

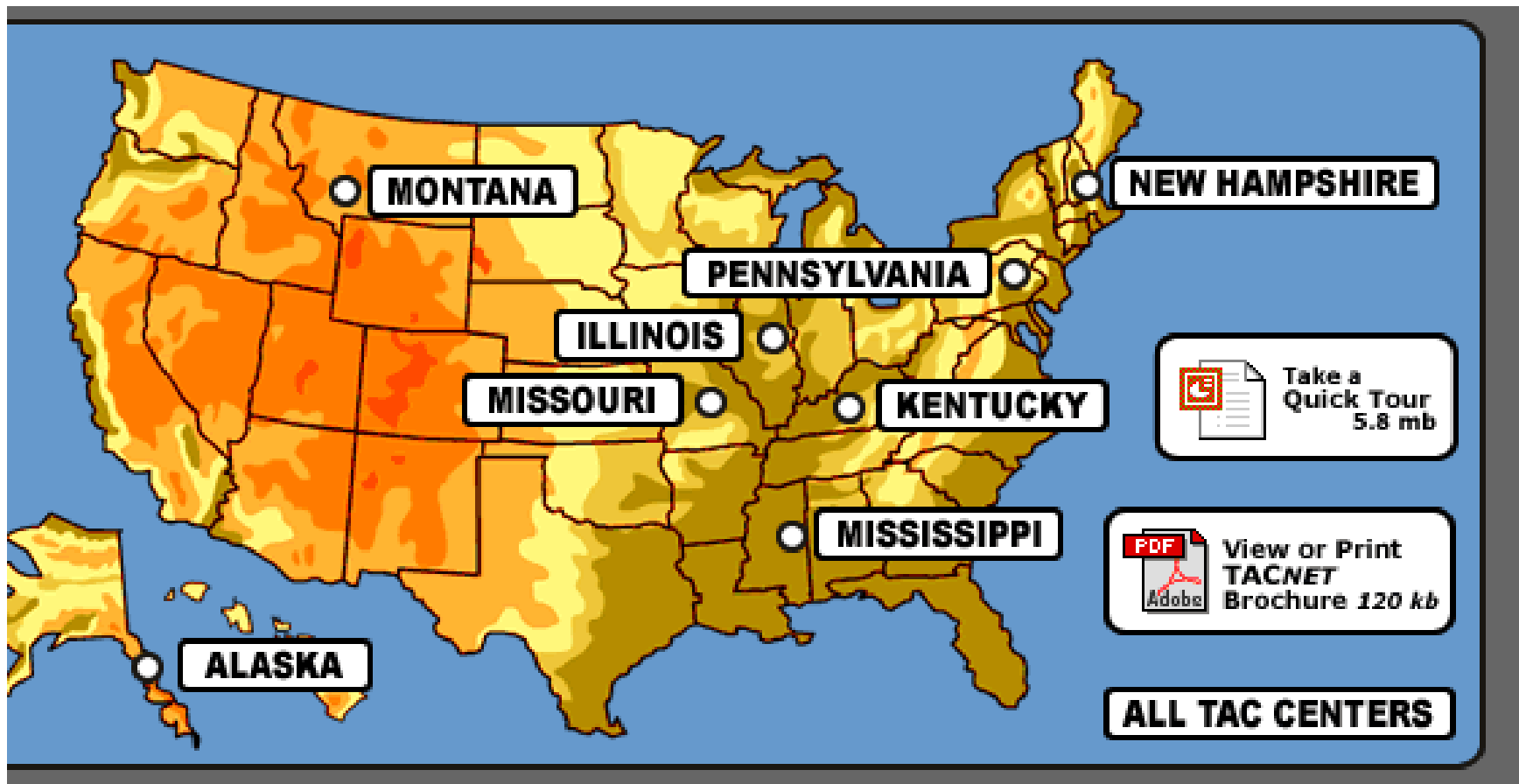
# **Reducing Disinfection By-Products in Small Drinking Water Systems**

by

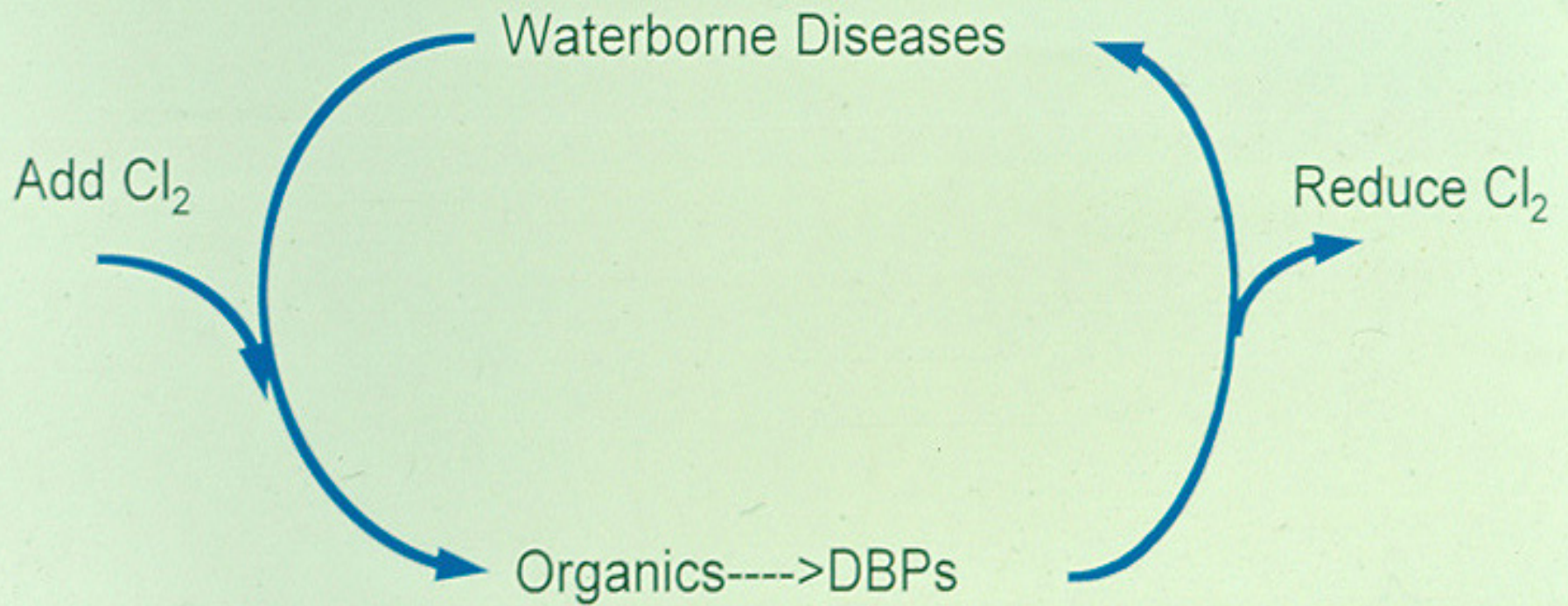
M. Robin Collins, James P. Malley, Jr, & Ethan Brooke  
Water Treatment Technology Assistance Center  
Department of Civil Engineering  
University of New Hampshire

# EPA TECHNICAL ASSISTANCE CENTER NETWORK (TACnet)

*Assisting Small Public Water Systems...Protecting Public Health*



# Catch - 22



# Disinfection Byproducts Formation

**NOM + Disinfectant = DBPs**

- **NOM=Natural Organic Matter=Organic Precursor**
- **Disinfectants=Chlorine, Chloramination, UV, Ozone, Chlorine Dioxide**
- **DBPs=Disinfection By-Products**  
Trihalomethanes (THMs), 80 ug/L  
Haloacetic Acids (HAAs), 60 ug/L

# DBP Control

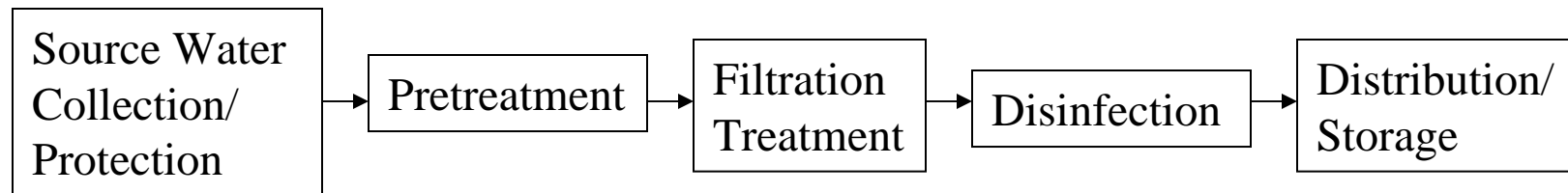
**NOM + Disinfectant = DBPs**

- NOM Removal/Reduction
- Alternative Disinfectants
- DBP Removal

# Viabile Water Treatment Options for Small Systems

- Packaged Coagulation Treatment Systems
- Pressure Filtration Systems
  - Granular Media
    - Ceramic Media
    - Diatomaceous Earth/Precoat
  - Membranes
- Biological Filtration Systems
  - Riverbank Filtration
  - Slow Sand Filtration

# MAJOR COMPONENTS OF A DRINKING WATER TREATMENT SYSTEM



# NOM Precursor Reduction Techniques

- Enhanced Coagulation/Clarification
- Activated Carbon/Media Adsorption
- Anionic Exchange Resins
- Biodegradation w/o & w/ Enhanced Biofiltration or Biological Activated Carbon (BAC)
- Membrane Filtration



# Enhanced Coagulation

# Surface Characteristics of Selected Particulates

	Zero Point of Charge, pH <sub>ZPC</sub>
INORGANIC (hydrophobic)	
“Al(OH) <sub>3</sub> ” (amorph)	7.5–8.5
Al <sub>2</sub> O <sub>3</sub>	9.1
CuO <sub>3</sub>	9.5
“Fe(OH) <sub>3</sub> ” (amorph)	8.5
MgO	12.4
MnO <sub>2</sub>	2–4.5
SiO <sub>2</sub>	2–3.5
Clays	
Kaolinite	3.3–4.6
Montmorillonite	2.5
Asbestos	
Chrysotile	10–12
Crocidolite	5–6
CaCO <sub>3</sub>	8–9
Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> OH	6–7
FePO <sub>4</sub>	3
AlPO <sub>4</sub>	4
ORGANIC (hydrophilic)	
Algae	3–5
Bacteria	2–4
Humic acid	3
Oil droplets	2–5

SOURCE: Parks (1967) and Stumm and Morgan (1981).

# What controls the coagulant dose?

- Particles versus Natural Organic Matter (NOM)?
- Characterize NOM/Aquatic Humic Substances using **Specific UV Absorbance (SUVA)**
- **SUVA = UV Absorbance @ 254 nm / mg/L of DOC**  
(typically expressed L/mg•m)
- Prof James Edzwald, UMass-Amherst

## **Guidelines: Coagulation Control**

- $SUVA < 2$ : NOM is non-humic; does not control coagulation
- $SUVA 2-4$ : NOM is a mixture of non-humics and humics; influences coagulation
- $SUVA > 4$ : NOM is high in aquatic humics; controls coagulation

# Enhanced Coagulation

- 1<sup>st</sup> Option: TOC Removal Based on Raw Water TOC & Alkalinity

Required Percent Removals of TOC

Raw Water TOC (mg/L)	Raw Water Alkalinity (mg/L CaCO <sub>3</sub> )		
	< 60	60 - 120	> 120
< 2	No Action	No Action	No Action
2 - 4	40	30	20
4 - 8	45	35	25
> 8	50	40	30

## ENHANCED COAGULATION LEVEL MAXIMUM pH\*

Alk mg/L CaCO <sub>3</sub>	Maximum pH
0 - 60	5.5
60 - 120	6.3
120 - 240	7.0
> 240	7.5

\*Enhanced Coagulation Requirement,  
Federal Register, Vol. 59, No. 145  
(July 29, 1994)

# Enhanced Coagulation

- 2<sup>nd</sup> Step: Bench or Pilot Testing Required
  - Addition of alum in 10 mg/L increments or equivalent amounts for ferric salts.
  - Desired dose based on point when an additional 10 mg/L alum does not decrease the residual TOC by 0.3 mg/L.

# Guidelines: Coagulant dosages for water supplies where NOM controls

- Aluminum Coagulants

**pH 6 to 6.5: 0.7 mg as Al/mg DOC**

**pH 7 to 7.5: 1 mg as Al/mg DOC**

## **Recommended pH for Alum**

**Water Temp: 10 °C or Above;**

**Use pH 6.1 - 6.5**

**Water Temp: Less than 10 °C**

**Use pH 6.5 - 6.8**

- Ferric Coagulants
  - pH 5.5: 2 mg as Fe per mg DOC
  - pH 7-7.5: 4 mg as Fe per mg DOC
  
- Organic Cationic Polymers
  - 0.65 – 1 mg active polymer per mg DOC



# Thusly, DOC Removals

- Depends on:
  - Nature of the NOM
  - Concentration of DOC
  - Coagulant Type and Dose
  - pH

# **Guidelines: Estimates of DOC Removal**

- **SUVA <2**
  - Aluminum & Ferric Coagulants ~ 20%
  - Organic Cationic Polymers ~ 10%
  
- **SUVA 2-3**
  - Aluminum & Ferric Coagulants ~ 20 to 50%
  - Organic Cationic Polymers ~ 10 to 30%
  
- **SUVA 3-4 and Higher**
  - Aluminum & Ferric Coagulants ~ 50 to 70%
  - Organic Cationic Polymers ~ 30 to 40%

# Empirical Model for Estimating DOC Removal (Edwards 1997)

- **DOC remaining after coagulation (mg/L) = non-adsorbable DOC fraction + adsorbable DOC fraction remaining after coagulation**

$$\text{DOC}_{\text{non-adsorb}} = (K_1 \cdot \text{SUVA}_{\text{Raw}} + K_2) \times \text{DOC}_{\text{initial}}$$

$$\text{DOC}_{\text{adsorb remain}} = \frac{-(MB + 1 - Ab) + ((MB + 1 - Ab)^2 + 4bA)^{1/2}}{2b}$$

where  $A = (1 - \text{SUVA}_{\text{Raw}} \cdot K_1 - K_2) \text{DOC}_{\text{initial}}$

$$B = (x_3 \text{pH}^3 + x_2 \text{pH}^2 + x_1 \text{pH})b$$

**Table 9-9**

Summary of best-fit model coefficients for DOC removal with iron and aluminum

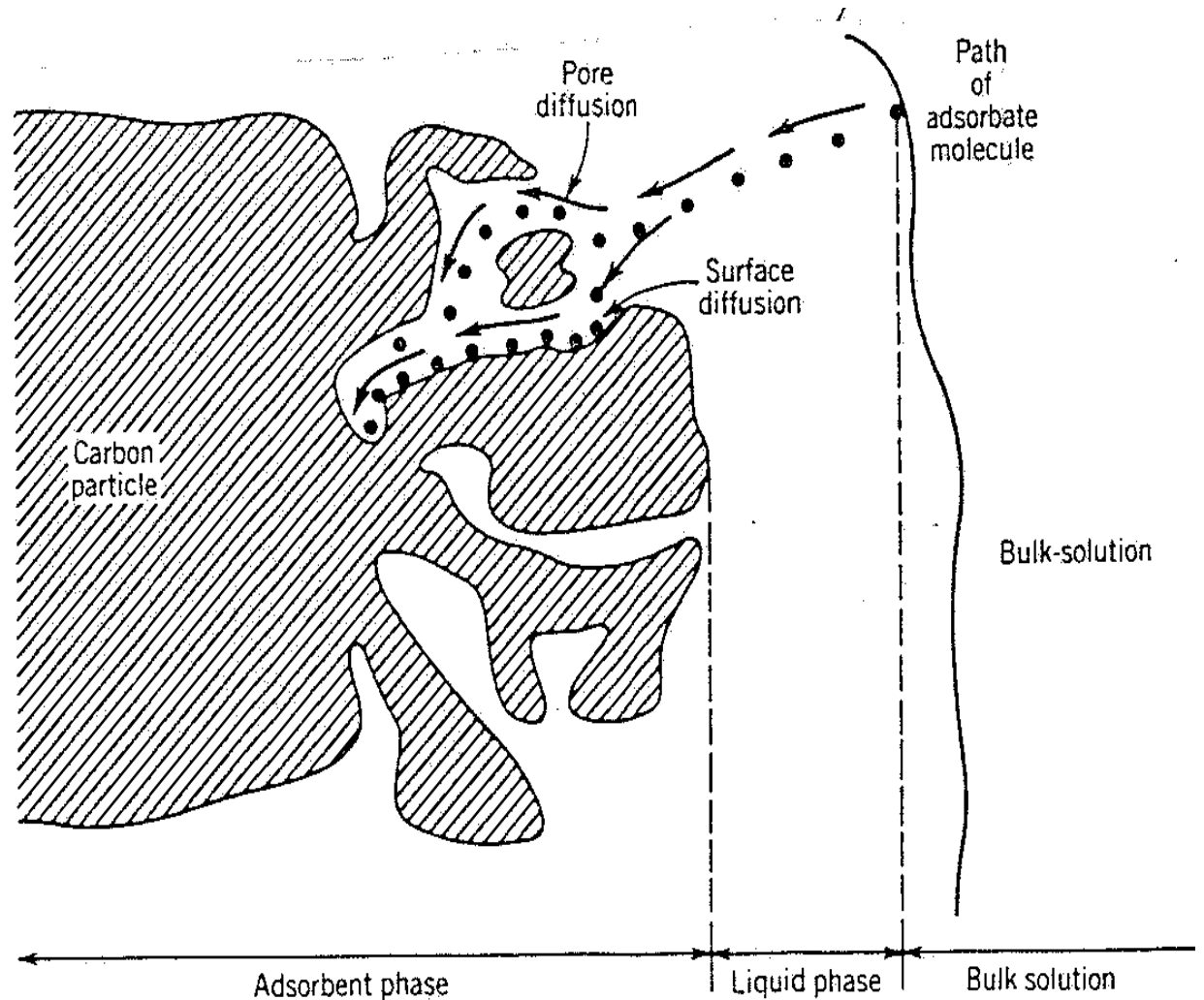
Parameter	DOC Model Coefficients	
	Iron	Aluminum
Standard error, mg/L	0.47	0.4
Standard error, %	9.3	9.5
90% confidence, %	±21	±21
$x_3$	4.96	4.91
$x_2$	-73.9	-74.2
$x_1$	280	284
$K_1$	-0.028	-0.075
$K_2$	0.23	0.56
$b$	0.068	0.147

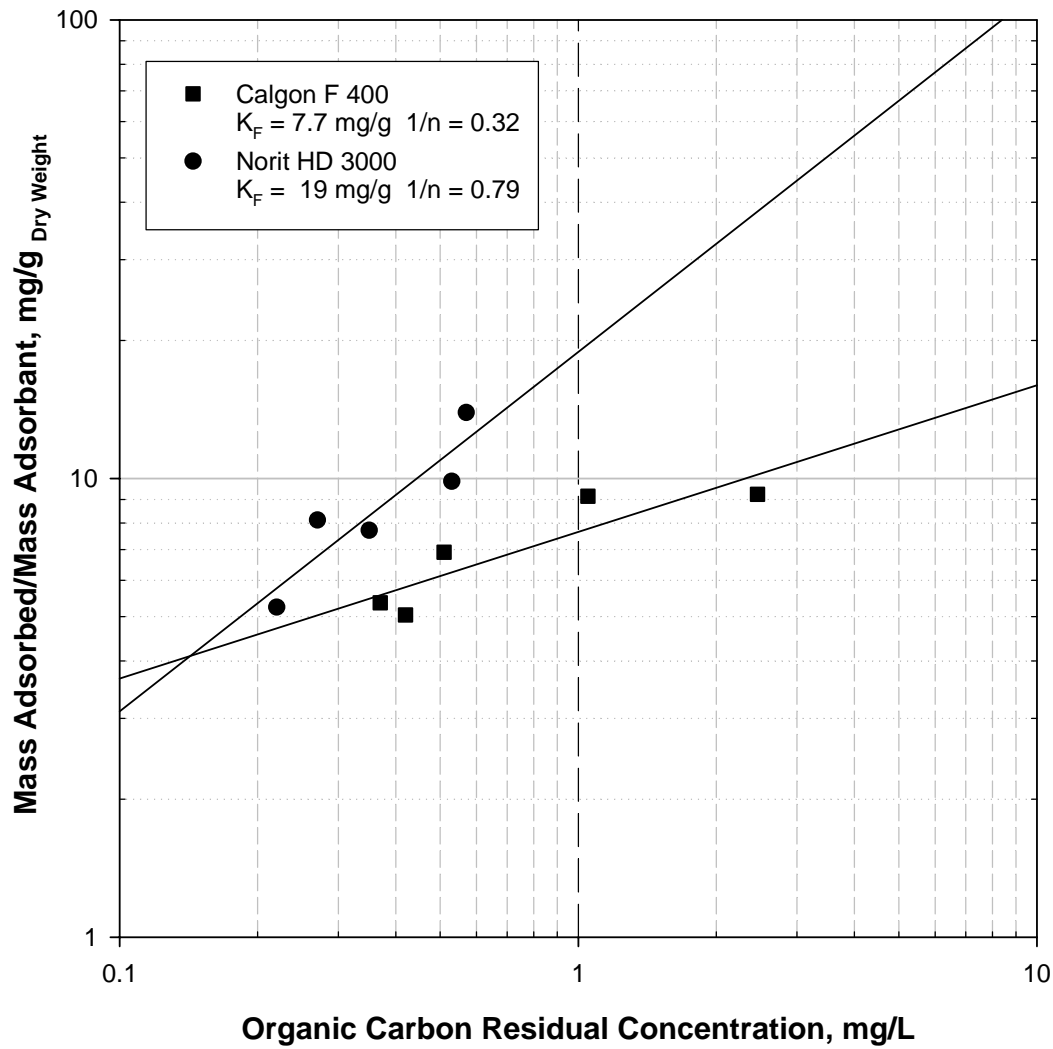
Source: Adapted from Edwards (1997).

# Activated Carbon/Media Adsorption

- Activated Carbon

- 1 gm = 1000m<sup>2</sup> surface area
- Adsorption – surface phenomenon
- Removal of organics by surface adsorption



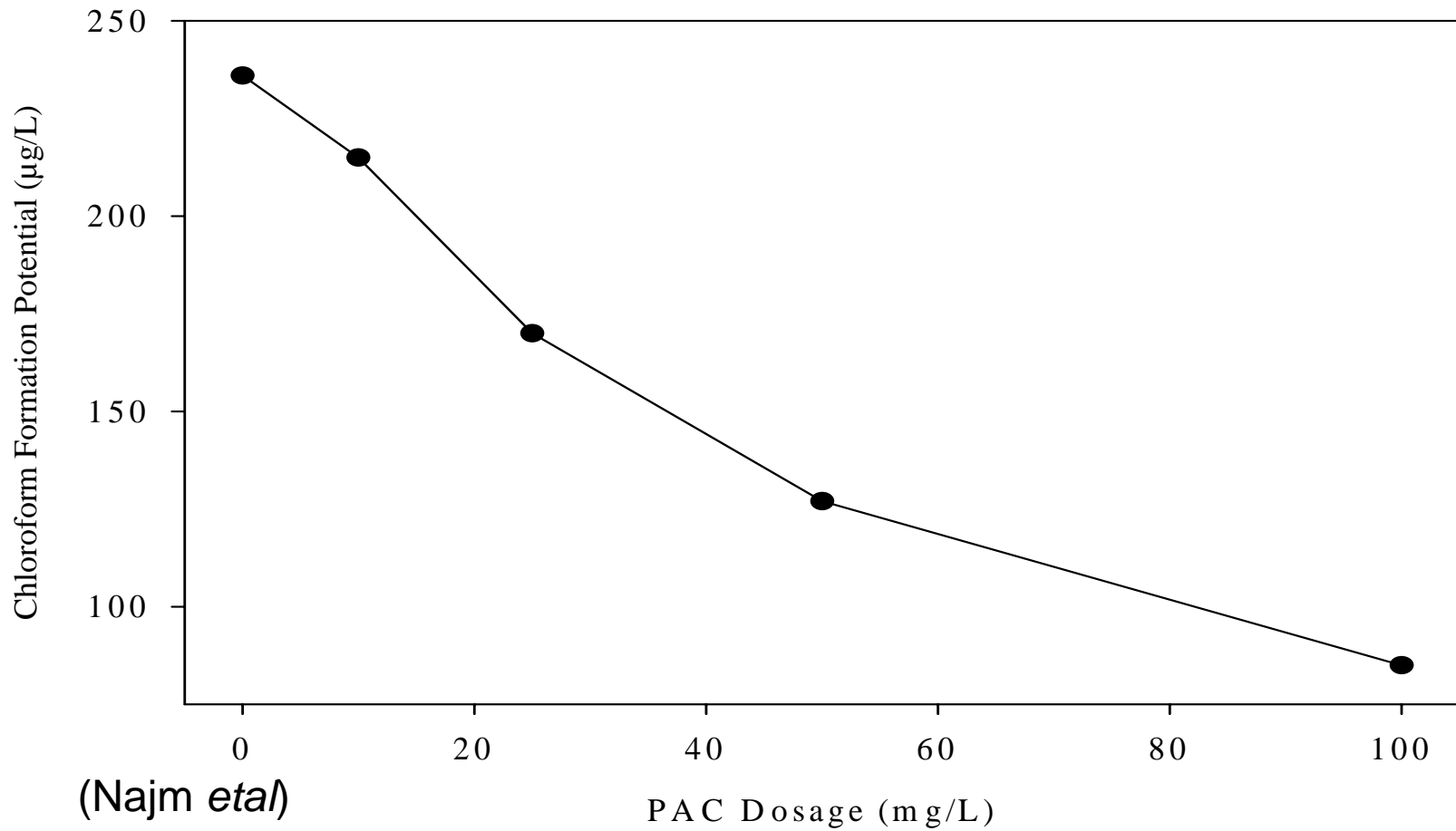


**Isotherm Challenge Conditions**

Initial Organic Carbon Concentration: 4.62 mg/L  
 pH Range: 7.00 to 7.69  
 Temperature: 20°C  
 Shaker Table: 1500 rpm  
 Time: 2 Hours

**Figure 6. Activated Carbon Isotherm Comparisons - Winthrop, Me**

# PAC on DBP formation

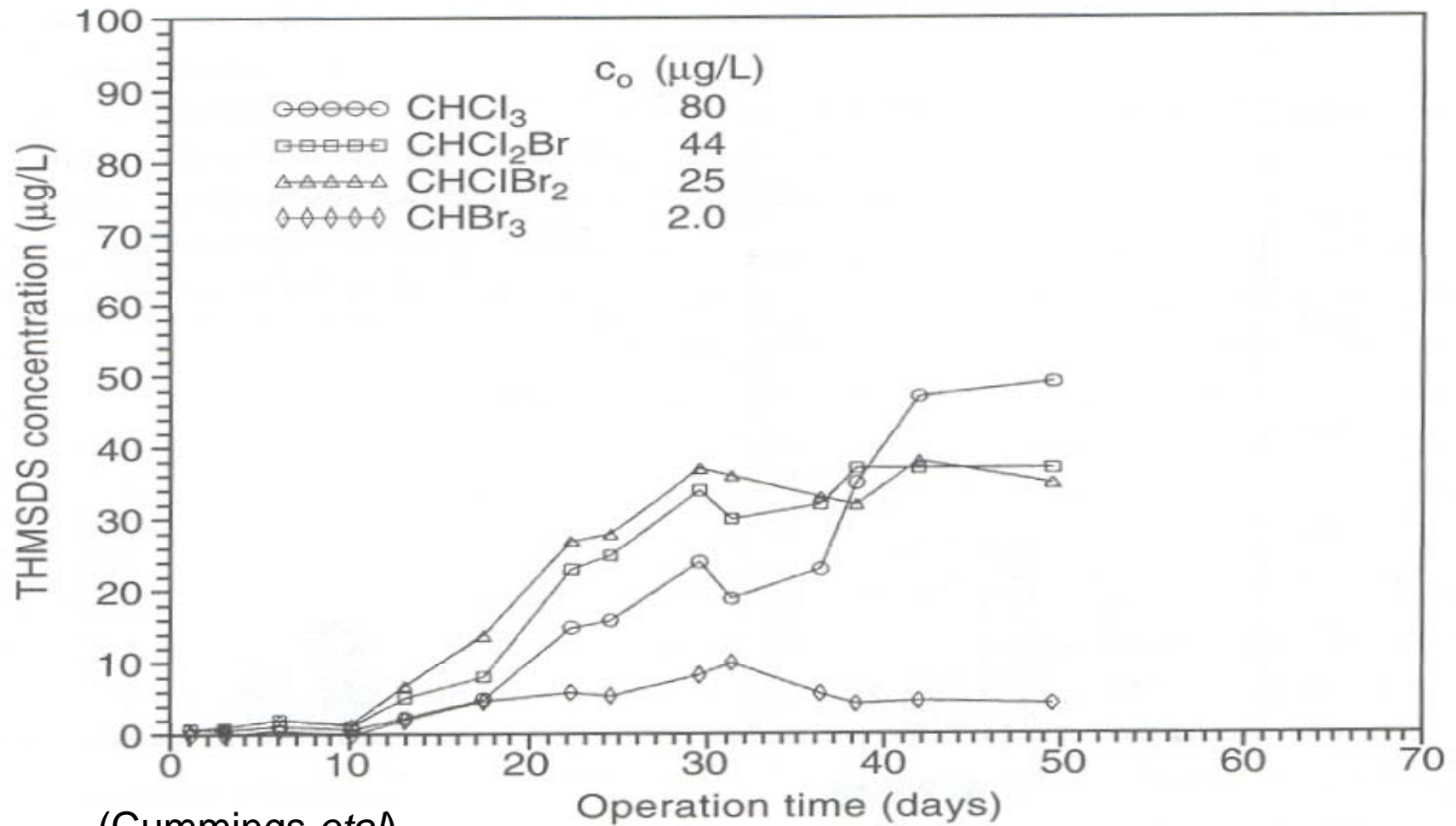




# PAC

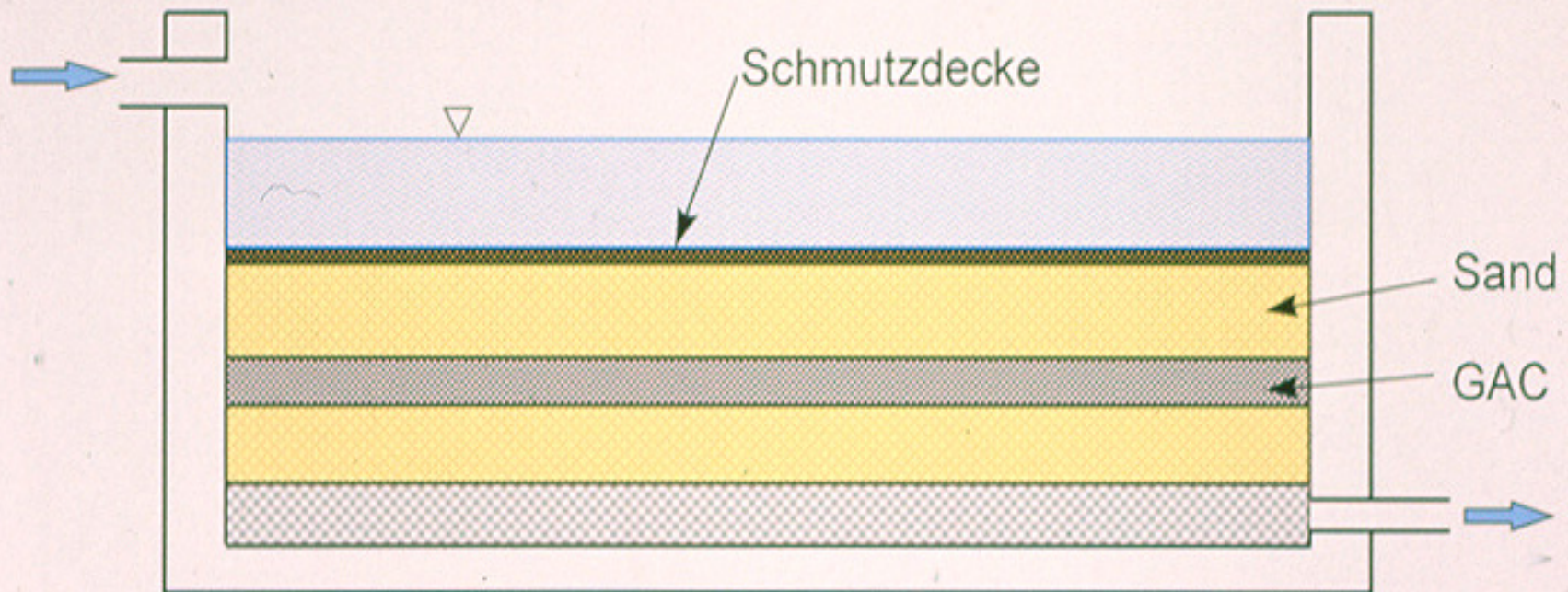
- NOM type
- Carbon type
- PAC dosage
- Contact time
- Taste, odor and color removal

# GAC for DBP precursor removal

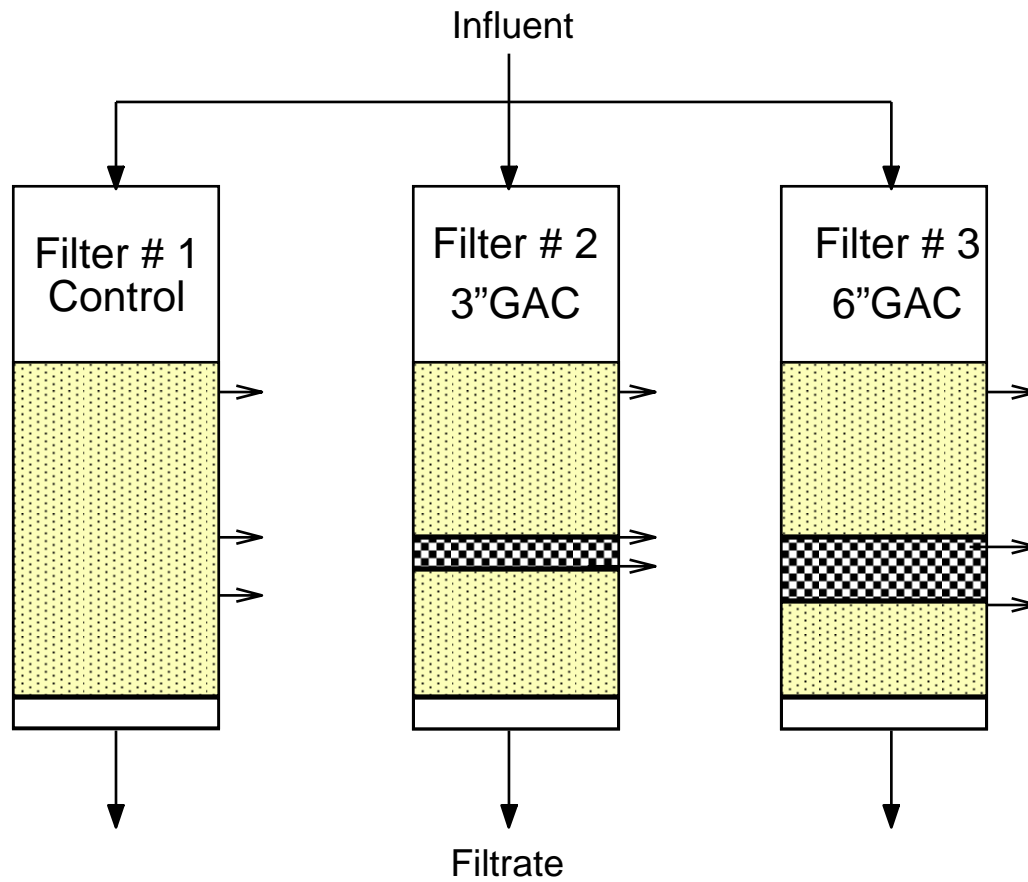


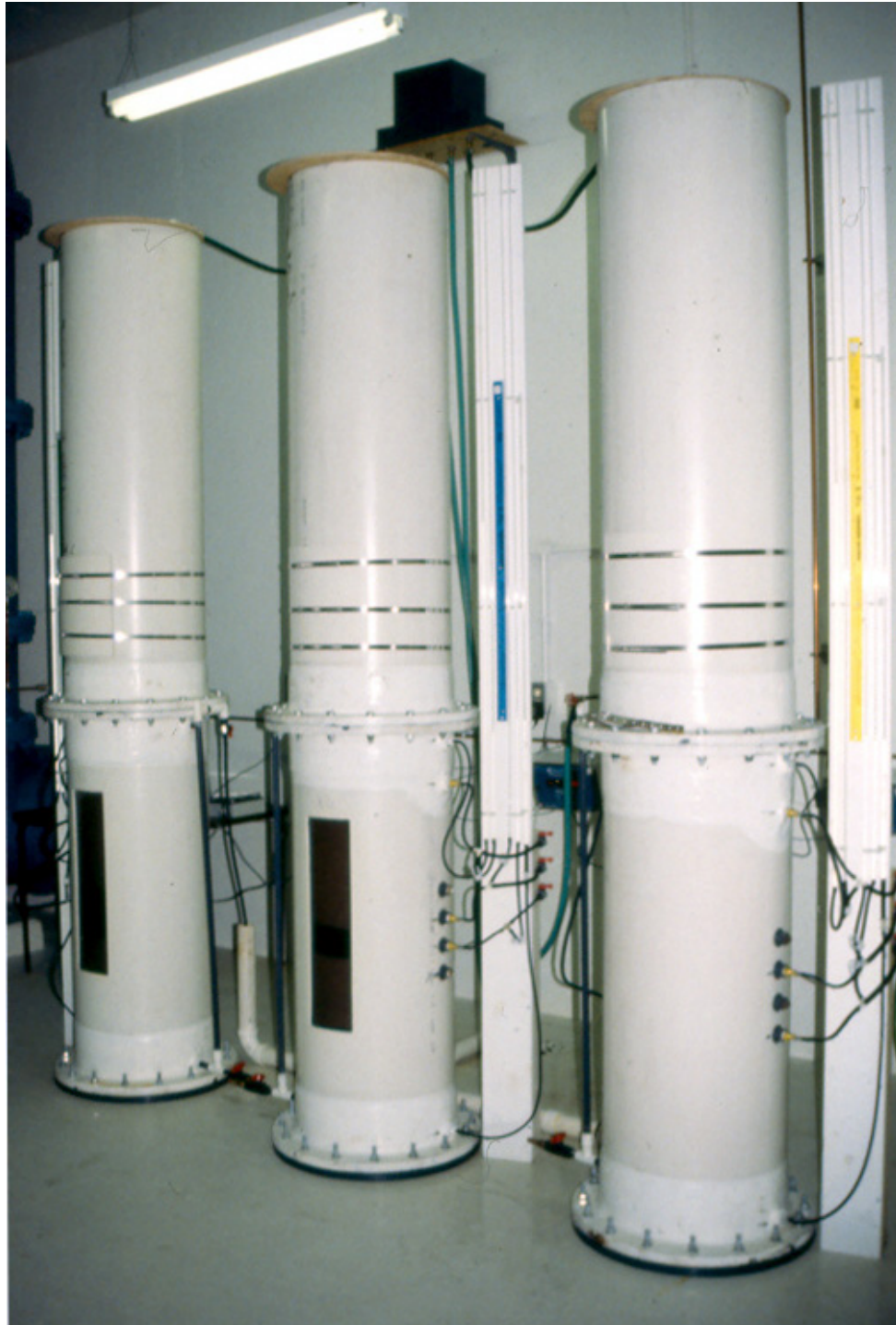
(Cummings *eta*)

# Slow Sand Filter / GAC Sandwich



# Experimental Design





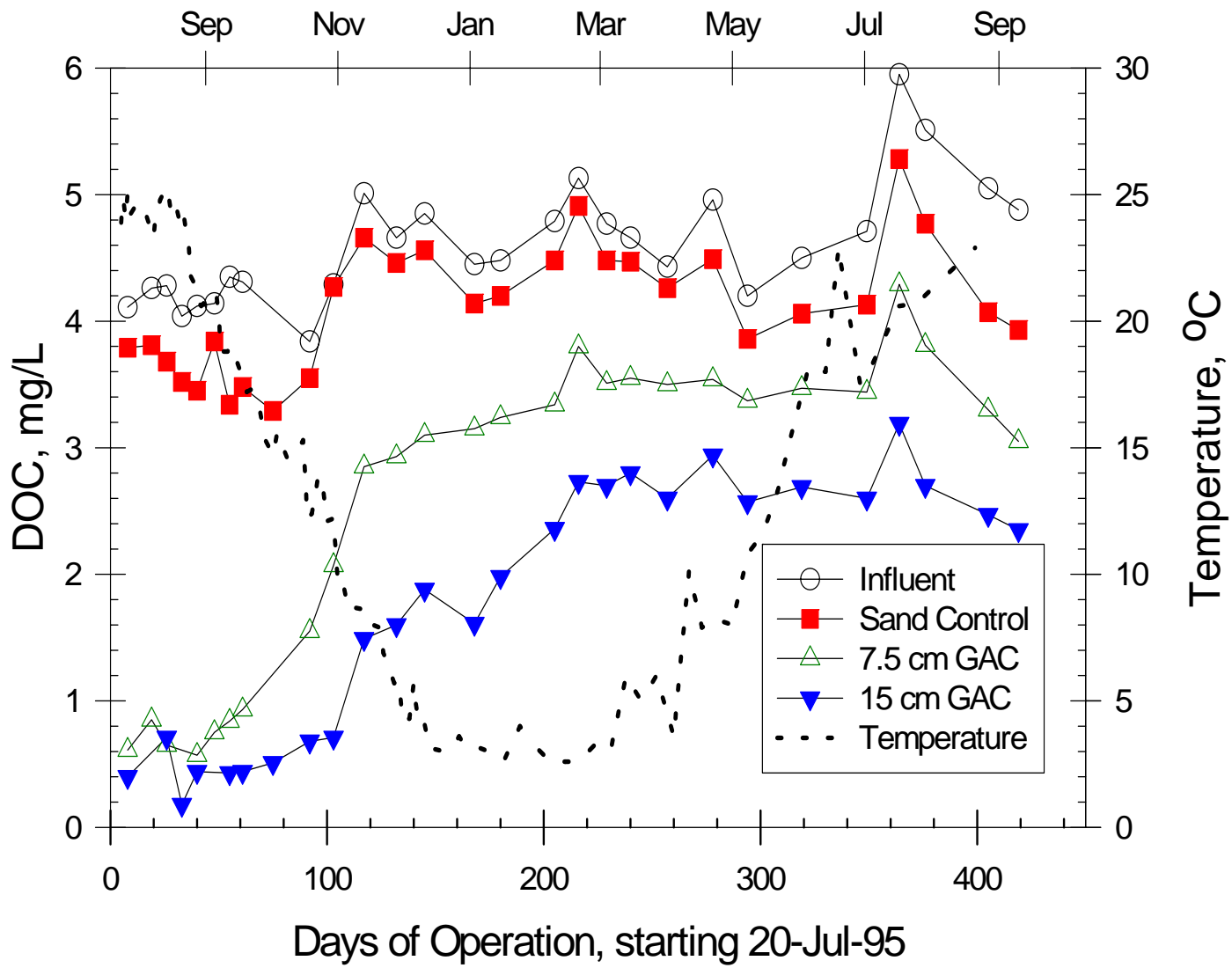


# Milo Raw Water Quality

(Jul 95 - Sep 96)

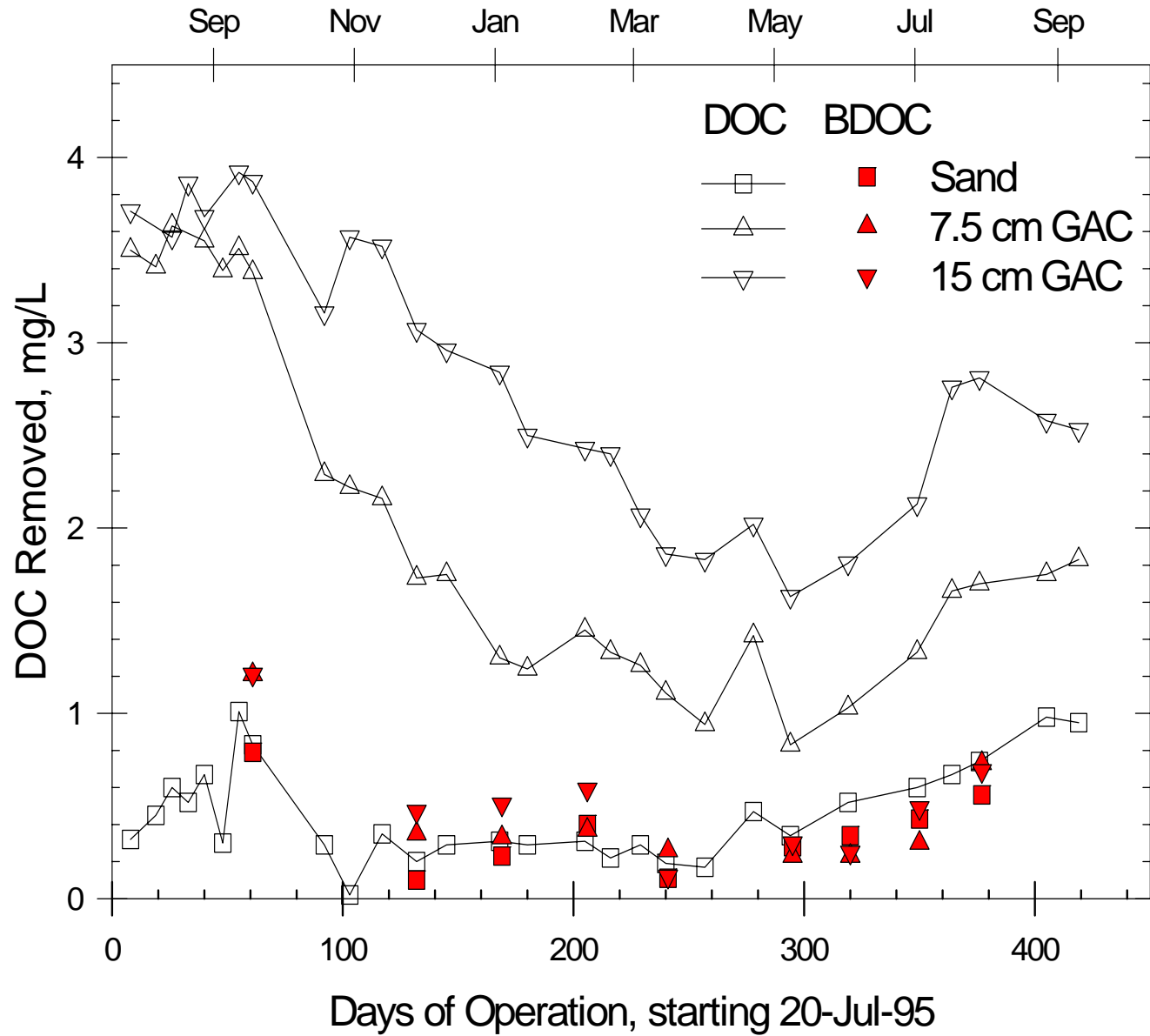
Parameter	Average	Range
Turbidity, NTU	0.43	0.25 - 1.49
Color, units PtCo	24	11 - 40
DOC, mg/L	4.6	3.8 - 6.0
BDOC, mg/L	0.6	0.4 - 1.2
UV Absorbance, $\text{cm}^{-1}$	0.153	0.098 - 0.229
THMFP, $\mu\text{g/L}$	430	331 - 570

# DOC Removal for Milo Pilot Filters



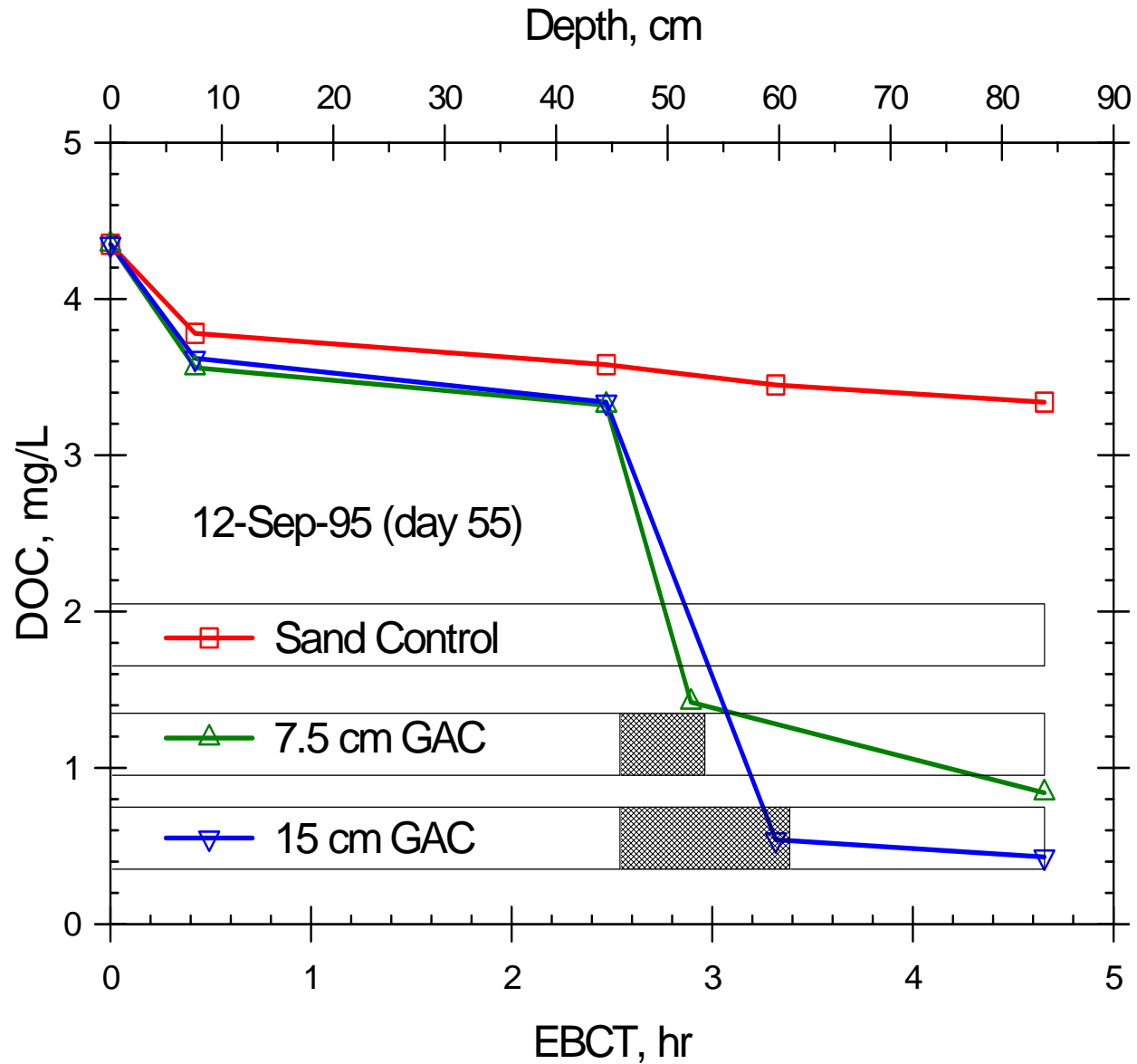


# DOC and BDOC Removal for Milo Pilot Filters



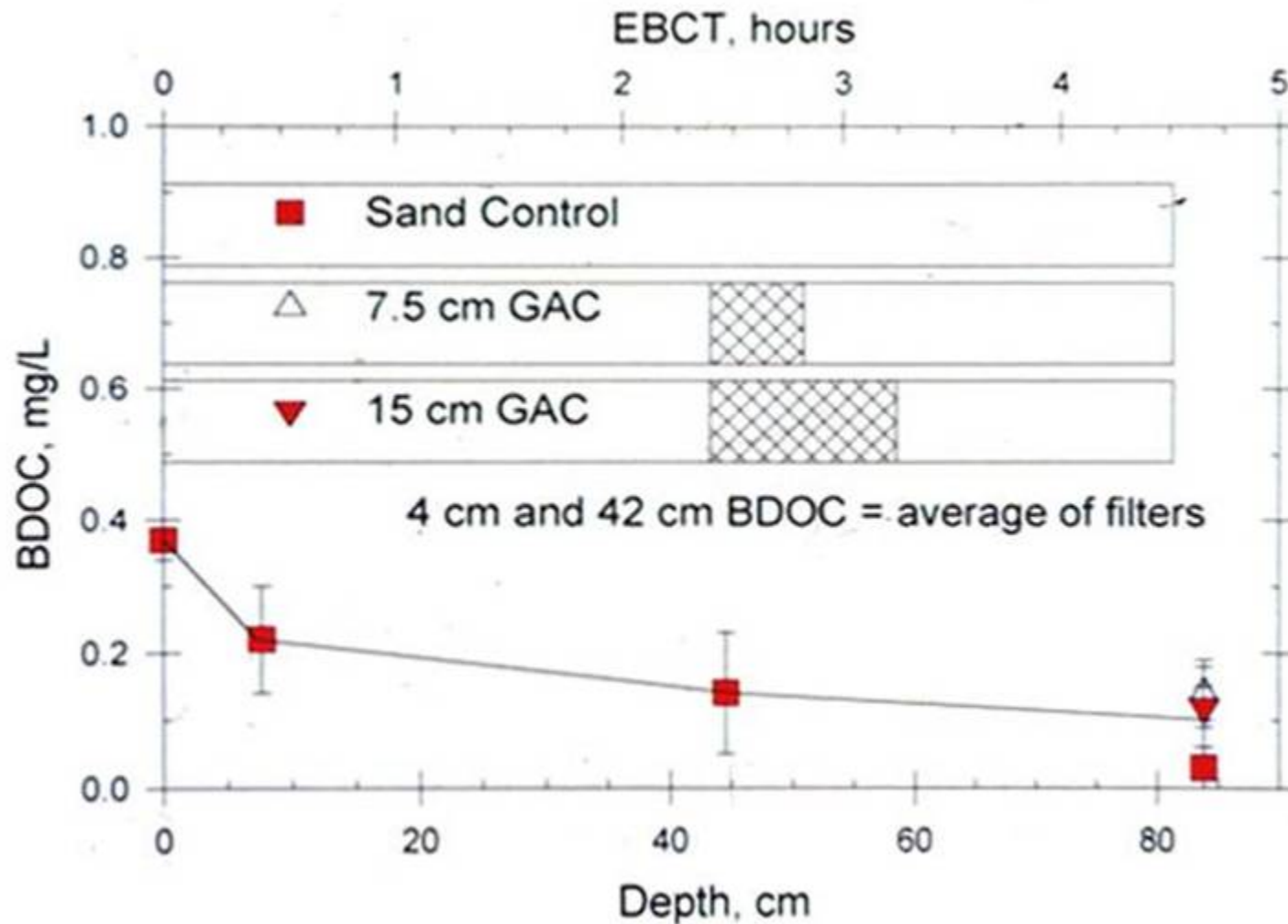


# DOC Removal with Depth, Milo Pilot Filters, 12-Sept-95

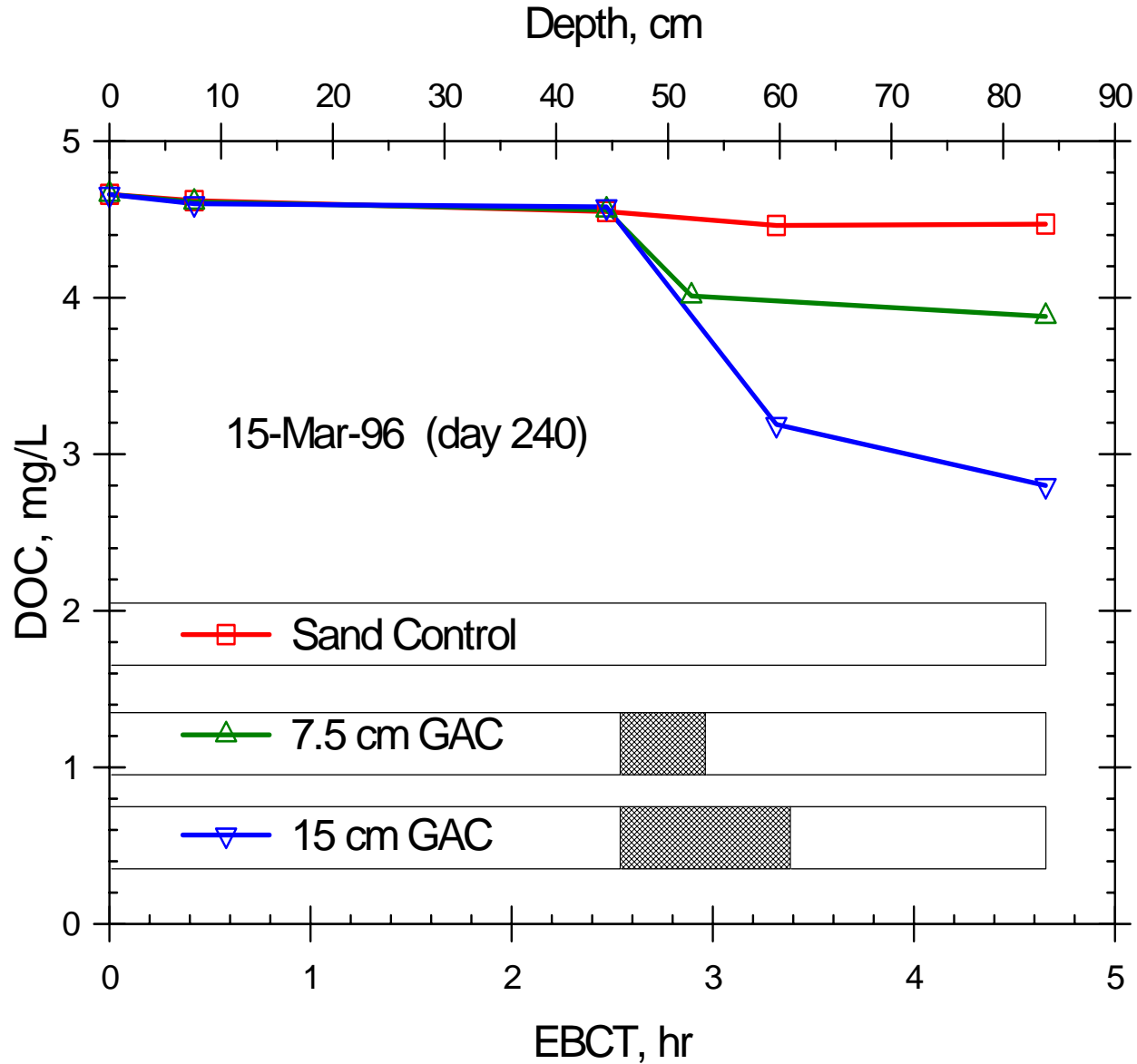


# BDOC Removal with Depth

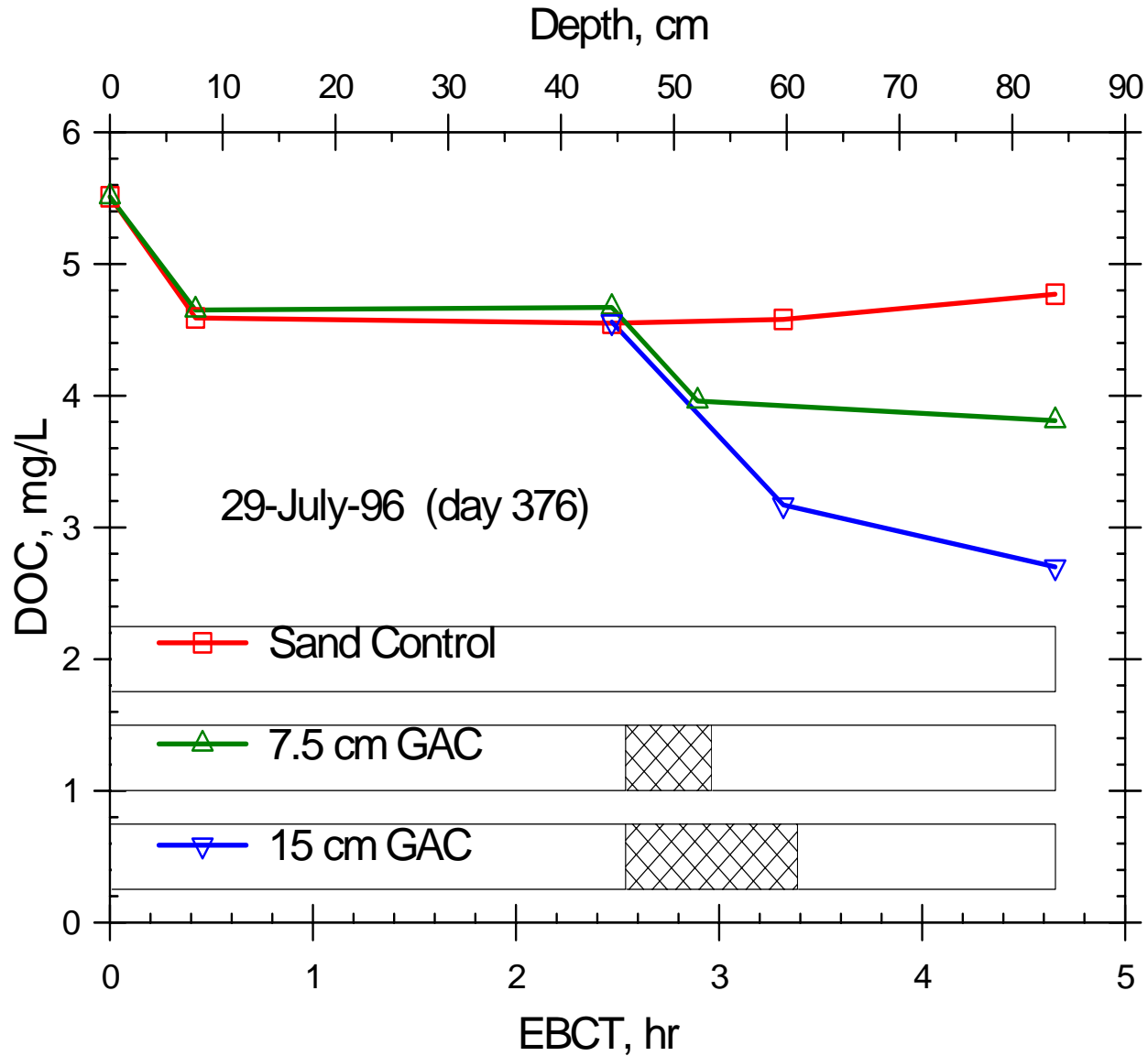
(SSF Pilot Tests at Milo, NH USA)



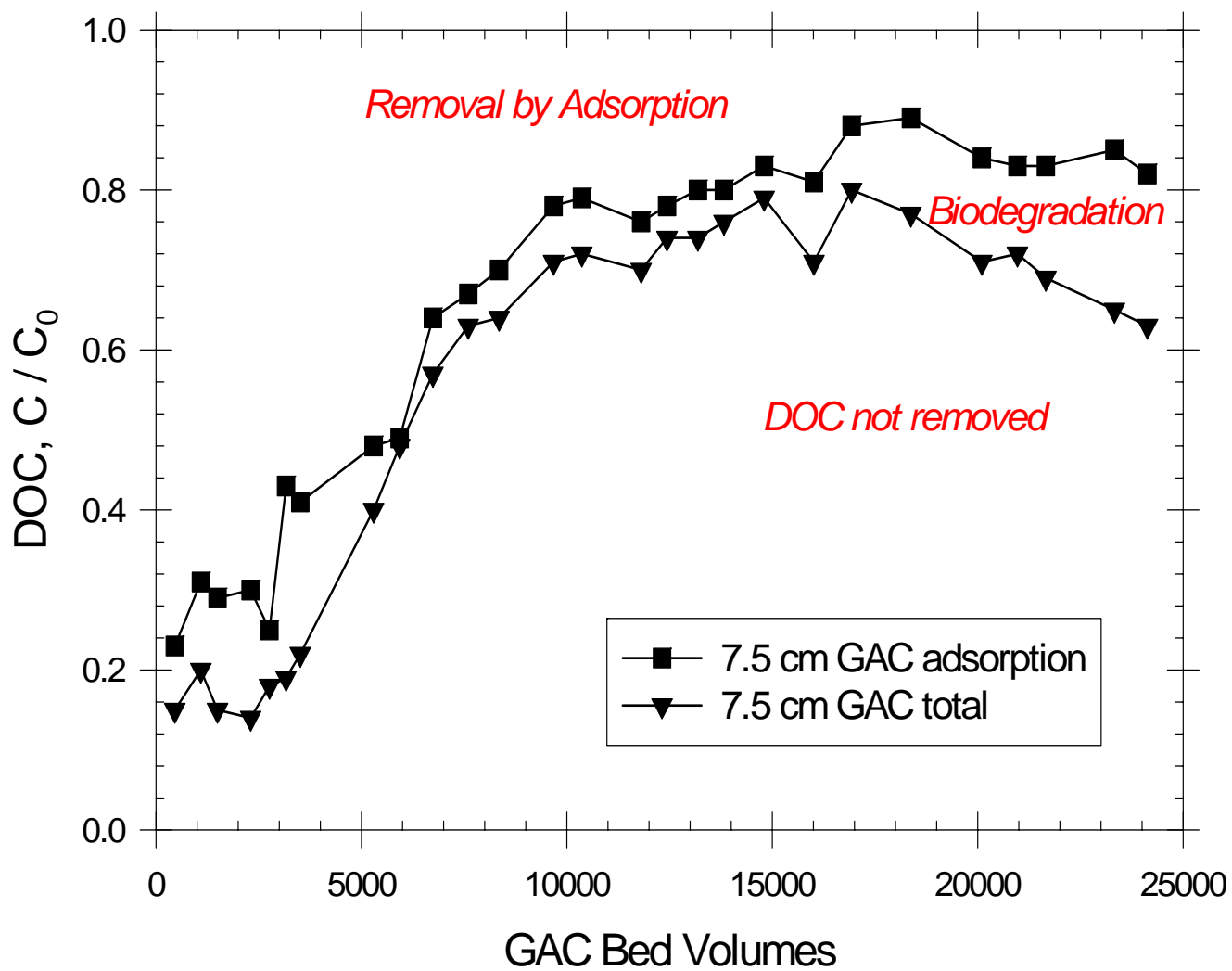
# DOC Removal with Depth, Milo Pilot Filters, 15-Mar-96



# DOC Removal with Depth, Milo Pilot Filters, 29-Jul-96



## DOC Removal by Adsorption and Biodegradation



# GAC Sandwich Summary

- Adsorption dominated first 7000 - 14000 GAC BVs.
- Removals reached pseudo steady-state after 200 - 300

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days:	Sand	7.5 cm GAC	15 cm GAC
Total	12%	28%	46%
Adsorption		16%	34%

---

## Evidence against Enhanced

### Biodegradation:

- Biomass levels and BDOC removals were similar in sand and GAC sublayers.

## Evidence for Slow Adsorption or

### Bioregeneration:

- Adsorption continued at a constant rate, even after 400+ days (11500 - 23000 GAC BVs).

Table 3. Summary of Average Total Organic Carbon and UV<sub>254</sub> Absorbance and % Removals for Winthrop Slow Sand Pilot Studies

<b>1<sup>ST</sup> PILOT STUDY PHASE (3/28/03 – 11/10/03)</b>						
<u>Filter</u>	<u>TOC</u>			<u>UV<sub>254</sub></u>		
	<u>n</u>	<u>mg/L</u>	<u>% Removal</u>	<u>n</u>	<u>cm<sup>-1</sup></u>	<u>% Removal</u>
<u>Raw</u>	<u>26</u>	<u>4.66 ± 0.46</u>	<u>--</u>	<u>26</u>	<u>0.113 ± 0.009</u>	<u>--</u>
<u>Plant 3</u>	<u>23</u>	<u>3.16 ± 0.36</u>	<u>32 ± 11</u>	<u>23</u>	<u>0.080 ± 0.011</u>	<u>29 ± 6</u>
<u>Pilot 1 (Old GAC)</u>	<u>26</u>	<u>3.01 ± 0.40</u>	<u>35 ± 11</u>	<u>26</u>	<u>0.061 ± 0.010</u>	<u>47 ± 8</u>
<u>Pilot 2 (Sand)</u>	<u>24</u>	<u>4.10 ± 0.36</u>	<u>13 ± 10</u>	<u>24</u>	<u>0.101 ± 0.011</u>	<u>11 ± 5</u>
<u>Pilot 3 (New GAC)</u>	<u>24</u>	<u>2.10 ± 0.47</u>	<u>54 ± 12</u>	<u>24</u>	<u>0.042 ± 0.011</u>	<u>63 ± 10</u>



# **BAC STUDY**

## ***Background***

FOUR SEPARATE TREATMENT TRAINS:

Train 1/DF Train = Ozone-Coag-BAC Direct Filtration

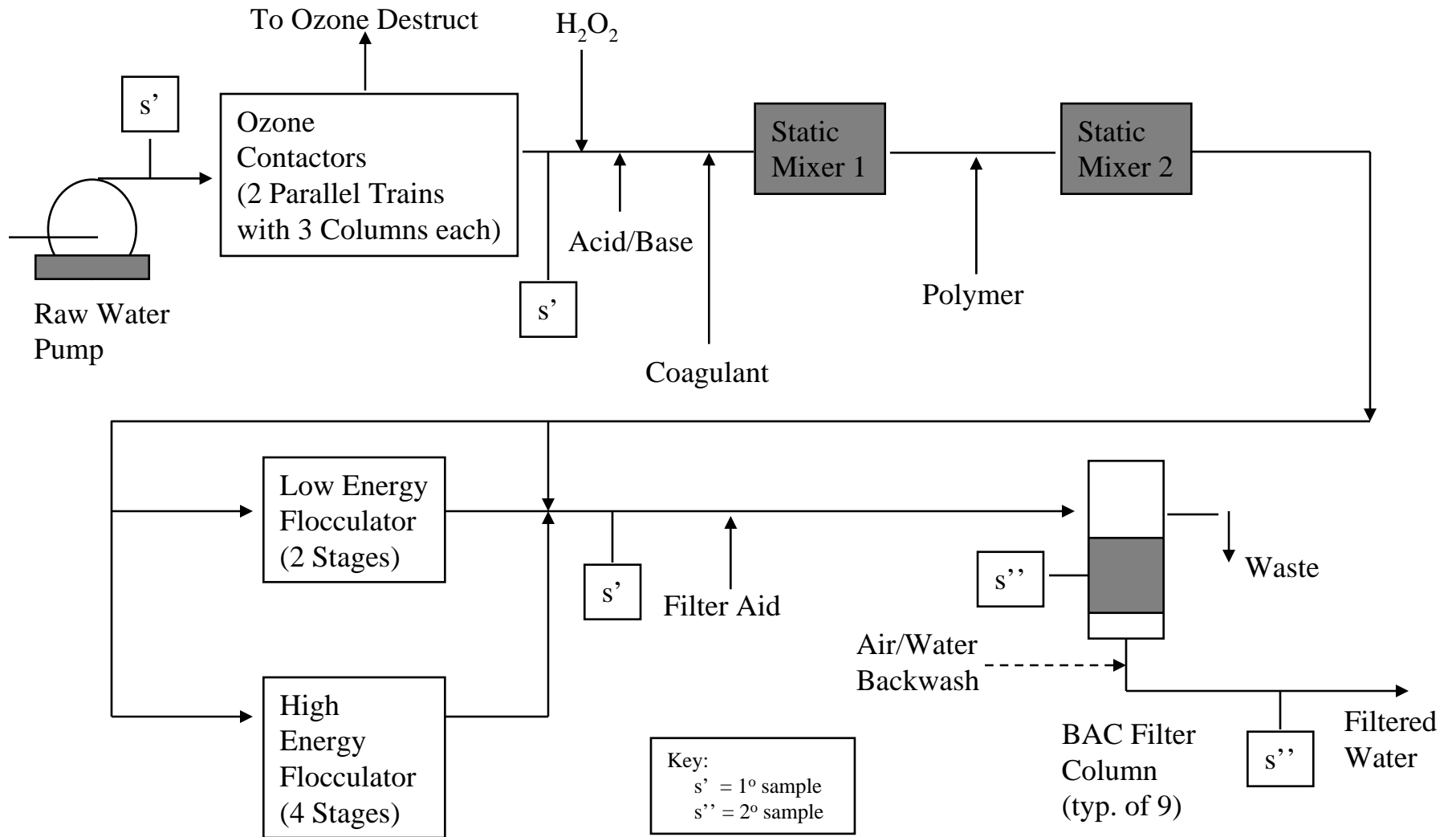
Train 2/DAF Train = Coag-DAF-Ozone-BAC Filtration

Train 3/DE Train = Ozone-BAC-DE Filtration

Train 4/MF Train = Membrane Filtration

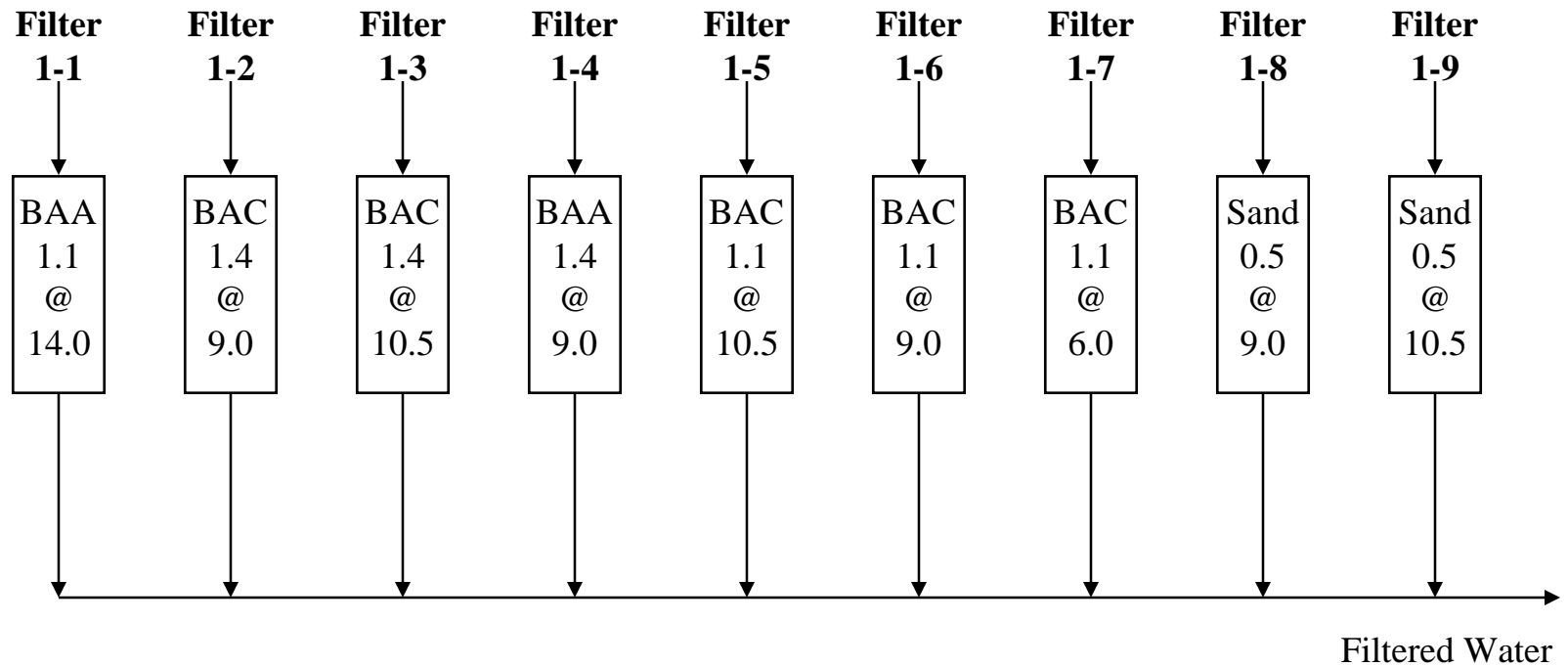
# Treatment Train No.1

## Ozone-BAC Direct Filtration



# Treatment Train No.1

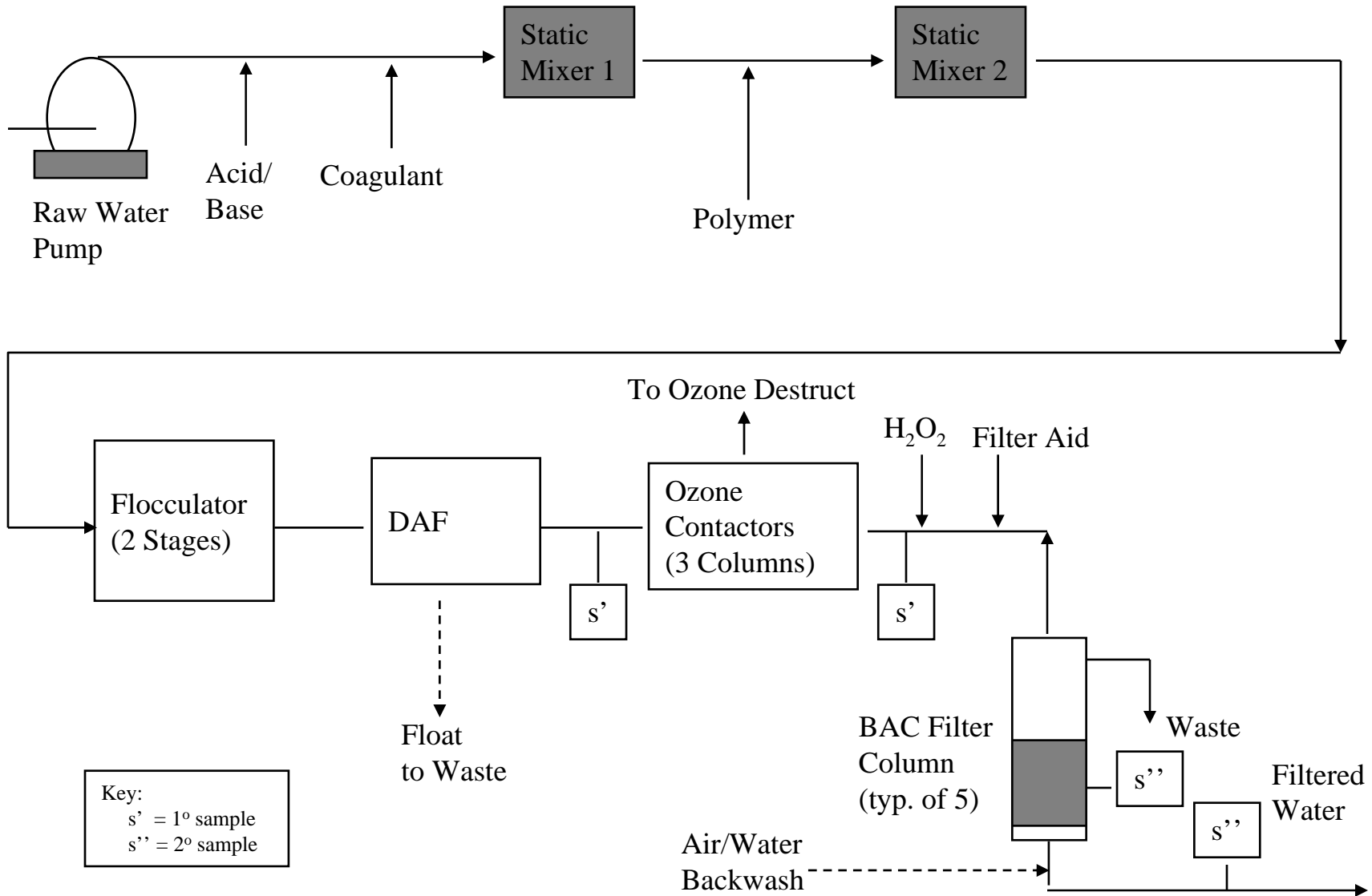
## DF Biological Filters



Key:  
grainsize (mm) @ loading rate (gpmsf)

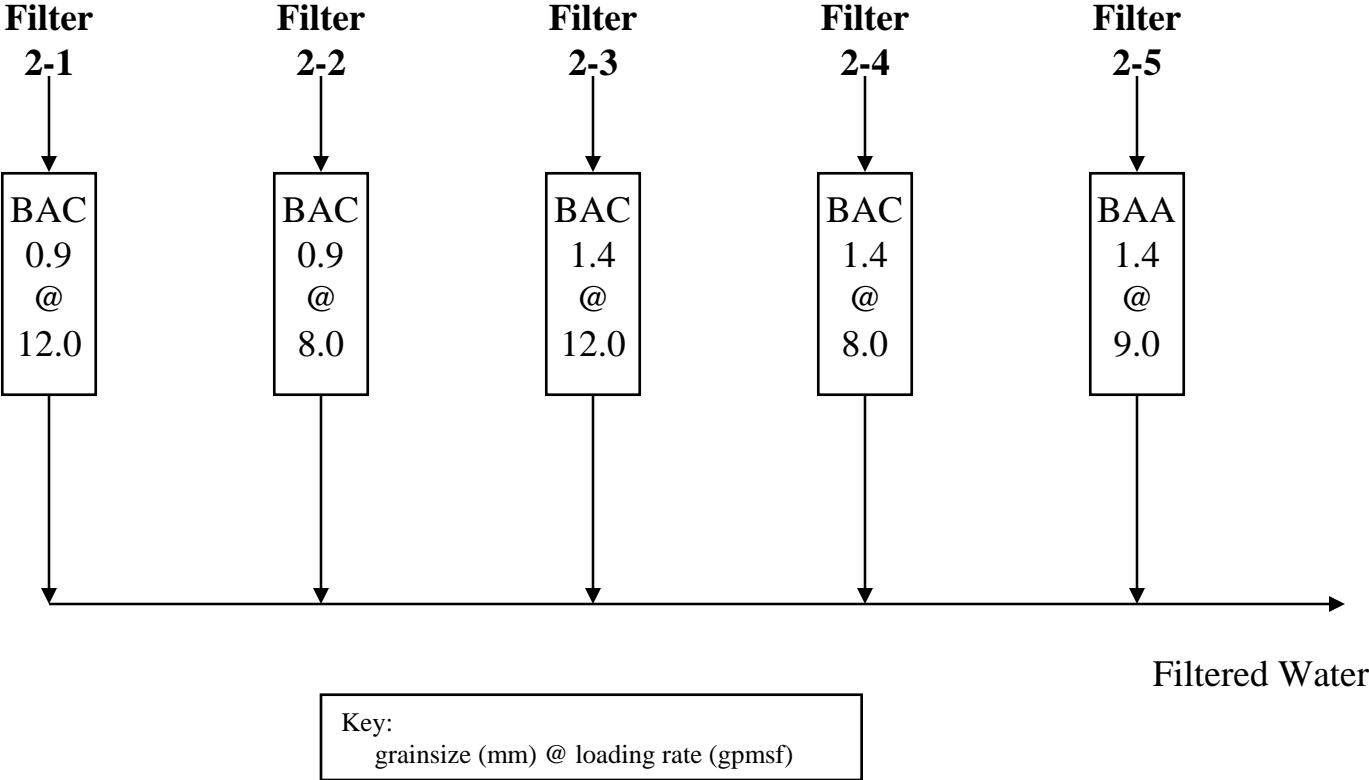
# Treatment Train No.2

## DAF-Ozone-BAC Filtration



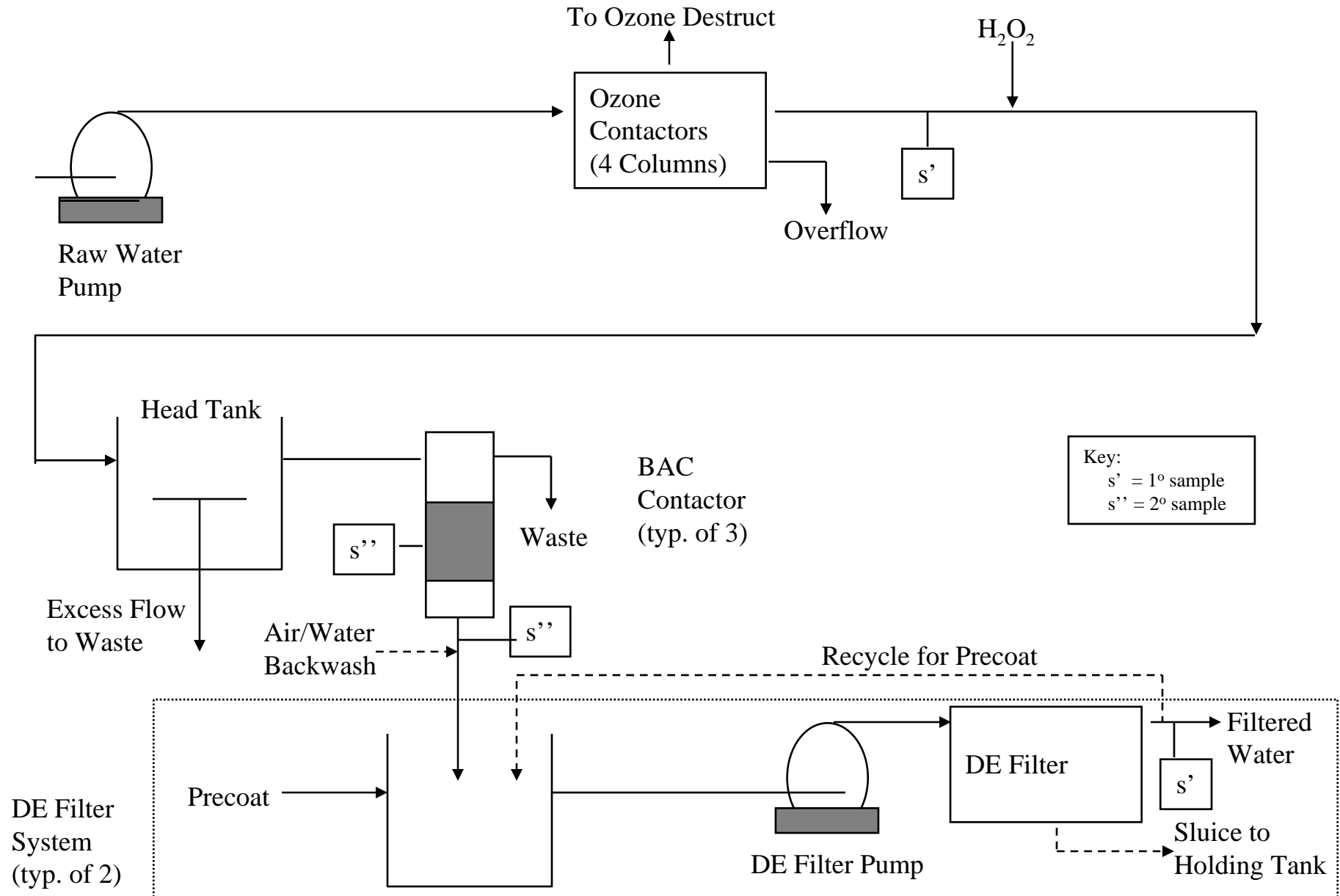
# Treatment Train No.2

## DAF Biological Filters



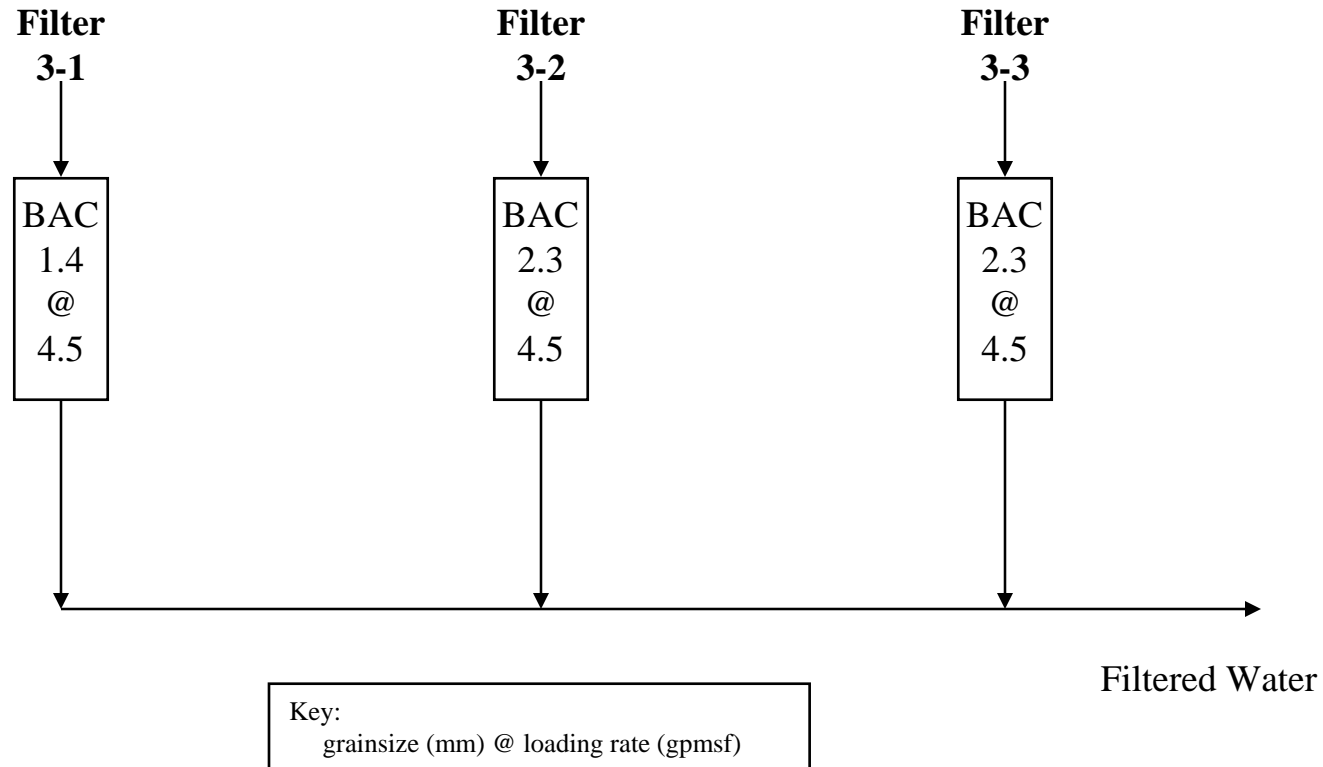
# Treatment Train No.3

## Ozone-BAC-DE Filtration



# Treatment Train No.3

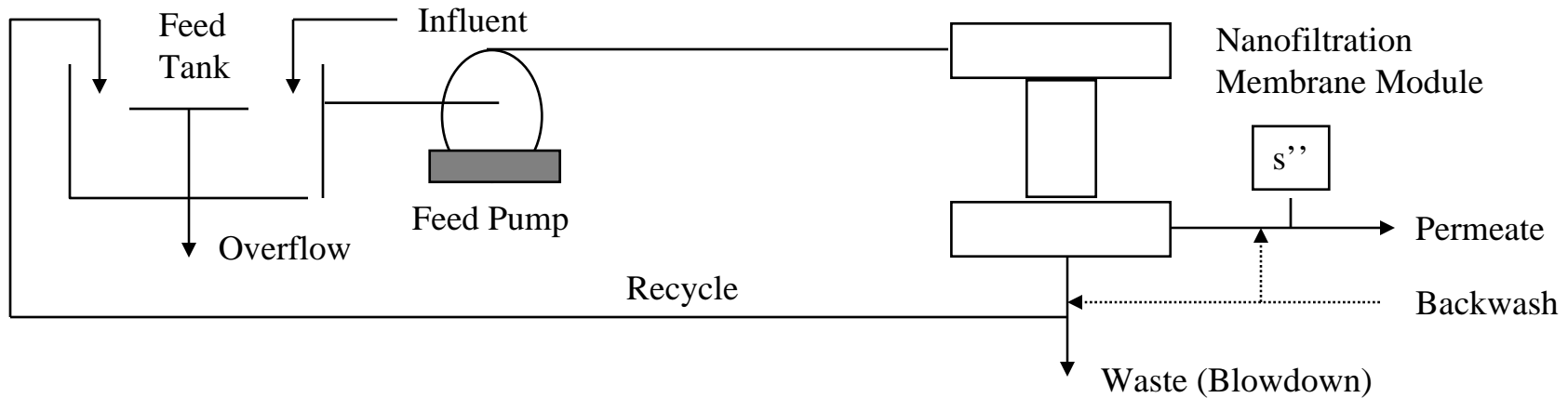
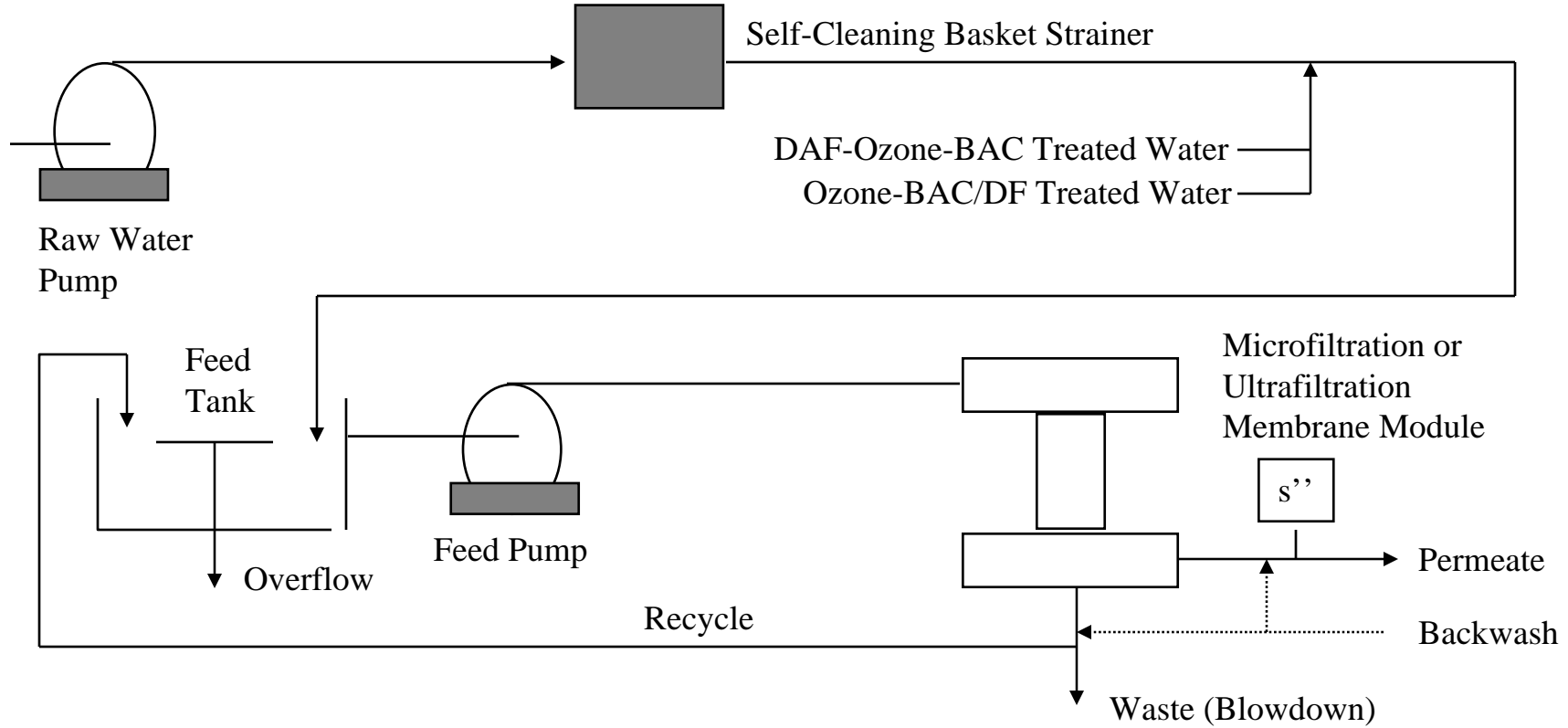
## Biological Contactors



# Treatment Train No.4

## Membrane Filtration

Key:  
 $s'$  = 1° sample  
 $s''$  = 2° sample





# OVERALL RESEARCH OBJECTIVES

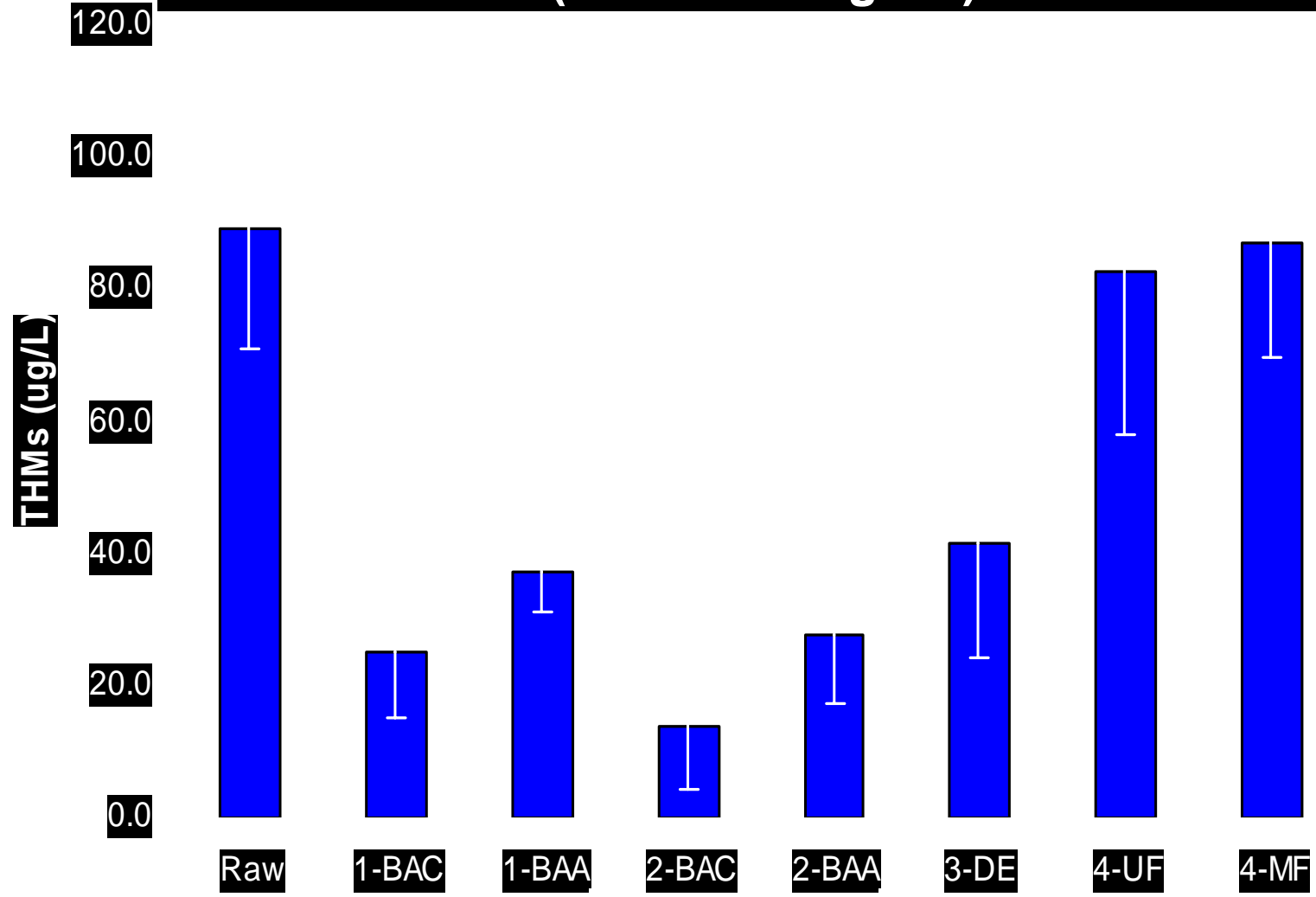
Which of the four pilot treatment trains will be most effective in removing the fractions of NOM that are:

- 1) Most amenable to reaction with chlorine, i.e. the formation of DBPs
- 2) Most available for biological activity and subsequent regrowth

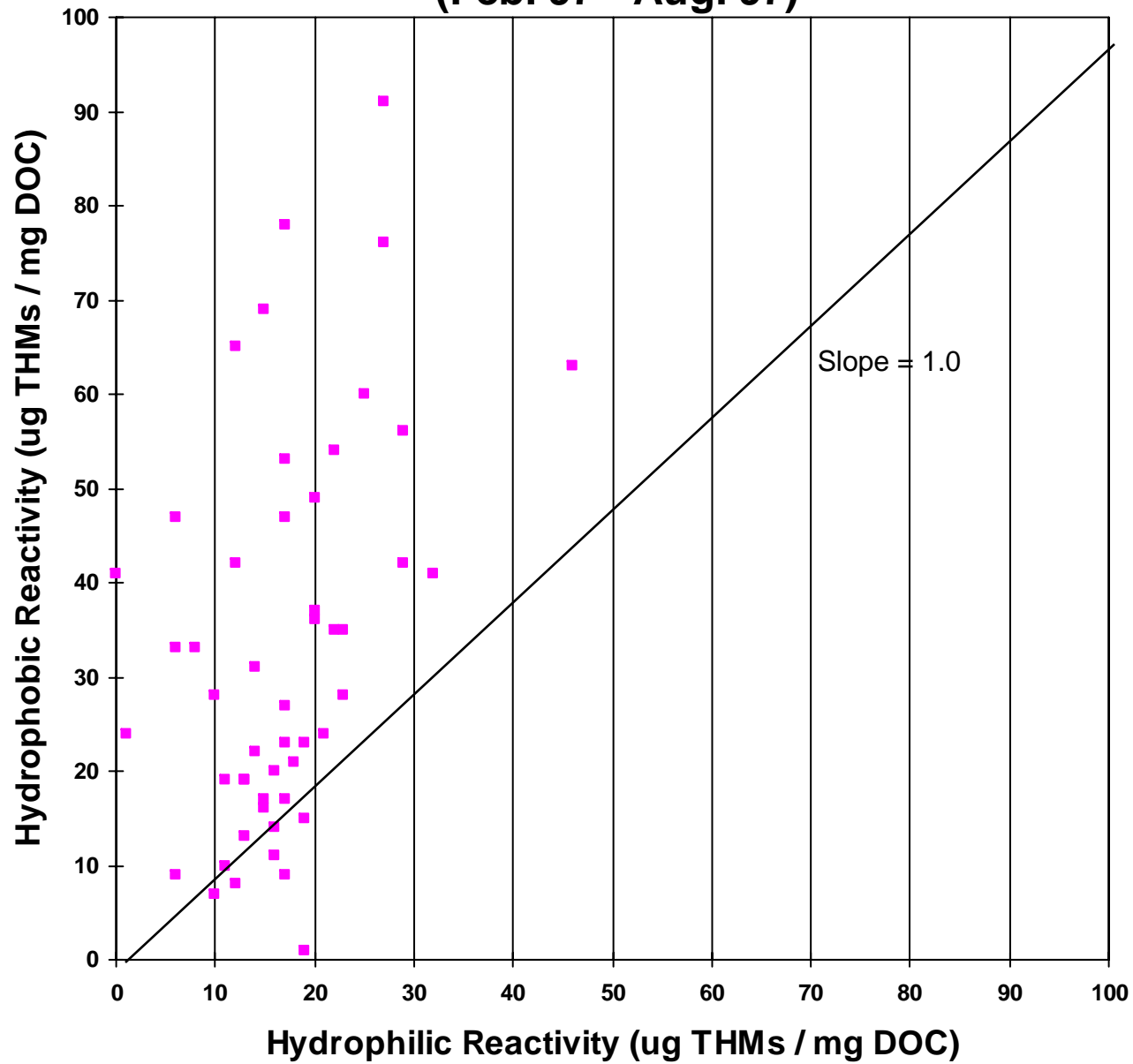
# **OVERALL RESEARCH OBJECTIVES**

- 1) Determine which of the four pilot treatment trains will be most effective in removing the fractions of NOM that are most amenable to reaction with chlorine**

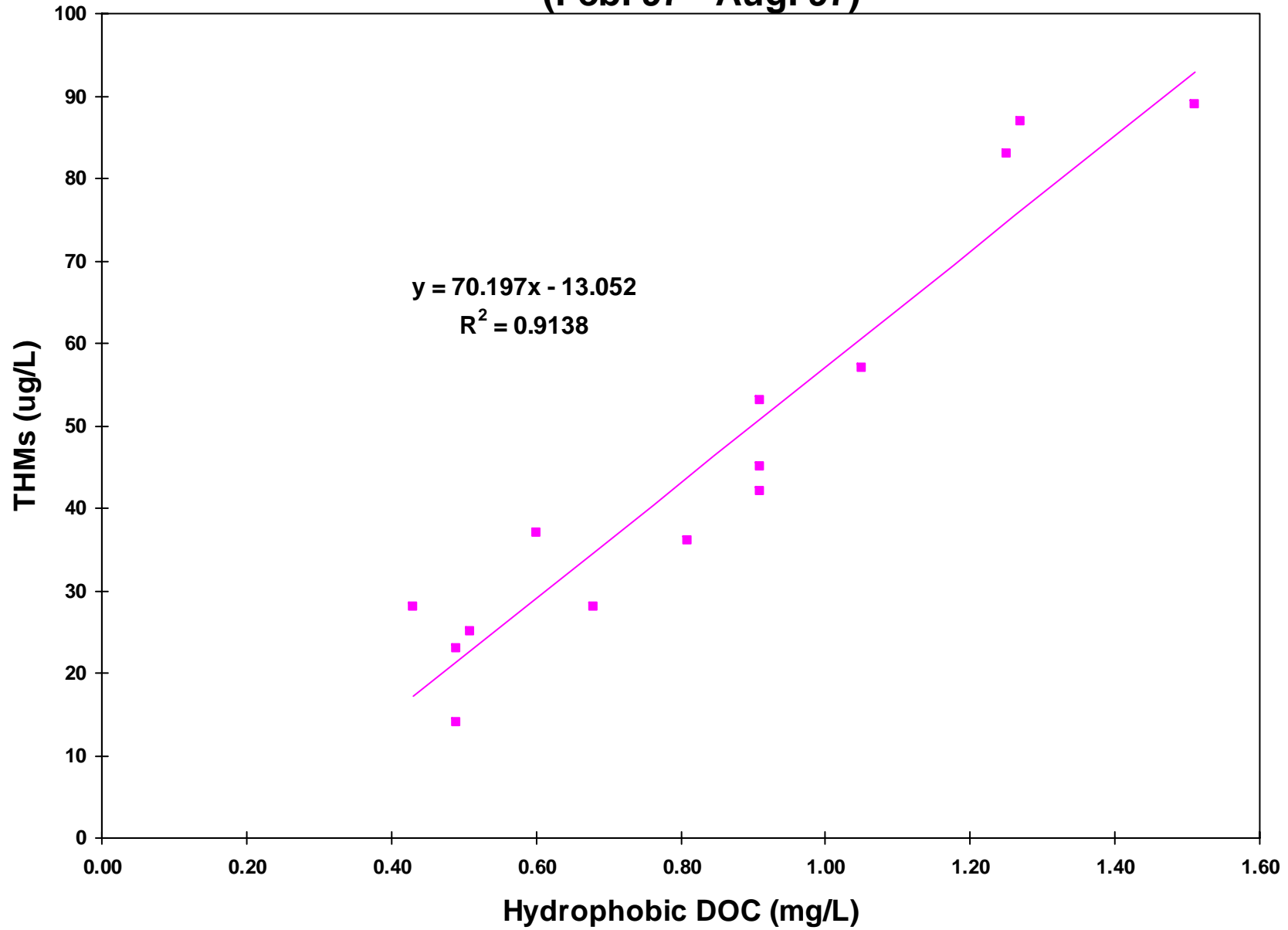
# Avg THMs For Each Treatment Train Final Effluent (Feb.'97 - Aug.'97)



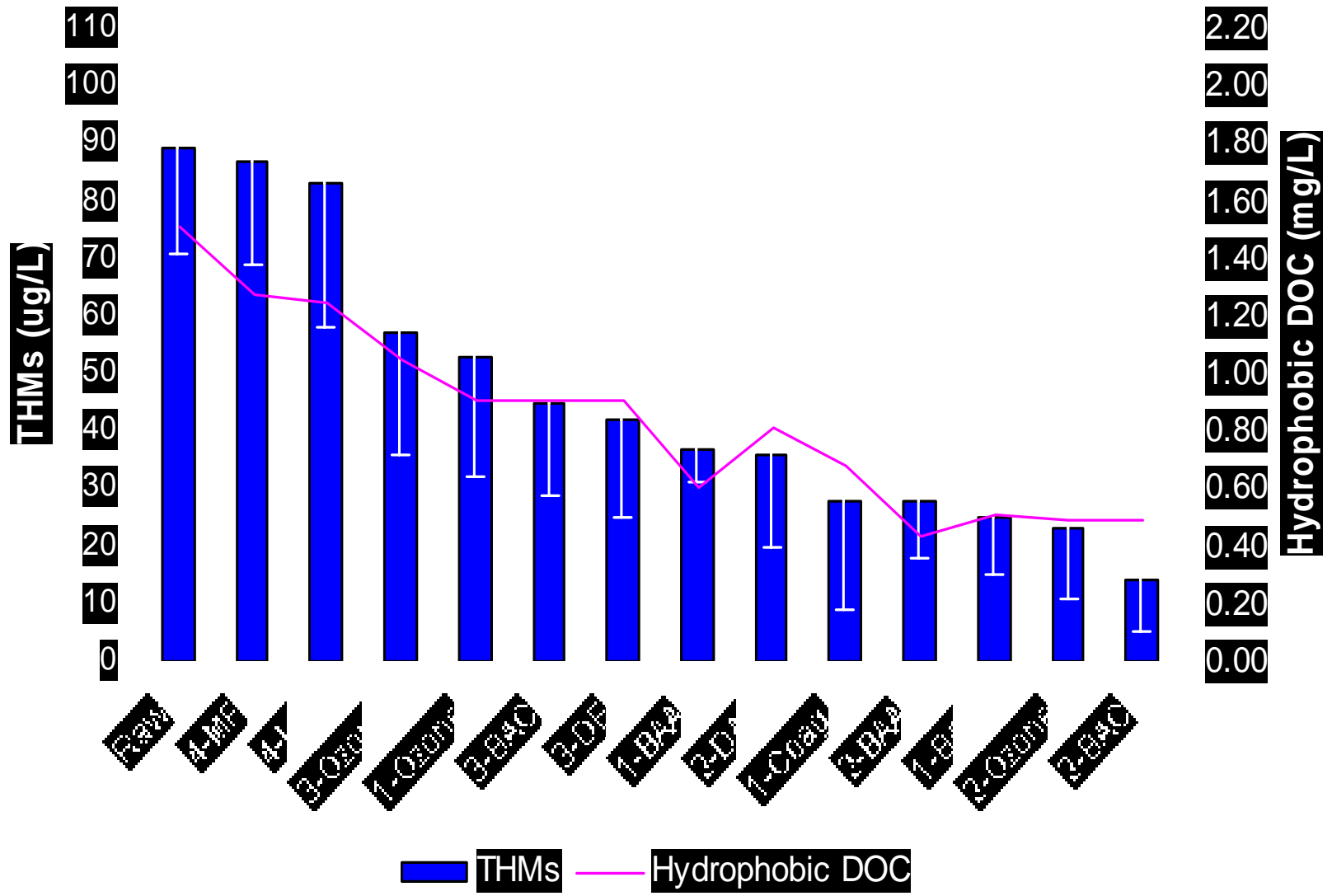
# Hydrophobic versus Hydrophilic Reactivity Data (Feb.'97 - Aug.'97)



# Avg THMs vs. Avg Hydrophobic DOC Thru Each Unit Operation (Feb.'97 - Aug.'97)



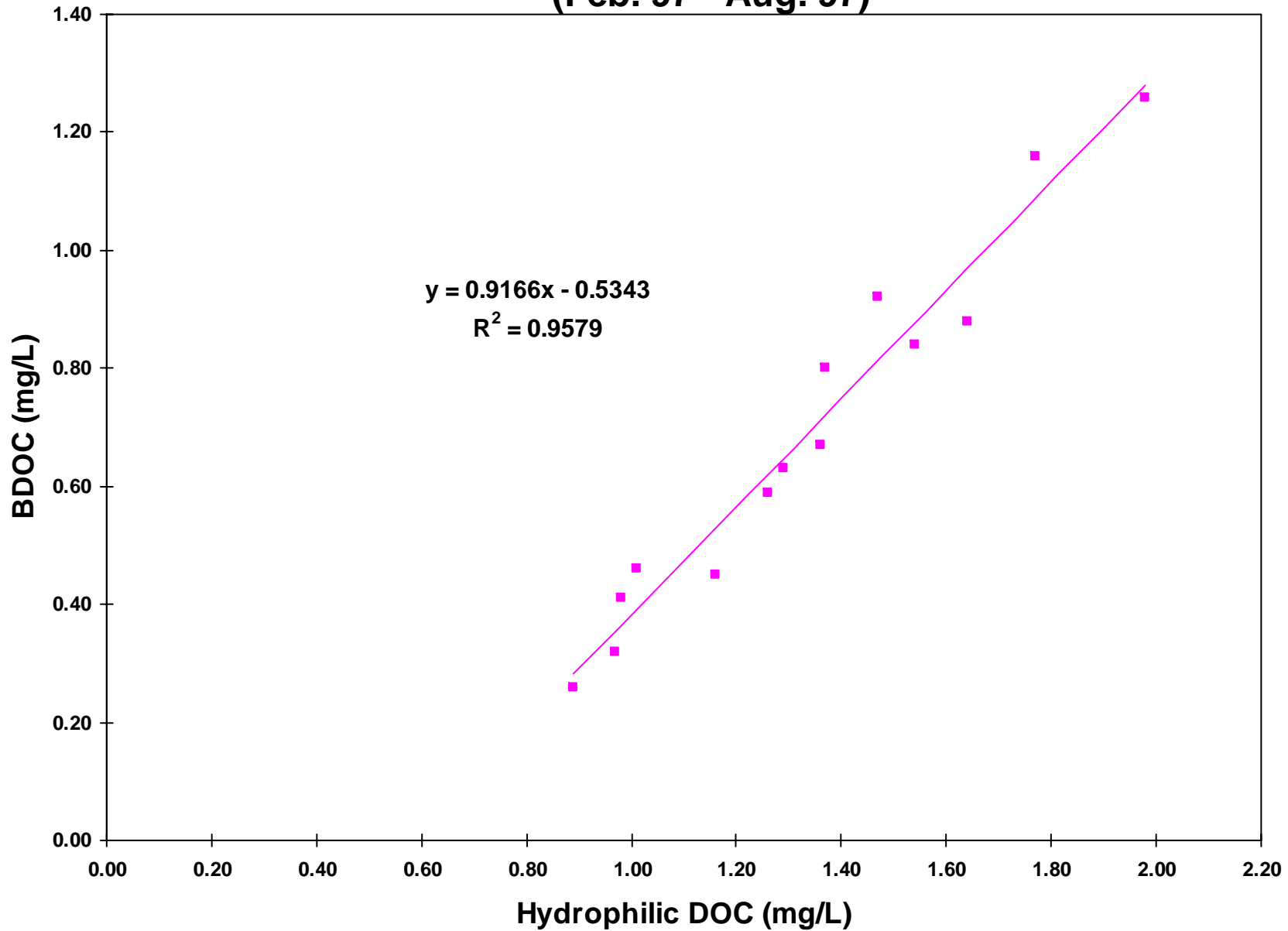
# Avg THMs/Phobic DOC Thru Each Unit Operation (Feb.'97 - Aug.'97)



# **OVERALL RESEARCH OBJECTIVES**

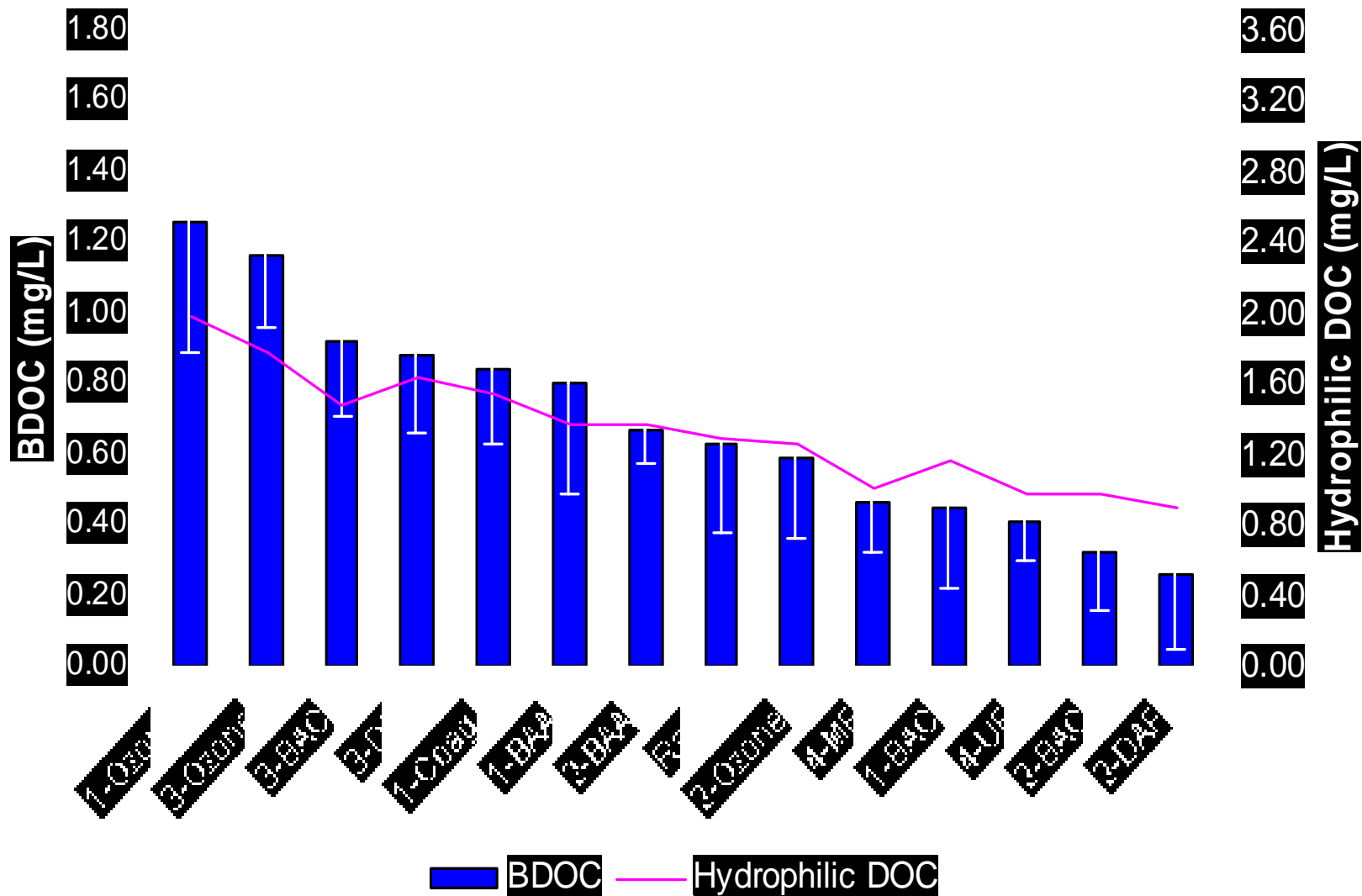
- 2) Determine which of the four pilot treatment trains will be most effective in removing the fractions of NOM that are most available for biological activity**

# Avg BDOC vs. Avg Hydrophilic DOC Thru Each Unit Operation (Feb.'97 - Aug.'97)

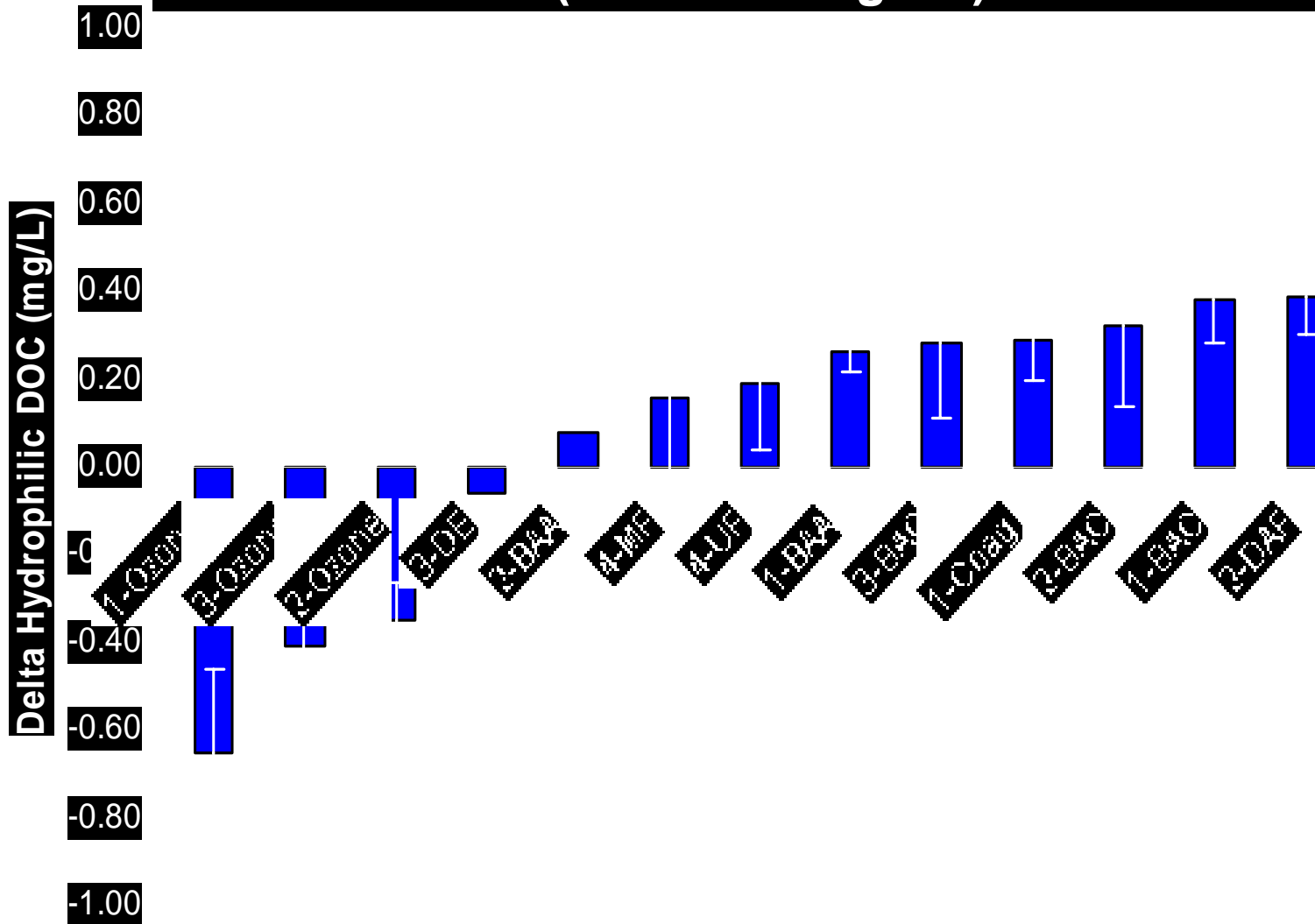




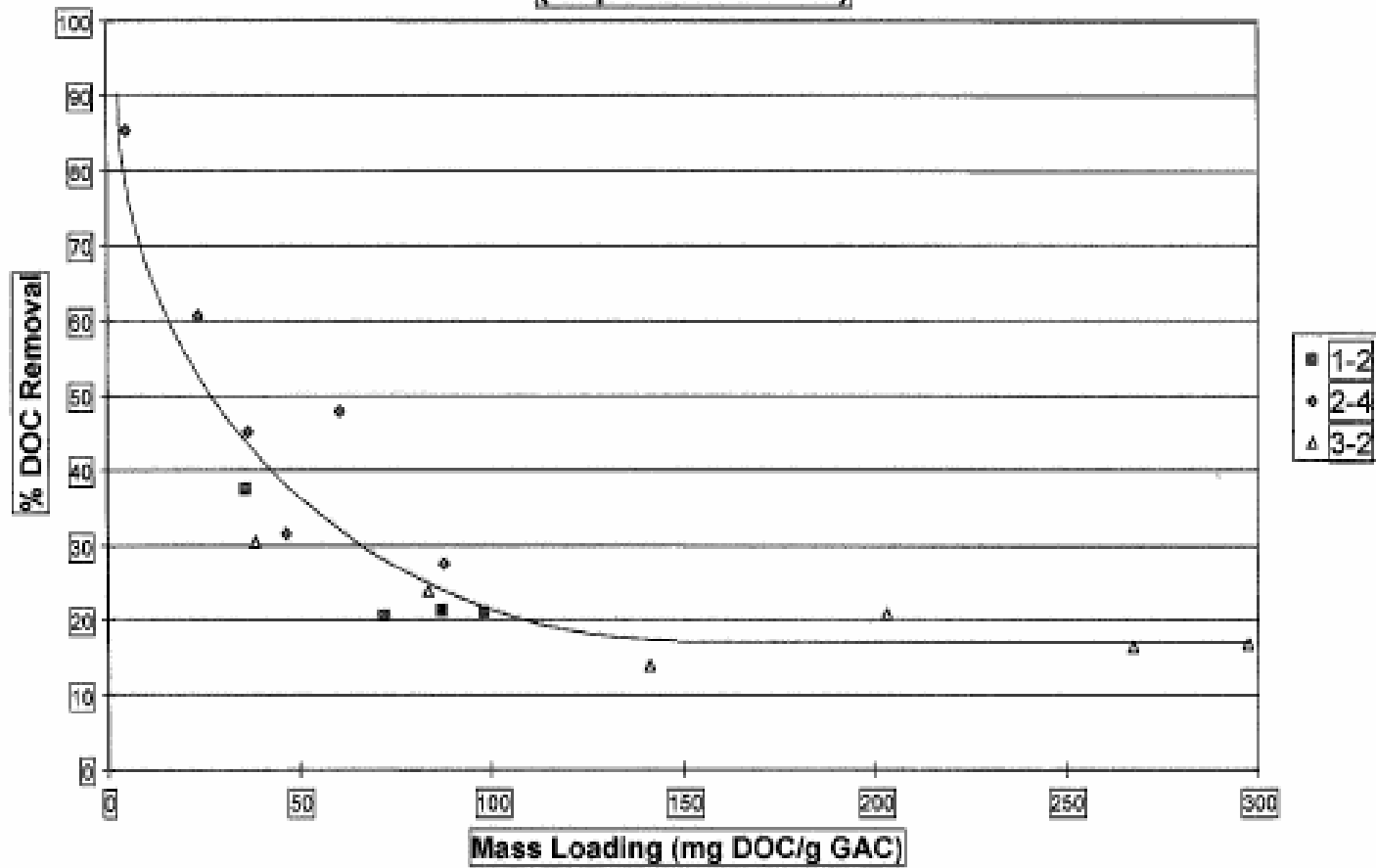
# Avg BDOC/Philic DOC Thru Each Unit Operation (Feb.'97 - Aug.'97)



# Avg Philic DOC Removal Thru Each Unit Operation (Feb.'97 - Aug.'97)



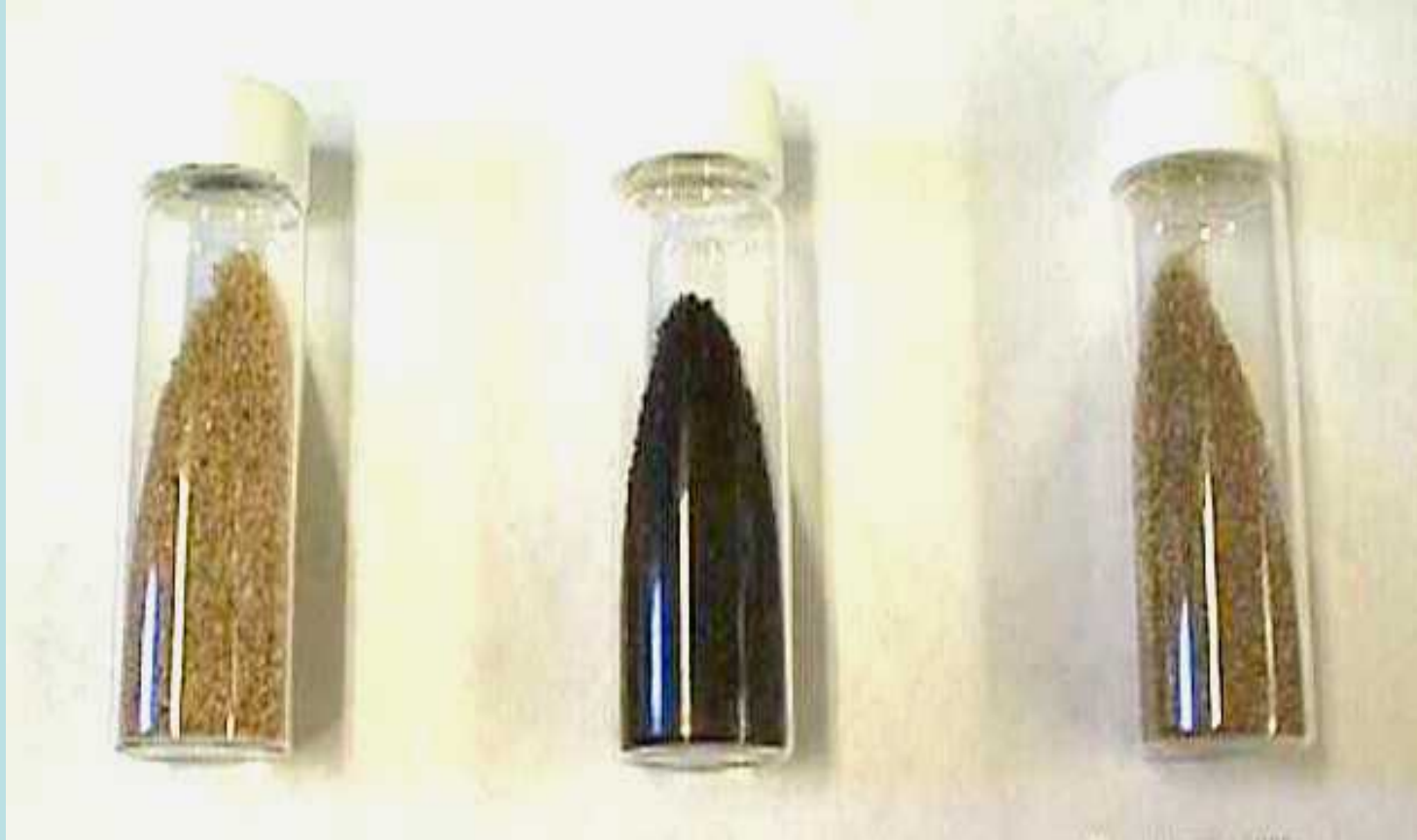
**% DOC Rem. Thru BAC Biofilters vs. Organic Mass Loading**  
**(Sep.'96 - Jun.'97)**



# BAC STUDY - CONCLUSIONS

- The treatment trains that removed the most organic precursor material were the DF and DAF Trains.
- The unit operations which resulted in the greatest reduction of THM formation were ozonation and coagulation.
- The DF and DAF Trains with BAC biofiltration produced the least biodegradable final effluents.
- The most effective unit operations for reducing biological regrowth potential were BAC biofiltration and coagulation.

# Filter Media

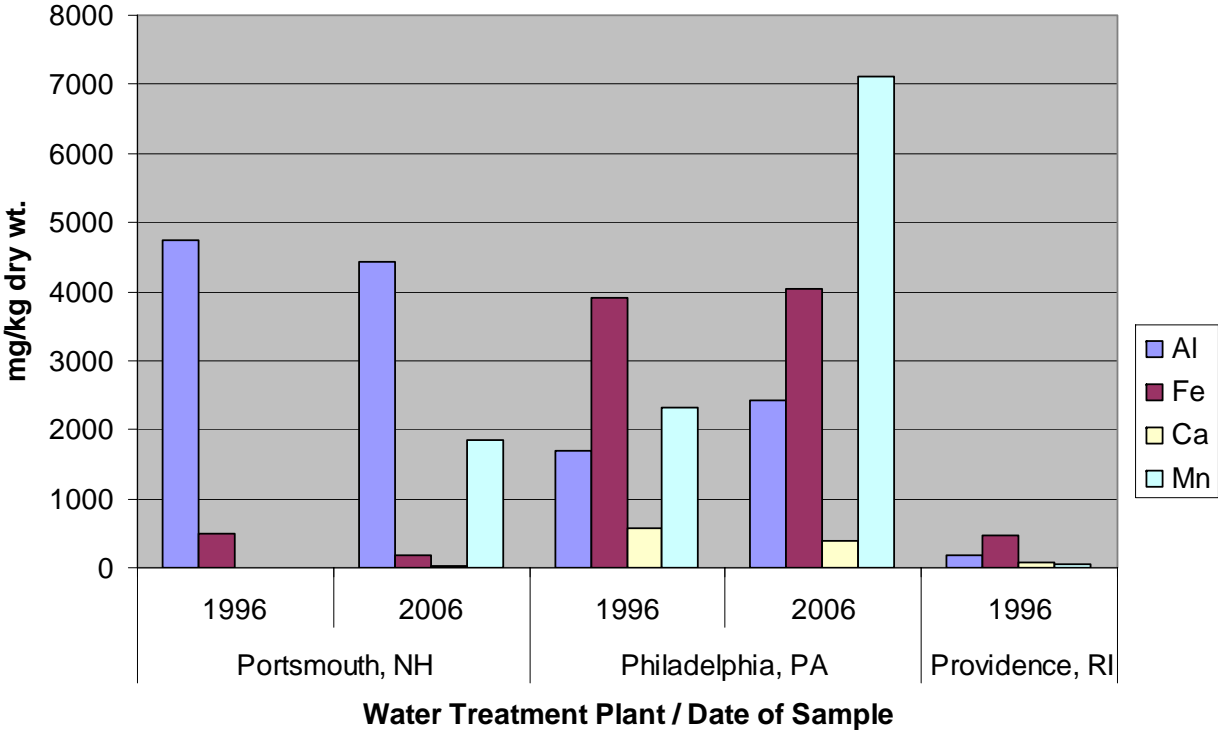


Portsmouth, NH

Philadelphia, PA

Providence, RI

# Average Metal Coating Content of Selected Rapid Sand Filters

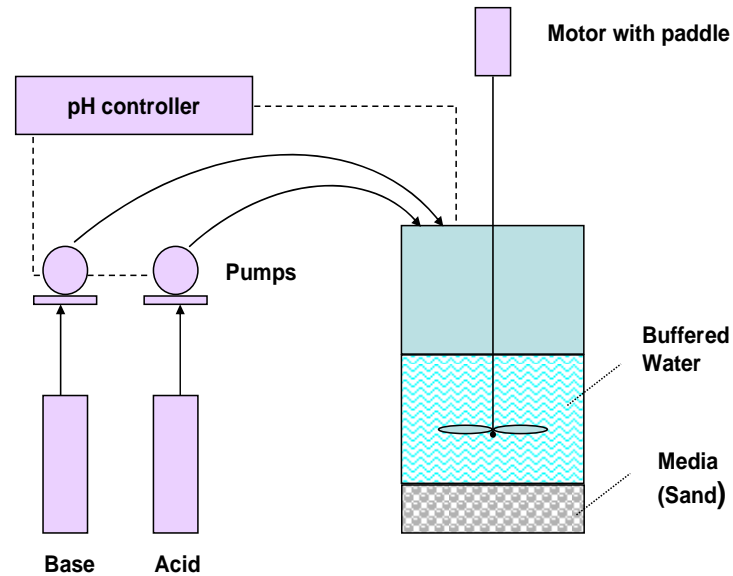


# RESEARCH OBJECTIVES

Explore the NOM removal potential of 'naturally' coated, regenerable sand filter media.

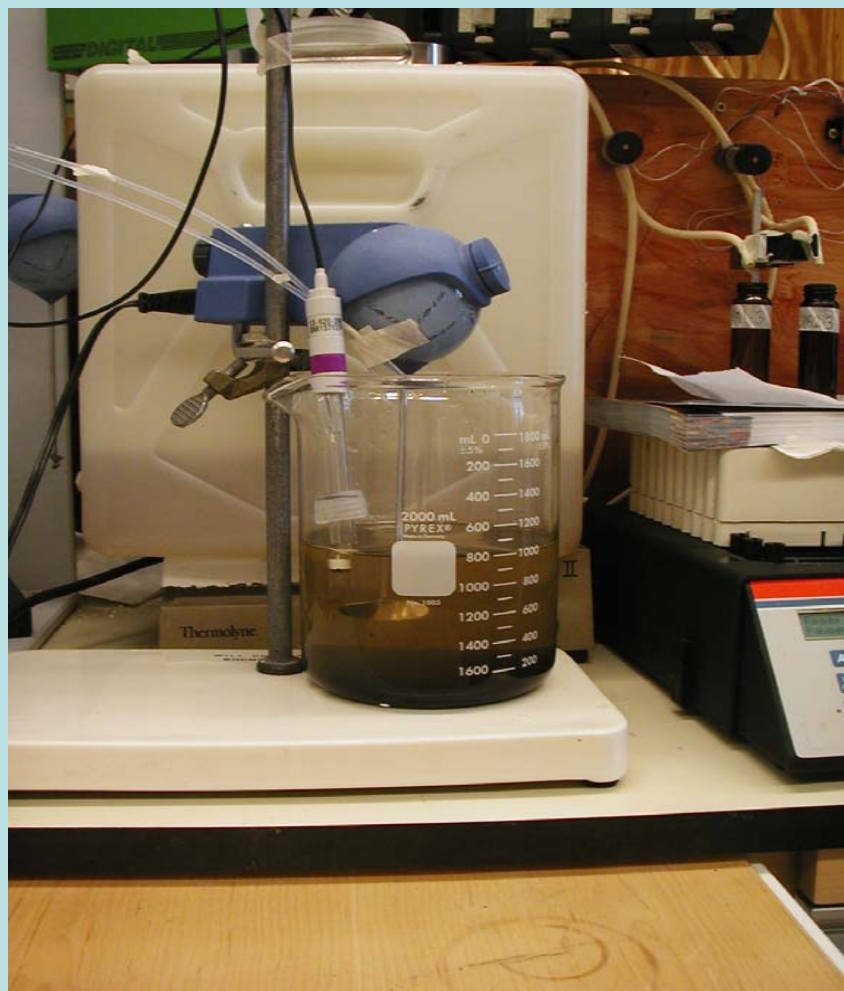
- 1) Assess coating characteristics of 'aged' rapid sand filter media.
- 2) Evaluate optimum initial cleaning/backwashing conditions.
- 3) Quantify NOM & Arsenic removal potentials using 'natural' Al or Fe oxide coatings on sand filter media.
- 4) Evaluate interferences associated with the adsorption capacity of the metal oxide coating.

# Backwash/Regeneration Set-Up



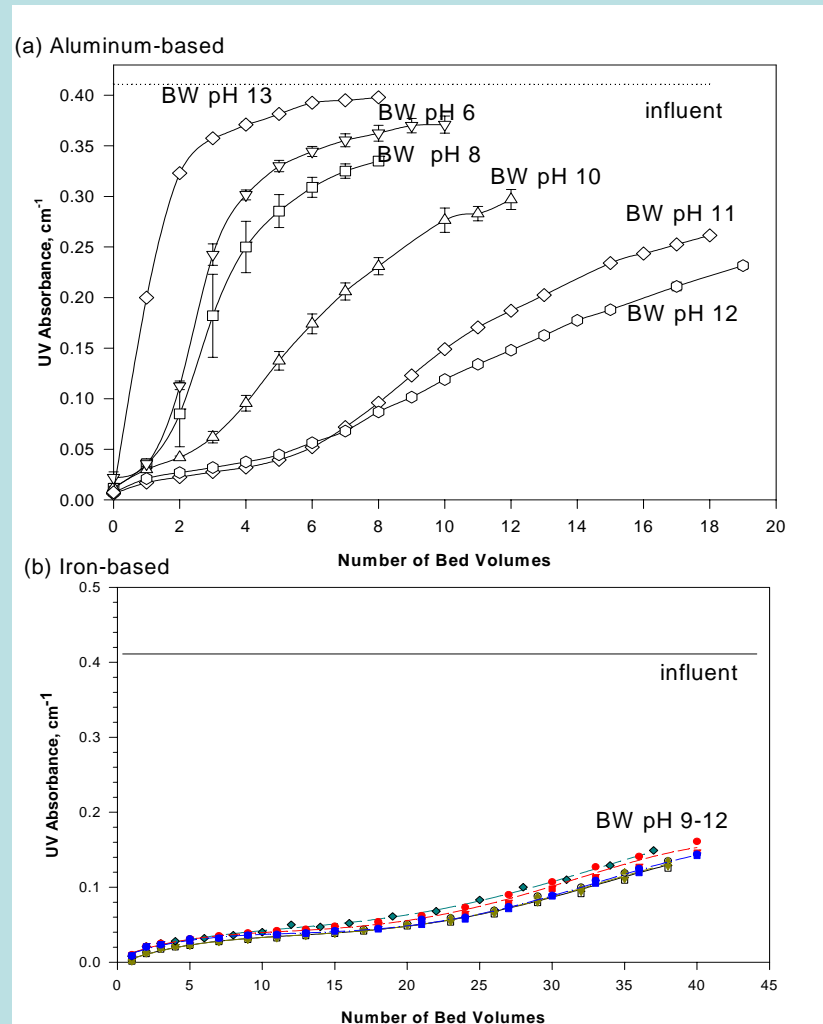


# BACKWASH SET-UP



# Effect of BW Regeneration pH on NOM Removal at pH 6 Challenges

(a) Aluminum-based coating and (b) Iron-based coating

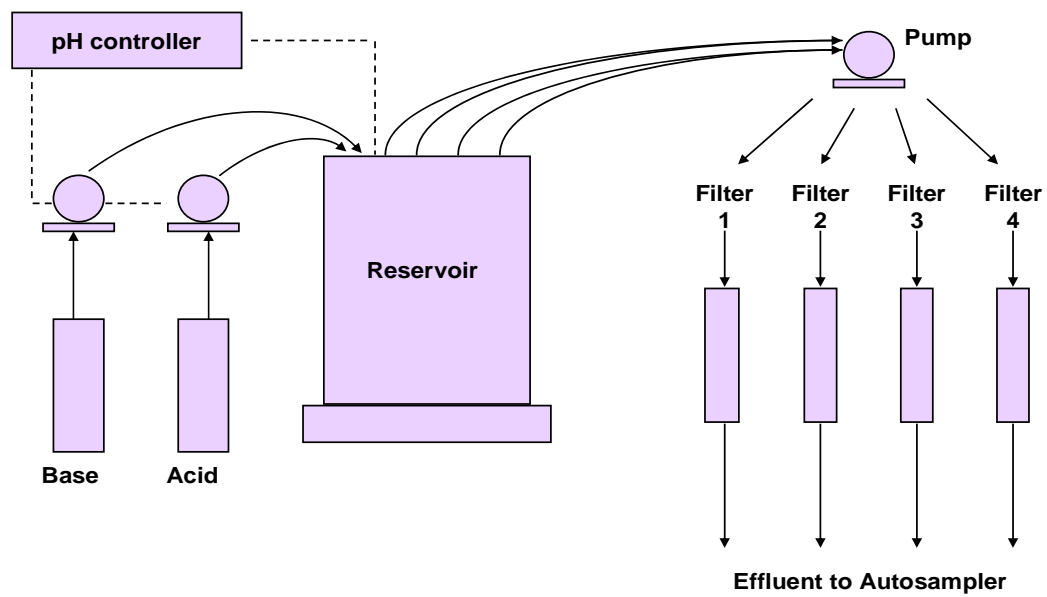


# RESEARCH OBJECTIVES

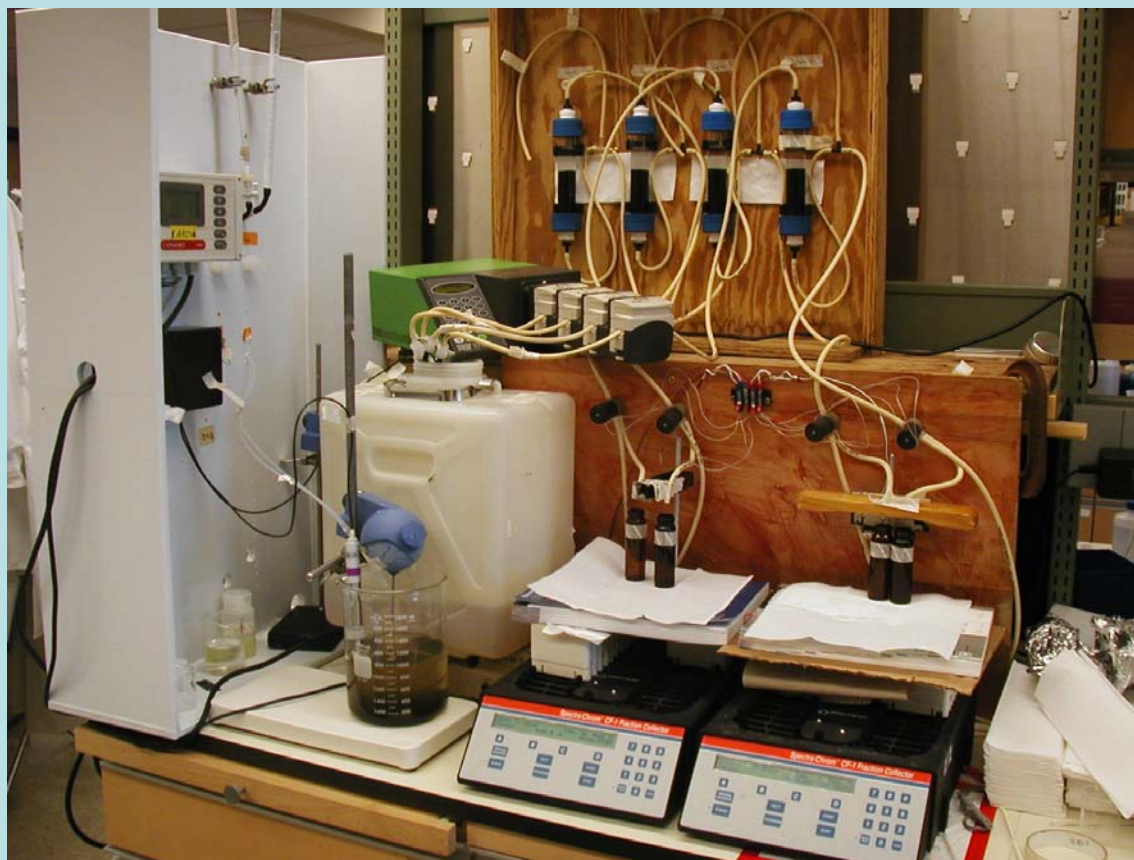
Explore the NOM removal potential of 'naturally' coated, regenerable sand filter media.

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- 2) Evaluate optimum initial cleaning/backwashing conditions.
- 3) Quantify NOM & Arsenic removal potentials using 'natural' Al or Fe oxide coatings on sand filter media.
- 4) Evaluate inorganic interferences regarding the adsorption capacity of the metal oxide coating.

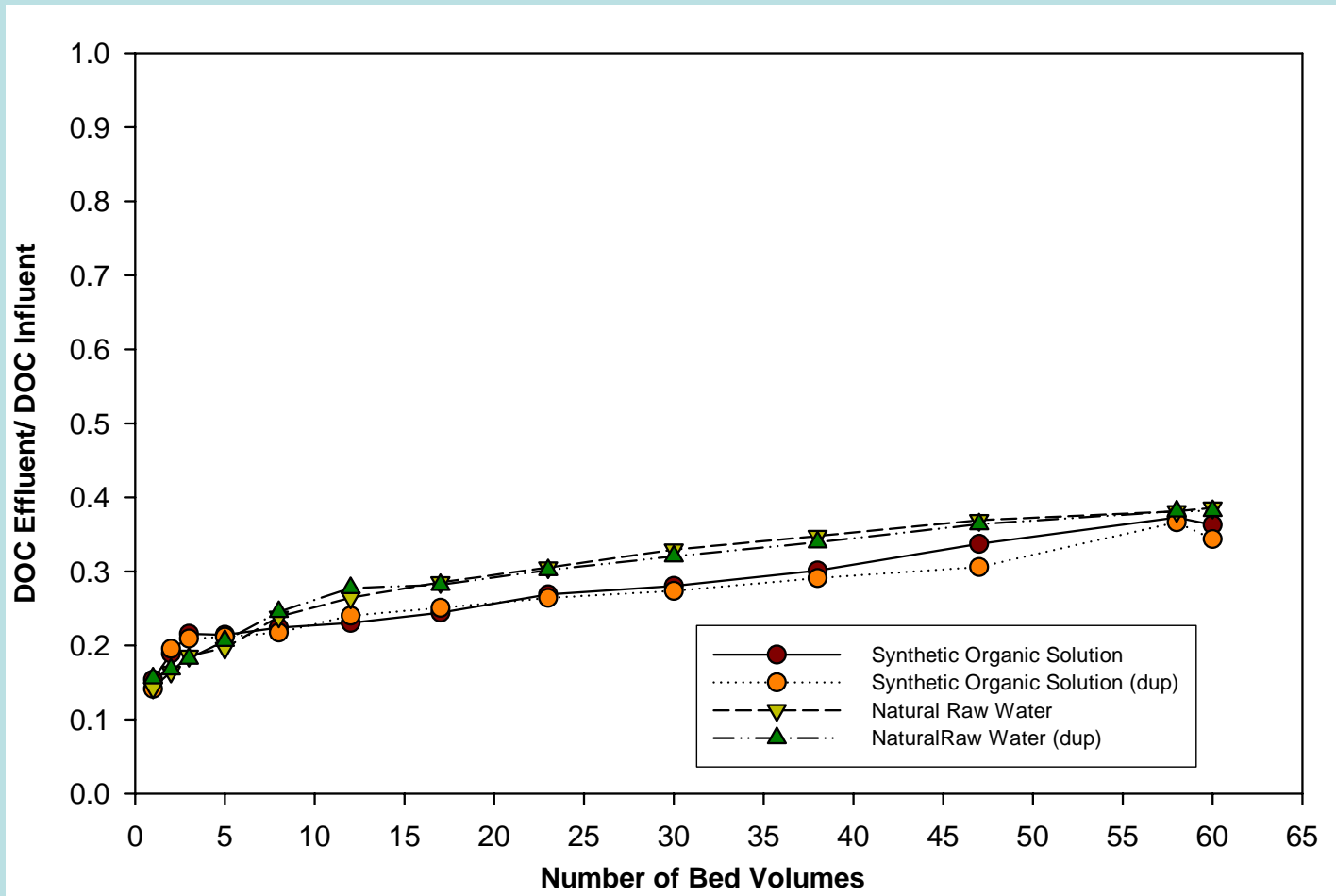
# Challenge Set-Up



# CHALLENGE SET-UP

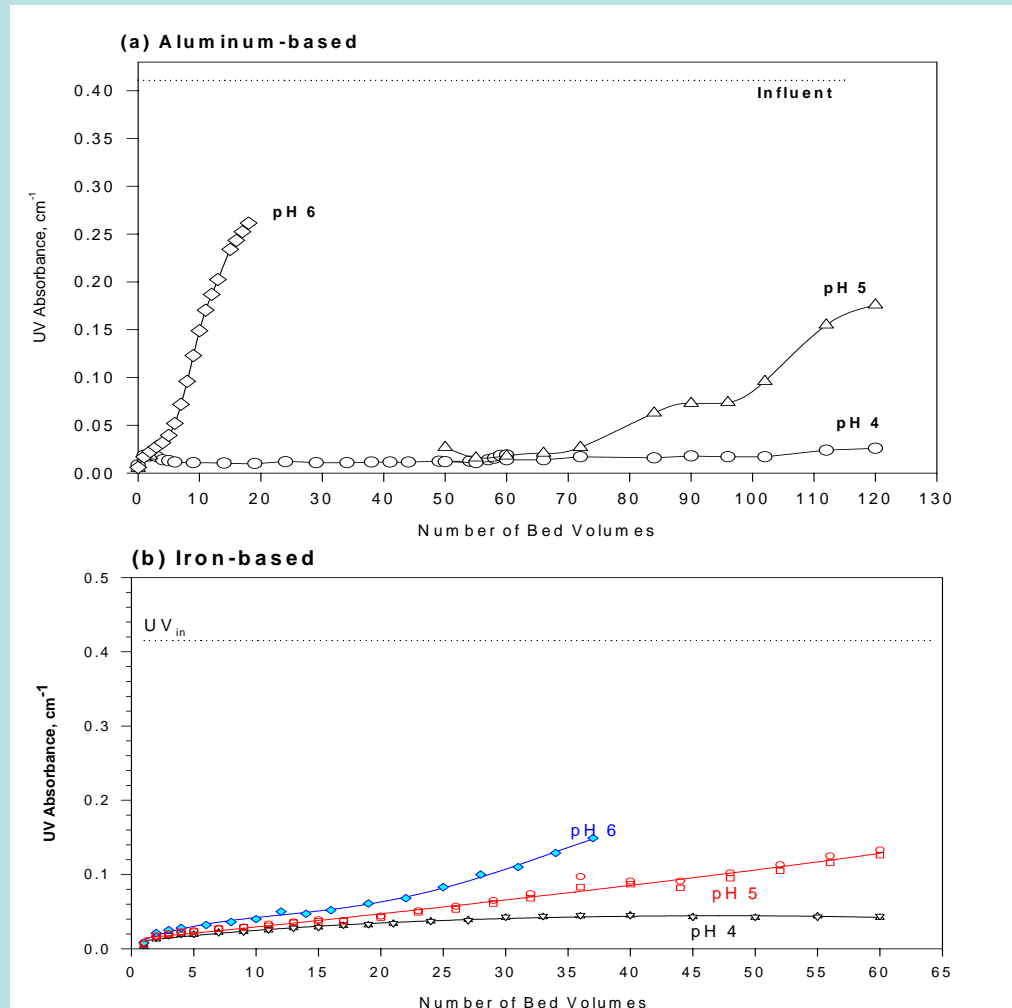


# Comparison of Synthetic and Natural DOC Challenge Solutions at pH 6 after Regeneration at pH 11 of Iron-Coated Sand



# Effect of Challenge Solution pH on NOM Removal after Regeneration at pH 11

(a) aluminum-based coating and (b) iron-based coating

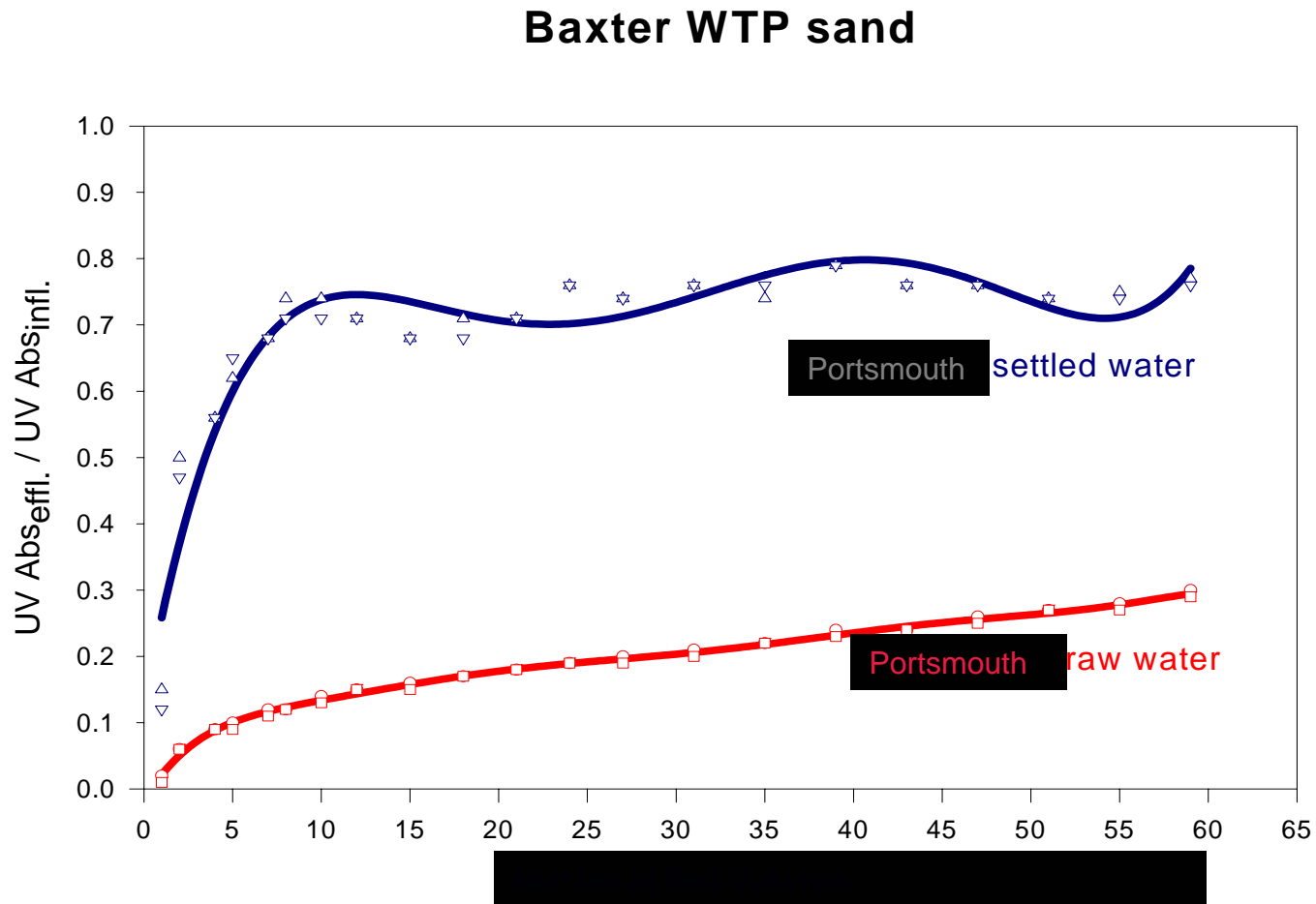


## Relating 60 Bed Volumes to Filter Run Times (hr)

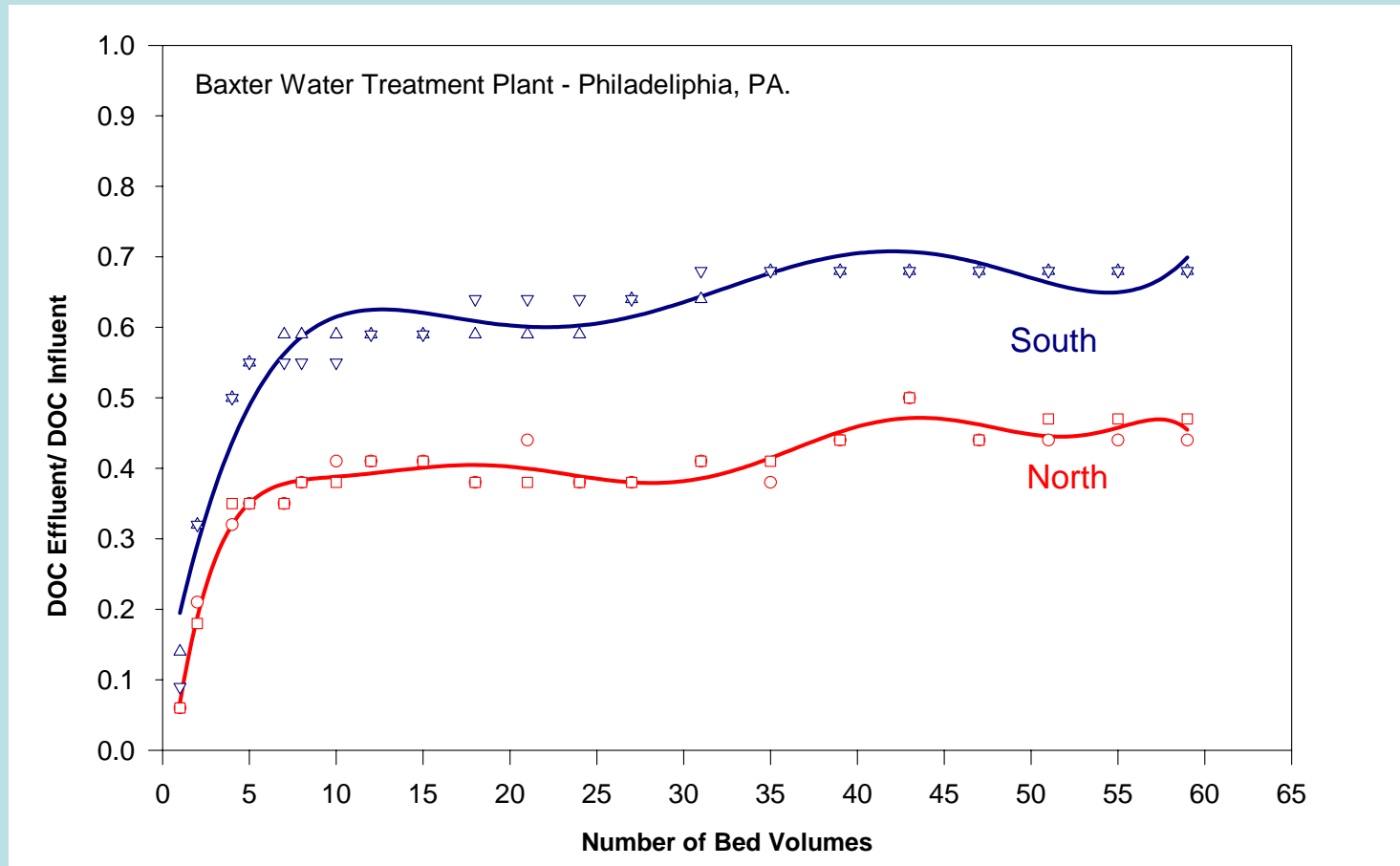
<u>Q, gpm/ft<sup>2</sup></u>	<u>Filter Bed Depth, ft</u>		
	<u>2</u>	<u>4</u>	<u>6</u>
2	7.5	15.0	22.4
4	3.7	7.5	11.2
6	2.5	5.0	7.5



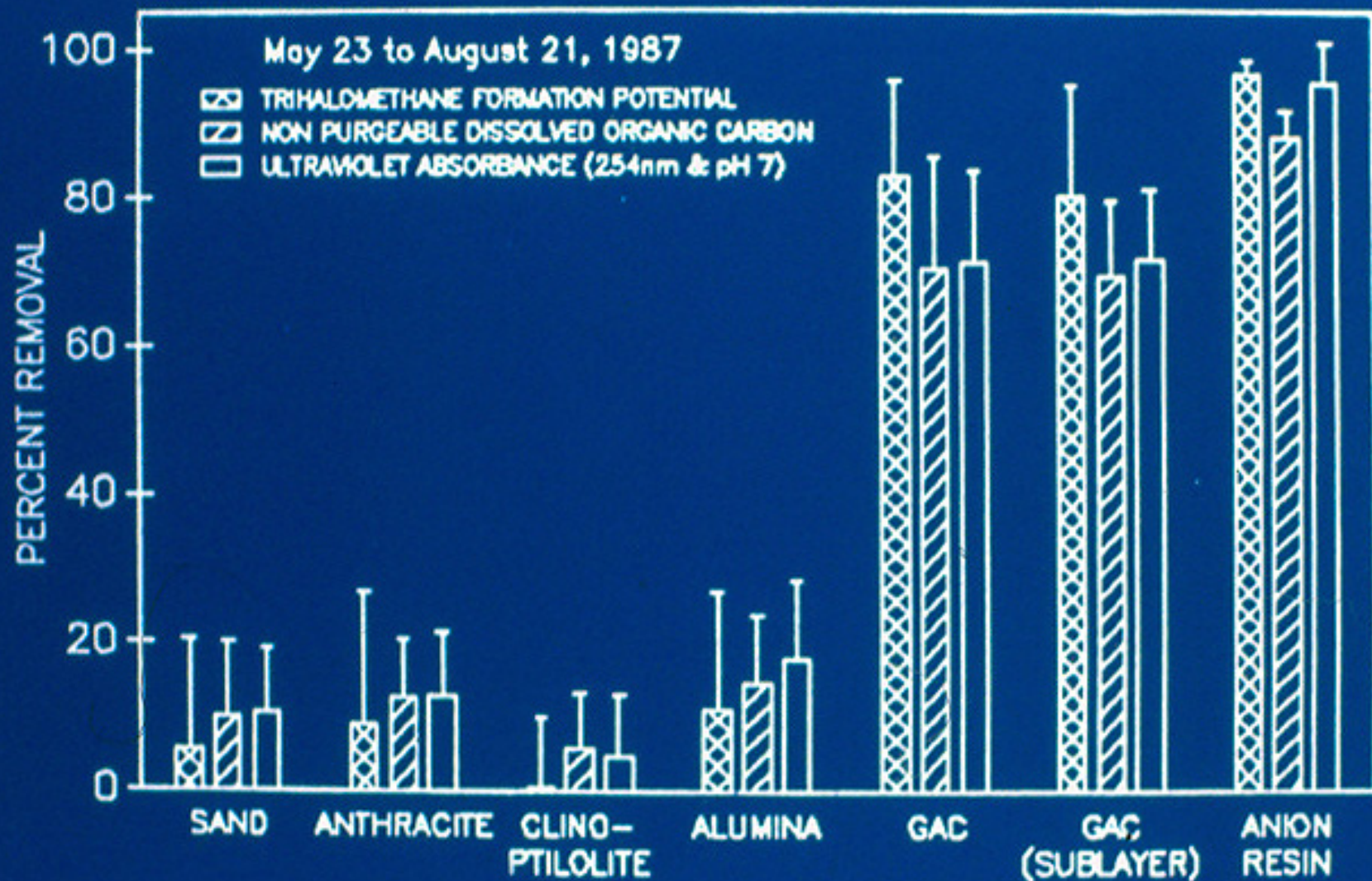
# Influence of Source Waters Adjusted to pH 5 on Organic Matter Removals after Regeneration of Iron-coated Sand at pH 11



# DOC Removals from a Clarified Source Water adjusted to pH 5 after Regeneration at pH 11 of an Iron-Coated Sand

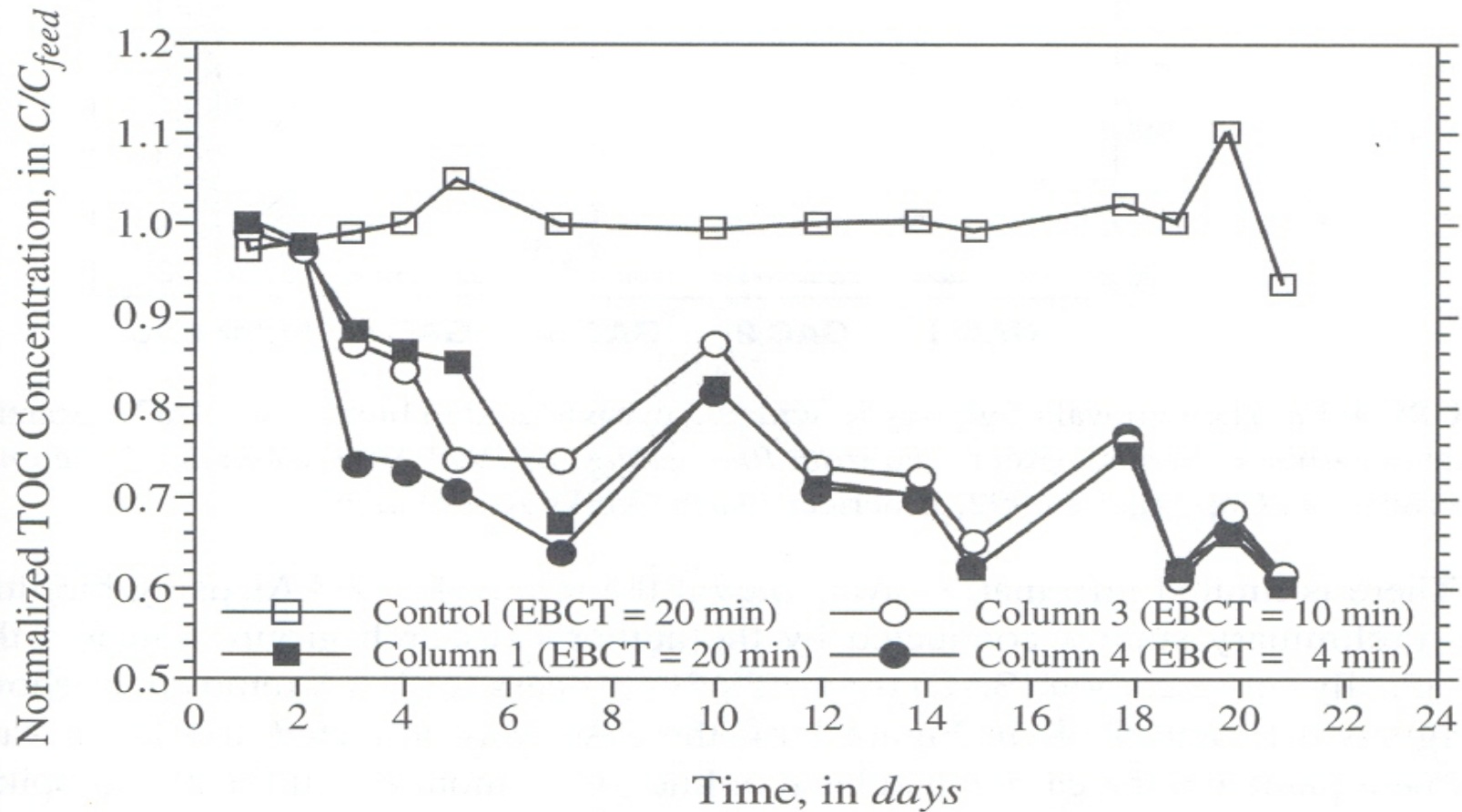


# Anionic Exchange Resins



# Biodegradation with and without Enhanced Biofiltration and BAC

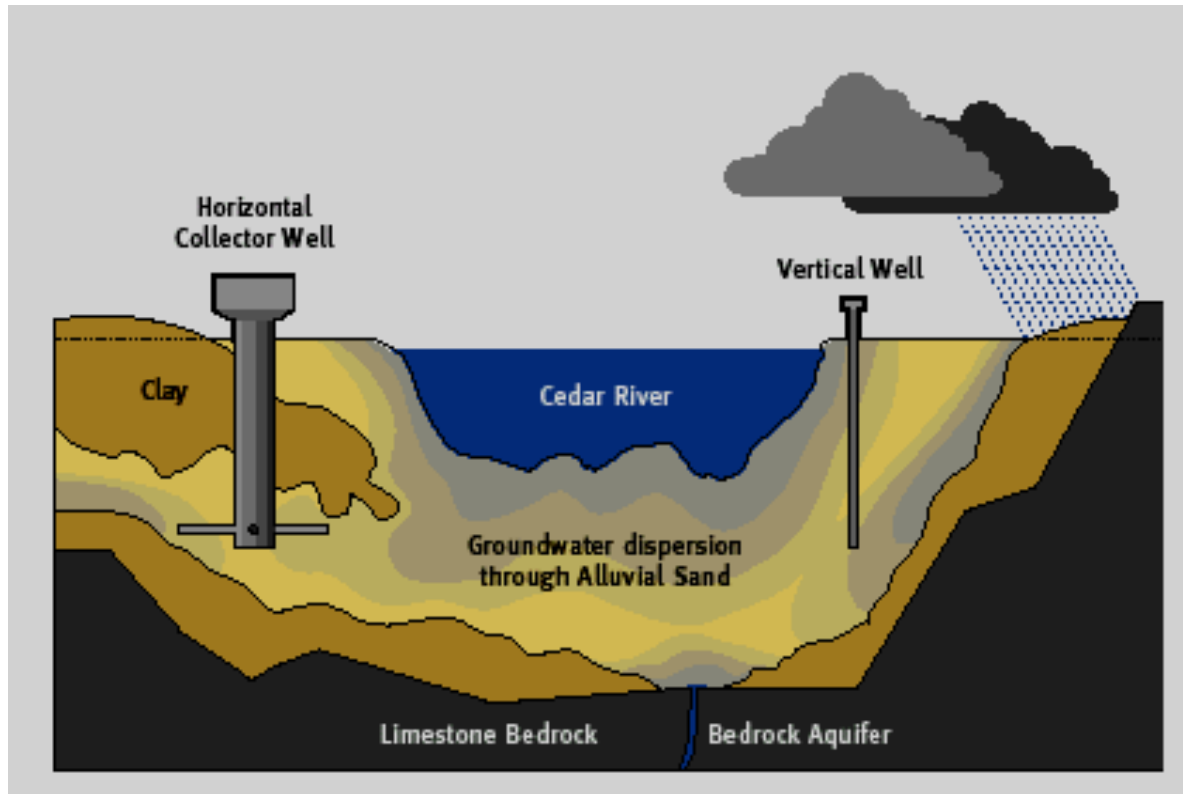
# Biofiltration for DBP precursor removal



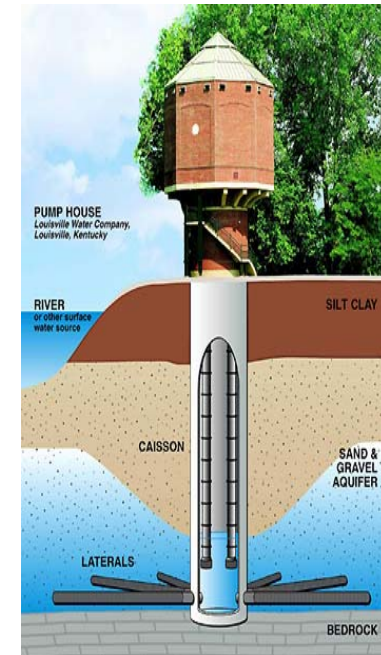
(Hozalski & Bouwer)



# Typical Layout of a RBF Well

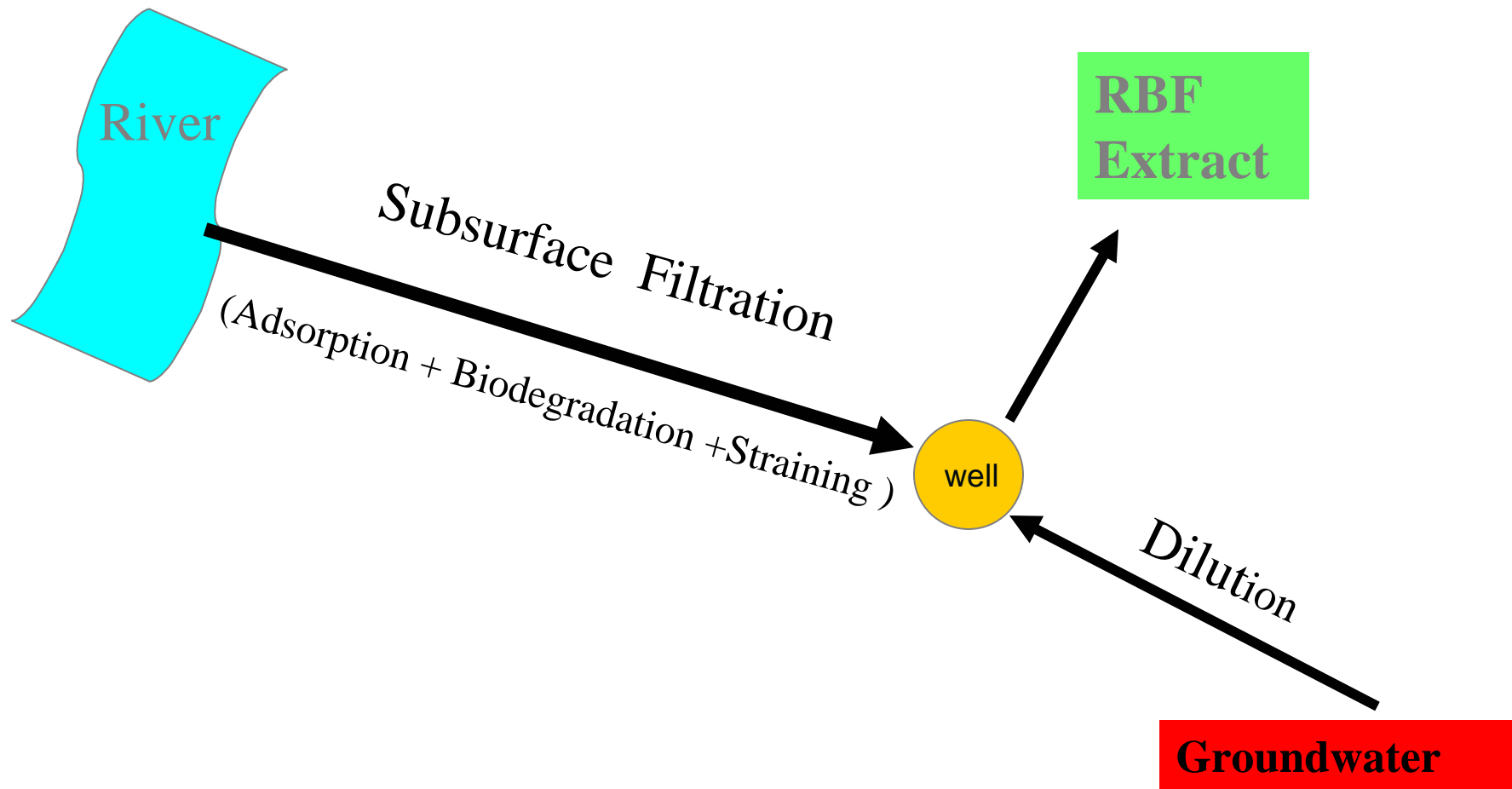


Cedar Rapids, IA



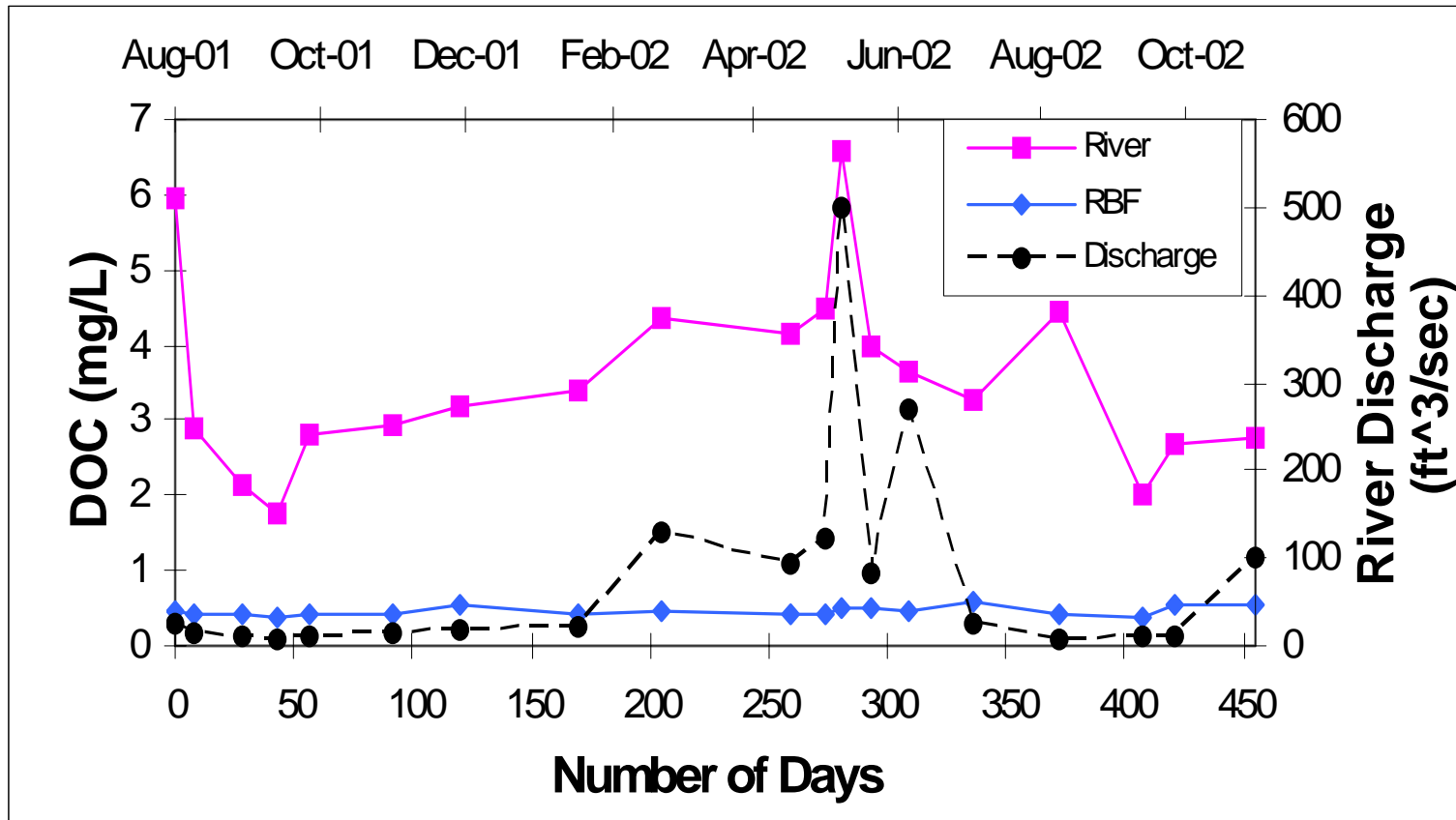
Louisville, KY

# Removal Processes Taking Place at an RBF Site

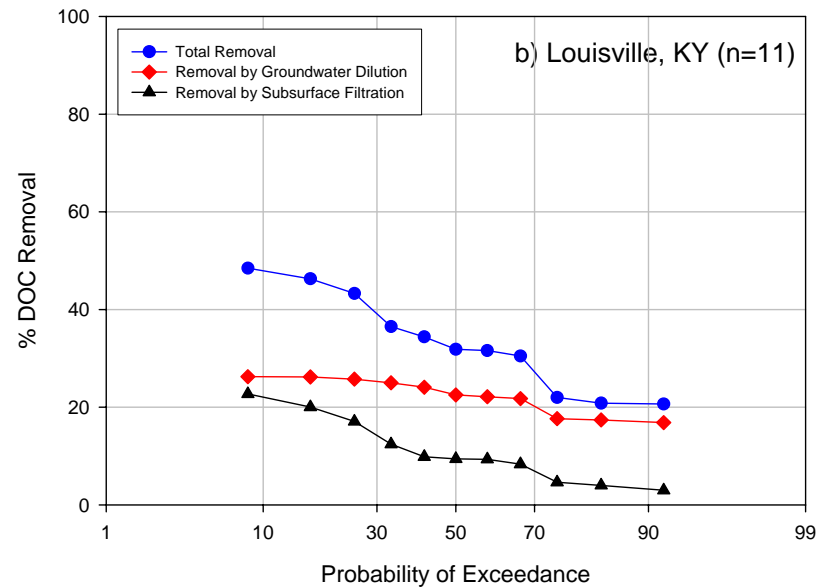
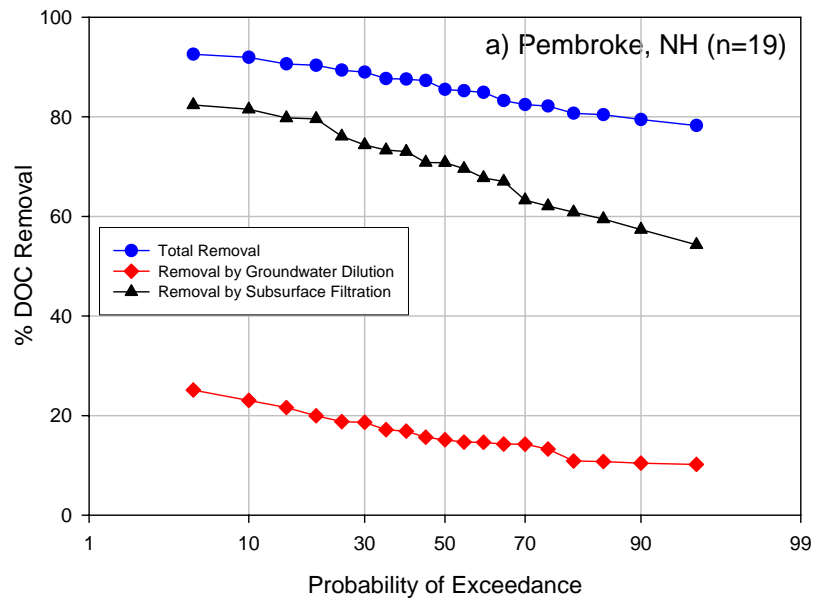




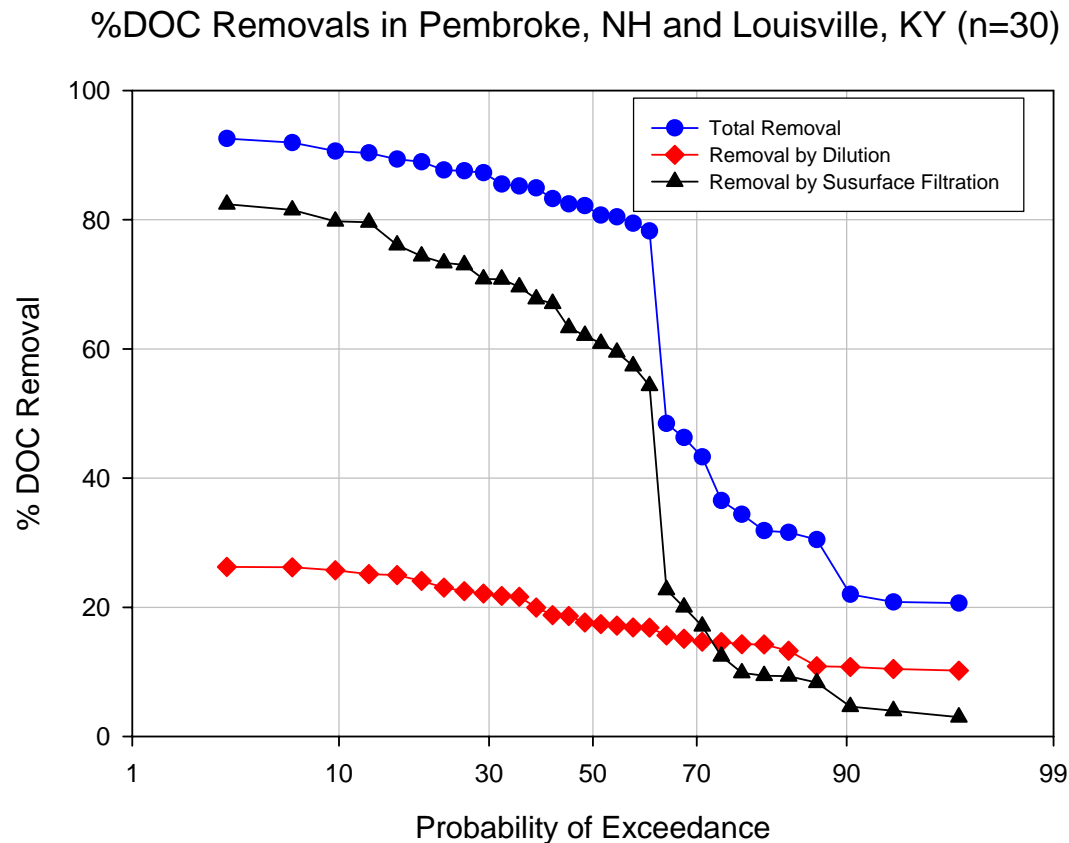
# Typical DOC variations as a function of river discharge in Pembroke, NH including groundwater dilution impacts.



# DOC Removals versus Probability of Exceedance in Pembroke, NH and Louisville, KY



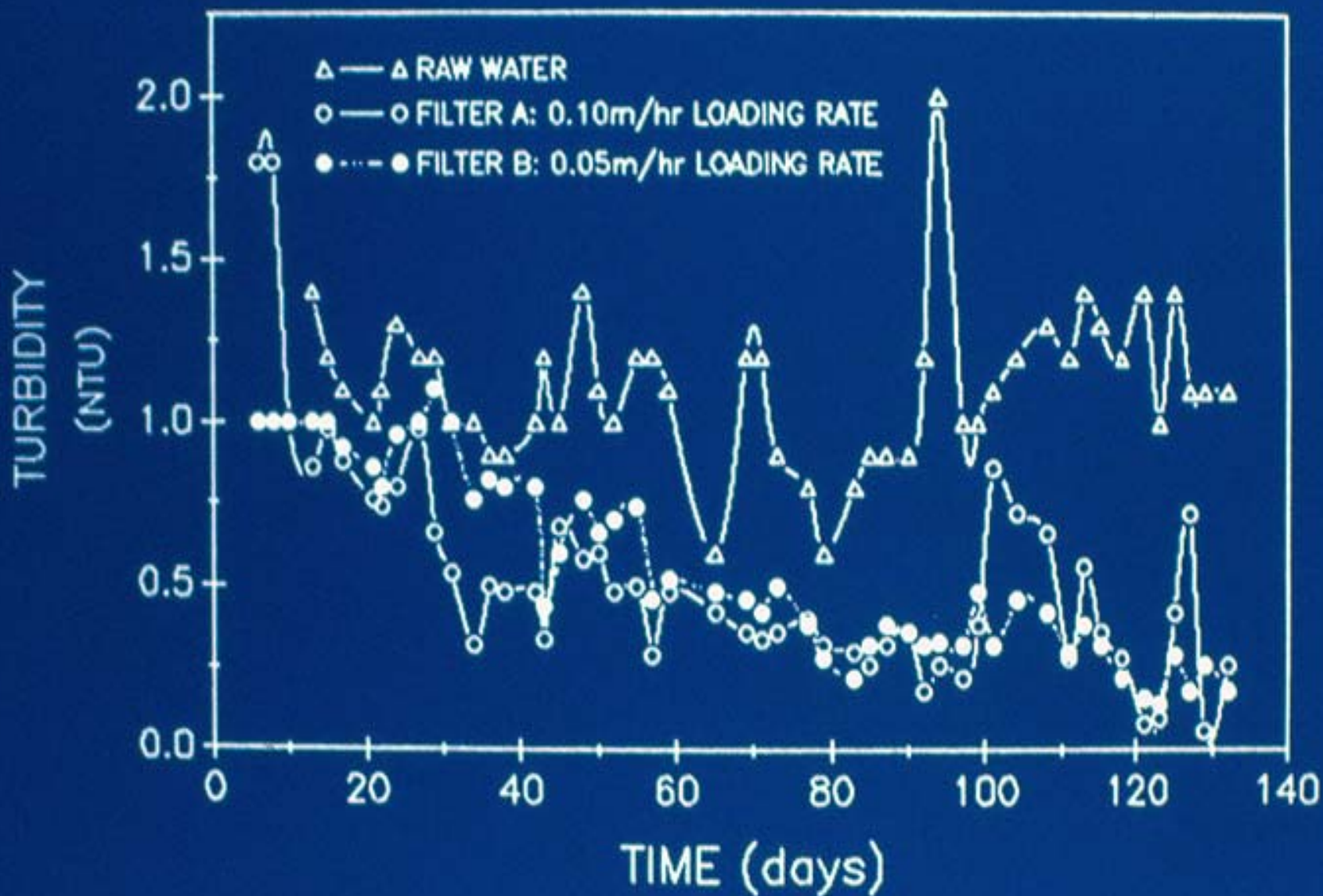
# DOC removal capability of exceedance comparison between Pembroke, NH and Louisville, KY



# ***Site Specific RBF Parameters Influencing DOC Removals***

- Initial DOC Concentration & Biodegradability
- Hydraulic Residence/Travel Time
- Aquifer Transmissivity
- Extent of Groundwater Dilution
- Composition of Subsurface Material
- Aerobic vs Anaerobic Subsurface Conditions
- Intermittent vs Continuous Operations

# TURBIDITY VALUES VERSUS TIME ASHLAND, NH, July 29 to December 8, 1987

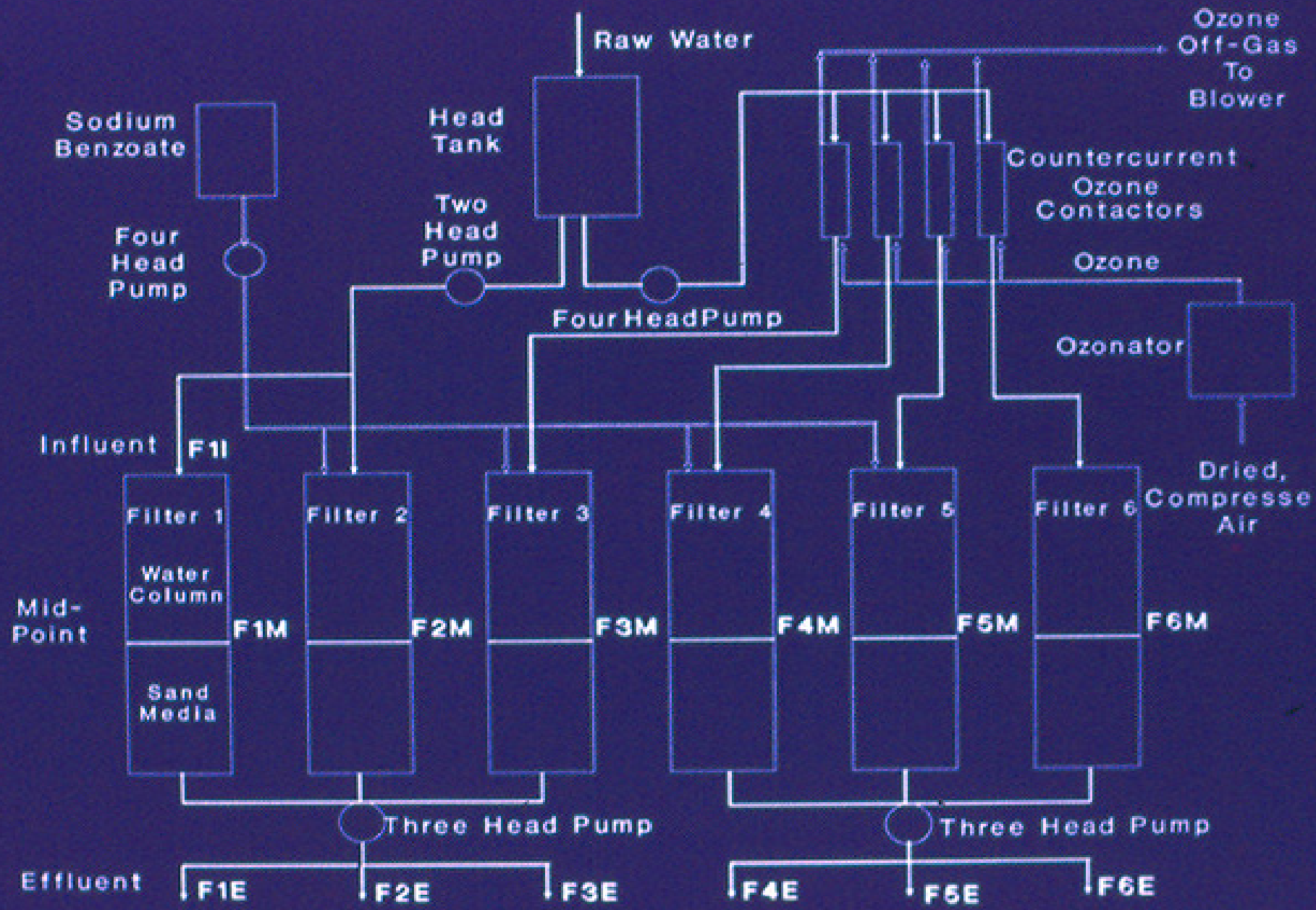






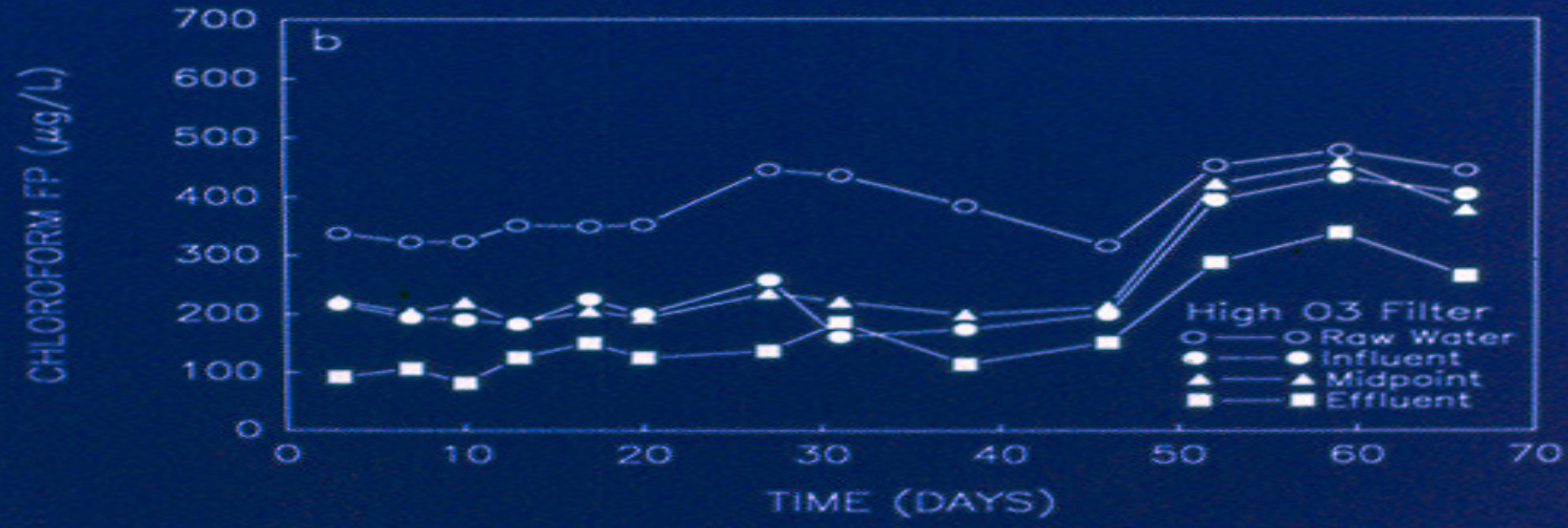
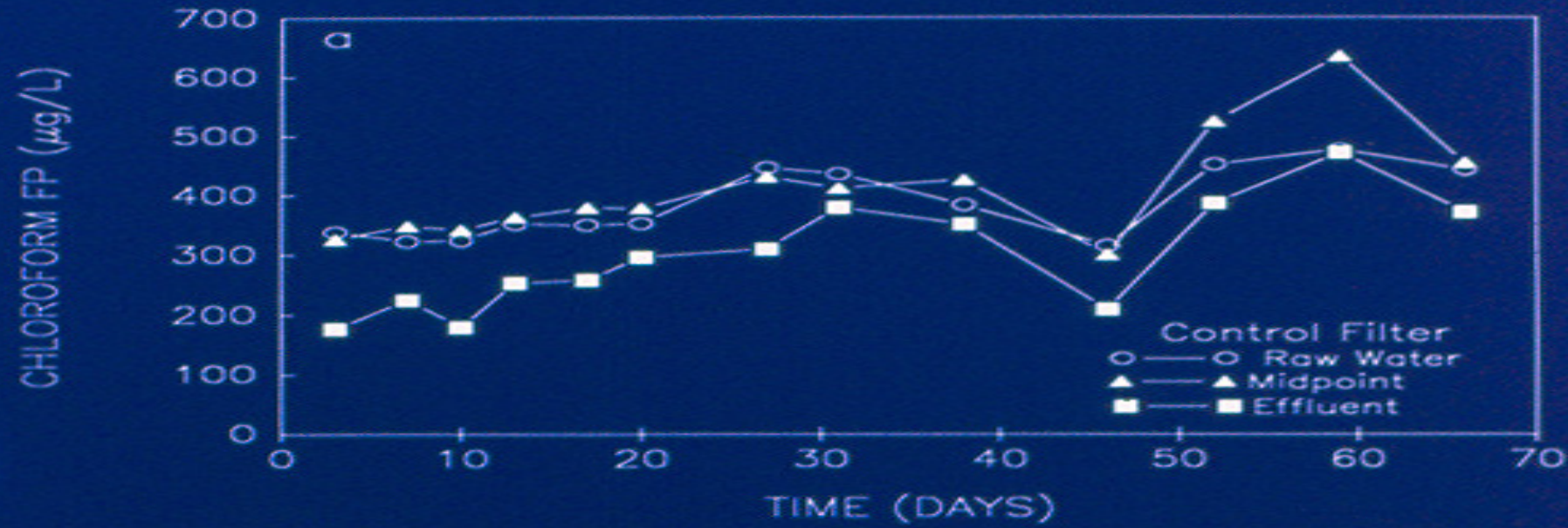


Filter #3  
CONTROL

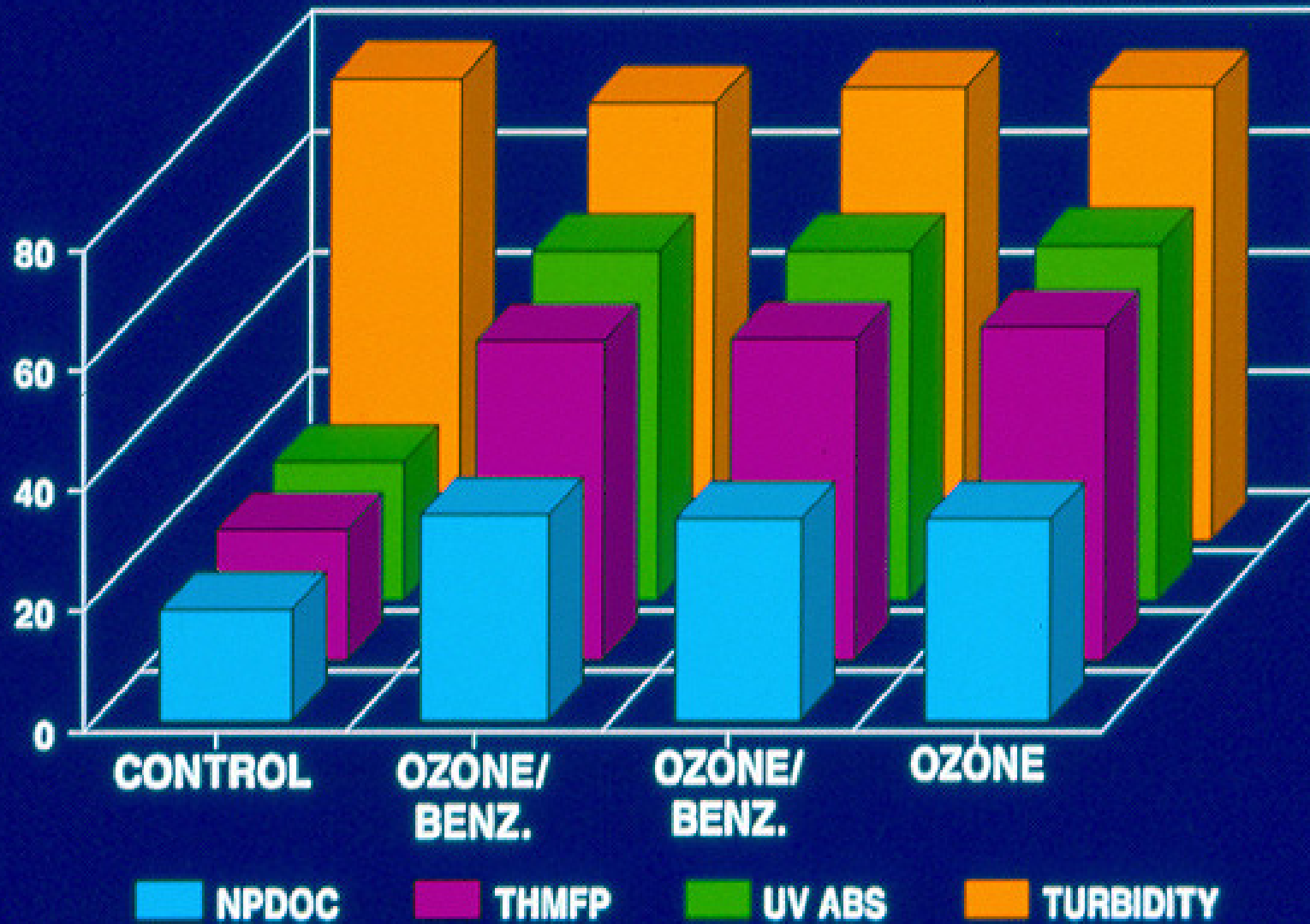




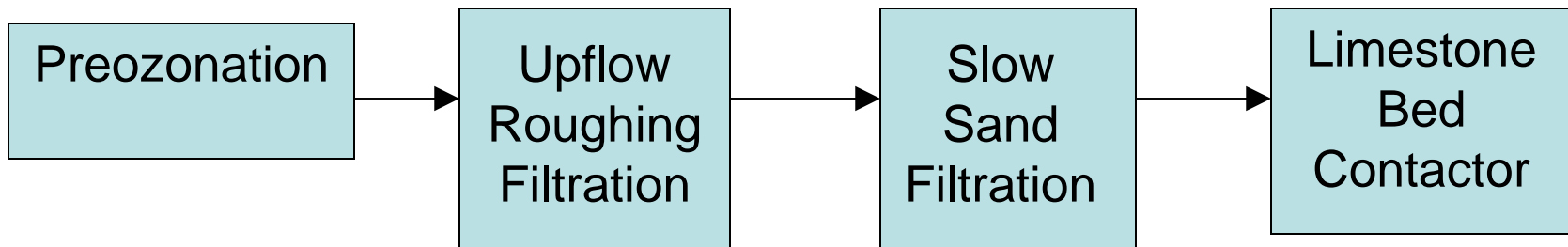
# PORTSMOUTH OZONE EFFECTS: THMFP

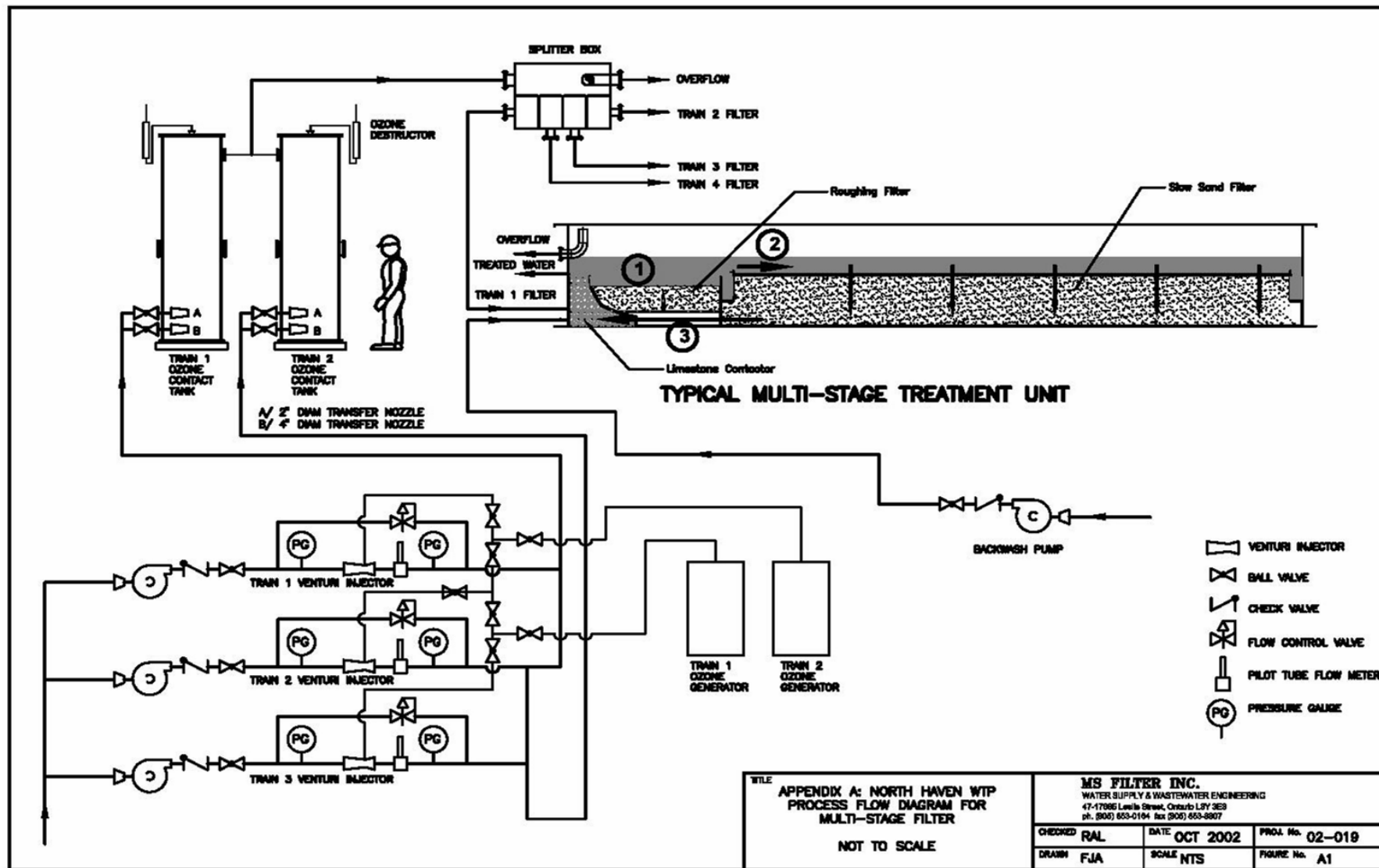


# AVERAGE PERCENT REMOVALS RUN 2



# Selected “Multi-stage” Prefabricated Treatment System

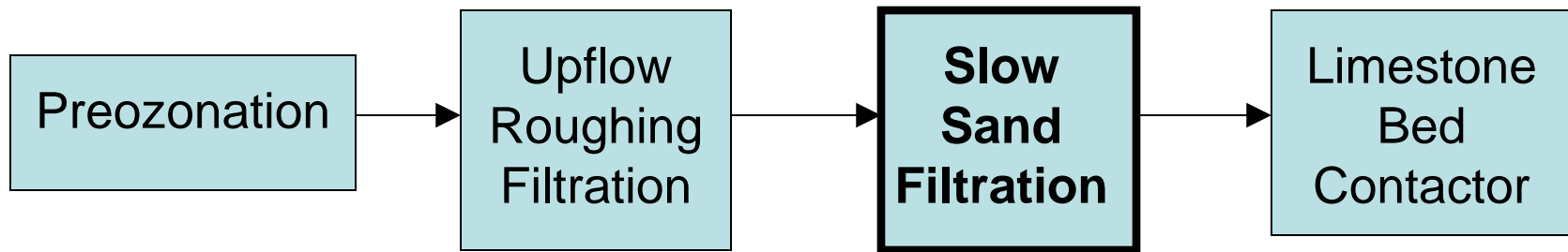








# Design Parameters



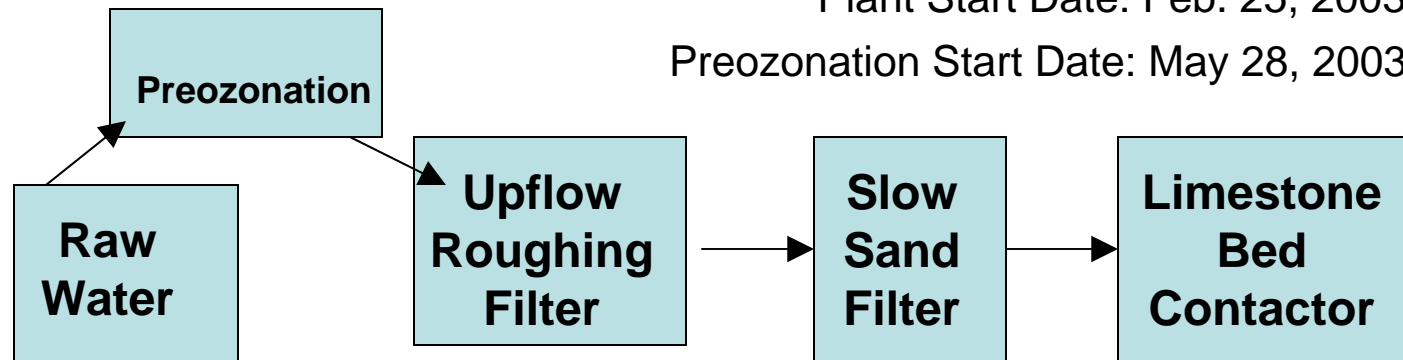
	<b>Peak Day</b>	<b>Average Summer Day</b>	<b>Average Winter Day</b>
Flow Rate, gpd	250,000	125,000	80,000
Slow sand filtration rate, gpm/ft <sup>2</sup>	0.12	0.06	0.04
Slow sand filter empty bed contact time, minutes	324	648	1,010

# Operational Summary

(5/28/03 – 6/12/03)

Plant Start Date: Feb. 25, 2003

Preozonation Start Date: May 28, 2003



Turbidity (NTU)	0.8	0.3	0.2	----
Color (CU)	25	----	5	----
UV Abs. (cm-1)	0.489	0.202	0.187	0.185
TOC (mg/L)	9.89	7.10	6.36	6.27

# “NEW” Modifications to SSF

- Replace limestone bed contactor with GAC or anionic resin with separate regeneration system
- Utilize an anionic resin “mat/quilt” on top of limestone bed contactor
- Use iron additions ( $<0.1$  ppm) to enhance NOM adsorption by iron-coated sand media



# Membrane Filtration (Nanofiltration)

Membrane Process	MWCO (daltons) <sup>a</sup> or Pore Size (μm) <sup>b</sup>	Operating Pressures	Recovery	Trans-membrane Flux	Primary Application
Microfiltration	0.05-5 <sup>b</sup>	5 to 30 psi	95 to 98%	100 to 1,000 gfd	Particle Removal Disinfection
Ultrafiltration	1,000-500,000 <sup>a</sup>	7 to 60 psi	80 to 95%	20 to 300 gfd	Partical Removal Disinfection
Nanofiltration	200-1,000 <sup>a</sup>	50 to 120 psi	70 to 90%	15 to 25 gfd	Softening NOM Removal
Reverse Osmosis	<200 <sup>a</sup>	200 to 1,500 psi	50 to 85%	3 to 20 gfd	Desalting, SOC IOC Removal

# Membranes for DBP precursor removal

**TABLE 4.1**  
**Summary of DBP Precursor Studies with Membrane Processes**

Water Source	Pretreatment	Membrane technology	Feed water THMFP (µg/L)	Treated THMFP (µg/L)	Percent THMFP removal
Ground	Antiscalant, Prefiltration	NF	961	28–32	97
		NF	961	31–39	96–97
		UF	961	326–947	2–66
Surface	Prefiltration	NF	157–182	55–84	49–70
Ground	Prefiltration	NF	176–472	6–95	78–98
Surface	None	MF	60–630	40–420	20
	Coagulation	MF	70–80	30–40	40–60
Ground	Prefiltration	NF	259	39	85
Ground	pH adjustment Prefiltration	NF	120	6	95
		UF	40–460	NA	<10
		NF	40–460	NA	30–90
Surface	Prefiltration UF	NF	40–460	NA	90
		NF	40–460	NA	90

*Source:* From Taylor, J.S., and Wiesner, M., Membranes, in *Water Quality and Treatment 5th ed.*, Letterman, R.D., Ed., Copyright ©1999 by The McGraw-Hill Companies, Inc. Reprinted by permission of the publisher.

(Taylor & Wiesner)

# Other Approaches to Reducing DBPs in Drinking Water

- Utilize “best” quality source water
  - Multilevel draw-offs from stratified reservoirs
  - Reduce exposure to algal blooms
  - Utilize selective pretreatment options, e.g. riverbank filtration, infiltration galleries, gravel roughing filters

- Minimize the use of chlorine
  - Replace chlorine with other disinfectant(s), e.g. UV+chloramination

- Utilize separate water system for residents close to WTP for CT purposes
- Reduce distribution system residence time from a single chlorination point by using disinfectant booster stations
- Reduce chlorine demand in distribution system by
  - Replacing old water mains
  - Initiating a strong flushing program

# General Comparison

	BAC	SSF	RBF	AR/SAT
Turbidity (NTU)	$\leq 1$ NTU	$\leq 1$ NTU	$\leq 1$ NTU	$\leq 1$ NTU
DOC Removal	$\geq 15$ %	$\geq 10$ %	$\geq 30$ %	$\geq 50$ %
Biostability: BDOC Removal	50 %	50 %	< MDL	< MDL

# General Comparison - cont

	BAC	SSF	RBF	AR/SAT
Effective Turbidity Removal	✓✓	✓✓	✓✓	✓✓
Effective DOC Removal	✓ (15-35%)	✓ (10-30%)	✓✓ (12-93+%)	✓✓ (10-93+%)
Biostability	✓✓	✓✓	✓✓	✓✓

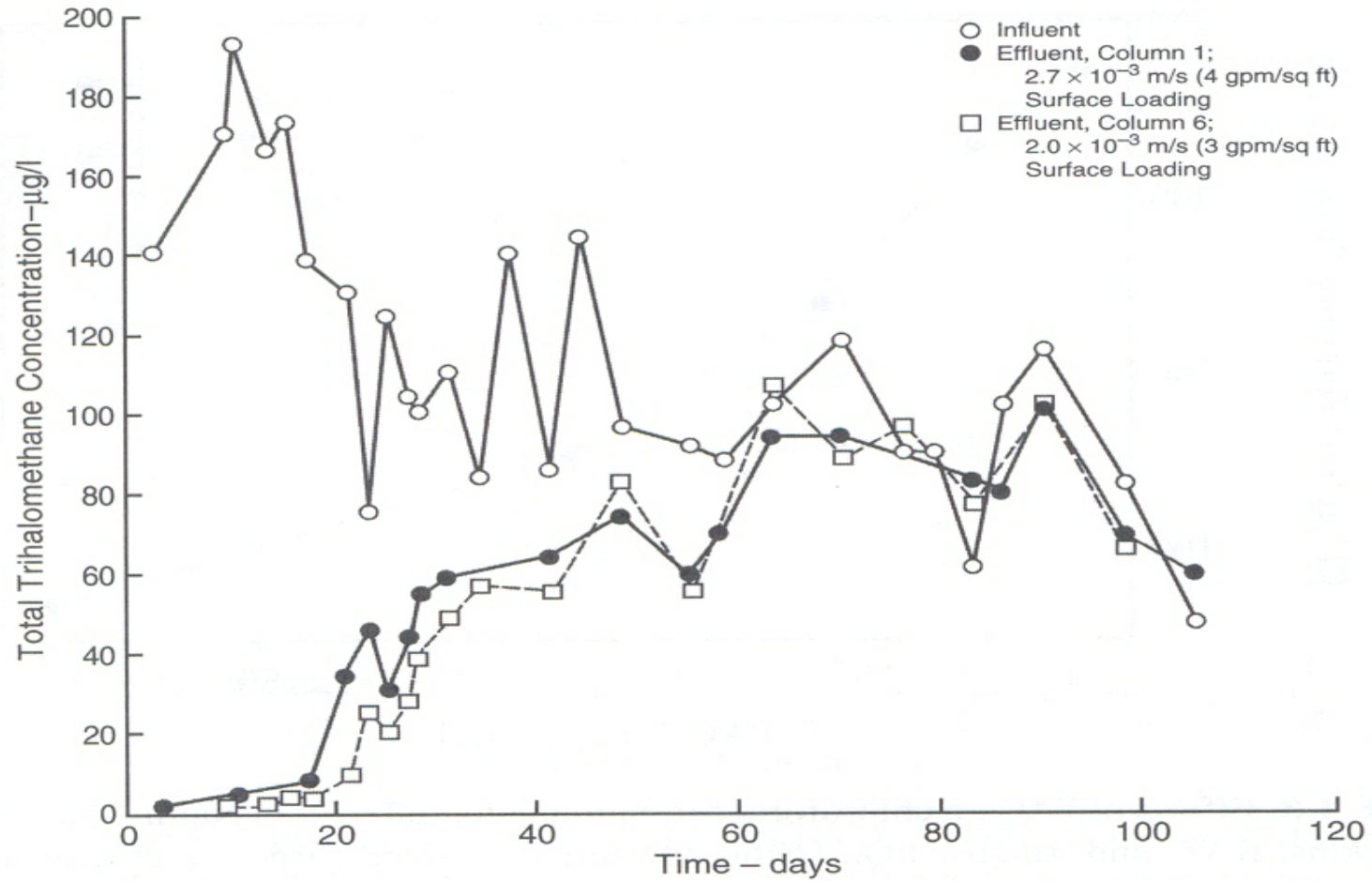


# Biodegradation of Disinfection By-Products

# DBP removal

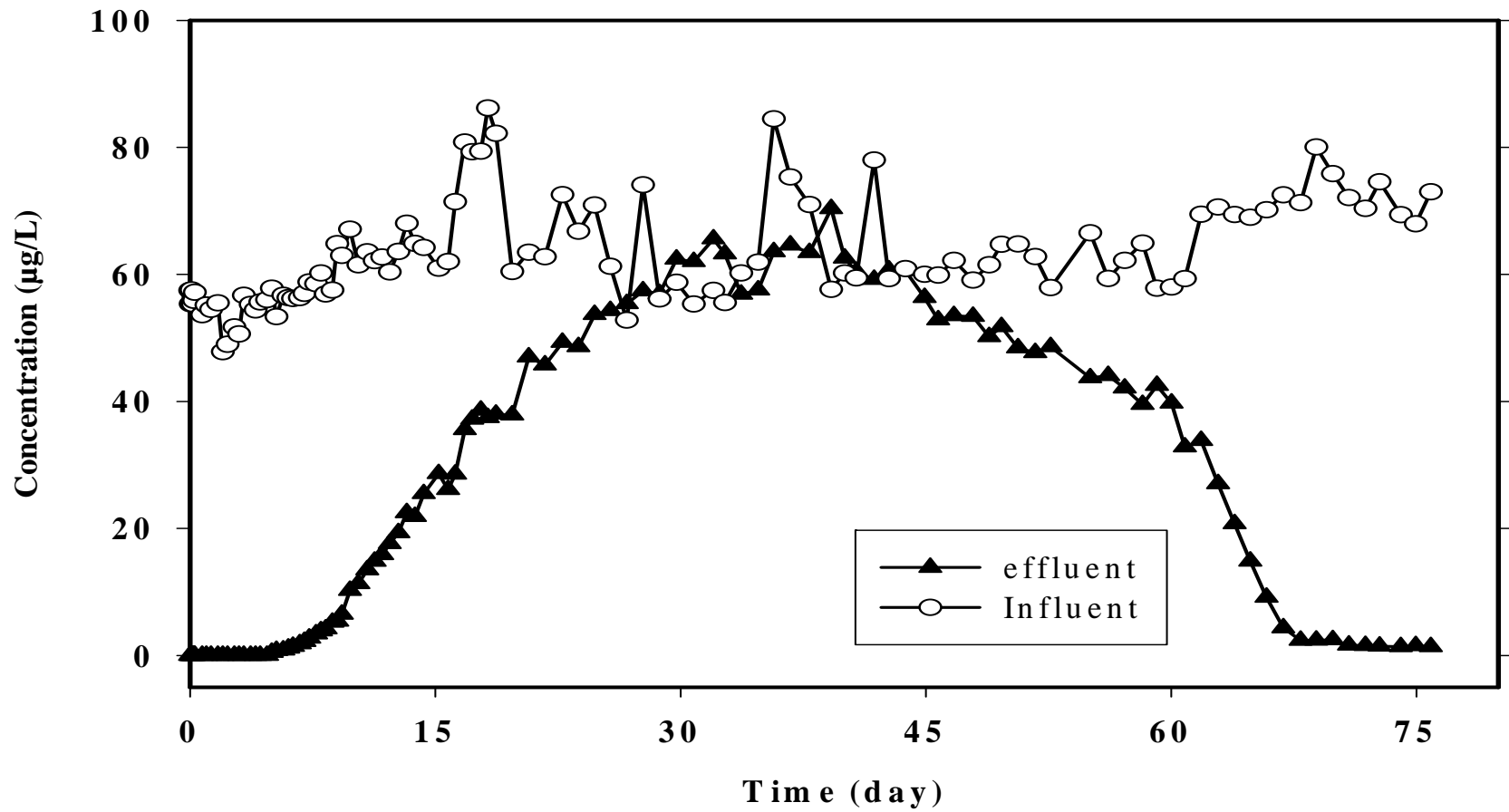
- GAC adsorption
  - Low carbon capacity
- Membranes
  - RO filtration; excellent for HAAs; OK for THMs
- Biofiltration
  - Biologically active carbon; HAAs not THMs
- Aeration
  - THMs, especially chloroform

# GAC for THM removal

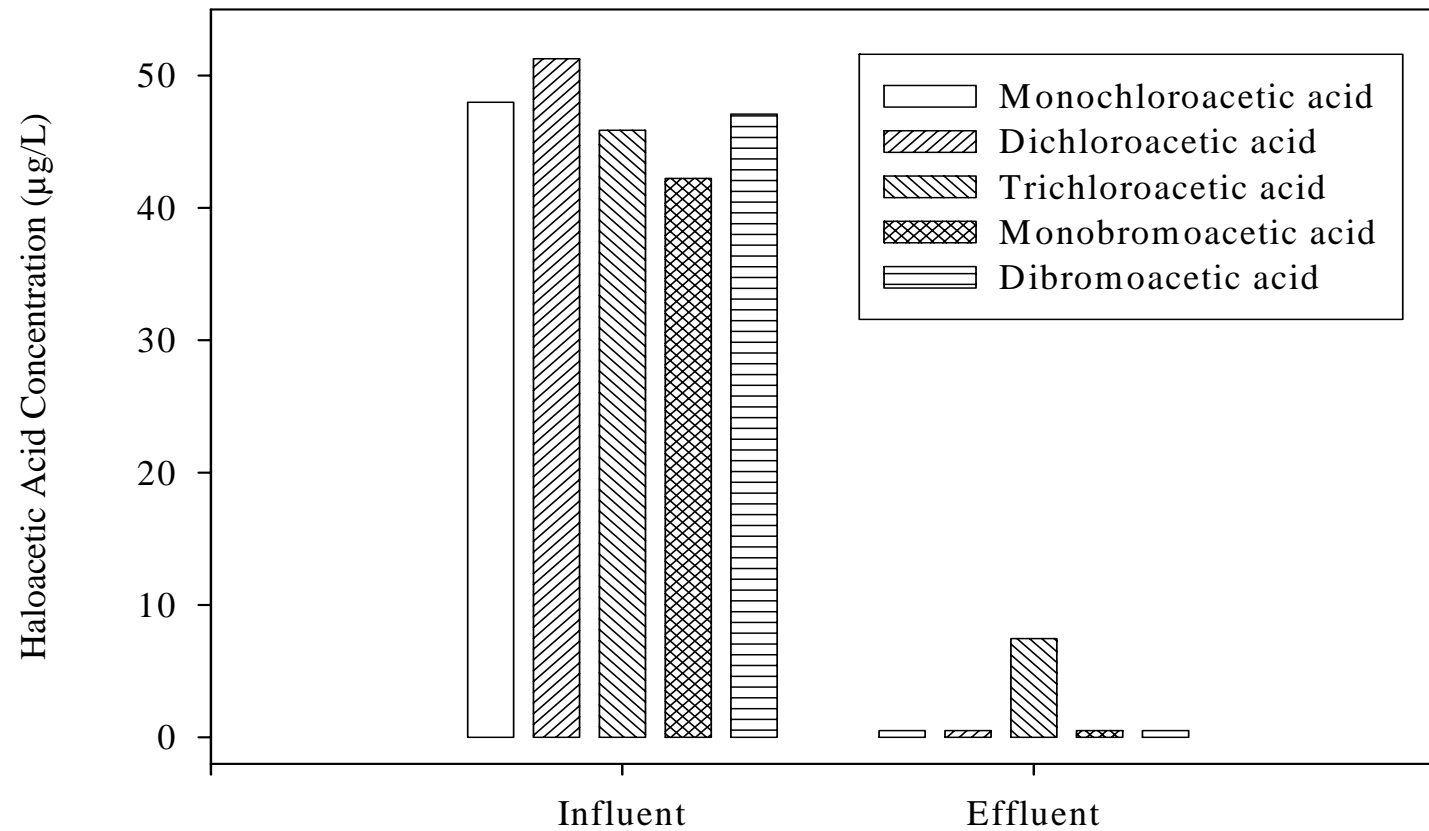


(McGuire & Suffet)

# GAC for haloacetic acid removal



# BAC filtration on HAAs



# BAC filtration on DBPs

