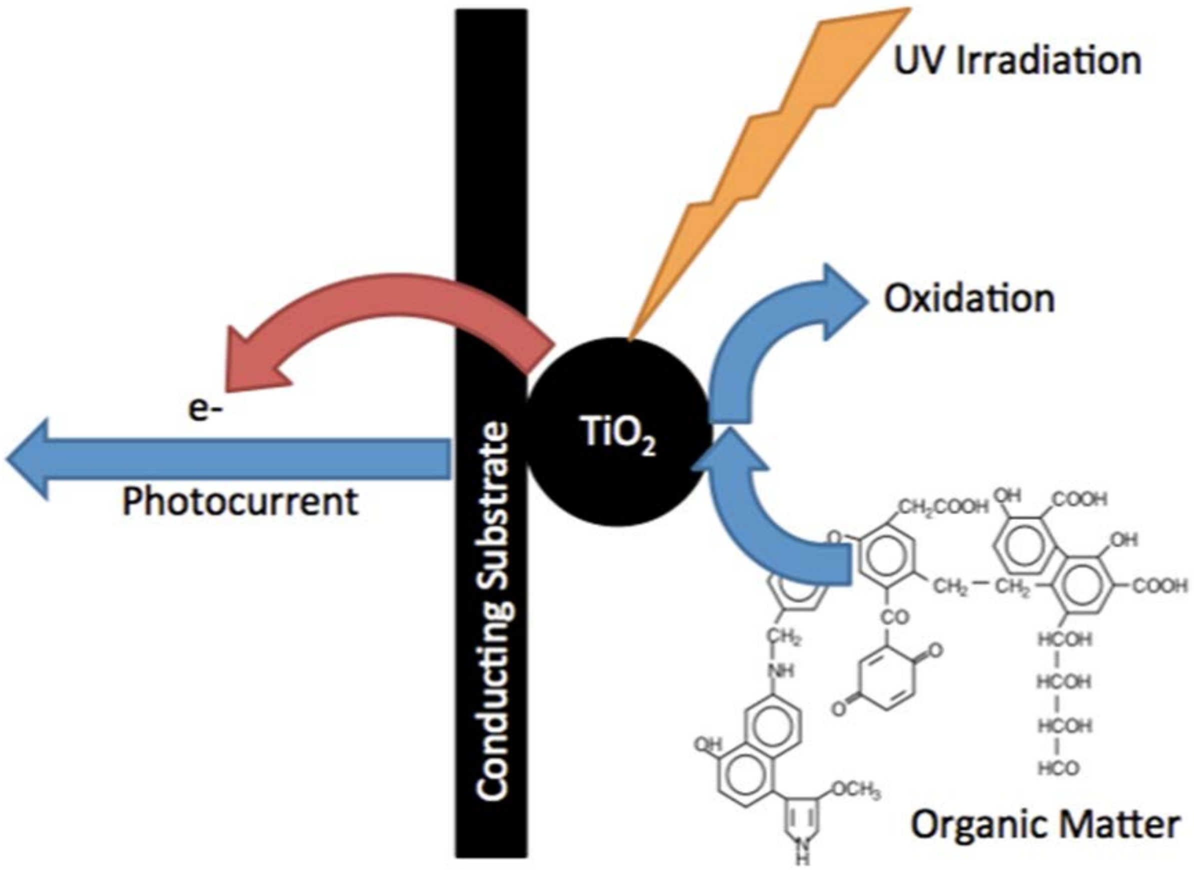


$$+ O_2 \rightarrow CO_2 + H_2O + NH_3 + e^-$$

COD measures demand for O_2

PeCOD measures generation of e-

PeCOD® COD Method



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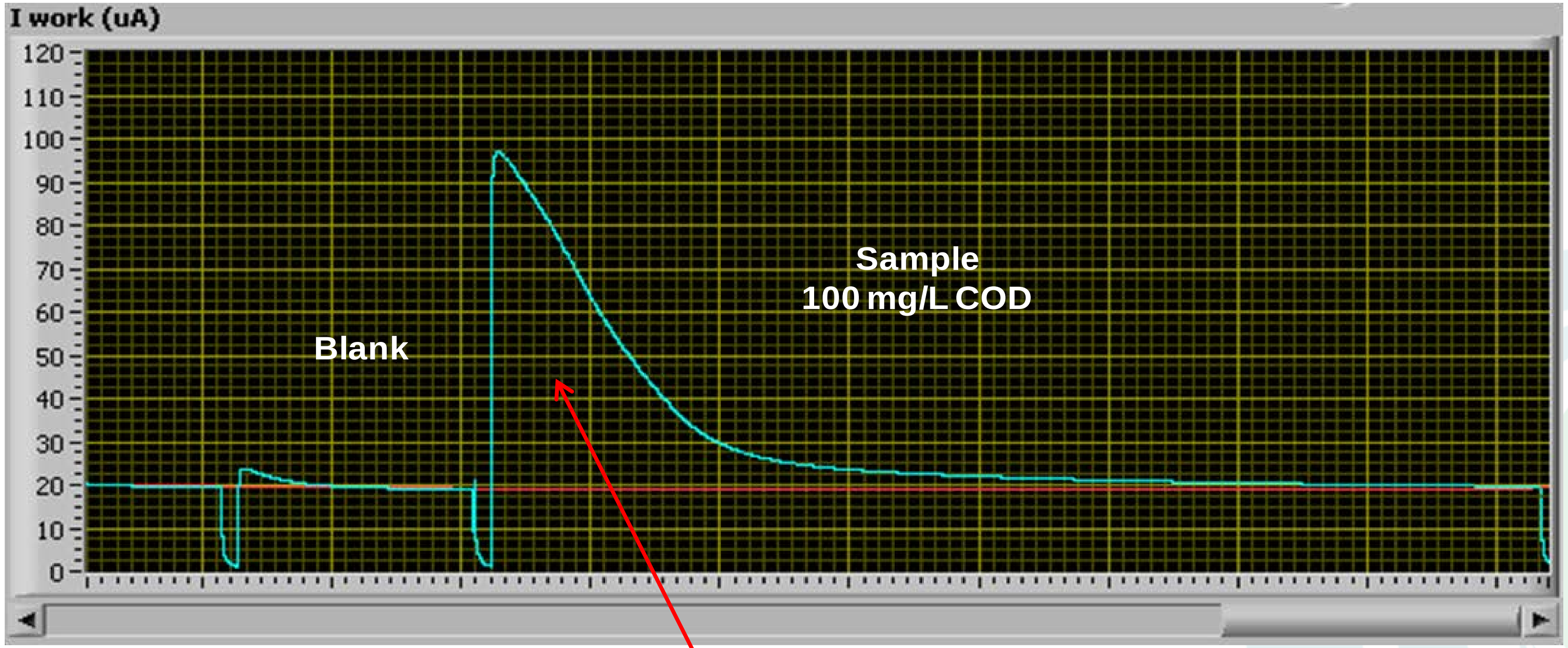
Electrons to COD



Time 4 min

Area under curve = Q_{net}

$$COD = k \cdot (Q_{net} - Q_{blank})$$

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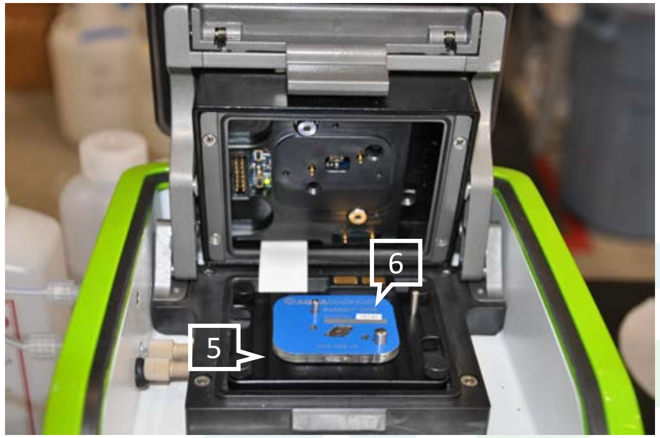
PeCOD® COD Analyzer Components

1. Port A – for sample and calibration solution
2. Port B – for blank control solution
3. Port W – for waste
4. Analyzer Lid
5. Electrode Block
6. Sensor



<u>Consumable Items:</u>

- Calibrant Solution - COD Standard
- Electrolyte
- Sensors

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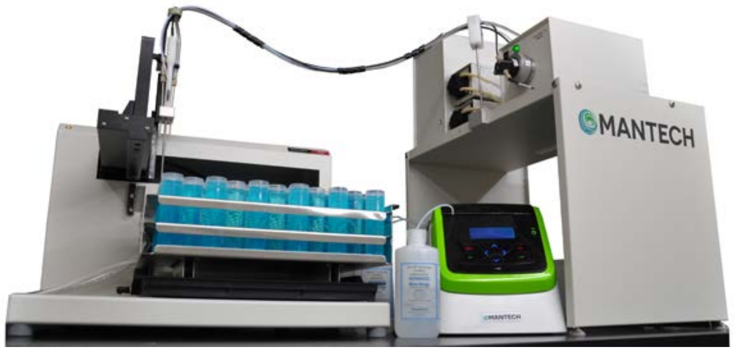
PeCOD® Configurations

Manual L100 PeCOD®	Automated L100 PeCOD®	Online L100 PeCOD®



Manual L100 PeCOD®

- Minimal bench space
- Manual sample prep
- Portable – optional battery operation

Automated L100 PeCOD®

- Run many samples without operator intervention
- Automated sample prep, calibrations, and rinsing
- Autodilution add-on available

Online L100 PeCOD®

- Online monitoring
- 4-20 mA output for SCADA connection
- Automated sample prep, calibrations and rinsing
- Connected directly to flowing sample stream

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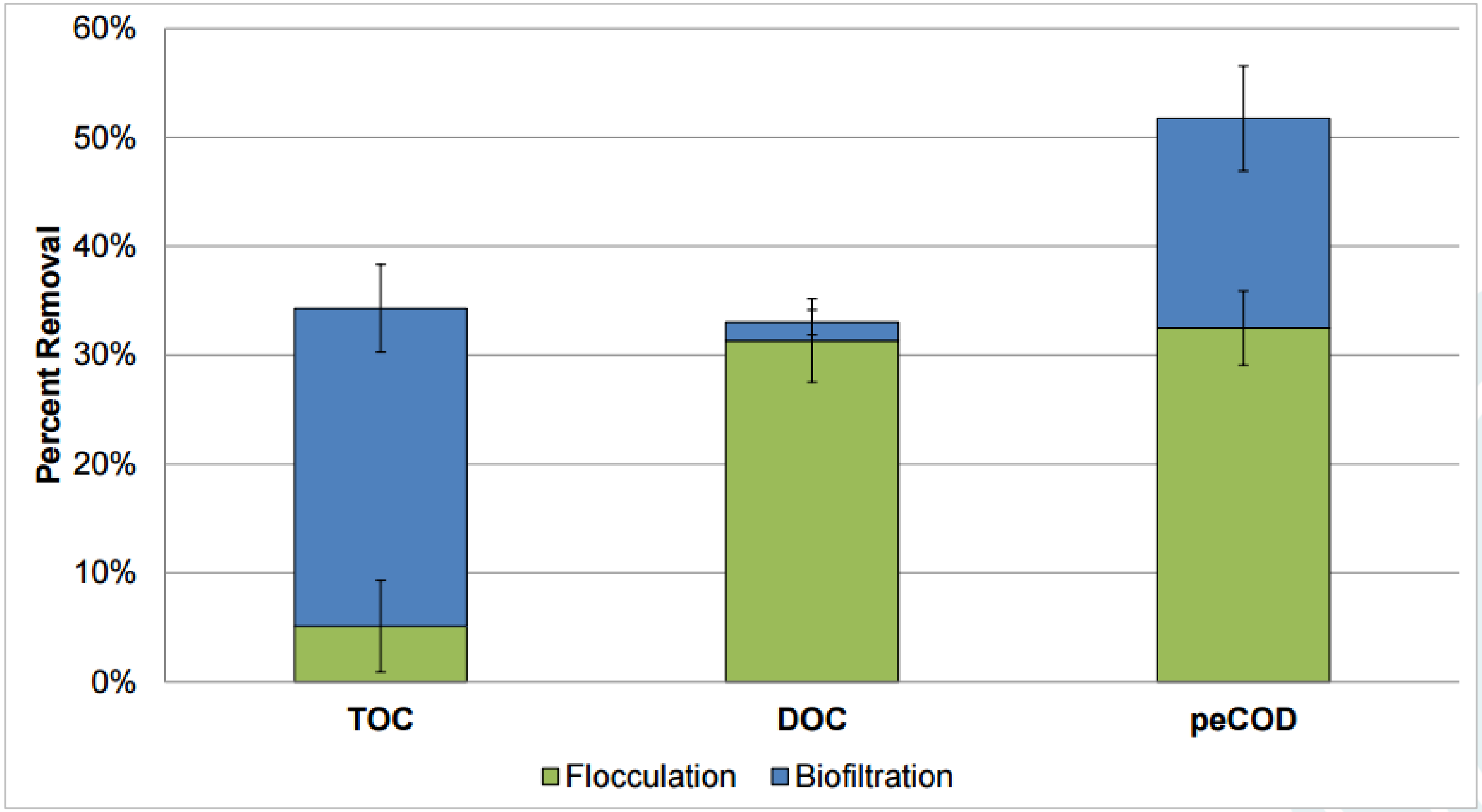
Current Research Focus

- Biofiltration, and BAC applications
- Determination of organic carbon oxidation state
- Surface water contamination monitoring
- Monitoring of ozonation in water treatment
- Detection of NOM related to taste & odour issues
- Direct potable reuse (DPR) pilot studies
- Predicting DBP formation potential
- Storm and event detection

Biofiltration: Dalhousie with Halifax Water



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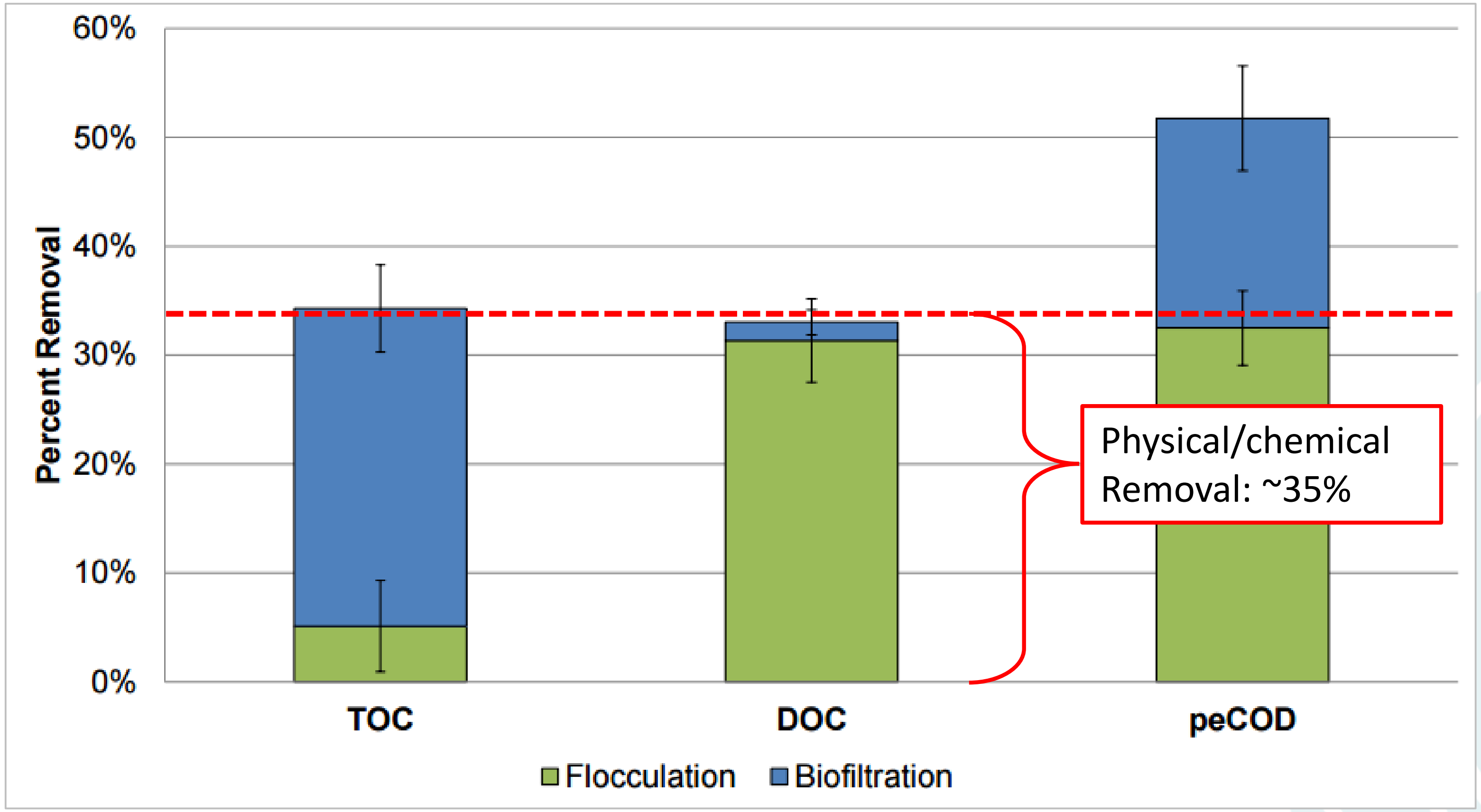
Biofiltration: Dalhousie with Halifax Water



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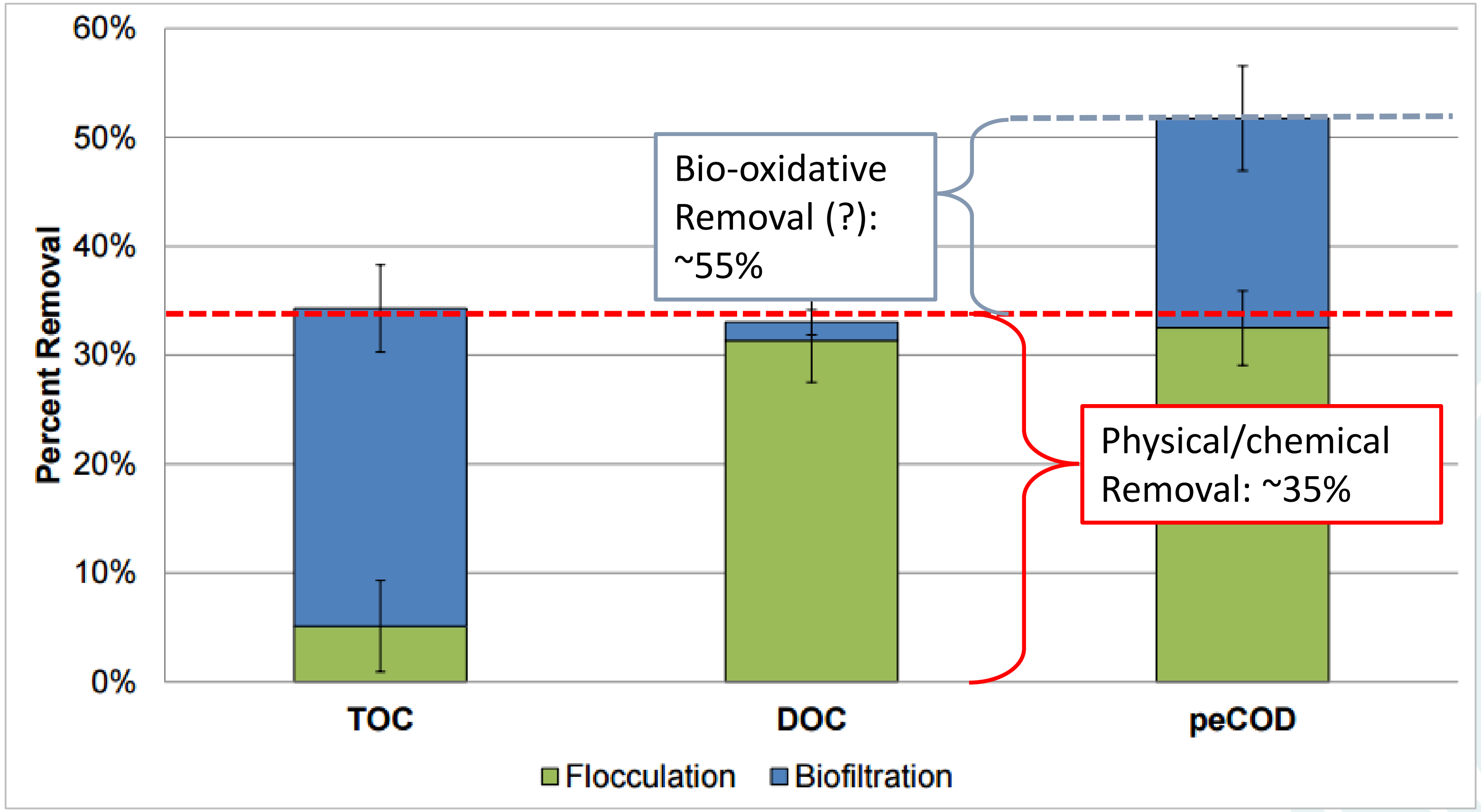
Biofiltration: Dalhousie with Halifax Water



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Mean Oxidation State of Organic Carbon

CHAPTER 12 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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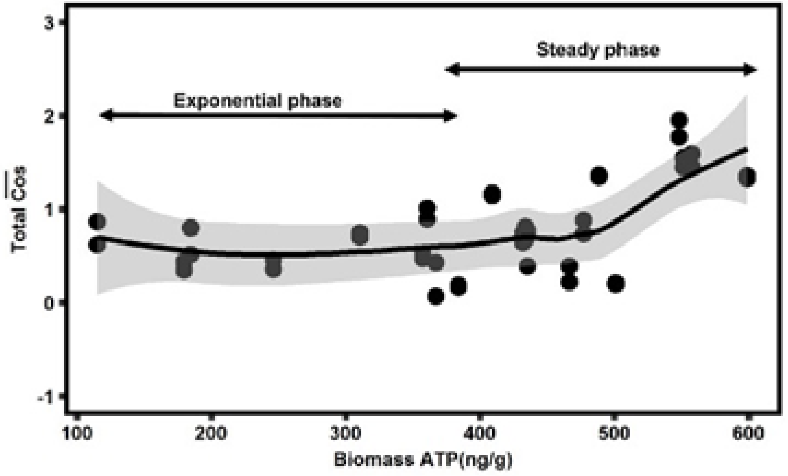
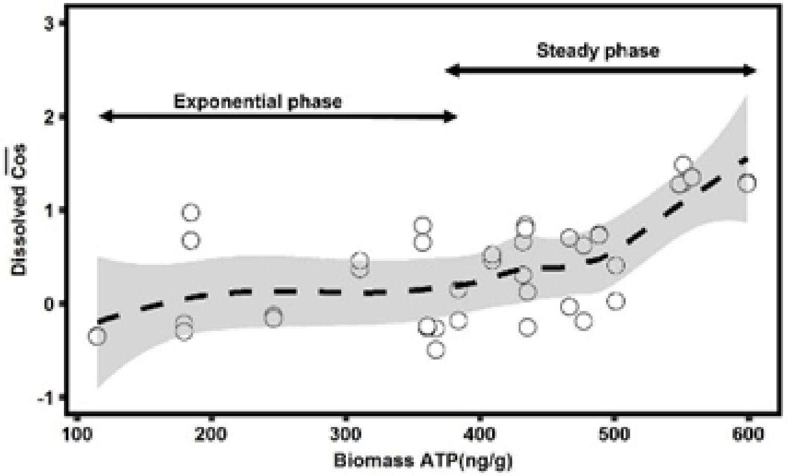
12.1 INTRODUCTION

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 by TOC/DOC overlooks the key feature of the biological instability of organic carbon: it is an electron donor (Rittmann and Huck, 1989). For example, the same TOC concentration of formic acid (HCOOH) and methanol (CH_3OH)

$$\overline{Cos} = \frac{\sum_1^i n_i OSC_i}{\sum_1^i n_i} = \frac{2j-m+3k+q}{y} = \frac{4(TOC - total\ peCOD)}{TOC} \quad \text{Equation 12.4}$$

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





Athabasca Watershed Case Study

- MANTECH collaboration with Canada's National Laboratory of Environmental Testing (NLET)
- Monitoring of various surface water samples in Athabasca watershed, in Alberta, Canada
- Hydrocarbon-associated contamination from natural bitumen deposits and anthropogenic activities such as oil sands mining

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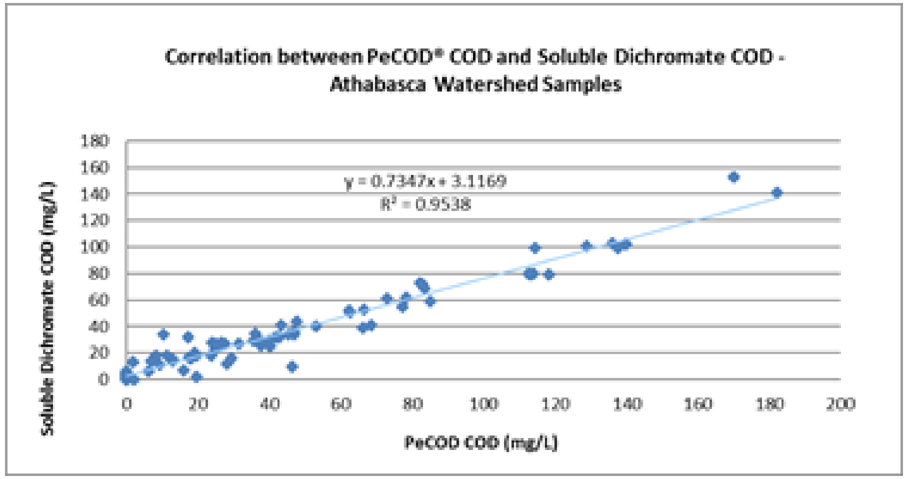
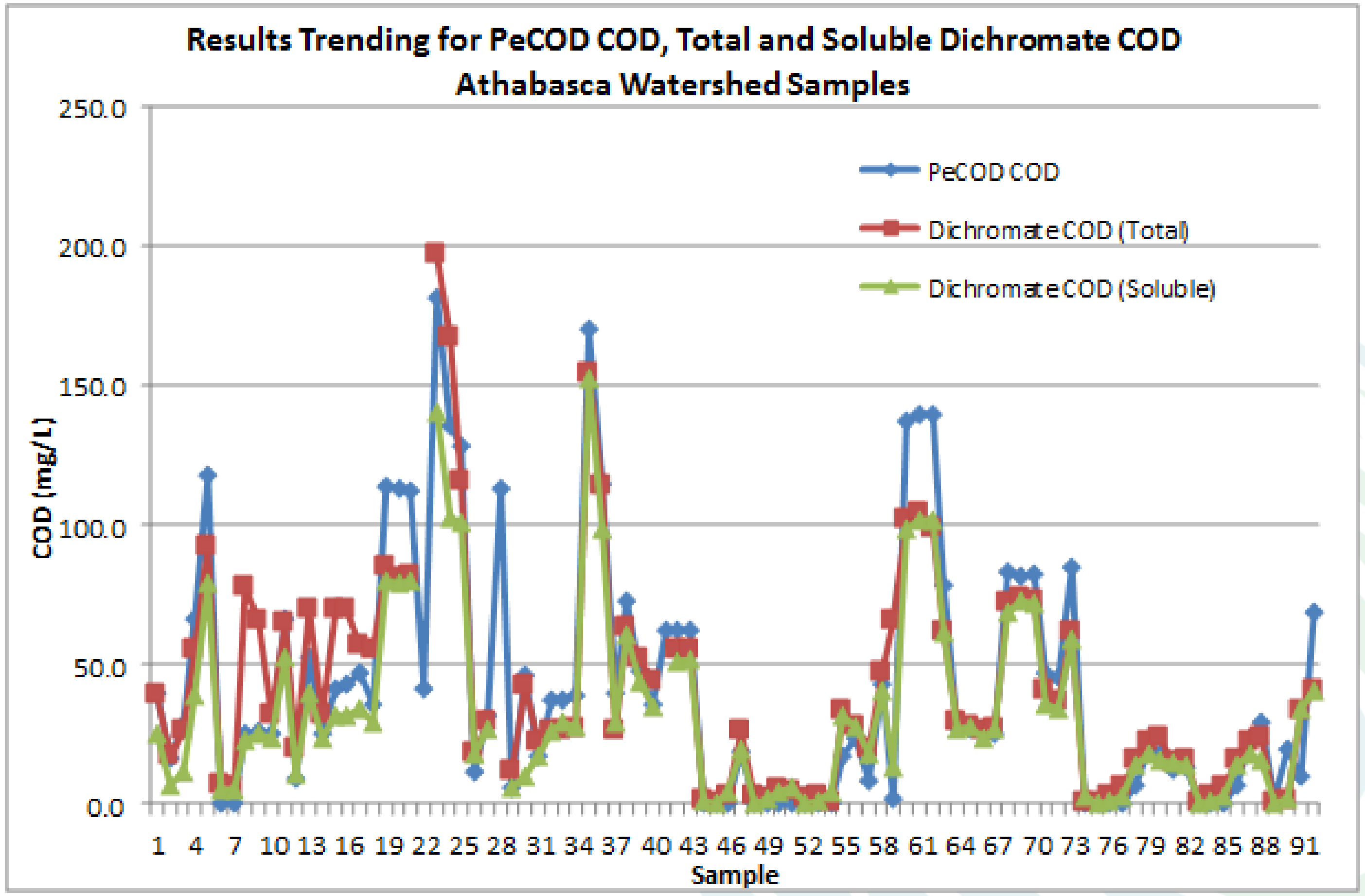
Athabasca Watershed Case Study

Soluble COD_{Cr} vs. PeCOD

$y=0.7347x + 3.1169$

$R^2 = 0.9538$





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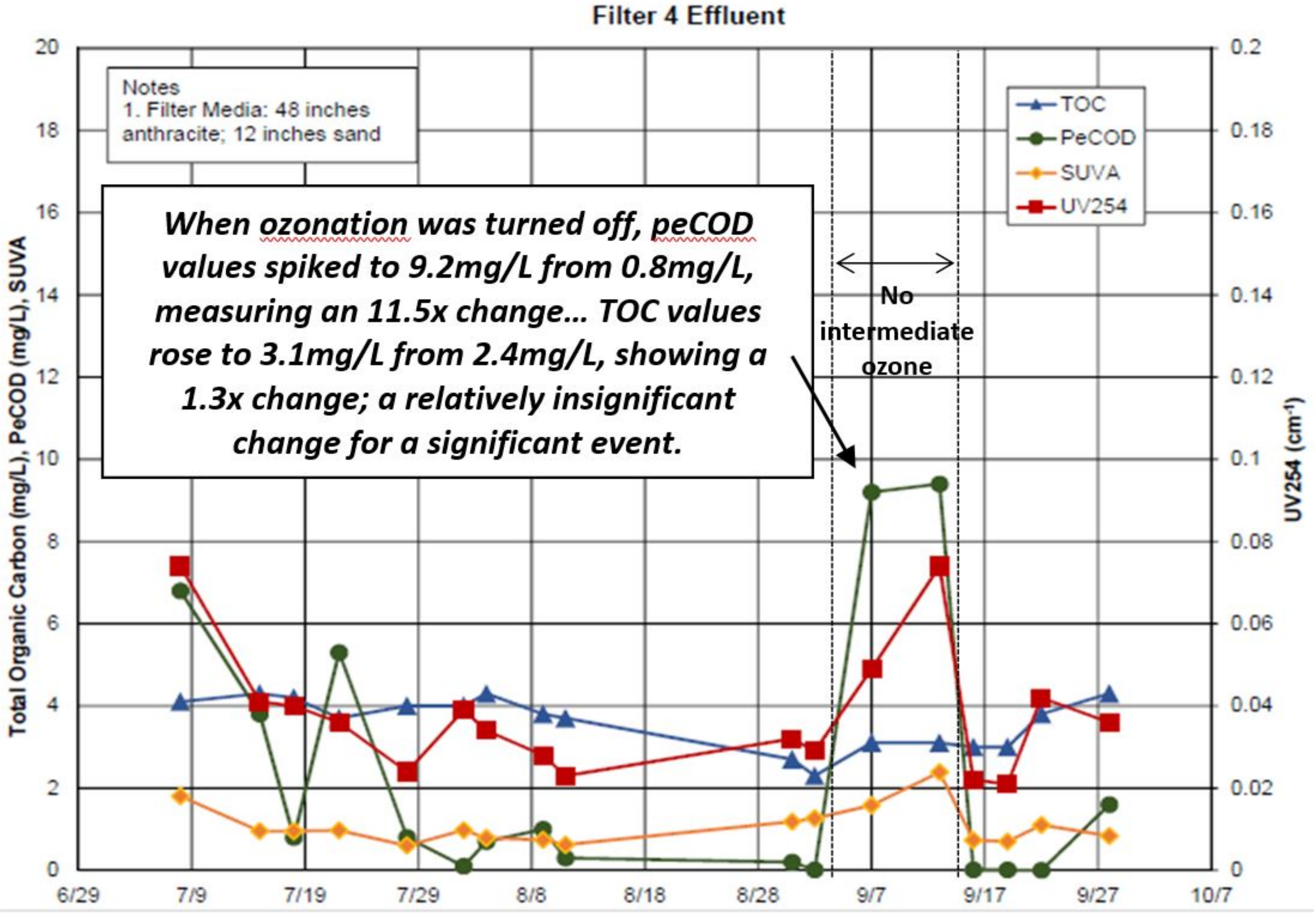
Ozonation Monitoring: Texas WTP

- Water treatment plant using ozonation in Texas monitoring peCOD, TOC, UV254, and SUVA
- Plant needed to turn off ozonation 1-2 weeks for maintenance
- When ozonation went off, PeCOD instantly spiked 11.5x
- UV254 slowly increased to about 2.5x
- TOC increased about 1.3x



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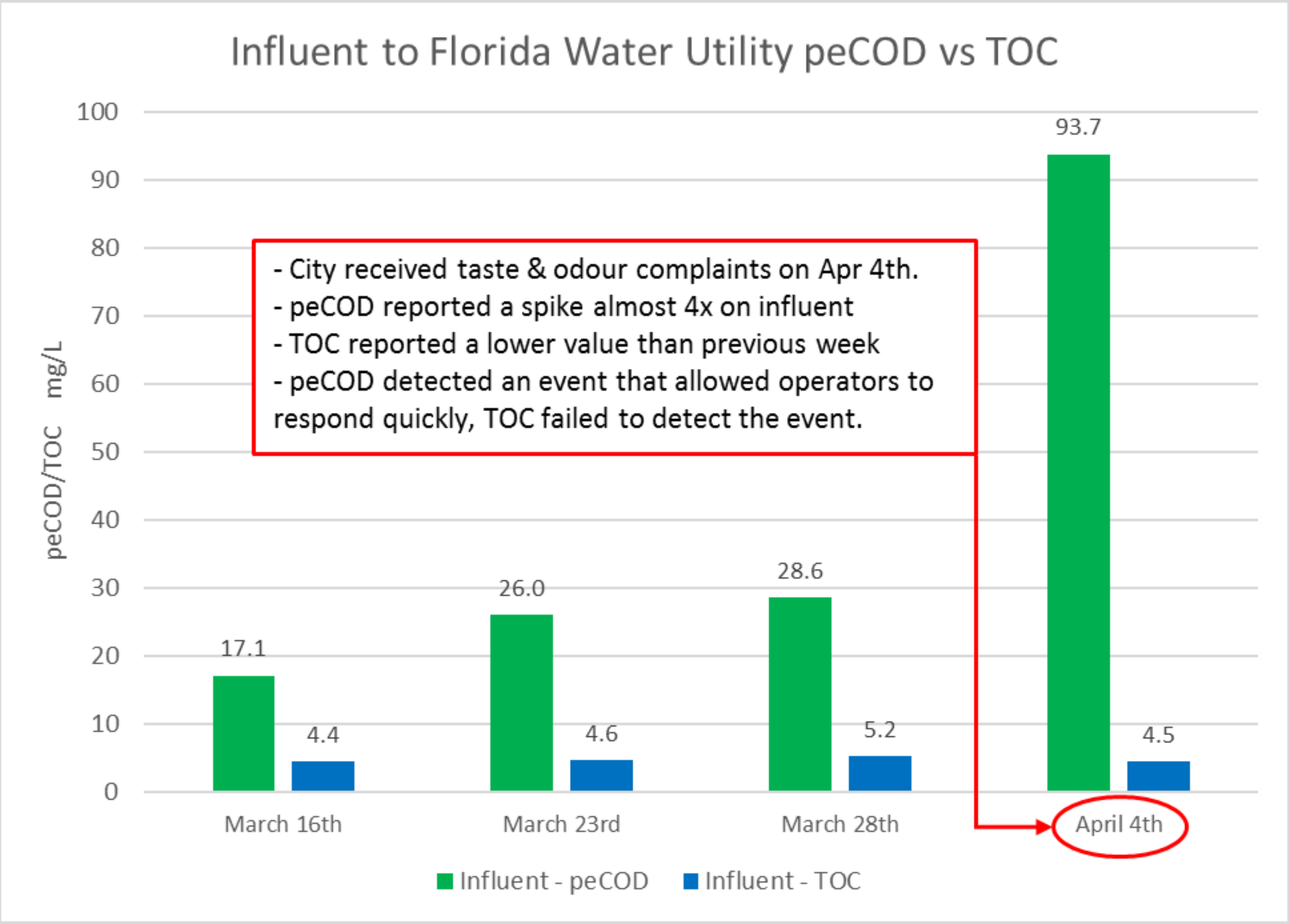
NOM Monitoring: US Municipal Water Utility

- Facility treating both ground water and surface water
  - Ground water supplied from a wellfield containing 48 wells
  - Surface water supplied by a local creek reservoir
- Ground water travels through a 9 mile pipeline to reach the Surface water treatment plant
- Need to isolate where NOM is being introduced
- Started a 3 month trial with a manual PeCOD unit
  - Grab sampling from 10 locations in the treatment and distribution plant
  - Goal is to isolate the critical locations for monitoring NOM

NOM Monitoring: US Municipal Water Utility

- PeCOD detected spike in NOM on April 4th
- City received complaints on this day for taste/colour /odor of water from distribution system
- PeCOD spike was the only indicator of this event
- Contamination was not picked up by TOC



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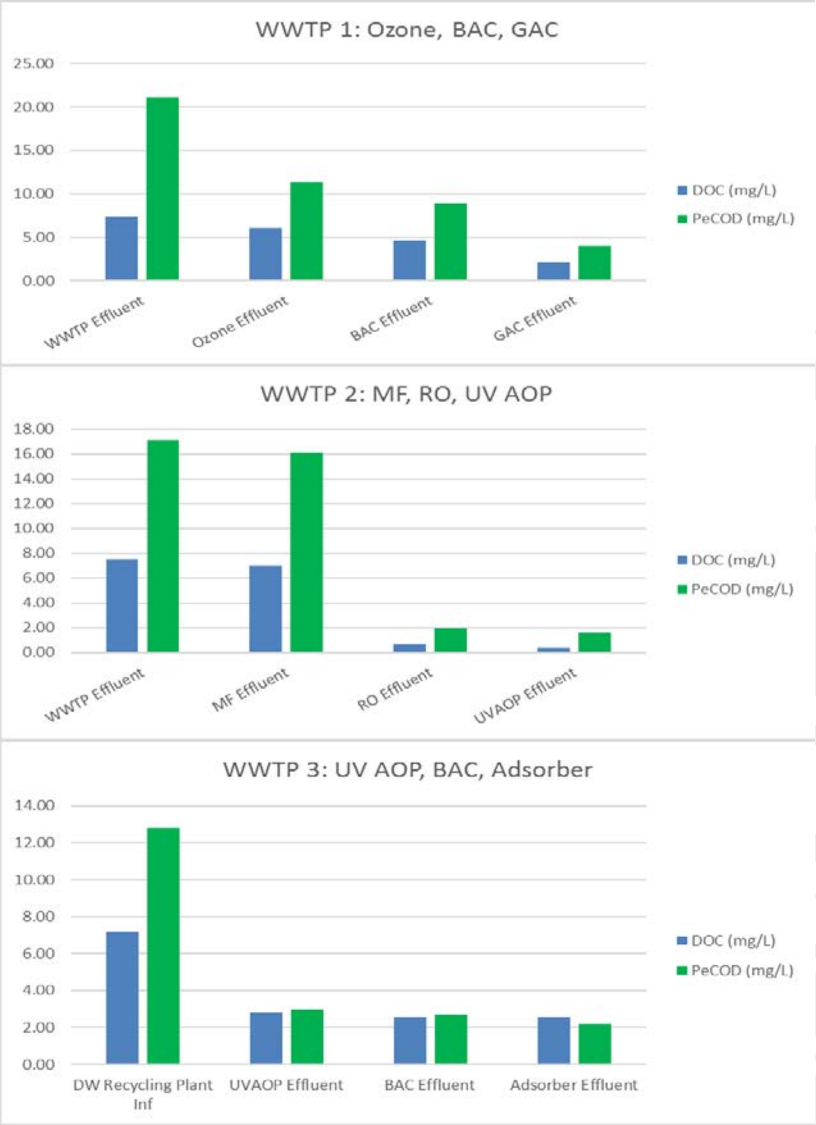
Direct Potable Reuse Study: U of Arizona

- 6 different DPR pilot facilities involved in this study
  - Africa, Singapore, and 4 US Utilities
- Final stages of sample collection and PeCOD analysis
  - PeCOD results demonstrate removal of NOM and treatment efficiency of different treatment trains
  - Correlation to DOC for this matrix
  - Can potentially provide information on the state of carbon in GAC filter



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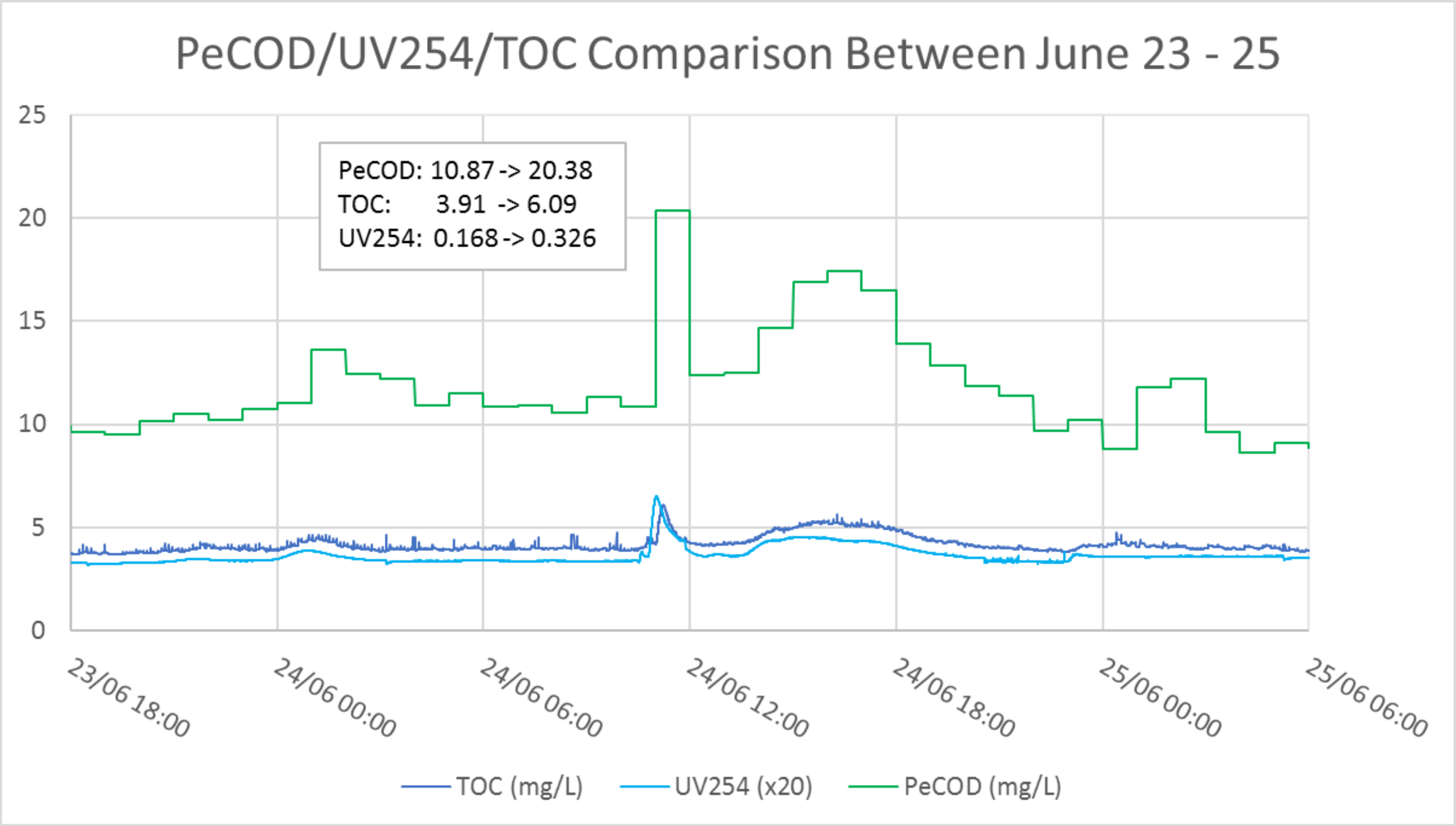
NOM Event Detection: Massachusetts Utility

- PeCOD being compared to TOC and UV254 in online setting.
- Focus on predicting formation of disinfection by-products (DBPs).
- Initial data shows PeCOD spikes related to storm events, with greater magnitude compared to other technologies.



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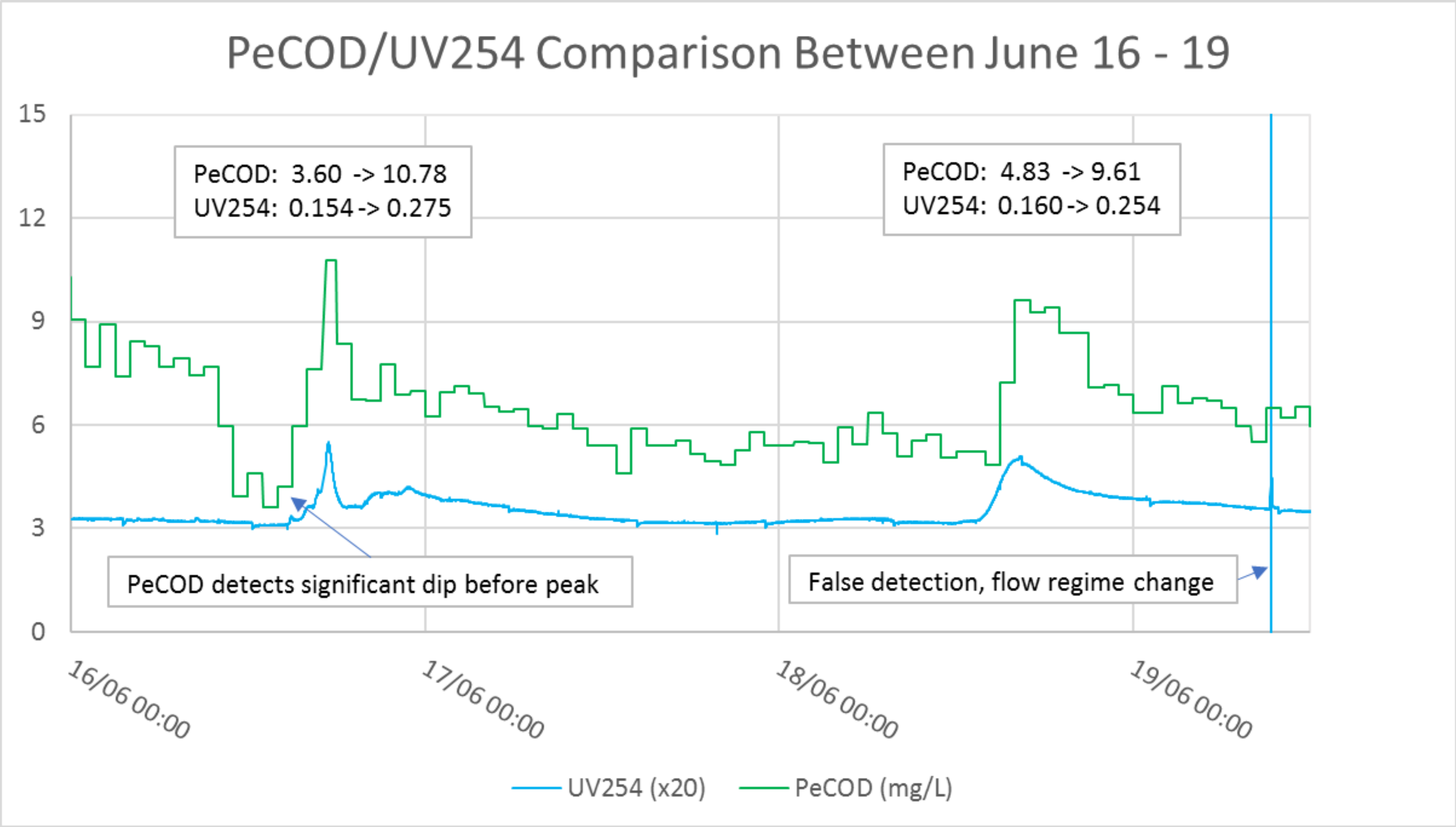
NOM Event Detection: Massachusetts Utility

- PeCOD detected all events that were also detected by UV254 and TOC
- Some events not captured by UV/TOC are captured by PeCOD
- Generally similar trends for most storms



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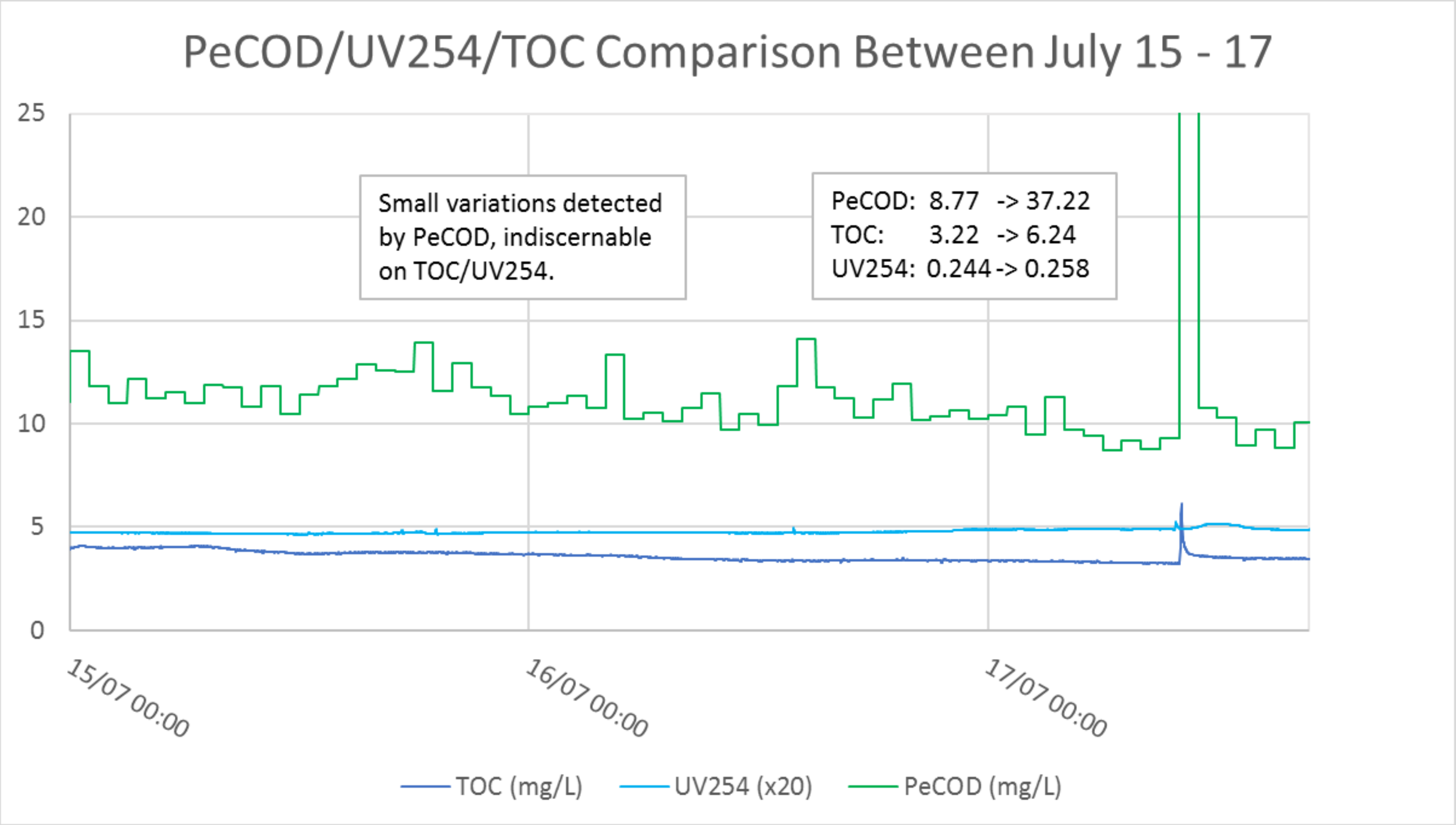
NOM Event Detection: Massachusetts Utility

- PeCOD displayed greater sensitivity to small changes
- This particular event was hypothesized to be contamination of the river, vastly different responses
- PeCOD 4.2x spike
- TOC 1.9x spike
- UV254 no significant spike



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PeCOD® COD Standard Methods

- ASTM International (D8084-17)
  - Freshwater sources for drinking water treatment plants
  - Treated drinking water
- Ontario MOECC (E3515)
  - Precipitation, groundwater, surface water
  - Effluent, industrial waste, raw sewage
  - Leachate

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Health Canada NOM Guidance Document

- Health Canada is soon releasing a guidance document for water utilities in relation to source-specific monitoring for NOM[1]
- COD listed as a treated water target parameter

Parameter	Units	Higher specific DBP yield or Extensive distribution system	Lower specific DBP yield
Colour	TCU	5–10	<15
UV254	cm^{-1}	0.02–0.04	0.02-0.07
UV transmittance	Percent	90–95	85–95
COD	mg/L O_2	<5	<5
DOC – for DBP control	mg/L C	<2	<4
DOC – for biological stability	mg/L C	<1.8	<1.8

Guidance Document Treated Water Targets – From Health Canada Presentation

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[1] MacDonald, J. (2018). *Natural organic matter in drinking water*

About MANTECH

- MANTECH Inc. is a manufacturer of online, portable and laboratory analyzers for water and wastewater.
- With over 1,900 analyzers installed in 45 countries, 100,000's of samples are analyzed everyday by MANTECH systems.

MANTECH's mission is to generate the highest quality results in the shortest amount of time with the goal of enabling our customers to have significant positive economic and sustainable impacts on their businesses and communities.

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Acknowledgements

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- Halifax Regional Water Commission
- Ontario MOECC
- Health Canada

Resources/Questions

- Website: http://mantech-inc.com/
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- Questions?

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