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Effect of Biological Activated Carbon Filters on the Removal of Biodegradable NOM and Molecular Weight

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Natural Organic Matter (NOM) is a complex mixture of organic materials (e.g. humic substances) present in natural waters[1].

- Chlorine disinfection has been shown to form potential carcinogenic compounds labelled disinfection by-products (DBPs)
- Disinfection By-Products have been of increasing concern and are now regulated by governing bodies (USEPA, Health Canada).
  - *Conventional treatment processes may not be capable of meeting current and future water quality guidelines[1].*

Integrated treatment processes that combine oxidation processes and activated carbon biofilters have been shown to be very effective at reducing natural organic matter (NOM) levels [1, 2, 3].

Oxidation Processes	• Increased concentration Biodegradable Organic Matter (BOM)
Biofiltration	• Removal of BOM, measured as Biodegradable Dissolved Organic Carbon (BDOC)

Ozone is a strong oxidant. Typical ozone doses result in[4]:

- Small destruction of TOC
- Increased polarity & decreased aromaticity
- Shift from HMW to LMW

→**Leads to an increase in the biodegradability of TOC after ozonation.**

Disinfection	• Only enough to inactivate organisms • Formation of BOM is undesirable
Reduction of DBPs	• Maximize production of BOM for removal by biofiltration

Advanced Oxidation Processes (AOPs)

Oxidation processes that generate hydroxyl free radicals (•OH)

Non-selective oxidant that quickly oxidizes most organic compounds (e.g. aromatic hydrocarbons)[5]

Many types of AOPs→ UV/H_2O_2

UV photolysis: H_2O_2 molecules produce •OH radicals

$$H_2O_2 + \Sigma hv \longrightarrow 2\ \bullet OH$$

Biofiltration is a critical part of this integrated process:

- Key purpose is to remove BDOC formed during oxidation, thereby reducing DBPFP & potential regrowth
- Insufficient or inadequate bacterial growth within the filter leads to[1,4]:
  - *Incomplete removal of biodegradable organic matter*
  - *Increased potential of DBP formation*
  - *Production of biologically unstable water*

    →Implications on treatment efficiency & distribution system health

Oxidation processes lead to the formation of biodegradable dissolved organic carbon (BDOC)

Studies show that there are three forms of BDOC[1,2,5,6]

Rapidly biodegradable ($BDOC_r$)

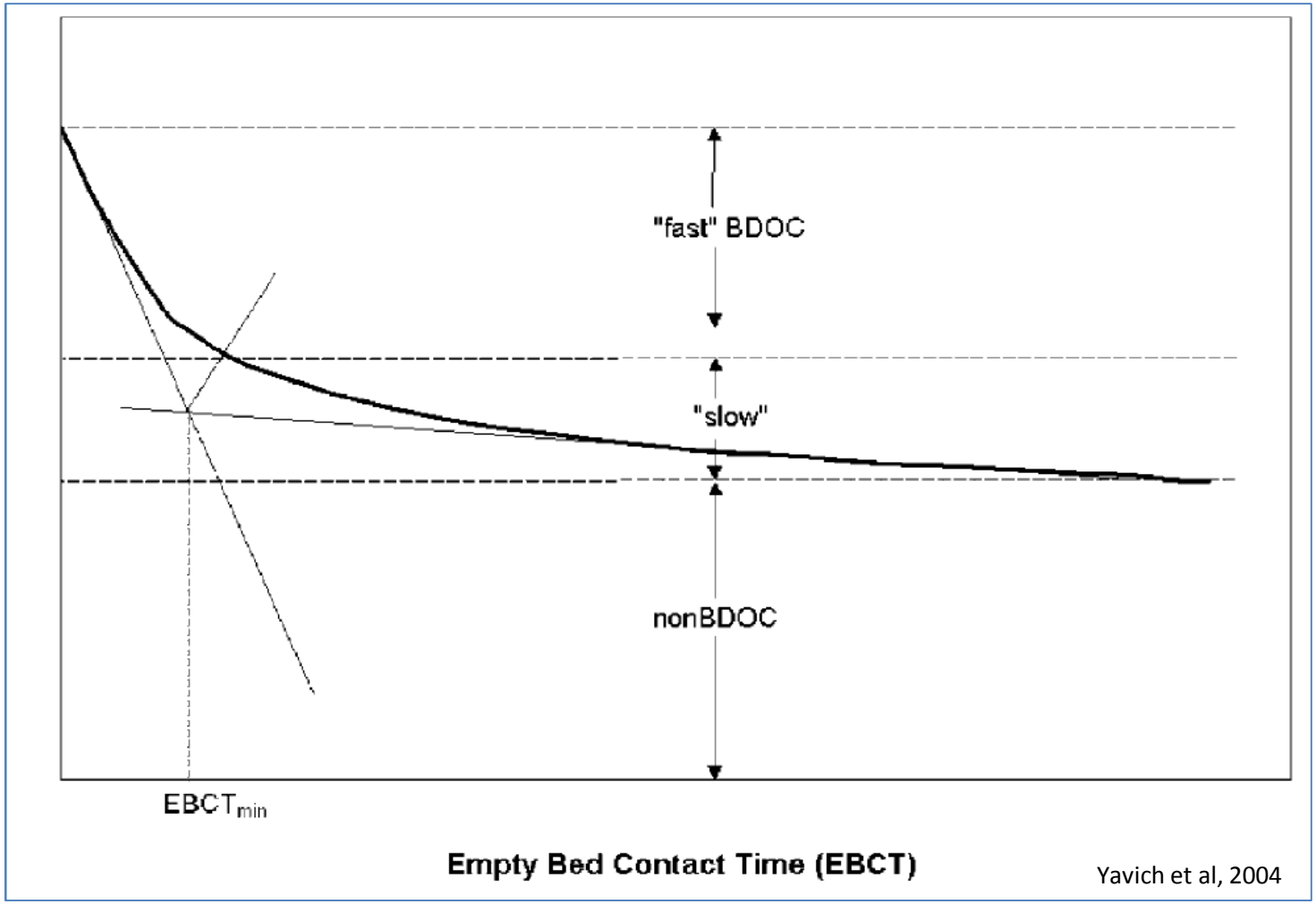
Slowly biodegradable ($BDOC_s$)

Non-biodegradable

WHY?

- Rapidly Biodegradable Organic Carbon leads to the potential formation of DBPs
- Slowly Biodegradable Organic Carbon leads to bacterial regrowth within the distribution system

Determination of Biodegradable Fractions

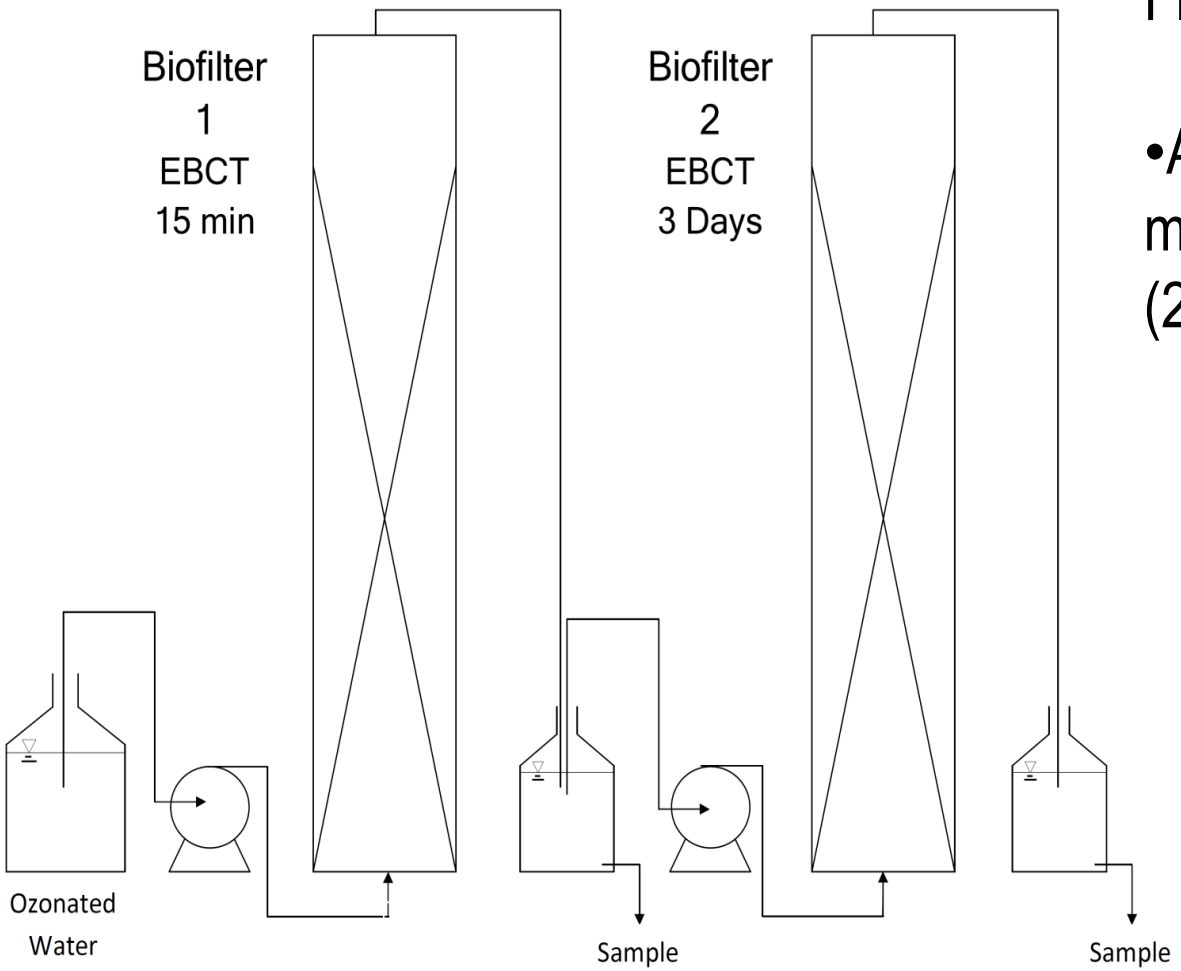


Yavich et al, 2004

Project focus:

- **Part 1 - Biofiltration Experiments: To assess the removal of NOM through biological activated carbon filtration.**
  - To assess the impact of ozonation and biofiltration on source water quality including TOC, UVA, SUVA, AMW and DBPFP.
  - To acclimatize biomass in order to perform the biodegradation experiments in Part 2.

Experimental Setup



- Granular Activated Carbon Filters, Picabiol®
- Acclimatization over 5 months with Ozonated water (2mgO_3/mg DOC)

Raw Water Characteristics:

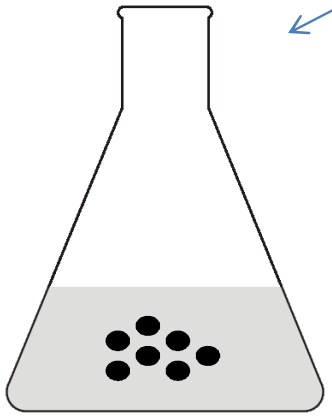
- *5 mg/L TOC*
- *Alkalinity 50 mg/L as $CaCO_3$*
- *Hardness, 50 mg/L as $CaCO_3$*
- *Temperature 22°C*
- *pH ~ 7*

Project focus:

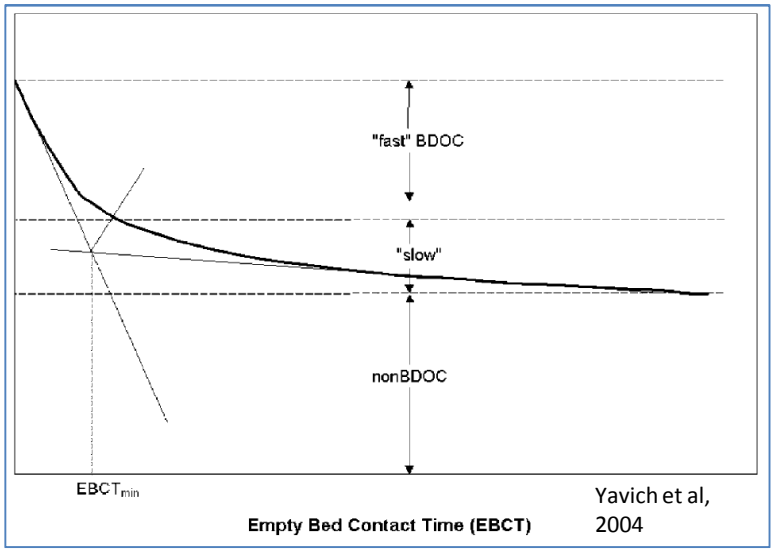
- **Part 2 - Biodegradation Experiments: To assess the effect of oxidation on the rate of biodegradation.**
  - To establish the effect of ozonation or UV/ H2O2 in combination with biological activated carbon filtration on the rate of biodegradation of organic matter and source water quality parameters including TOC, UVA, SUVA, AMW and DBPFP.
  - To develop a technique to evaluate biodegradation within activated carbon biofilters by determining the rate kinetics governing the removal of DOC over time.

In series with filtration experiments, biodegradation tests were performed to determine removal of biodegradable organic carbon during oxidation and biofiltration.

Harvest Acclimated Biomass → Place in a Reactor with Treated Water → Place in Shaker at 22°C for Various Times → Measure DOC, SUVA, AMW



4, 8, 12, 18 hrs; 1, 2, 3, 4, 5, 6, 7 days

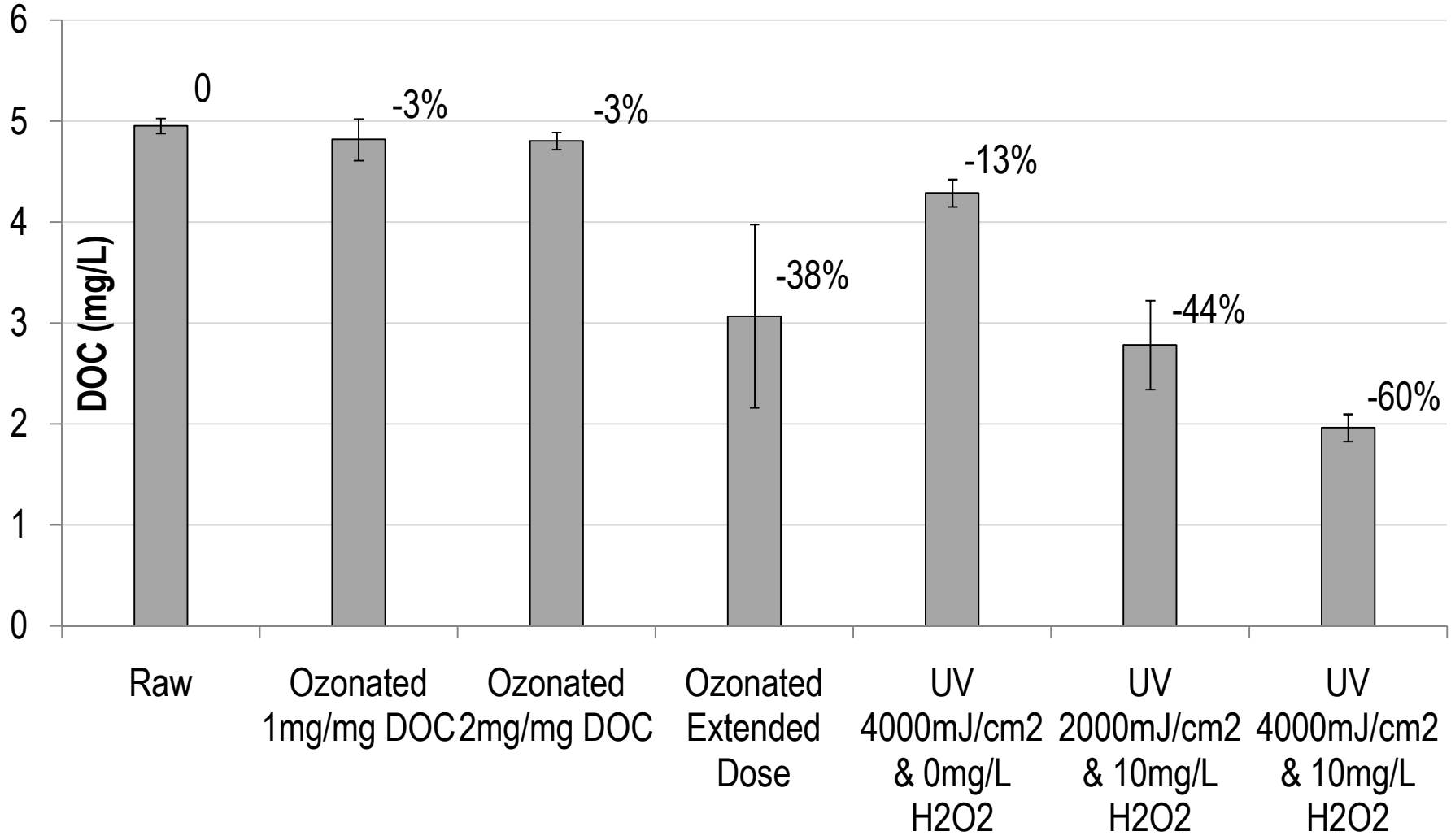


Yavich et al, 2004

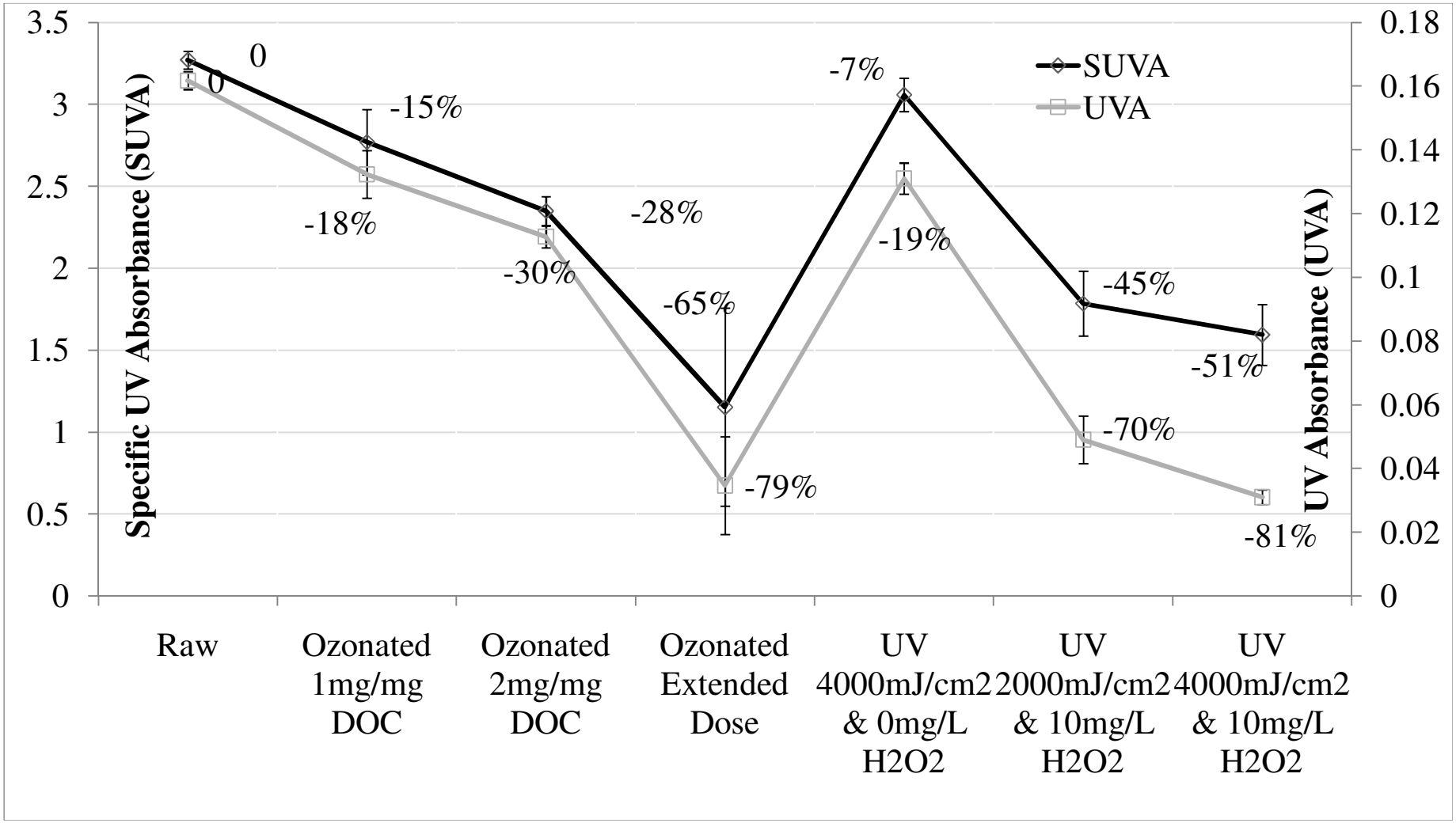
Source of Biomass	Oxidant	Dose	Reaction Times
BAC Column 1 & 2	*None*	-	
	Ozone	1 mg/ mg DOC	
	Ozone	2 mg/ mg DOC	4, 8, 12,
	Ozone	Extended Dose (≈25 mg/mg DOC)	18 hrs; 1, 2, 3, 4, 5,
	AOP	2000 mJ/cm2 & 10 mg/L H_2O_2	6, 7 days
	AOP	4000 mJ/cm2 & 10 mg/L H_2O_2	
	AOP	4000 mJ/cm2 & 0 mg/L H_2O_2	

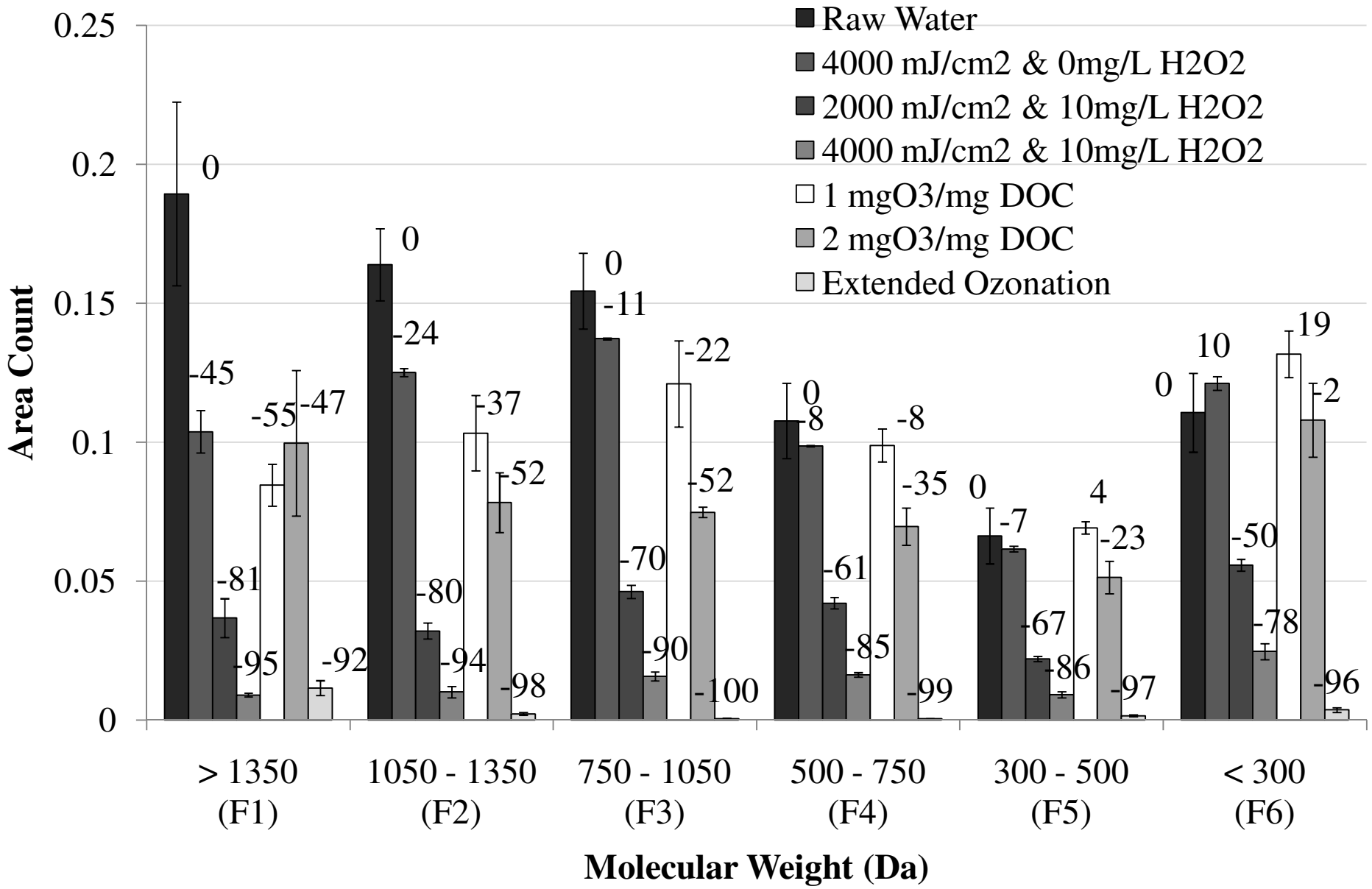
RESULTS

Part 2 - Effect of Oxidation on DOC

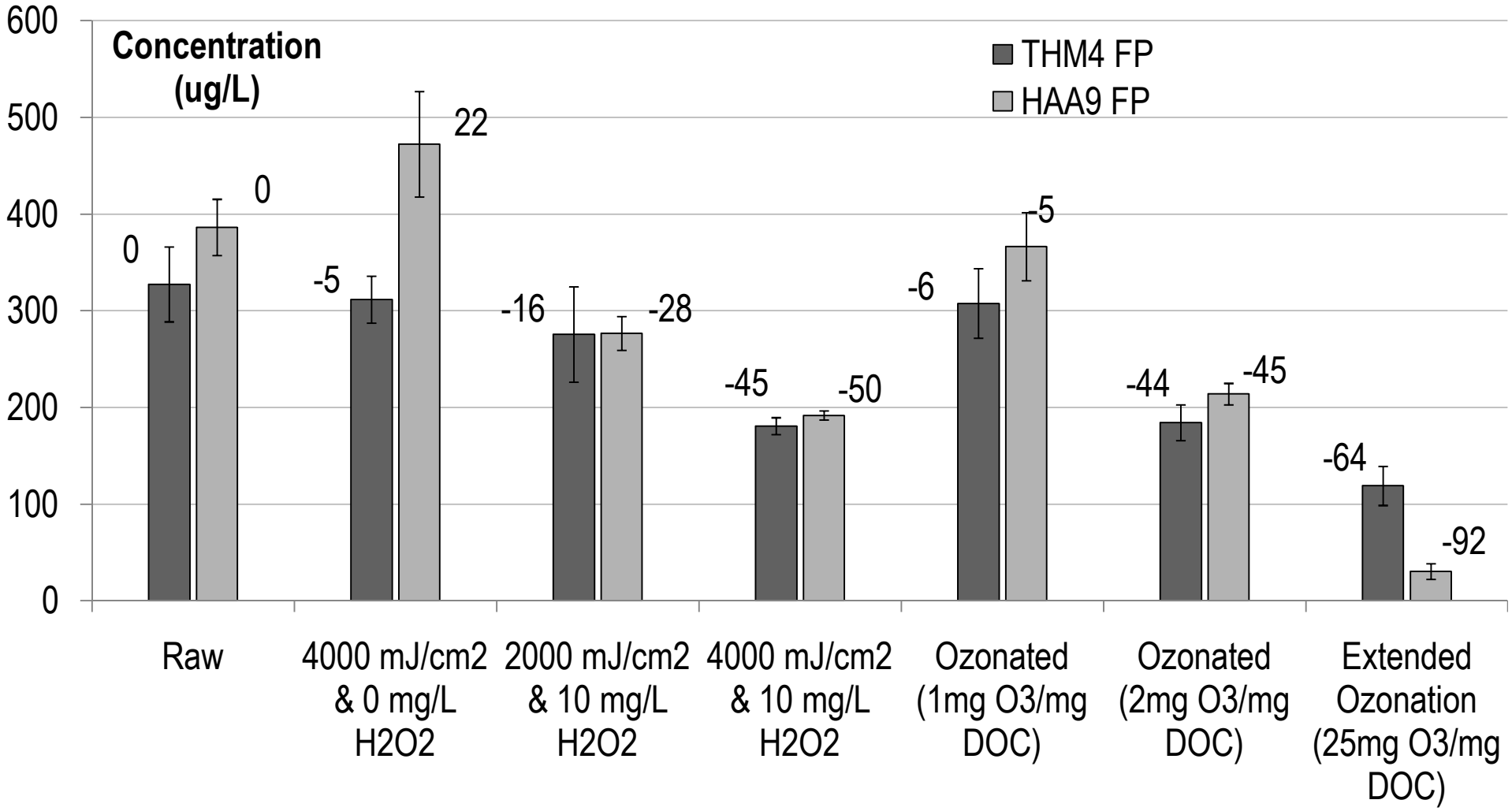


Part 2 - Effect of Oxidation on UVA

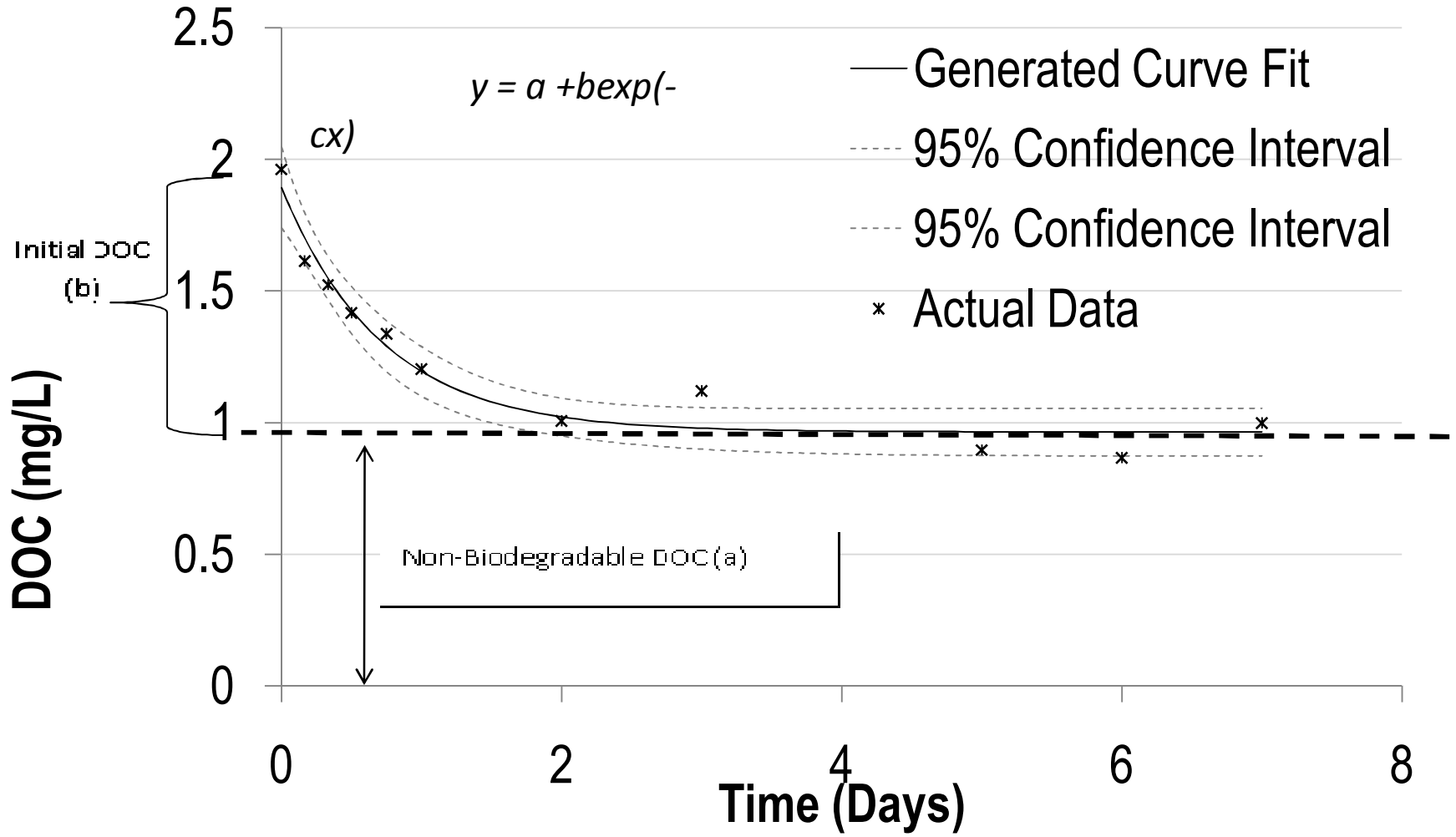


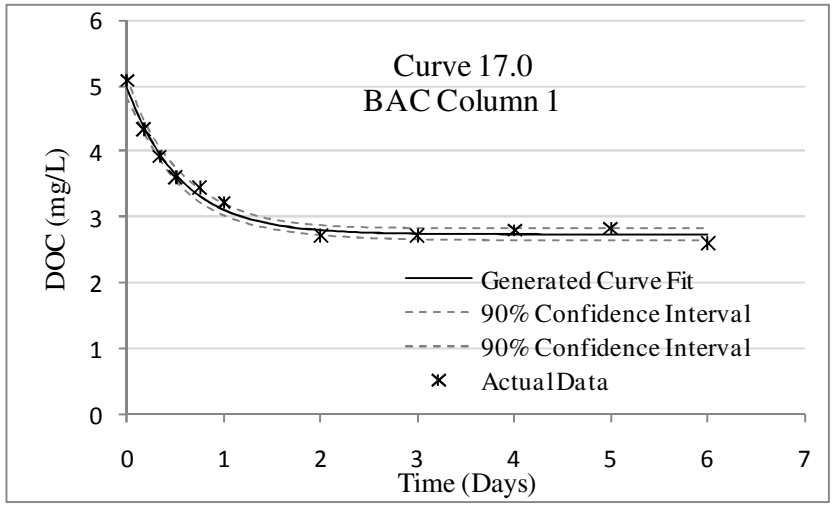

Raw Water
4000 mJ/cm2 & 0mg/L H2O2
2000 mJ/cm2 & 10mg/L H2O2
4000 mJ/cm2 & 10mg/L H2O2
1 mgO3/mg DOC
2 mgO3/mg DOC
Extended Ozonation
Area Count
0.25
0.2
0.15
0.1
0.05
0
0 -45 -81 -95 -55 -47 -92
0 -24 -80 -94 -37 -52 -98
0 -11 -70 -90 -22 -52 -100
0 -8 -61 -85 -8 -35 -99
0 -7 -67 -86 4 -23 -97
0 10 -50 -78 19 -2 -96
> 1350 (F1)
1050 - 1350 (F2)
750 - 1050 (F3)
500 - 750 (F4)
300 - 500 (F5)
< 300 (F6)
Molecular Weight (Da)

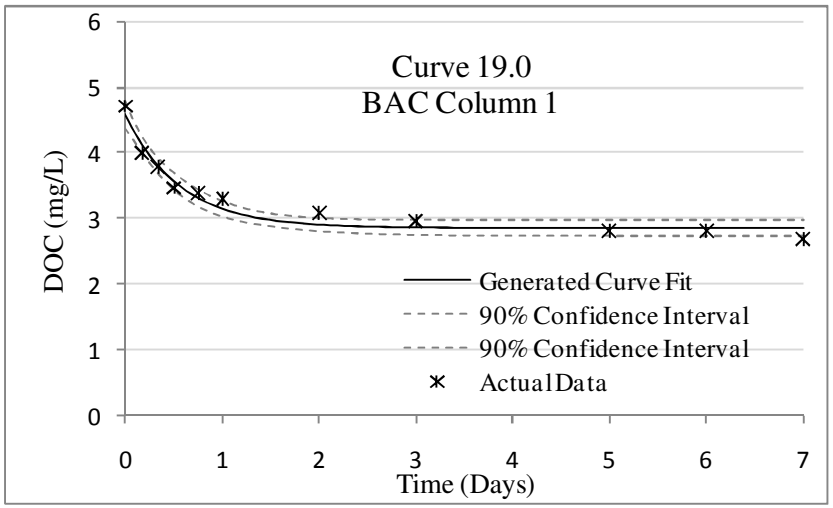
Part 2 - Effect of Oxidation on DBPFP

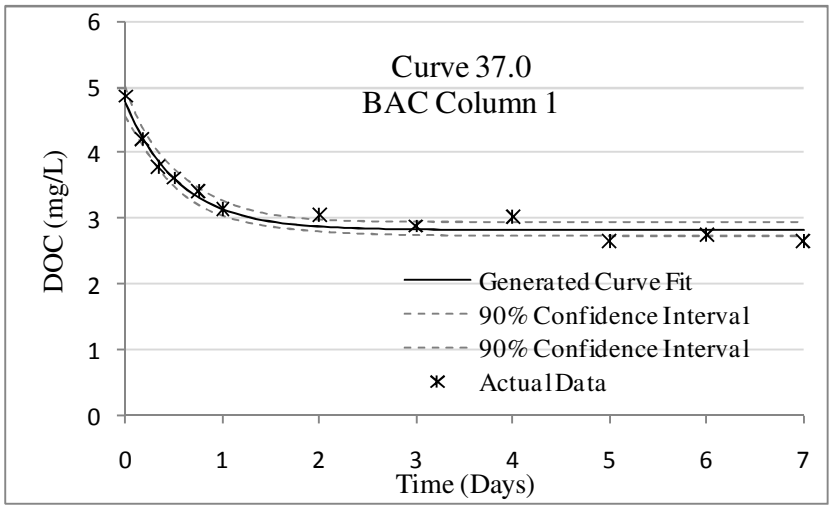


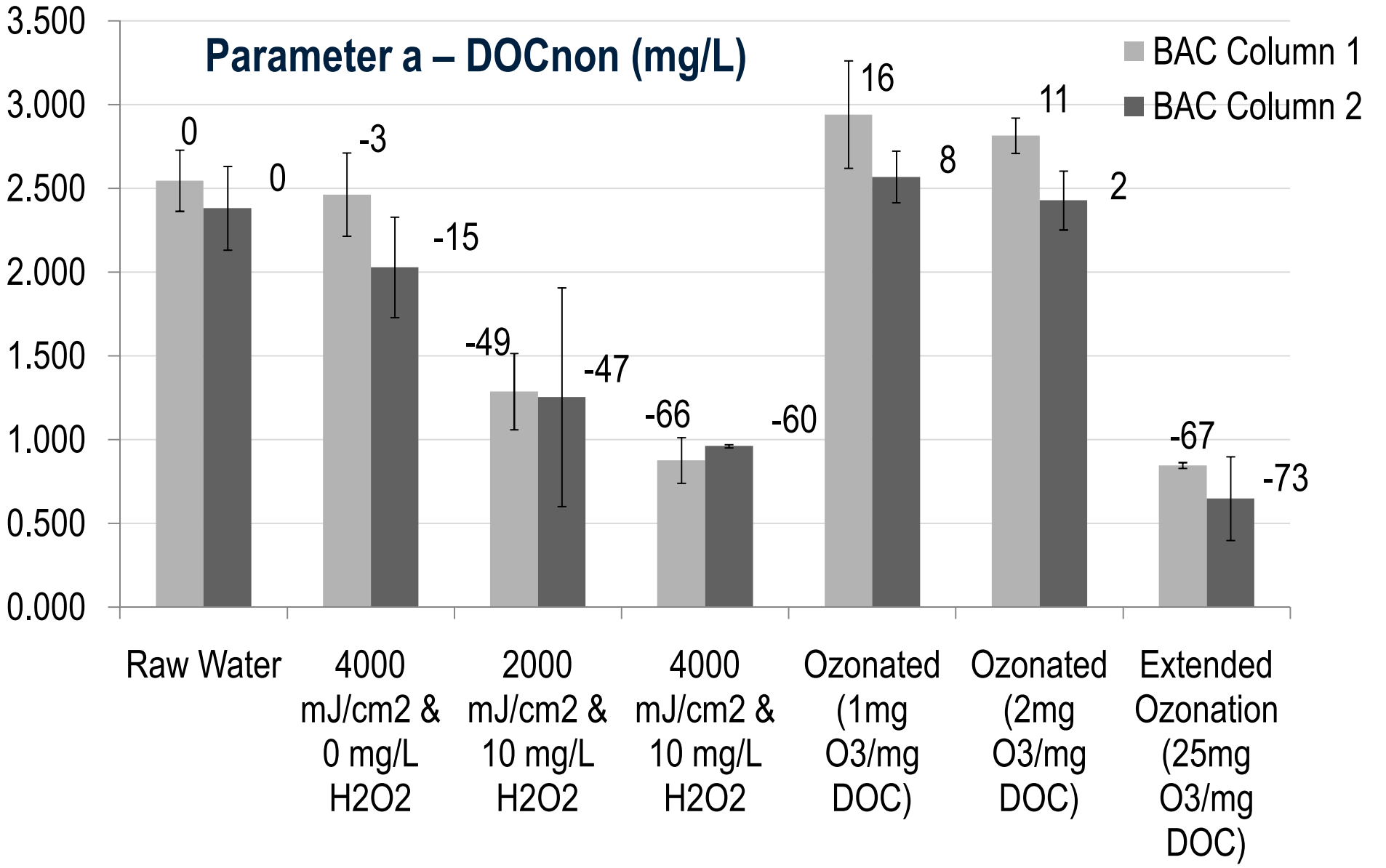
Part 2 - Effect of Biodegradation on NOM

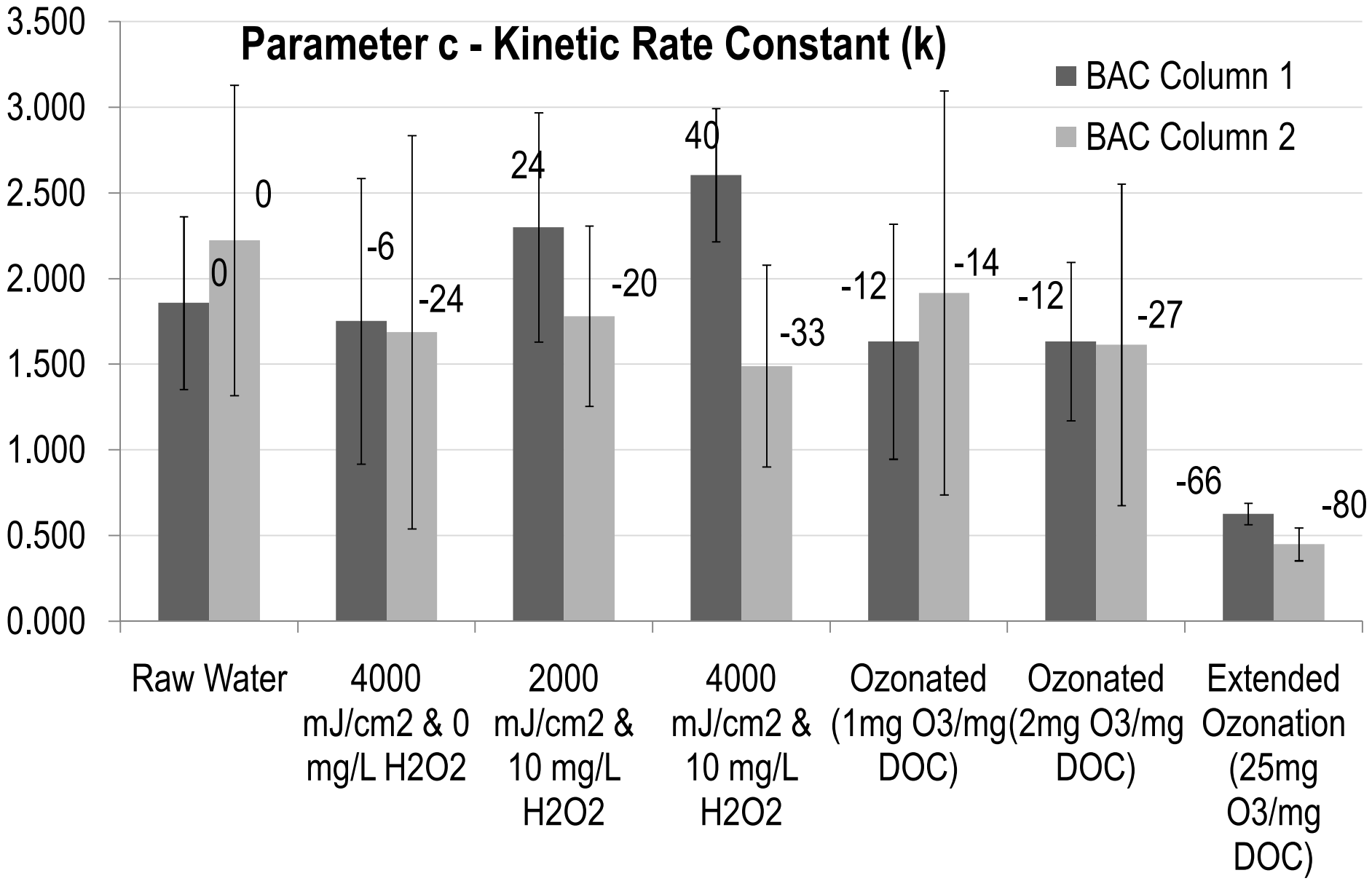


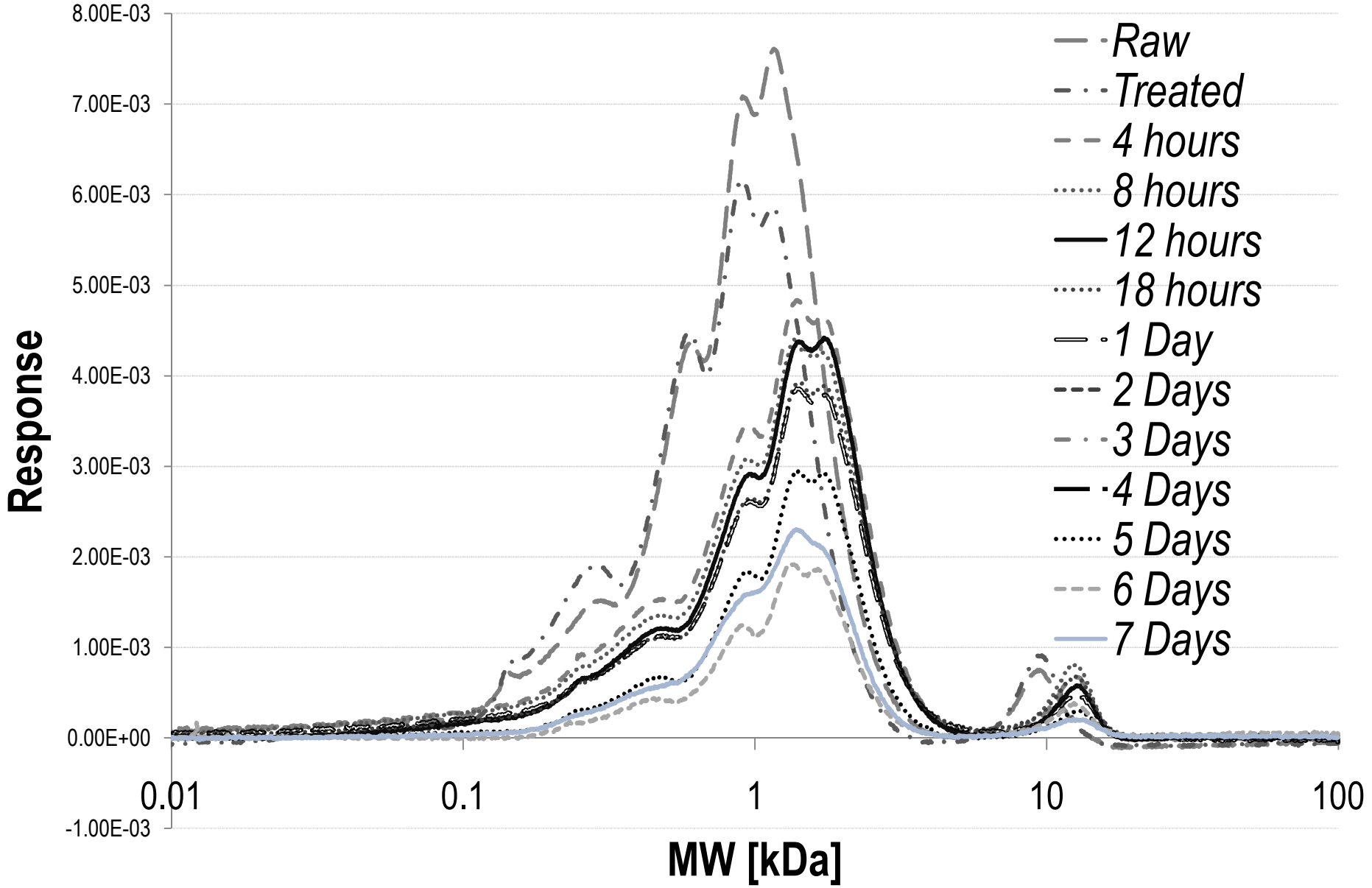

Curve 17.0
BAC Column 1
DOC (mg/L)
Time (Days)
Generated Curve Fit
90% Confidence Interval
90% Confidence Interval
Actual Data


Curve 19.0
BAC Column 1
DOC (mg/L)
Time (Days)
Generated Curve Fit
90% Confidence Interval
90% Confidence Interval
Actual Data

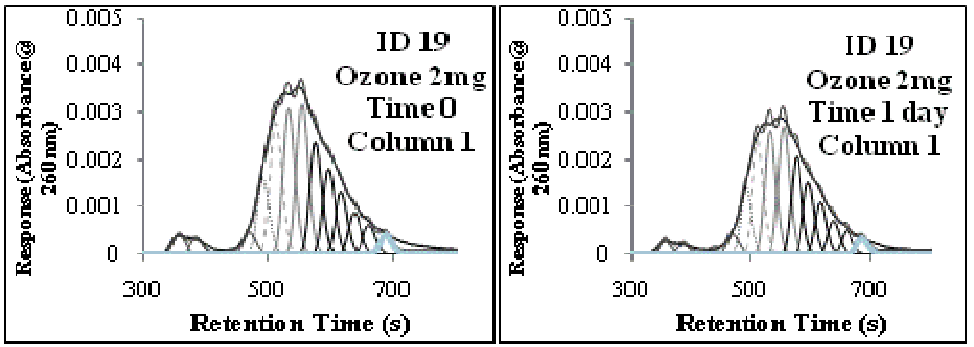

Curve 37.0
BAC Column 1
DOC (mg/L)
Time (Days)
Generated Curve Fit
90% Confidence Interval
90% Confidence Interval
Actual Data

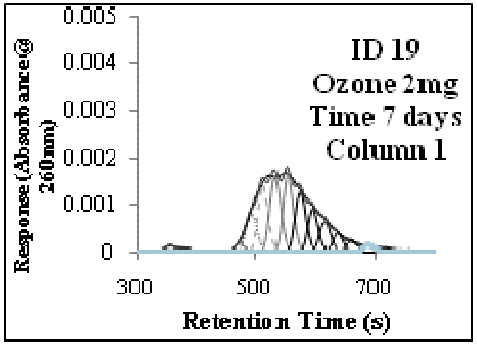

Parameter a – DOCnon (mg/L)
BAC Column 1
BAC Column 2
3.500
3.000
2.500
2.000
1.500
1.000
0.500
0.000
0
0
-3
-15
-49
-47
-66
-60
16
8
11
2
-67
-73
Raw Water
4000 mJ/cm2 & 0 mg/L H2O2
2000 mJ/cm2 & 10 mg/L H2O2
4000 mJ/cm2 & 10 mg/L H2O2
Ozonated (1mg O3/mg DOC)
Ozonated (2mg O3/mg DOC)
Extended Ozonation (25mg O3/mg DOC)

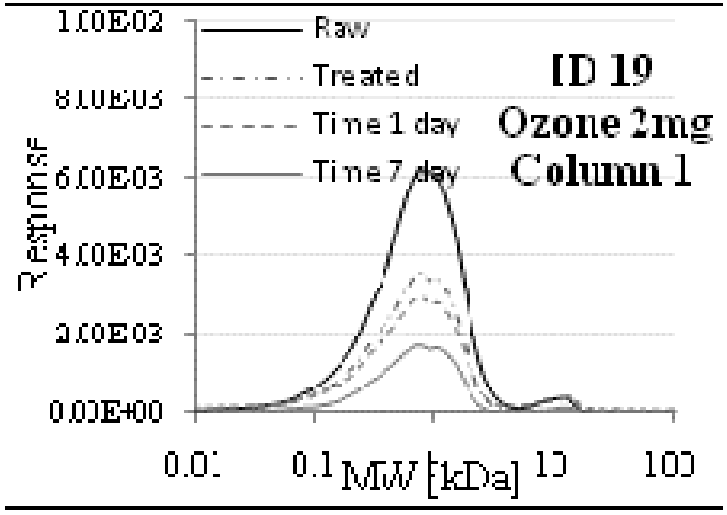

Parameter c - Kinetic Rate Constant (k)
BAC Column 1
BAC Column 2
3.500
3.000
2.500
2.000
1.500
1.000
0.500
0.000
0
0
-6
-24
24
-20
40
-33
-12
-14
-12
-27
-66
-80
Raw Water
4000 mJ/cm2 & 0 mg/L H2O2
2000 mJ/cm2 & 10 mg/L H2O2
4000 mJ/cm2 & 10 mg/L H2O2
Ozonated (1mg O3/mg DOC)
Ozonated (2mg O3/mg DOC)
Extended Ozonation (25mg O3/mg DOC)

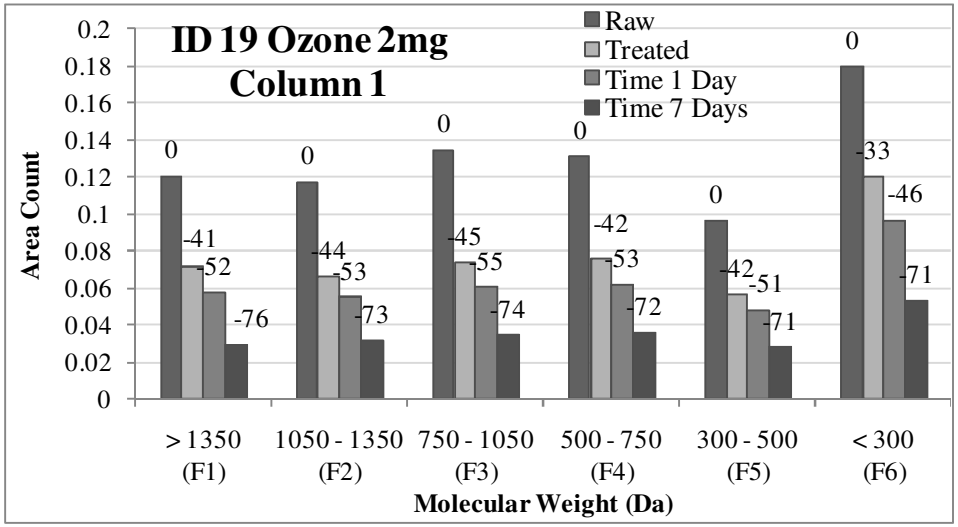

8.00E-03
7.00E-03
6.00E-03
5.00E-03
4.00E-03
3.00E-03
2.00E-03
1.00E-03
0.00E+00
-1.00E-03
Response
0.01
0.1
1
10
100
MW [kDa]
Raw
Treated
4 hours
8 hours
12 hours
18 hours
1 Day
2 Days
3 Days
4 Days
5 Days
6 Days
7 Days

Part 2 - Effect of Biodegradation on NOM









Part 1 Conclusions

- Ozonation at 2 mg O_3/mg DOC did not result in a significant reduction in DOC, but did have a significant effect on UVA & AMW.
- DBPFP was significantly reduced following ozonation; However, overall ozonation was unable to lower DBPFP below the Canadian Drinking Water Guideline values.
- Subsequent biofiltration resulted in significant reduction in DOC levels.
- BAC Column 1 preferentially biodegraded the smaller molecular weight NOM that was more biodegradable.
- Only BAC Column 2 was able to lower the DBPFP and generate THM and HAA concentrations that were below the Health Canada Canadian Drinking Water Guideline values.

Part 2 Conclusions

- High dose oxidation is required to lower DOC levels significantly.
- High dose ozonation & UV/H2O2 was successful at significantly lowering the fraction and amount of aromatic material present in feed water.
- Ozonation at 2mg O3/mg DOC and UV/H2O2 treatment at 2000mJ/cm2 and 10 mg/L resulted in a shift from high AMW to low AMW NOM. This effect was not as noticeable for the higher ozonation and AOP doses.
- Only the extended ozonation dose of 25 mgO3/mg DOC was able to meet the Canadian Drinking Water Guideline limits for THMs and HAAs.

Part 2 Conclusions

- *Results suggest that the amount of non-biodegradable DOC is a function of the type and dose of oxidant used.*
- *With the exception of the ozonation at 25mgO3/mg DOC, kDOC was not a function of the type or dose of oxidant used.*
- *Very little biodegradation occurred at the high dose UV/H2O2 and extended ozonation doses – in contrast to the lower doses.*
- *Results suggest that lower AMW NOM is preferentially biodegraded during biofiltration.*
- *Biomass from BAC Column 1 and BAC Column 2 resulted in similar biodegradation kinetics*

THANK YOU!

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1) Yavich, A.A., Lee, K.H., Chen, K.C., Pape, L. & Masten, S.J. (2004). Evaluation of biodegradability of NOM after ozonation. Water Research. 38 (12) pp. 2839 - 2846.
2) Health Canada. (2008). Guidelines for Canadian Drinking Water Quality. Federal-Provincial-Territorial Committee on Drinking Water. May, 2008. Available at http://www.hc-sc.gc.ca/ewh-semt/alt_formats/hecs-sesc/pdf/pubs/water-eau/sum_guide-res_recom/summary-sommaire-eng.pdf
3) Cipparone L.A., Diehl A.C. & Speitel, Jr. G.E. (2007). Ozonation and BDOC removal: effect on water quality. J. Am. Water Works Assoc. 89 2 (1997), pp. 84–97.
4) Carlson, K.H. & Amy, G.L. (1997). The Formation of Filter-Removable Biodegradable Organic Matter During Ozonation. Ozone: Science & Engineering. 19(2) pp 179-199.
5) Speitel, G.E., Wanielista, M.M., Symons, J.M. , Davis, J.M. (1999). Advanced Oxidation and Biodegradation Processes for the Destruction of TOC and DBP Precursors. AWWARF, 90758. 138p.
6) Klevens, C.M., Collins, M.R., Negm, R., Farrar, M.F. & Fulton, G.P. Natural Organic Matter characterization and treatability by biological activated carbon filtration. In: Disinfection by-products and NOM precursors: chemistry, characterization, control; proceedings, ACS Symposium, 1996, Washington DC, p. 211-246.