DALHOUSIE UNIVERSITY

Photoelectrochemical Chemical Oxygen Demand Analysis in Drinking Water

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Introduction

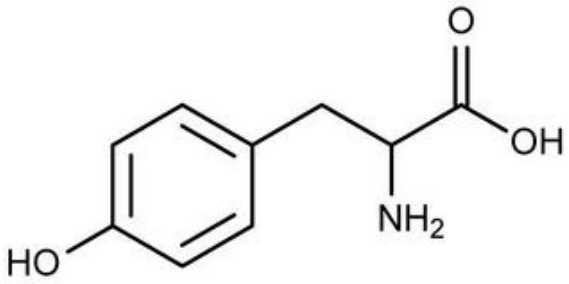
- Natural organic matter (NOM) is a critical target for drinking water treatment
- NOM can be associated with
  - Taste, odour, colour issues
  - Coagulant, oxidant demand
  - **DBP precursors**

– We have a number of tools for bulk NOM estimation: DOC, TOC, UV_{254}, SUVA

Chemical Oxygen Demand (COD) Measurement in Drinking Water

- Traditional NOM surrogates may not be suitable for assessing NOM removal in all cases
  - UV_{254}, SUVA
    - Rely on aromaticity, which is not a chemical feature of many organic compounds, example sugars
  - Carbon (e.g., as TOC, DOC)
    - Does not quantify the reactivity of the organic

What is Chemical Oxygen Demand?



$+ O_2 \rightarrow CO_2 + H_2O + NH_3$

TOC measures conversion to CO_2

What is Chemical Oxygen Demand?

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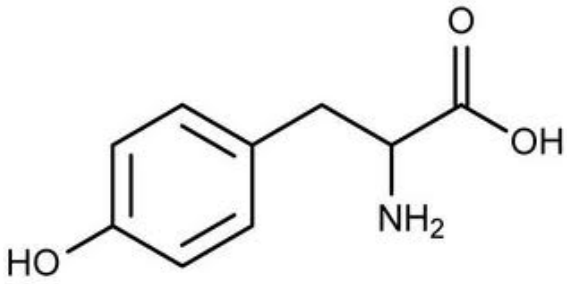


$$+ O_2 \rightarrow CO_2 + H_2O + NH_3$$

COD measures “demand” for oxygen

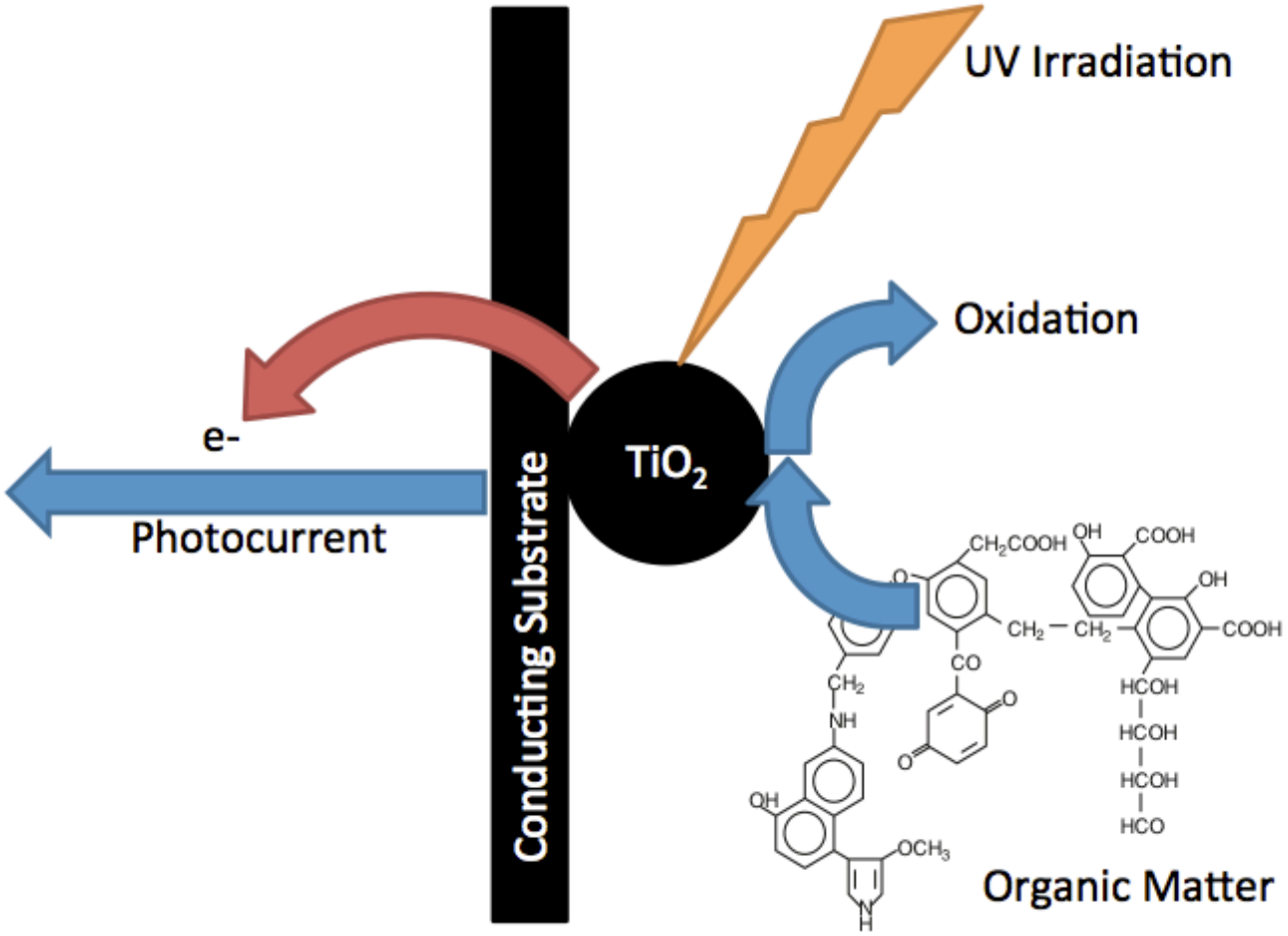
Why is COD not often used in Drinking Water?

- The traditional method for COD determination is to oxidize with potassium dichromate under acidic conditions
- Issues:
  - Sensitivity
  - Use of hazardous chemicals
    - Dichromate, mercury, surfuric acid
  - Analysis time
    - Hours

Photoelectrochemical COD (peCOD) Analysis

- Safe for operator
  - No hazardous chemicals
  - Single reagent (electrolyte)
- Takes 5-10 min
  - Can automate
  - Potential for online measurement
- Low range
  - MDL = 0.5 mg/L (using modified procedure)
- Uses green chemistry
  - No hazardous wastes

Working Principle: peCOD



Technical Approach

1. Conducted initial method validation with model organic compounds
   a. Compared peCOD of carboxylic acids, amino acids and reference compounds to the calculated theoretical oxygen demand (ThOD)
   b. Verified peCOD applicability in the drinking water NOM range of concern
2. Tested technology at various drinking water treatment plants
3. Monitored full-scale drinking water biofiltration

Method Validation: Comparison of peCOD and ThOD for *Amino Acids*

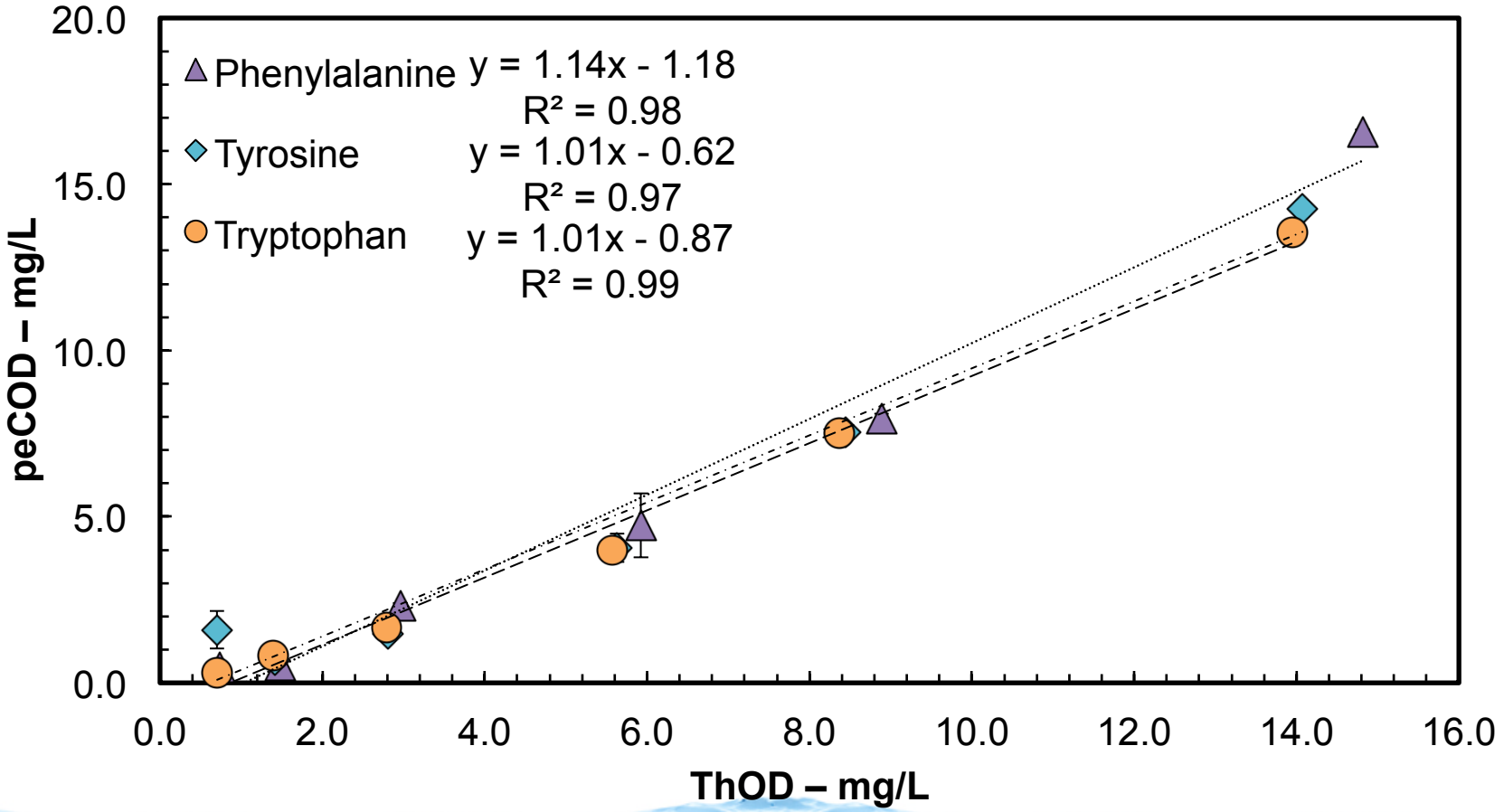


Figure: Stoddart, A. K., & Gagnon, G. A. (2014). Application of photoelectrochemical chemical oxygen demand to drinking water. *Journal: American Water Works Association*, *106*(9).

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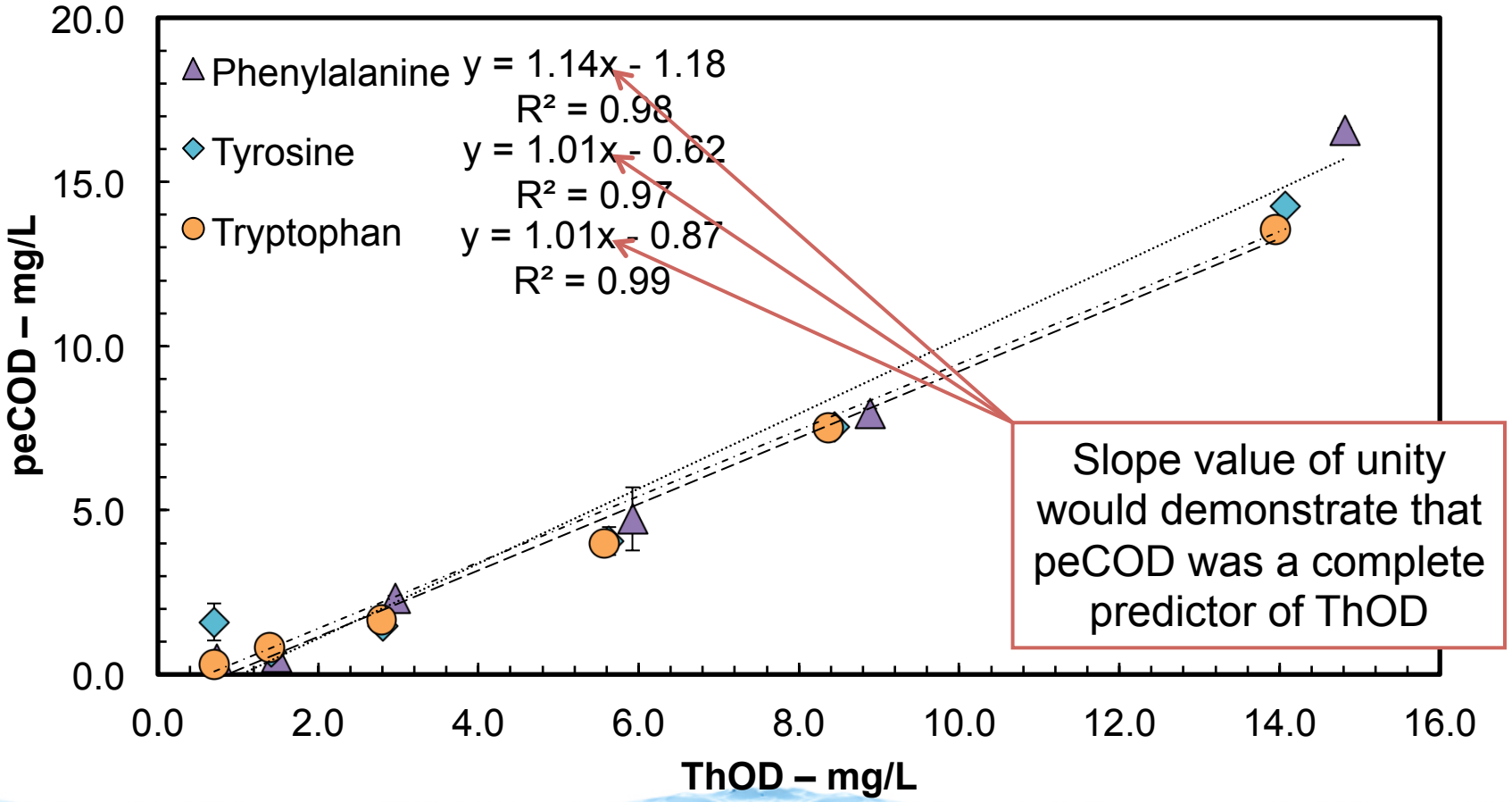

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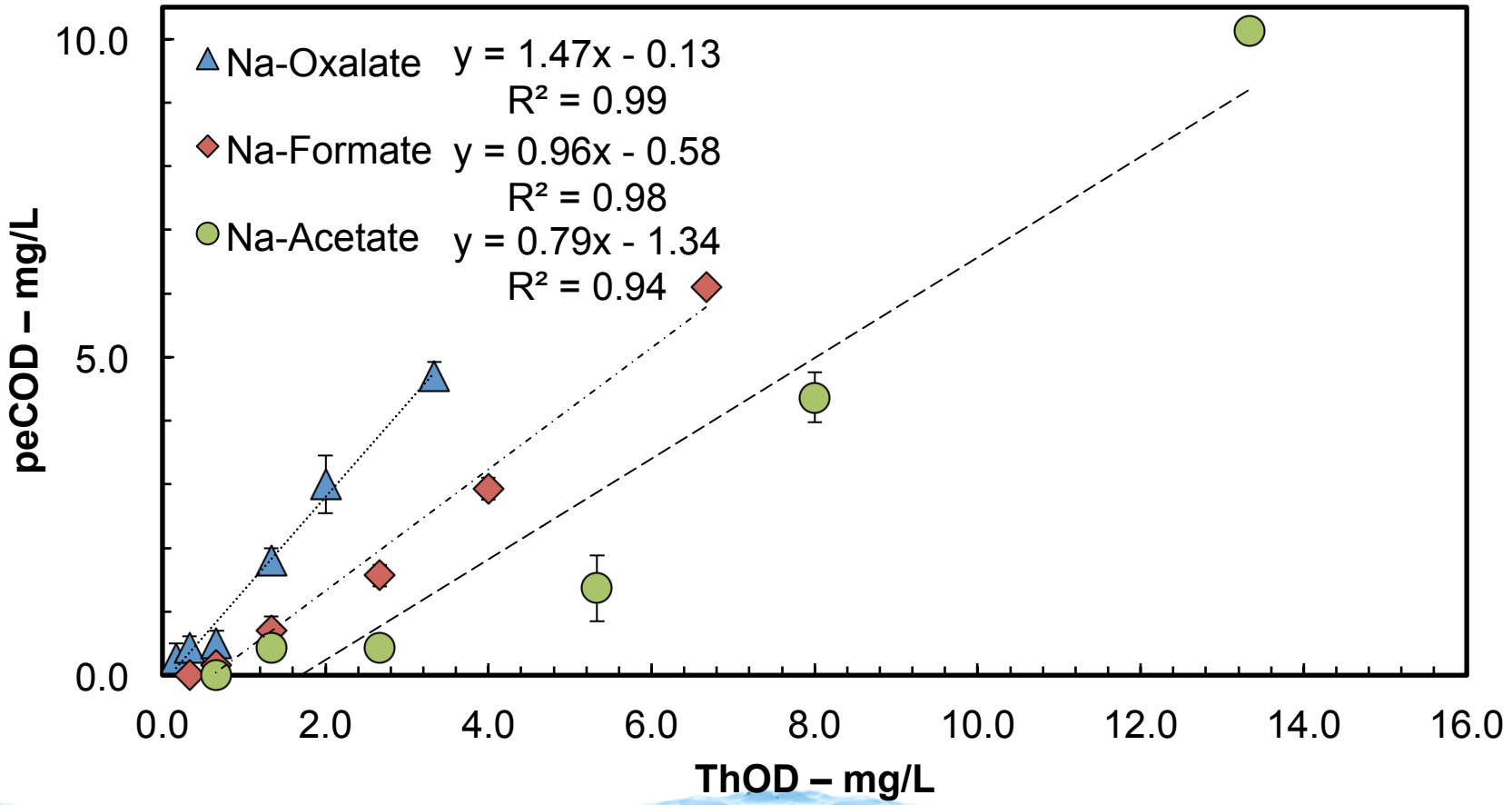
Method Validation: Comparison of peCOD and ThOD *Carboxylic Acids*



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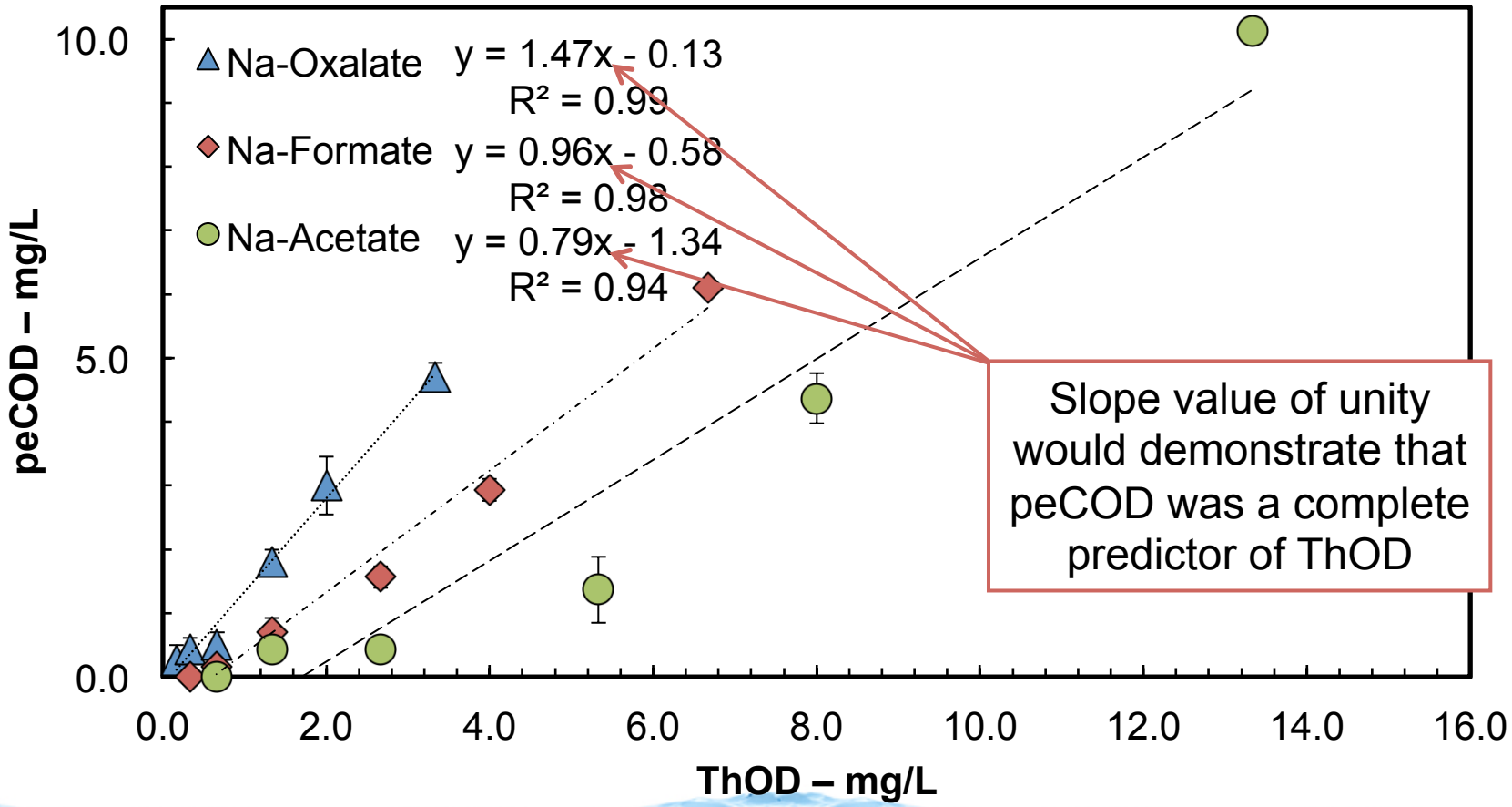

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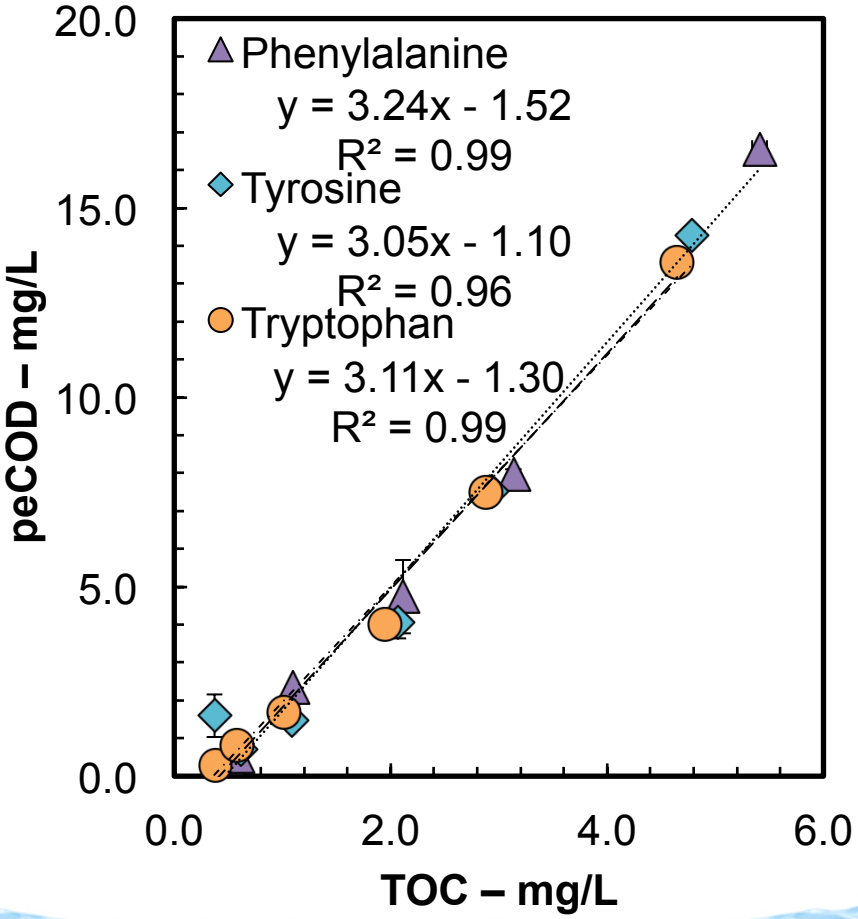
Method Validation:
Comparison of peCOD and TOC



- peCOD detectable at TOC concentrations characteristic of raw and treated water
  - i.e., 1-5 mg C/L
- peCOD:TOC ratios were predictable based on stoichiometry of the oxidation reaction
  - i.e., oxygen to carbon ratio

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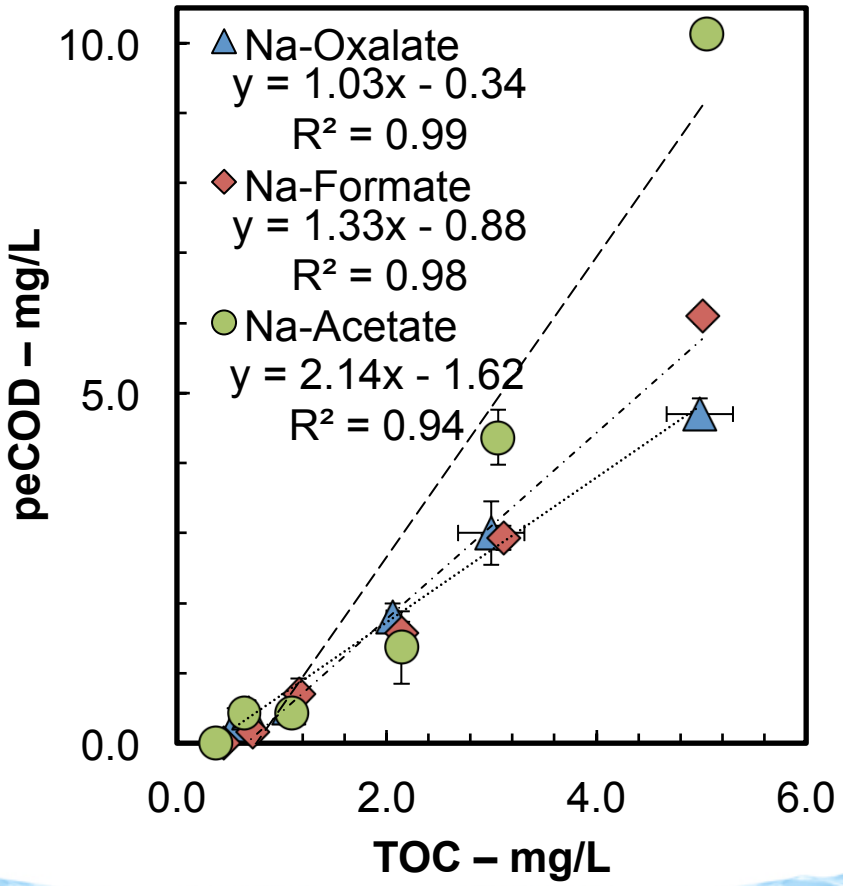

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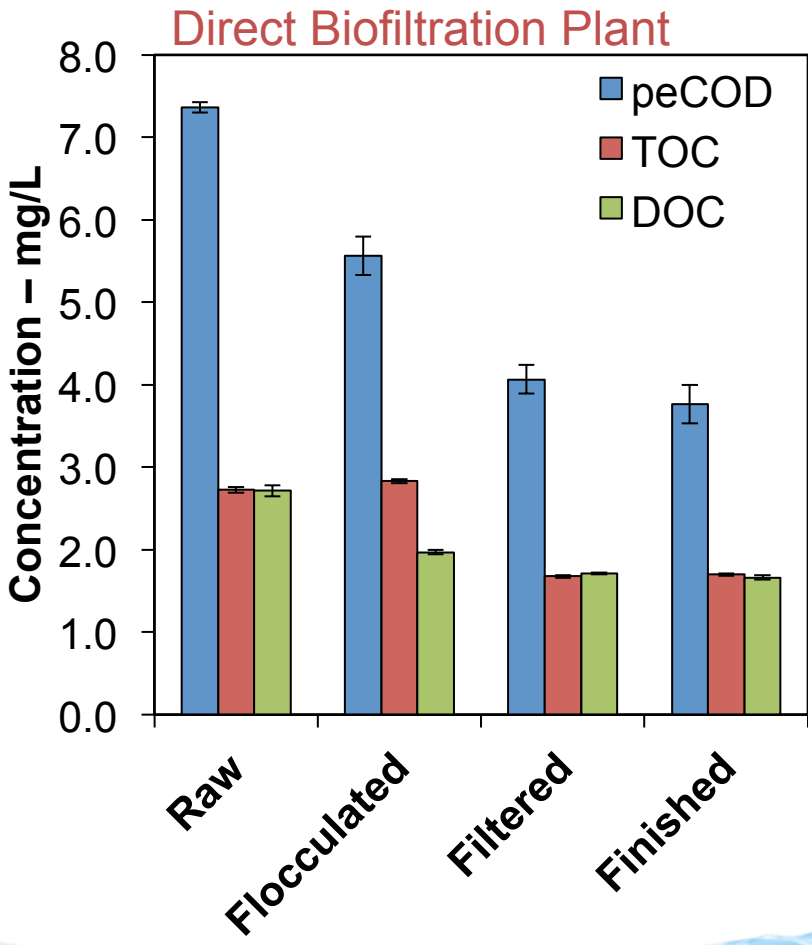
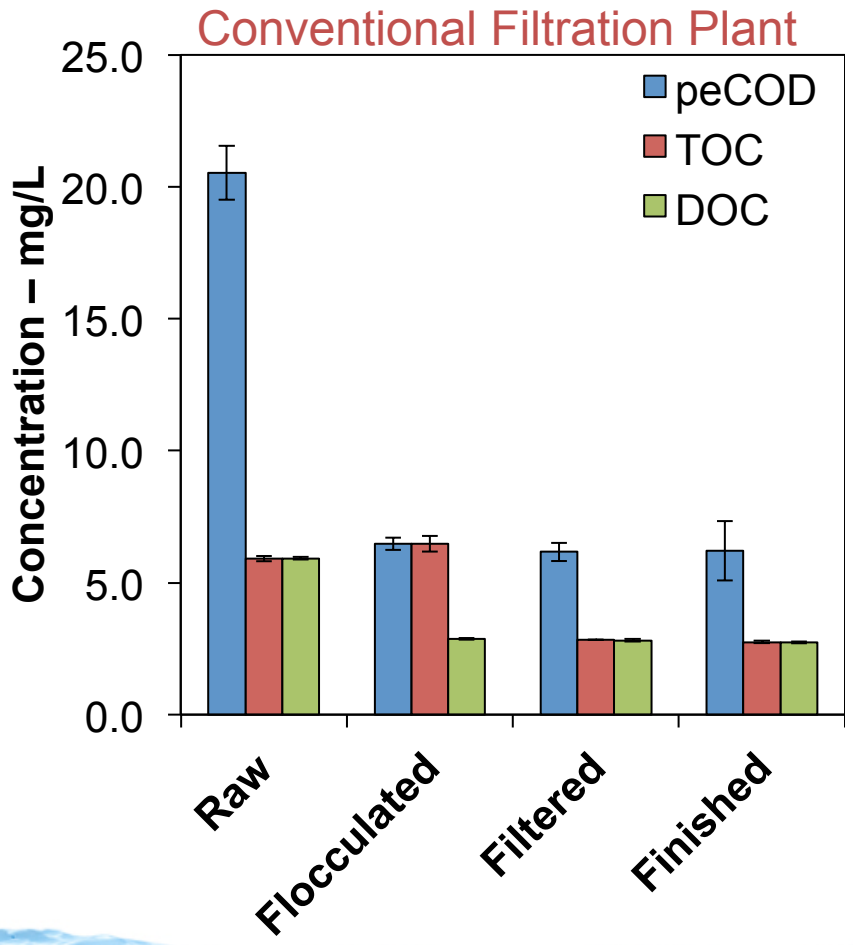
Method Validation:
Various Treatment Plants





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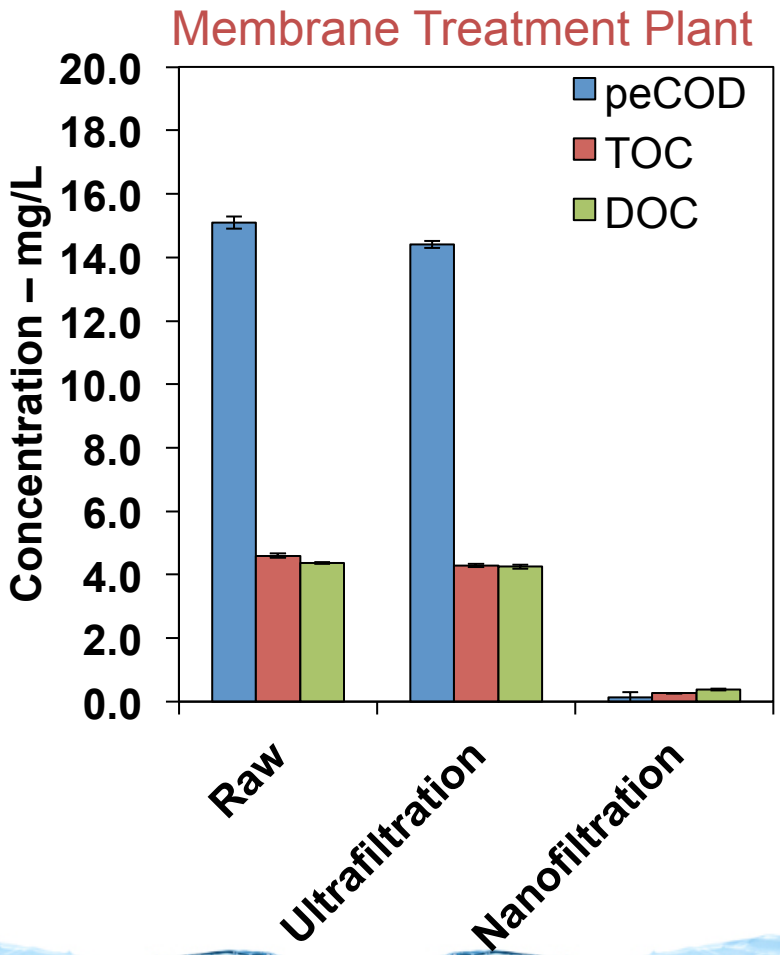

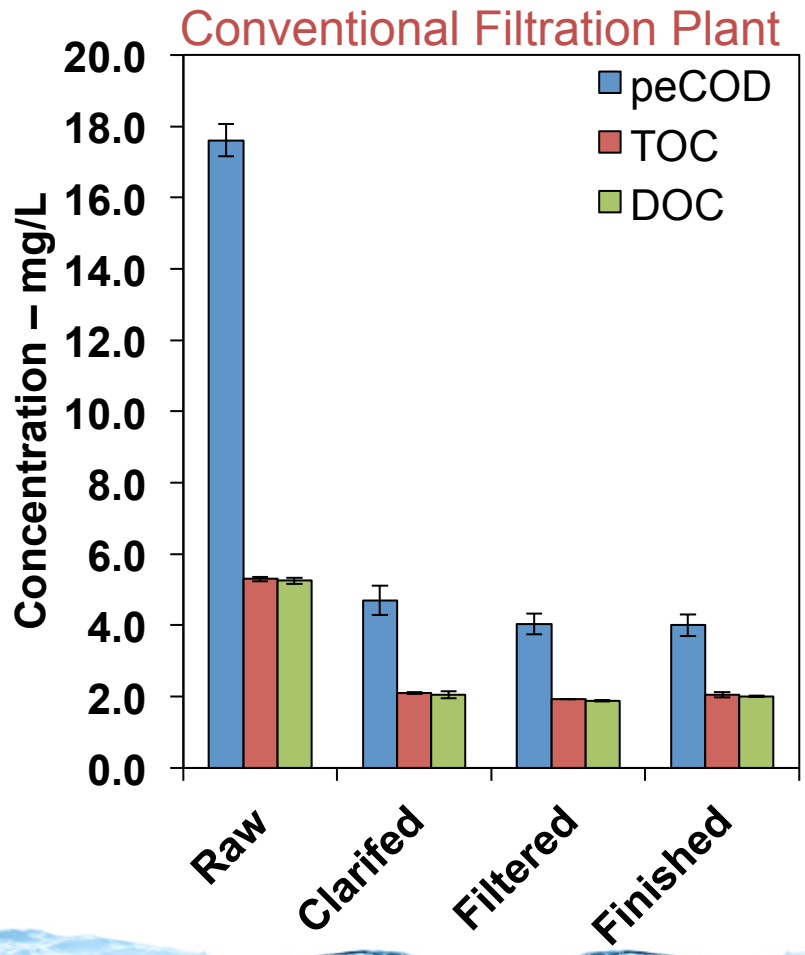

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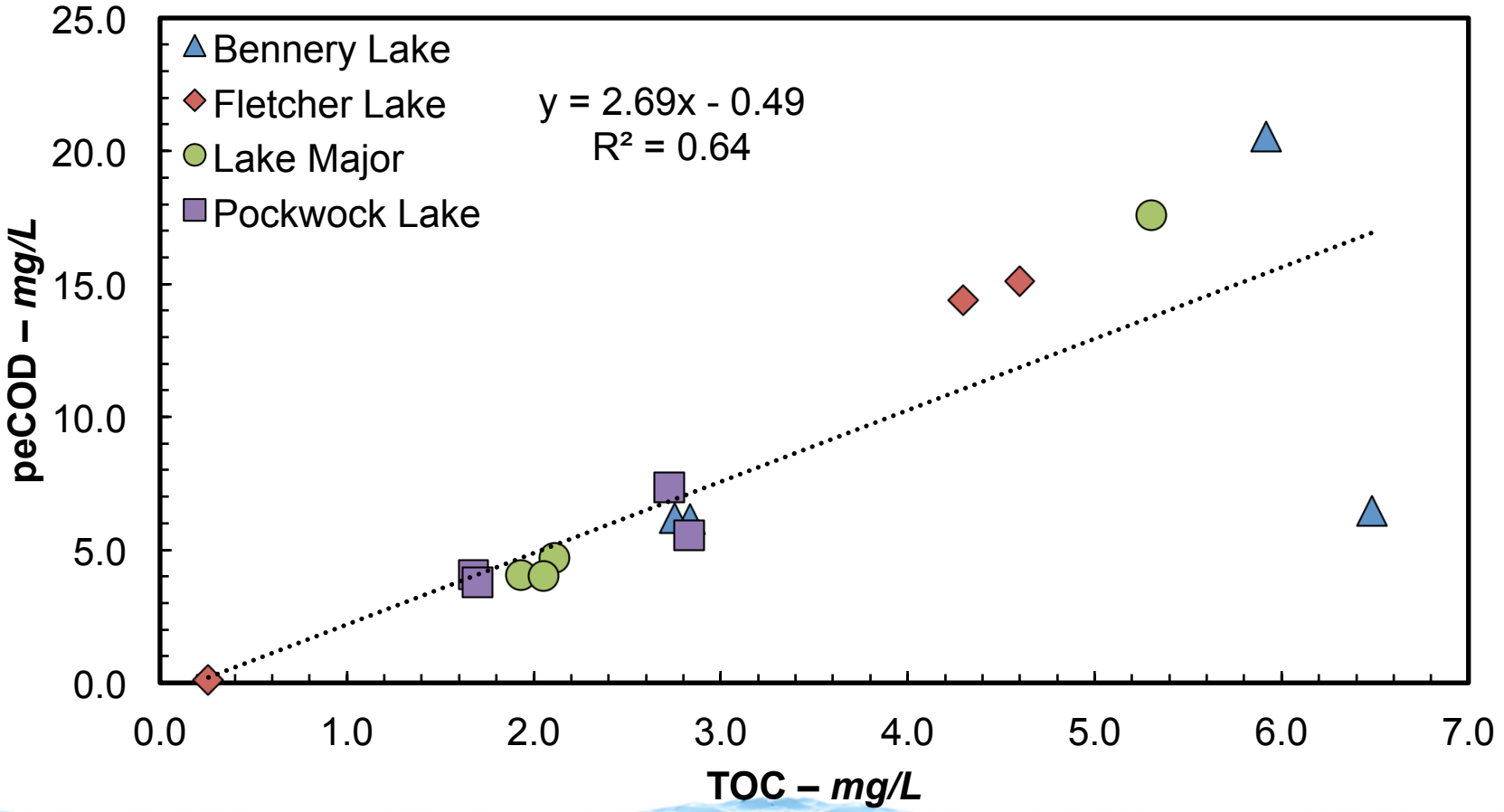
Method Validation:

Various Treatment Plants in Nova Scotia - **peCOD and TOC**



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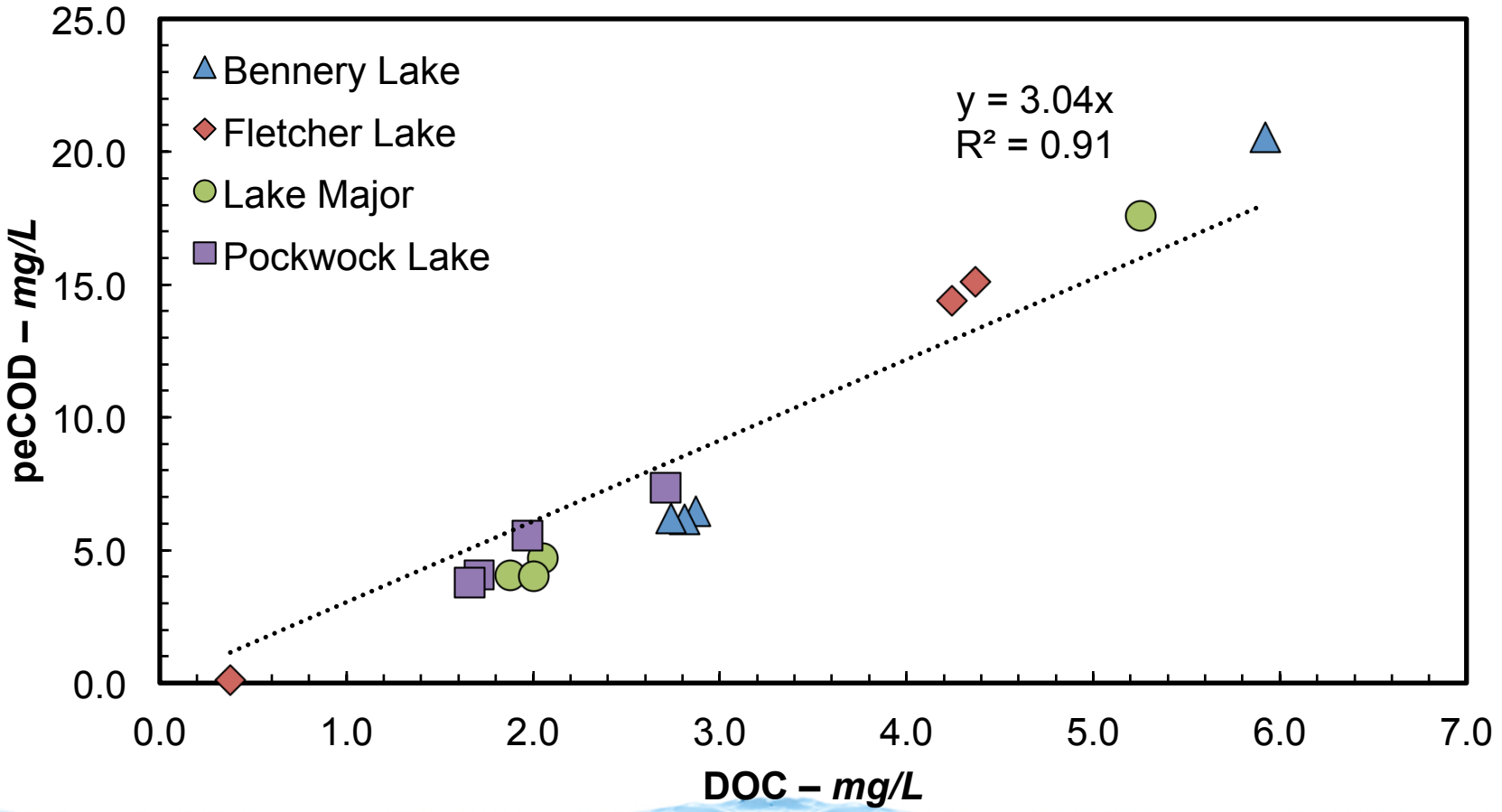
Method Validation: Various Treatment Plants in Nova Scotia - **peCOD and DOC**



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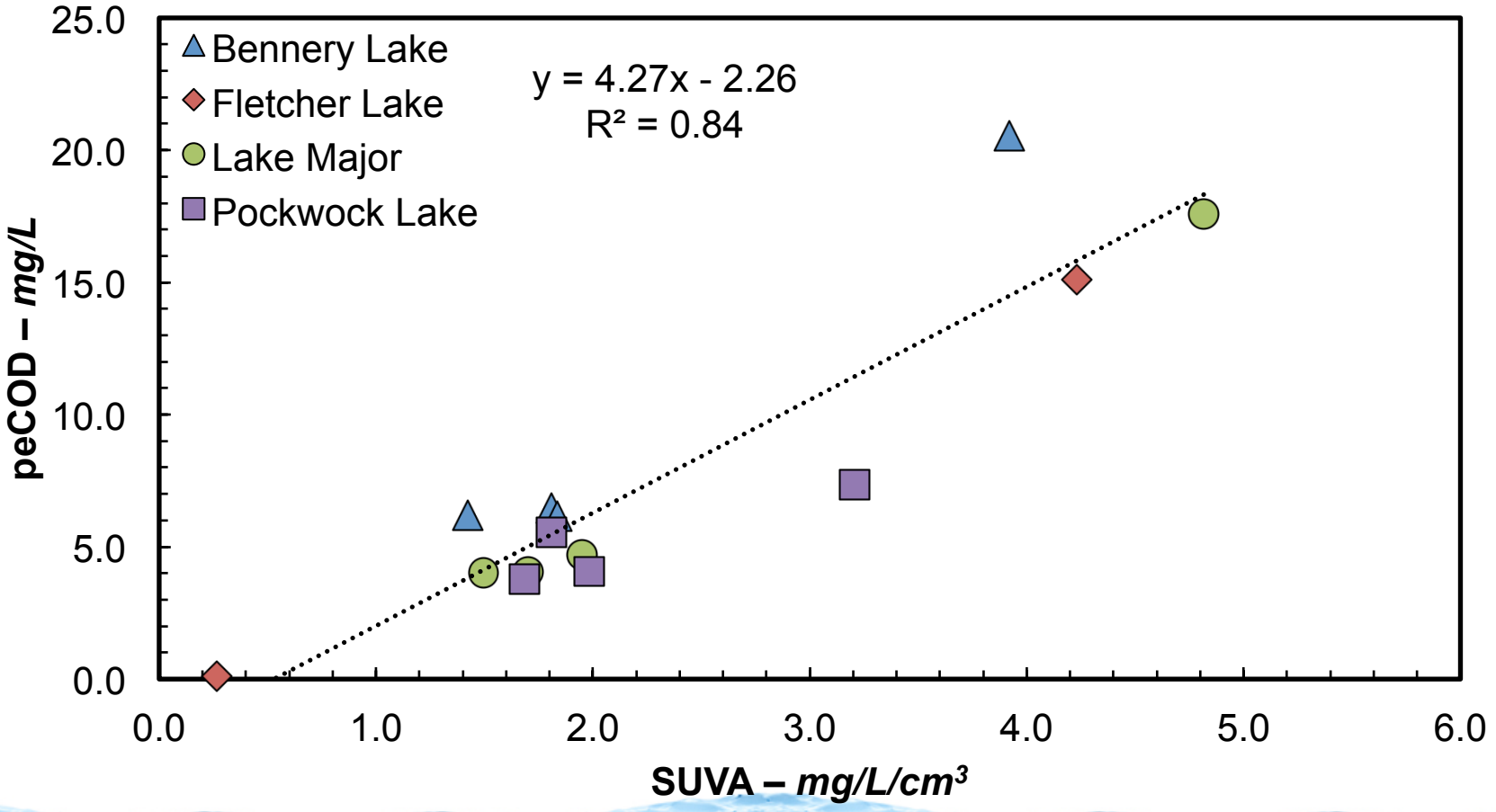
Method Validation:

Various Treatment Plants in Nova Scotia – **peCOD and SUVA**



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Case Study: Biofiltration Monitoring

Biofiltration Monitoring : Background

- Direct filtration drinking water treatment plant underwent conversion to biofiltration through removal of pre-chlorination
- Conversion resulted in
  - Reduction in HAAs (~40-60%) and THMs (~20-60%)
  - Increase in bioactivity on the filter media
    - 40 ng ATP/cm^3 to 200-300 ng ATP/cm^3
- However, limited DOC removal across the filter occurred, making it difficult to assess treatment performance

Decrease in THM and HAA concentrations as a result of conversion

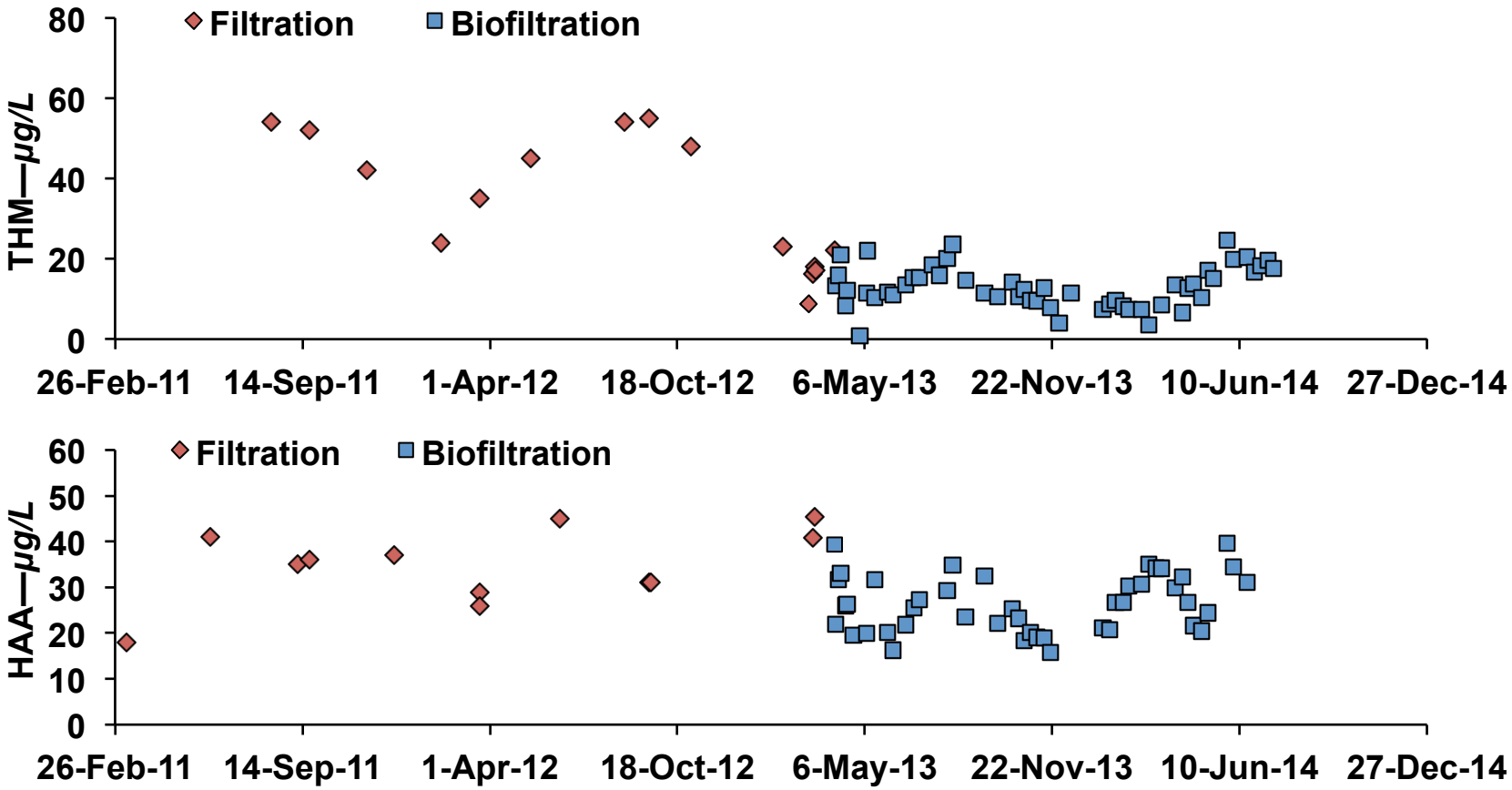
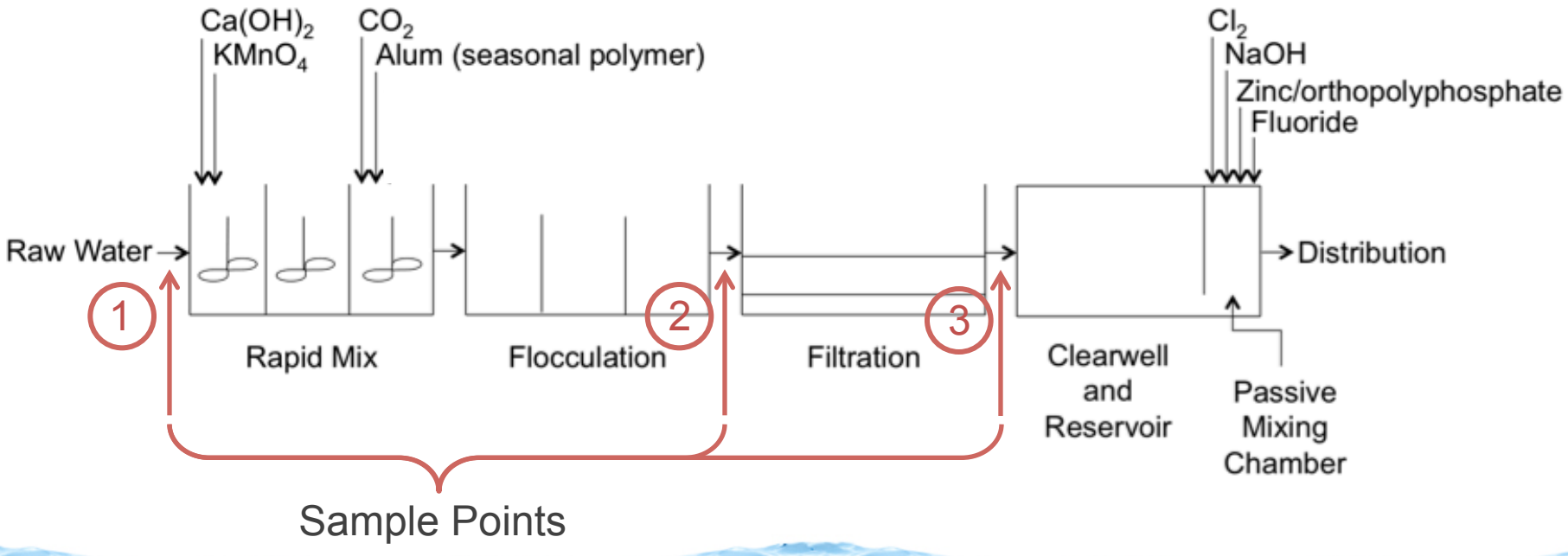


Figure adapted from: Stoddart, A. K., & Gagnon, G. A. (2015). JAWWA.

Biofiltration Monitoring : Approach

- Monitored NOM surrogates (TOC, DOC and peCOD) at 3 locations for a period of 9 months



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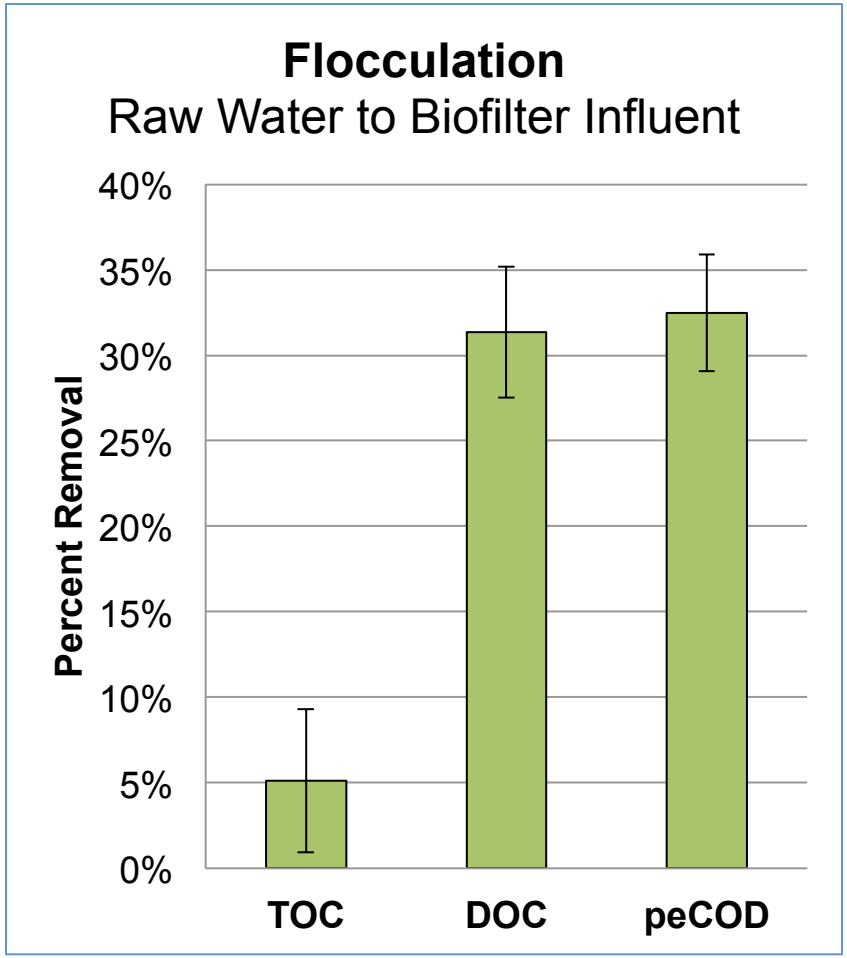
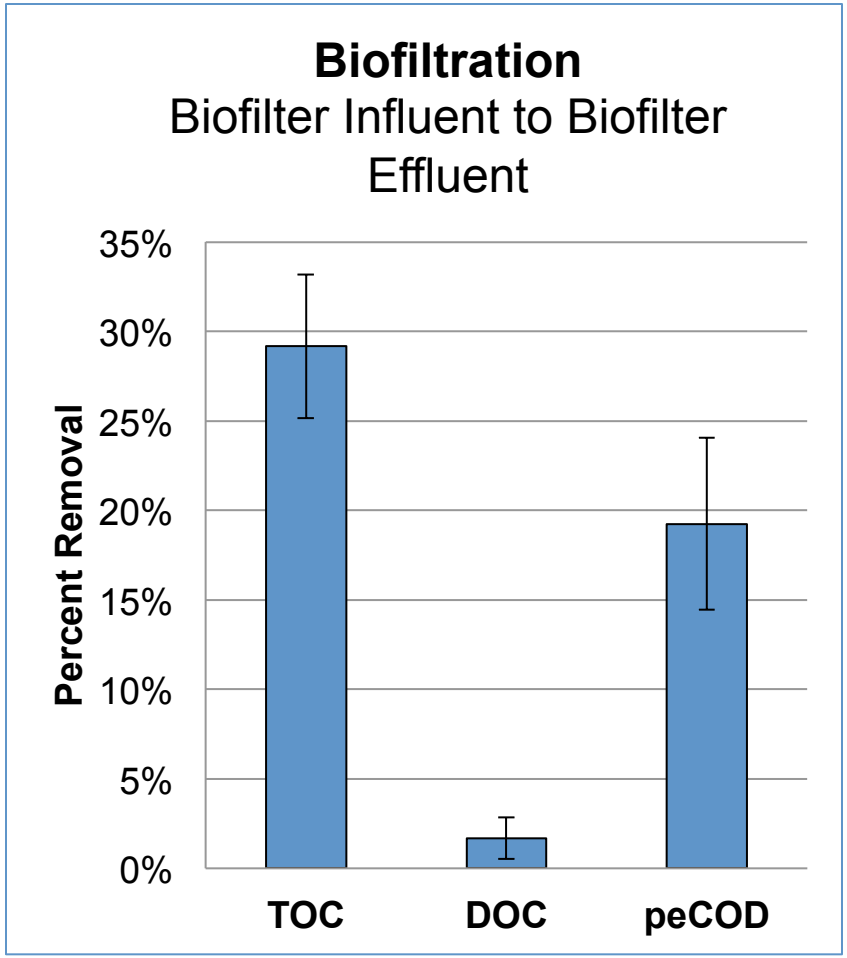
Effect of Flocculation



Error bars represent 95% CI

- Limited removal of TOC
  - TOC: 5 ± 4%
  - Includes flocculated material
- Similar removal of DOC and peCOD
  - DOC: 31 ± 4%
    - Does not measure flocculated material (0.45 µm filtration as sample preparation)
  - peCOD: 32 ± 3%
    - Assumed to measure only soluble portion

Effect of Biofiltration



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- Greatest average removal of TOC
  - TOC: 29 ± 4%
  - Flocculated material filtered out
- Limited average removal of DOC
  - DOC: 2 ± 1%
- More peCOD removal
  - peCOD: 19 ± 5%

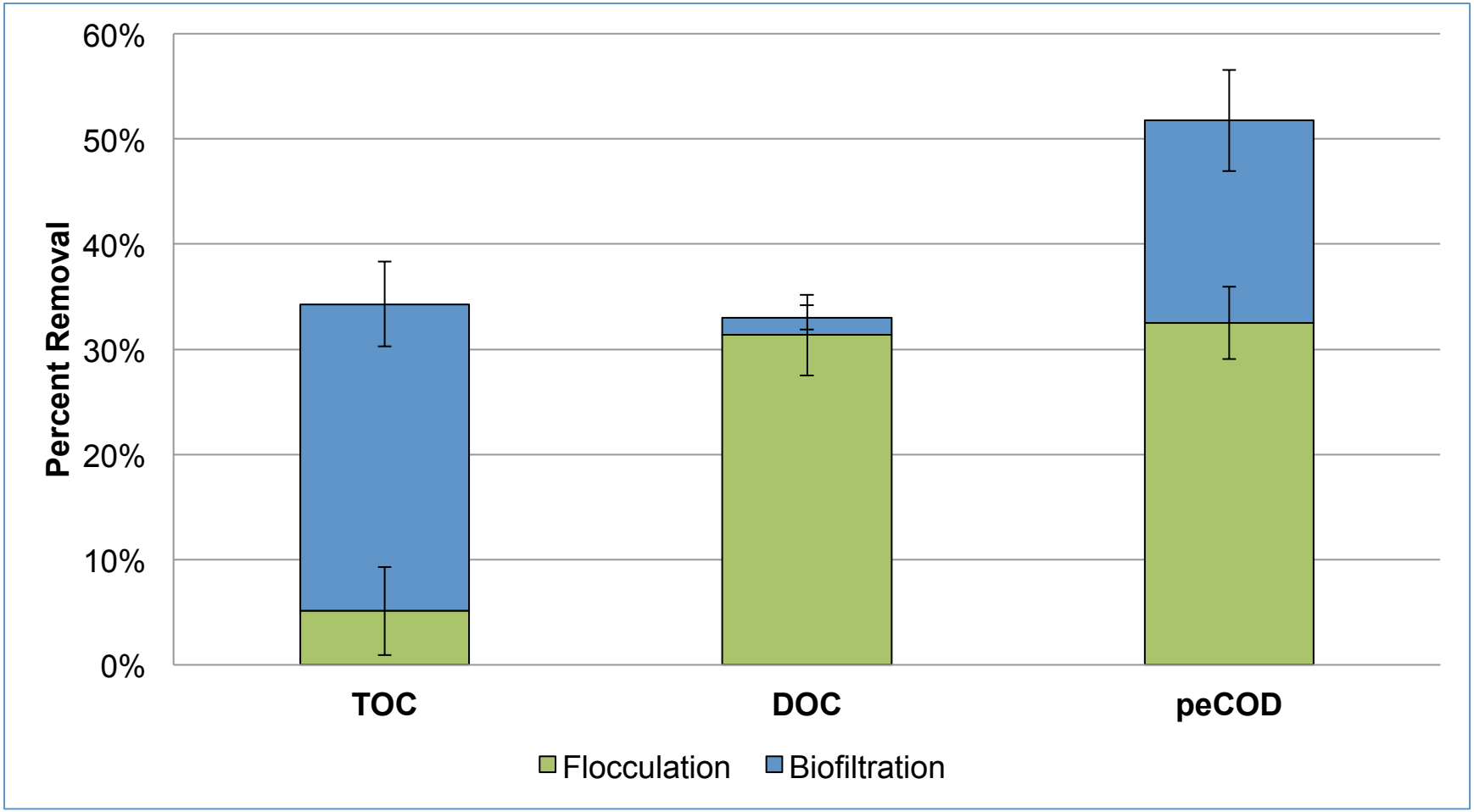
Effect of Flocculation and Biofiltration

NOM Surrogate	Raw Water	Flocculated Water	Biofiltered Water
TOC—*mg/L*	3.16 ± 0.13	3.00 ± 0.16	2.06 ± 0.07
DOC—*mg/L*	3.04 ± 0.34	2.07 ± 0.06	2.09 ± 0.12
peCOD—*mg/L*	8.51 ± 0.55	5.90 ± 0.46	4.64 ± 0.42

Effect of Flocculation and Biofiltration

NOM Surrogate	Raw Water	Flocculated Water	Removal	Biofiltered Water	Removal
TOC—*mg/L*	3.16 ± 0.13	3.00 ± 0.16	0.16	2.06 ± 0.07	0.94
DOC—*mg/L*	3.04 ± 0.34	2.07 ± 0.06	0.97	2.09 ± 0.12	-0.05
peCOD—*mg/L*	8.51 ± 0.55	5.90 ± 0.46	2.61	4.64 ± 0.42	1.26

Treatment Train: Combined Effect of Flocculation and Biofiltration



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Treatment Train: Combined Effect of Flocculation and Biofiltration

SUVA	Expected DOC Removal Using Alum
>4	>50%
2-4	25-50%
<2	<25%

Source water SUVA:
3.4 ± 0.1

Expected DOC removal with alum[1]:
25-50%

Table. Adapted from Edzwald and Tobiason, 1999; [1]Edzwald and Tobiason, 1999

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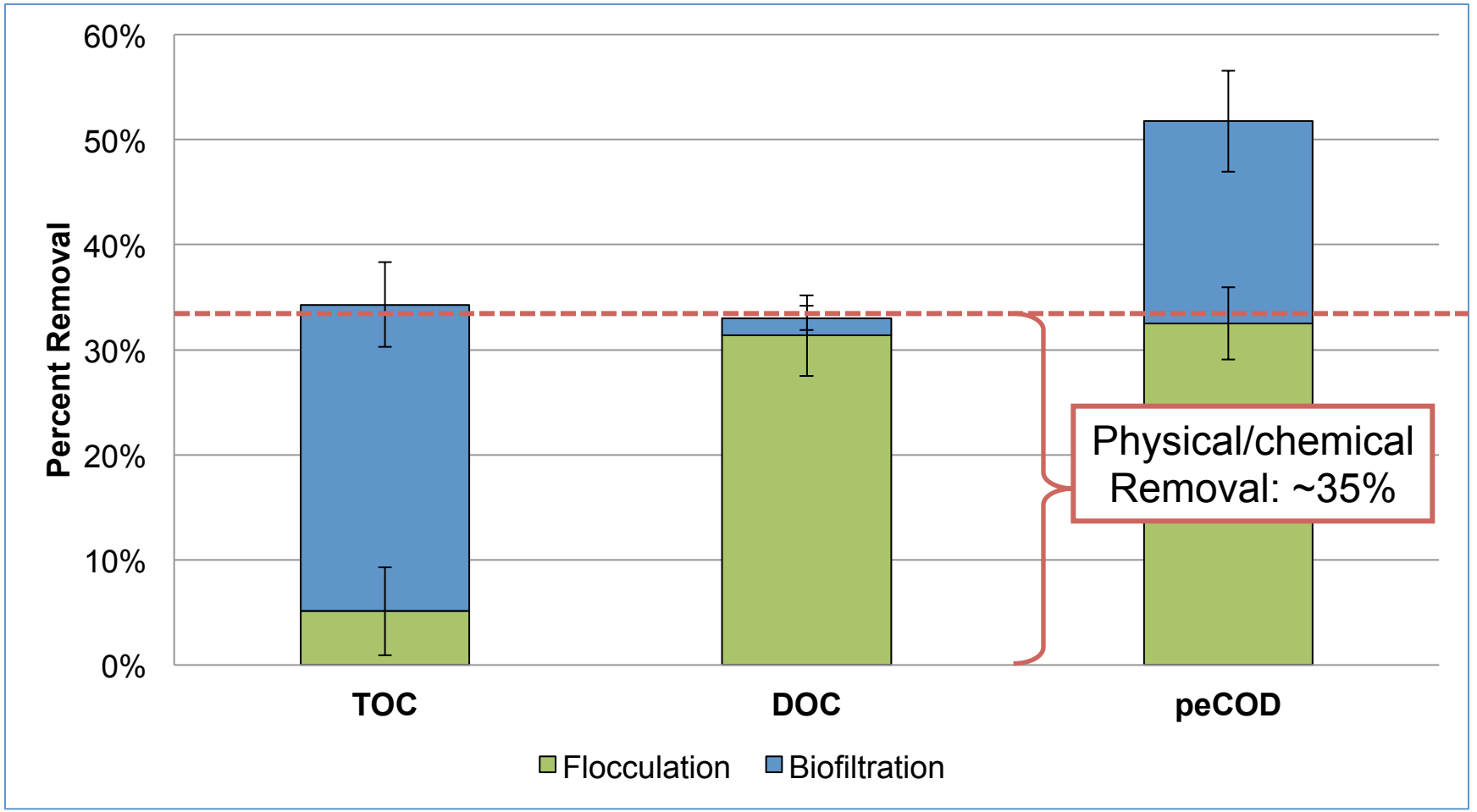

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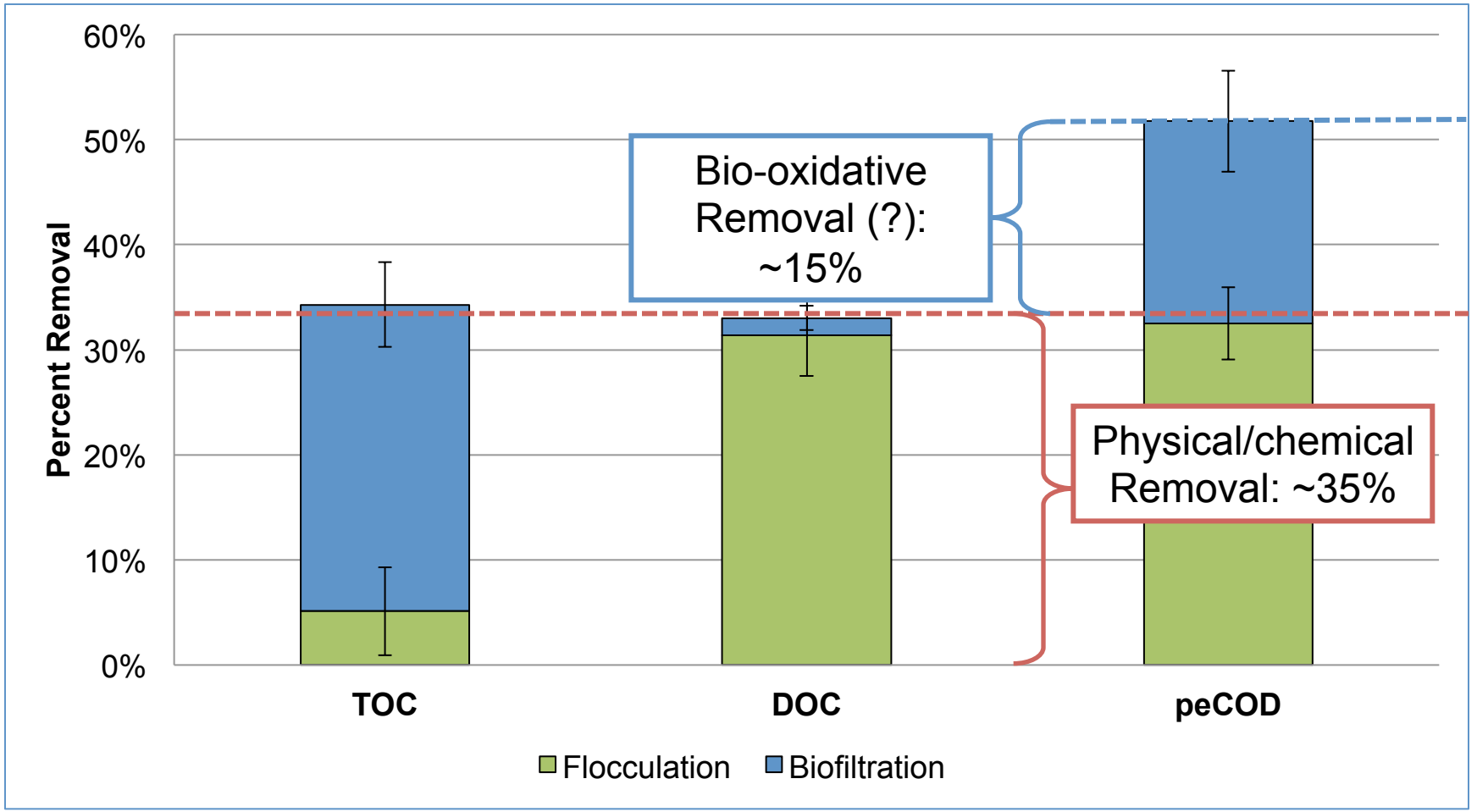

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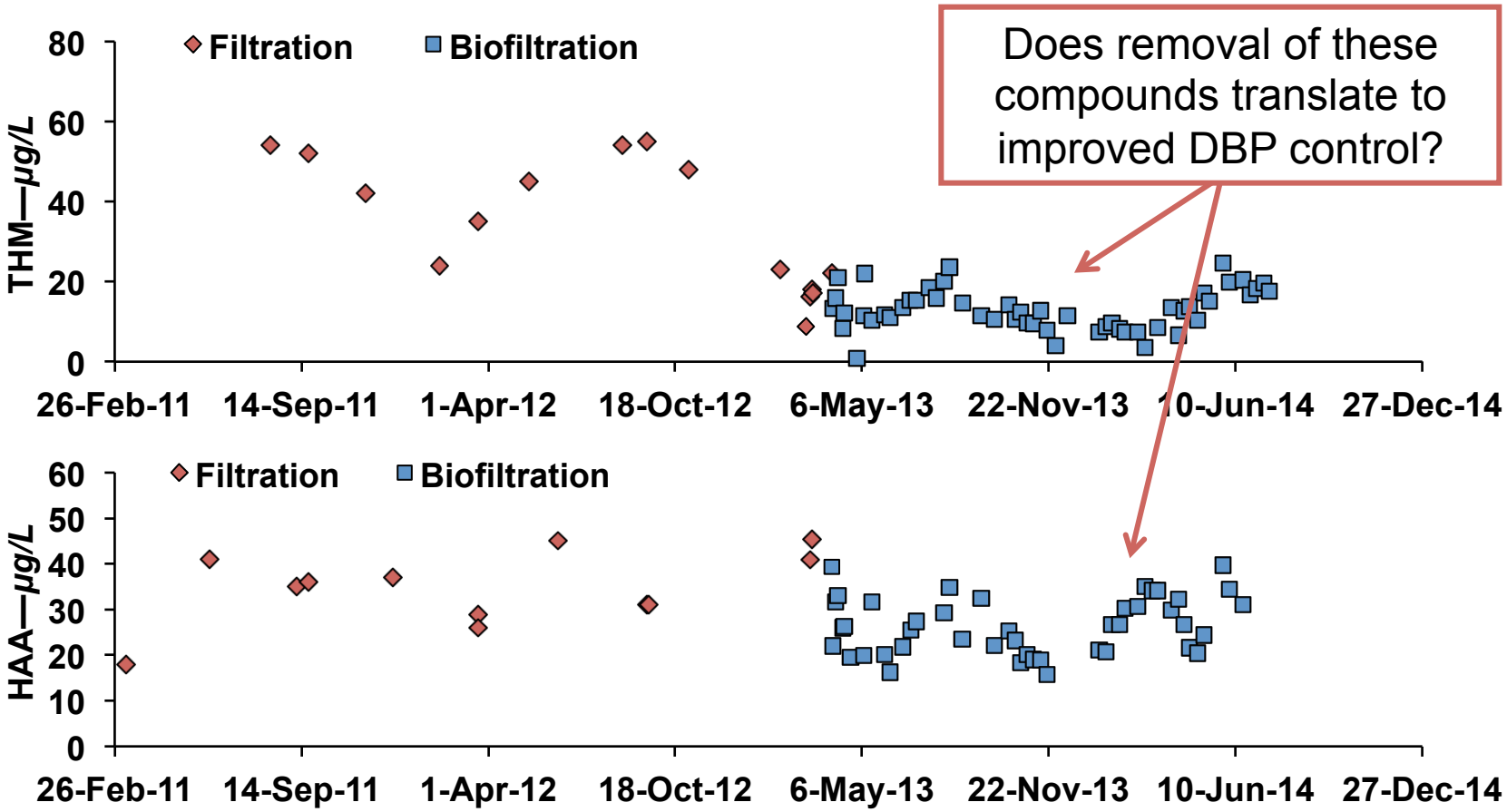

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Conclusions

- peCOD can measure NOM rapidly, at low concentrations and without the use of hazardous chemicals
- peCOD is an appropriate bulk NOM parameter
- The use of peCOD to monitor biofiltration may provide additional information on NOM removal and subsequent biofilter performance to compliment other NOM surrogates