Biscayne Bay Coastal Wetlands Rehydration Pilot Project

Stakeholder Meeting
August 25, 2009

Joan Oppenheimer
MWH

MWH

MIAMI-DADE COUNTY

1

Next Steps

- Microconstituents and Treatment Efficiencies
  - Nitrification/Denitrification
  - Microfiltration (MF)
  - Reverse Osmosis (RO) and/or Chem P
  - Advanced Oxidation Process (AOP)
  - Other Processes

MWH

MIAMI-DADE COUNTY

2

Process Train Configurations

Train A (Baseline)

Nitrification	Denitrification	Chemical P Removal	Membrane Separation: MF	Advanced Oxidation: AOP	Product Stabilization

Train B

Nitrification	Denitrification	Membrane Separation: MF	Membrane Separation: RO	Advanced Oxidation: AOP	Product Stabilization

Train C

Nitrification	Denitrification	Chemical P Removal	Membrane Separation: MF	Membrane Separation: RO	Advanced Oxidation: AOP	Product Stabilization

MWH

MIAMI-DADE COUNTY

3

Predominant mechanisms

- Nitrification/Denitrification:
  - biodegradation, sorption, volatilization
- Low Pressure Membranes
  - sieving effect, surface effects
- High Pressure Membranes:
  - diffusion barrier, surface effects
- Chem P:
  - coagulation
- AOP:
  - free radical oxidation

MWH

MIAMI-DADE COUNTY

4

Treatment Studies : Nitrification / Denitrification

MWH

MIAMI-DADE COUNTY

5

Fate of Pharmaceuticals and Personal Care Products Through Municipal Wastewater Treatment Processes (WERF Project 03-CTS-22UR)

Joan Oppenheimer, M.S.P.H.
Roger Stephenson, Ph.D., P.E., DEE

WERF Webseminar on Trace Organic Compounds
Wednesday, July 9th 2008

MWH

MIAMI-DADE COUNTY

Study Goals and Objectives

- Surveyed occurrence/passage of PPCPs through soluble phase of full-scale WWTP facilities
- PPCP passage through activated sludge facilities with wide range of nutrient removal capabilities (SRTs)
- Included passage through media filters, MF/RO, and pilot MBRs

MWH

MIAMI-DADE COUNTY

PPCP Occurrence & Treatment Bins – Activated Sludge Process

Treatment / Occurrence	Bin TI Good Removal	Bin T2 Moderate Removal	Bin T3 Poor Removal
Bin O1 Infrequent	Methyl-3-phenylpropionate	Octylphenol	TCEP Triphenyl-phosphate
Bin O2 Intermediate		Ethyl-3-phenylpropionate	BHA DEET Musk Ketone
Bin O3 Frequent	9 compounds	Triclosan Benzophenone	Galoxolide

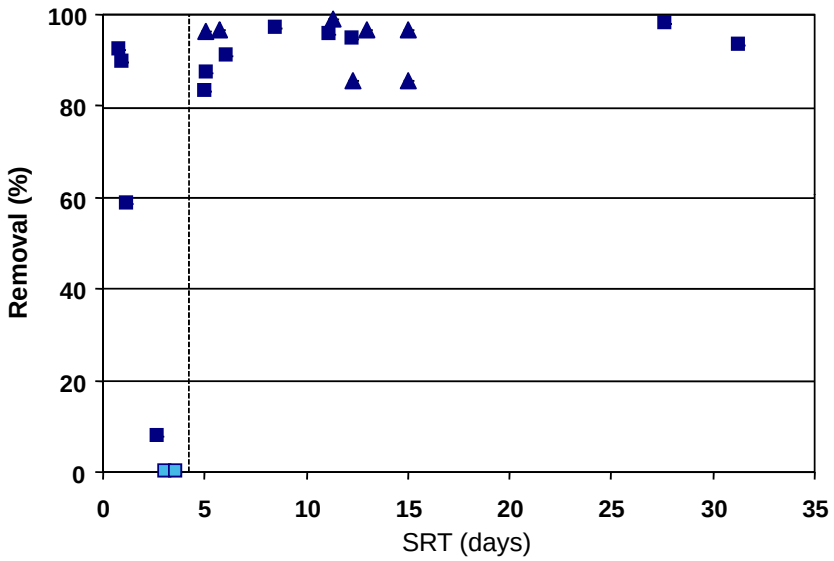
PPCP Occurrence & Treatment Bins – Activated Sludge Process

Treatment / Occurrence	Bin TI Good Removal	Bin T2 Moderate Removal	Bin T3 Poor Removal
Bin O1 Infrequent			
Bin O2 Intermediate			
Bin O3 Frequent			

$SRT_{80} \leq 5$ Days

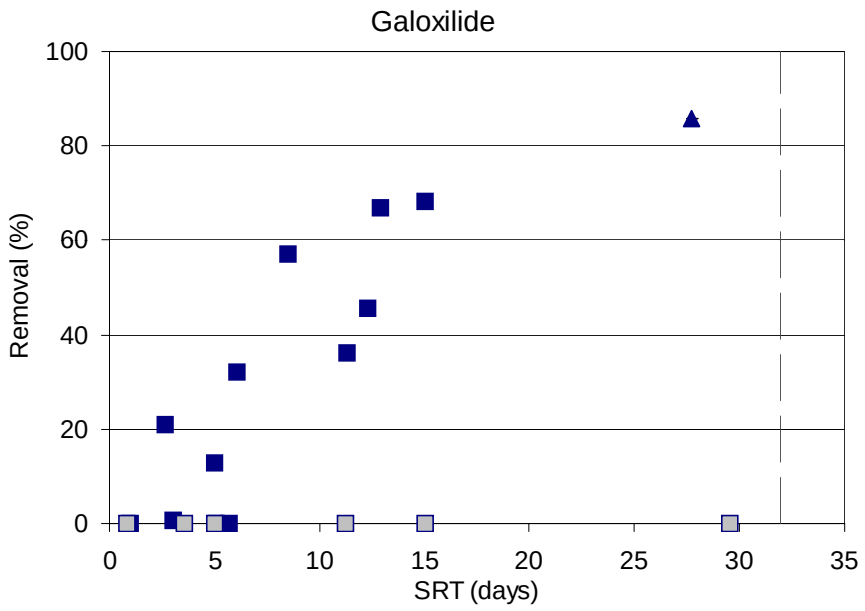
- Caffeine
- Ibuprofen
- Oxybenzone
- Chloroxylenol
- Methylparaben
- Benzyl salicylate
- 3-phenylpropionate
- Butylbenzylphthalate
- Octylmethoxycinnamate

SRT for Oxybenzone (Bin T1)



= Effluent > Influent

SRT for Galoxolide (Bin T3)



Post RO Treatment

	Plant F	Plant D
Chloroxylenol	-27%	ND
Methylparaben	>97%	ND
DEET	26%	0.050
Benzophenone	-88%	ND
TCEP	-17%	ND
Galoxilide	-18%	ND
Musk Ketone	12%	ND
Oxybenzone	0%	ND
Triclosan	15%	ND

MWH

MIAMI-DADE COUNTY

WERF Study Conclusions

- SRT dependence demonstrated for PPCPs:

$SRT_{80} \leq 5$ days	:10 compounds on target list
$5 \leq SRT_{80} \leq 15$ days:	benzophenone
	triclosan
	DEET
$SRT_{80} \geq 15$ days:	musk ketone
	galaxolide
	TCEP

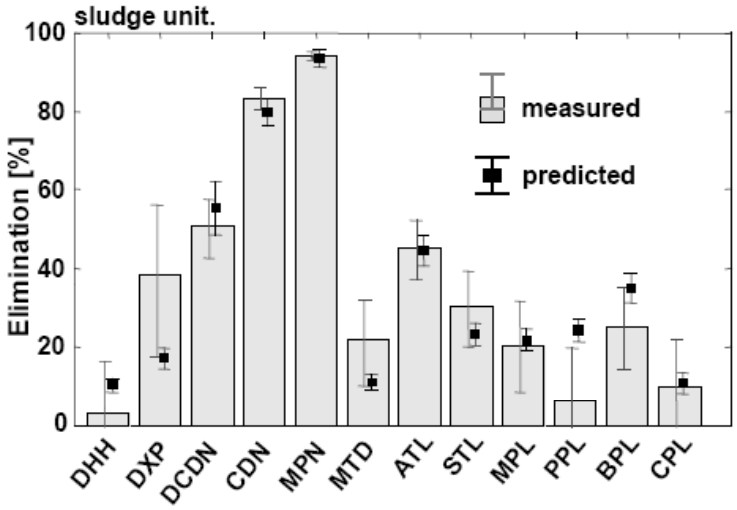
- Media filtration shows little removal
- RO is very effective
- MBR performance equivalent to activated sludge operated above 10 days

MWH

MIAMI-DADE COUNTY

EU Neptune Study (Psycho-actives and Beta blockers)

Measured vs. predicted elimination [%] of selected betablockers and psycho-active drugs in an activated sludge unit.



Authors: A. Wick and T. A. Ternes
BfG, Germany
Wick@bafg.de

MWH

MIAMI-DADE COUNTY

14

University South Florida Study: Antibiotics through Denitrification

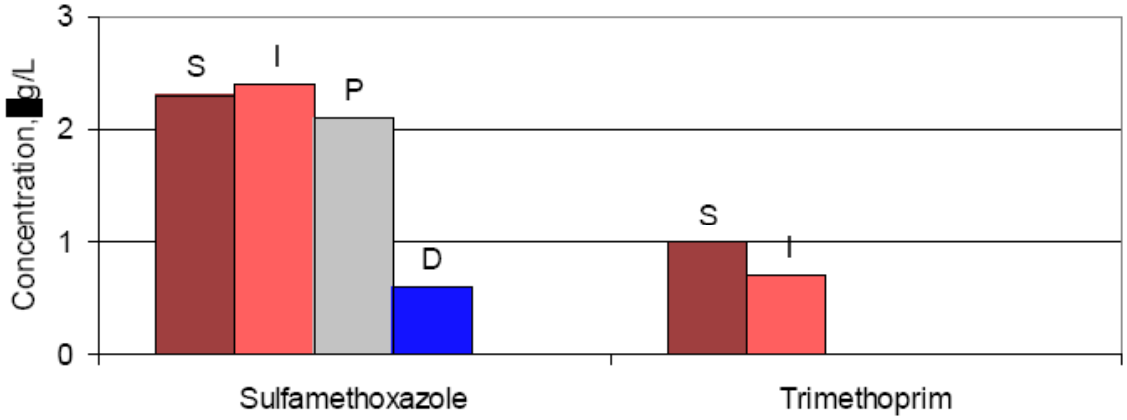


Figure 2. Comparison of concentrations of detected antibiotics in samples from sewer(S), wastewater treatment plant influent (I), primary effluent (P), denitrified effluent (D), and final disinfected effluent (F). Detection limits were 50 ppt for Sulfamethoxazole and 10 ppt for Trimethoprim.

Impact of pure oxygen nitrification treatment on removal of antibiotic residues and patterns of antibiotic resistance in reclaimed water

Audrey D. Levine[1], Valerie J. Harwood[2], and Michael T. Meyer[3]

MWH

MIAMI-DADE COUNTY

15

University of South Florida Study: *E. Coli* Antibiotic Resistance

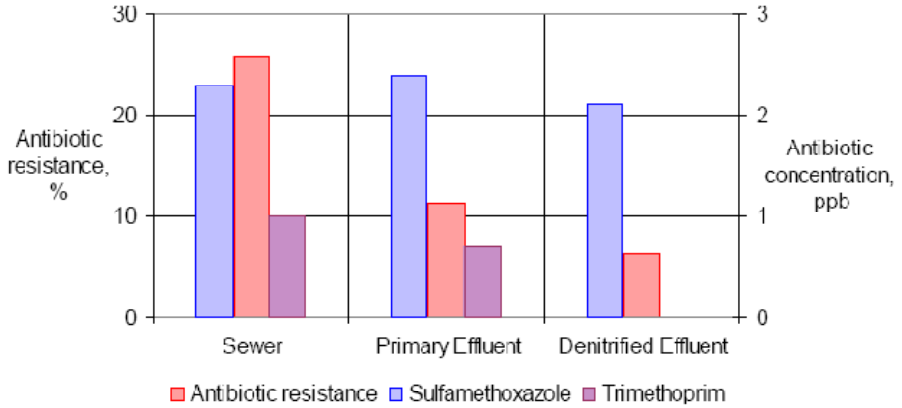


Figure 3. Comparison of antibiotic resistance of *E. Coli* and concentrations of Sulfamethoxazole and Trimethoprim in samples from sewer, primary effluent, and denitrified effluent. Detection limits were 50 ppt for Sulfamethoxazole and 10 ppt for Trimethoprim.

Impact of pure oxygen nitrification treatment on removal of antibiotic residues and patterns of antibiotic resistance in reclaimed water

Audrey D. Levine[1], Valerie J. Harwood[2], and Michael T. Meyer[3]

MWH

MIAMI-DADE COUNTY

16

Estrogenic Compounds

- Most estrogencity (E2/EE2)
- Most persistant (E1)
- No demonstrated relationship to SRT
- Evidence E1 removal via autotrophs
- Evidence E2 removal due to heterotrophs
- BNR aids in treatment

MWH

MIAMI-DADE COUNTY

17

Treatment Studies : Membranes

MWH

MIAMI-DADE COUNTY

18

ACE 2009, San Diego
June 15, 2009

Ensuring High Pressure Membrane Performance for the Removal of EDCs, Pharmaceuticals, and Personal Care Products from Potable Supplies

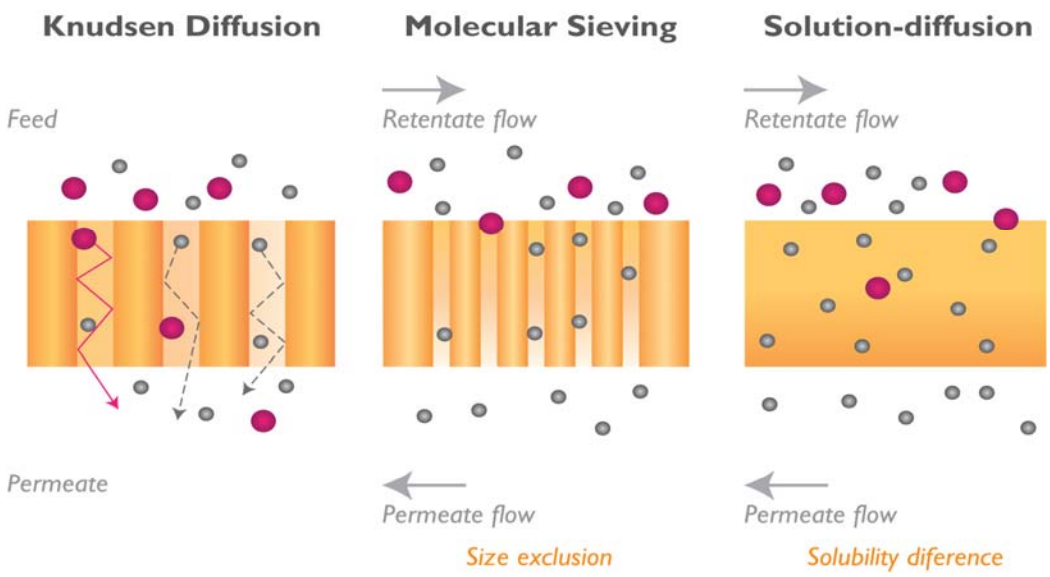
Presentation Outline

- Factors Impacting Rejection
  - Compound characteristics
  - Membrane characteristics
- Data Observations
  - Literature
  - Pilot
- Ongoing Studies

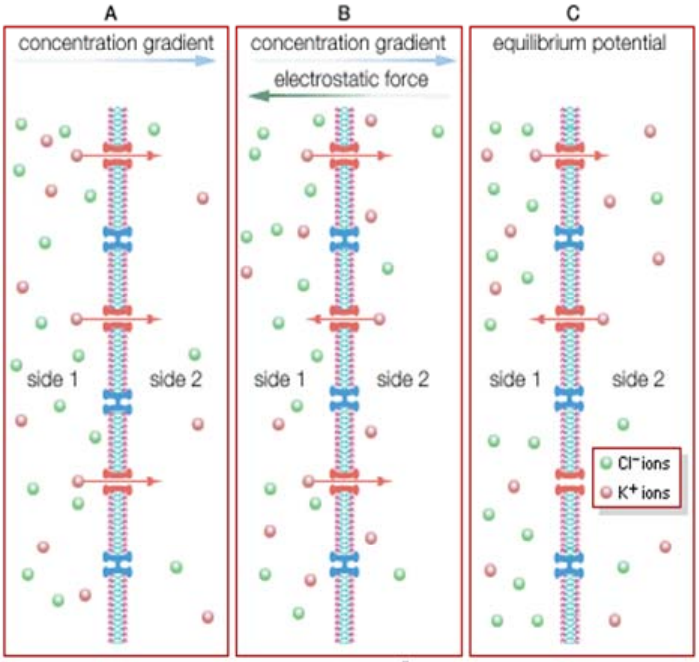
MWH

MIAMI-DADE COUNTY

Membrane Diffusivity and Sieving or Solubility Effects



Electrostatic Repulsion at Membrane Surface



© 2002 Encyclopædia Britannica, Inc.

MWH

MIAMI-DADE COUNTY

Solute Characteristics Affecting Rejection

- Size
  - Molecular weight
  - Molecular size
    - length, width, volume
    - Stokes' radius
    - molecular mean size
- Charge
  - pK_a or pK_b
  - Dipole moment
- Diffusivity
  - Diffusion coefficient
- Hydrophobicity
  - Solubility
  - Kow; Hammett numbers
- Volatility
  - Henry's constant
  - Vapor pressure
- Other Relevant QSAR

MWH

MIAMI-DADE COUNTY

Membrane Characteristics Affecting Rejection

- Size
  - MWCO
  - Pore size
- Charge
  - Zeta potential (surface charge)
  - Contact angle (hydrophobicity)
- Diffusivity
  - Porosity / Permeability
  - Surface roughness
  - Polymeric Composition

MWH

MIAMI-DADE COUNTY

Literature Findings on Compound Passage

- Ionic (pk_a <5) (BEST REJECTION)
  - High rejection, independent of time
  - Impacted by solvent pH
- Hydrophilic neutrals
  - High rejection at bench and with fouled membrane at pilot
- Hydrophobic neutrals (LEAST REJECTION)
  - high initial rejection, then low rejection for virgin membrane
  - stable intermediate rejection for fouled membrane
  - Poorer rejection more polar compounds (H-containing)

MWH

MIAMI-DADE COUNTY

Predicting Qualitative Rejection Categories (continued)

- **Poor Rejection**
  - No steric exclusion (MW<MWCO)
  - No electrostatic exclusion (pH<pKa)
  - Hydrophilic (Log Kow <2)
  - Small molecule (MWd<pore size)

(Bellona, Drewes, Xu, and Amy (2004) Wat. Res. 38(2795)
Amy (2008) AWWA WQTC Proceedings

Example Compounds:
- N-Nitrosodimethylamine (NDMA)
- Ammonia (NH3)

MWH

MIAMI-DADE COUNTY

Compounds Detected at Trace Levels in RO Pilot-scale or Full-scale Testing

Caffeine	TFC-HR, FS ESPA2
DEET	Saehan FL
Galaxolide	ESPA2
Gemfibrozil	ESPA2
Iopromide	TFC-HR
Meprobamate	Saehan RE-FRM
Oxybenzone	TFC-HR
Pentoxifylline	TFC-HR
Sulfamethoxazole	Saehan FL, ESPA2, Saehan RE-FRM
TCEP	Osmonics AK

- Snyder (2007)Removal of EDCs and Pharmaceuticals in Drinking and Reuse Treatment, AwwaRF Report

MWH

MIAMI-DADE COUNTY

Excellent RO Performance for Single Stage

Compound	Units	MDL	RO Feed	RO 1 Permeate	RO 2 Permeate	RO 3 Permeate	RO 4 Permeate
Hydrocodone	ng/l	1	49.5	<1.0	<1.0	<1.0	<1.0
Trimethoprim	ng/l	1	227	<1.0	<1.0	<1.0	<1.0
Acetaminophen	ng/l	1	<20	<1.0	<1.0	<1.0	<1.0
Caffeine	ng/l	10	<200	<10	<10	<10	<10
Erythromycin-H_2O	ng/l	1	224	<1.0	<1.0	<1.0	<1.0
Sulfamethoxazole	ng/l	1	584	<1.0	<1.0	<1.0	<1.0
Fluoxetine	ng/l	1	30	<1.0	<1.0	<1.0	<1.0
Pentoxifylline	ng/l	1	<20	<1.0	<1.0	<1.0	<1.0
Meprobamate	ng/l	1	200.5	<1.0	<1.0	<1.0	<1.0
Dilantin	ng/l	1	211.5	<1.0	<1.0	**1.0**	<1.0
TCEP	ng/l	10	215	<10	<10	<10	<10
Carbamazepine	ng/l	1	300	<1.0	<1.0	**1.1**	<1.0
DEET	ng/l	1	172	<1.0	<1.0	**1.2**	<1.0
Atrazine	ng/l	1	<20	<1.0	<1.0	<1.0	<1.0
Diazepam	ng/l	1	<20	<1.0	<1.0	<1.0	<1.0
Oxybenzone	ng/l	1	<20	<1.0	<1.0	<1.0	<1.0
Estriol	ng/l	5	<100	<5.0	<5.0	<5.0	<5.0
Ethynylestradiol	ng/l	1	<20	<1.0	<1.0	<1.0	<1.0
Estrone	ng/l	1	32	<1.0	<1.0	<1.0	<1.0
Estradiol	ng/l	1	<20	<1.0	<1.0	<1.0	<1.0
Testosterone	ng/l	1	<20	<1.0	<1.0	<1.0	<1.0
Progesterone	ng/l	1	<20	<1.0	<1.0	<1.0	<1.0
Androstenedione	ng/l	1	<20	<1.0	<1.0	<1.0	<1.0
Iopromide	ng/l	1	521	**1.0**	<1.0	<1.0	<1.0
Naproxen	ng/l	1	84	<1.0	<1.0	<1.0	<1.0
Ibuprofen	ng/l	1	23	<1.0	<1.0	<1.0	<1.0
Diclofenac	ng/l	1	51.5	<1.0	<1.0	<1.0	<1.0
Triclosan	ng/l	1	<20	<1.0	<1.0	<1.0	<1.0
Gemfibrozil	ng/l	1	529	<1.0	<1.0	<1.0	<1.0

TFC 4820-HR 4
RE 4040-BLR
TM710
ESPA2-4040

MWH

MIAMI-DADE COUNTY

RO Performance with Staging

Compound	Units	MDL	RO Feed	RO 4 Permeate Combined	RO 4 Permeate Stage 1	RO 4 Permeate Stage 2
Hydrocodone	ng/l	1	102	<1.0	<1.0	<1.0
Trimethoprim	ng/l	1	328	<1.0	<1.0	**1.6**
Acetaminophen	ng/l	1	<10	<1.0	<1.0	<1.0
Caffeine	ng/l	10	<100	<10	<10	<10
Erythromycin-H_2O	ng/l	1	211	<1.0	<1.0	<1.0
Sulfamethoxazole	ng/l	1	574	<1.0	<1.0	**1.9**
Fluoxetine	ng/l	1	55	<1.0	<1.0	<1.0
Pentoxifylline	ng/l	1	<10	<1.0	<1.0	<1.0
Meprobamate	ng/l	1	262	<1.0	<1.0	**1.2**
Dilantin	ng/l	1	130	<1.0	<1.0	<1.0
TCEP	ng/l	10	273	<10	<10	<10
Carbamazepine	ng/l	1	413	<1.0	<1.0	**1.8**
DEET	ng/l	1	376	**1.1**	<1.0	**2.1**
Atrazine	ng/l	1	<10	<1.0	<1.0	<1.0
Diazepam	ng/l	1	<10	<1.0	<1.0	<1.0
Oxybenzone	ng/l	1	<10	<1.0	**1.1**	**1.0**
Estriol	ng/l	5	<5.0	<5.0	<5.0	<5.0
Ethynylestradiol	ng/l	1	<1.0	<1.0	<1.0	<1.0
Estrone	ng/l	1	35	<1.0	<1.0	<1.0
Estradiol	ng/l	1	5.0	<1.0	<1.0	<1.0
Testosterone	ng/l	1	<1.0	<1.0	<1.0	<1.0
Progesterone	ng/l	1	<1.0	<1.0	<1.0	<1.0
Androstenedione	ng/l	1	3.8	<1.0	<1.0	<1.0
Iopromide	ng/l	1	10	<1.0	<1.0	<1.0
Naproxen	ng/l	1	139	<1.0	<1.0	<1.0
Ibuprofen	ng/l	1	23	<1.0	<1.0	<1.0
Diclofenac	ng/l	1	157	<1.0	<1.0	<1.0
Triclosan	ng/l	1	34	<1.0	<1.0	<1.0
Gemfibrozil	ng/l	1	357	<1.0	<1.0	<1.0

RE 4040-BLR

MWH

MIAMI-DADE COUNTY

Ongoing Studies

- Studying critical compound properties and critical membrane characteristics by commercial designation impacting compound property rejection
- Evolving developments of integrity monitoring methods/surrogates

MWH

MIAMI-DADE COUNTY

Treatment Studies : Chemical P

MWH

MIAMI-DADE COUNTY

31

Coagulation Process

- Process that removes particles
- Relationship to compound Kow demonstrated
  - Kow > 5 needed for more than 10-20% removal
- <20% removal demonstrated in DW and WW

MWH

MIAMI-DADE COUNTY

32

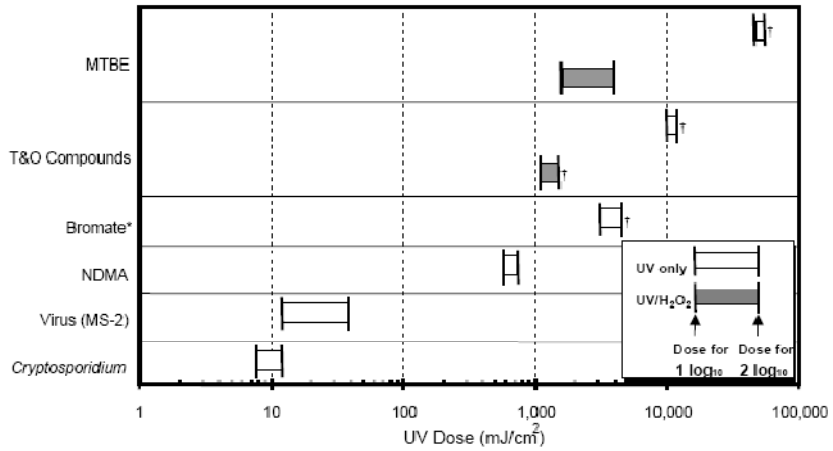
Treatment Studies : AOP Processes

MWH

MIAMI-DADE COUNTY

33

UV Reduction of Water Contaminants



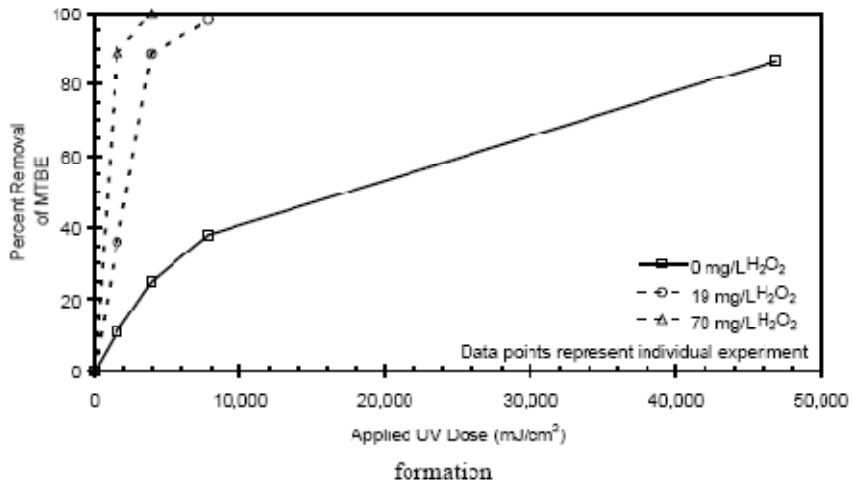
* Bromate reduction in laboratory water, all other data for natural waters

† 2 $\log_{10}$ reduction estimated based on data from this study

Figure ES1. UV Dose Range for 1 to 2 $\log_{10}$ Reduction of Water Contaminants

Taken from Mofidi et al., MWDSC January 2002 Study for CEC

Impact of Peroxide Addition to UV Reduction of MTBE



Taken from Mofidi et al., MWDSC January 2002 Study for CEC

Pharmaceutical 2º Rate Constants ($M^{-1} \cdot S^{-1}$)

Ozone		OH Radicals
9.6	ibuprofen	$7.4 \cdot 10^9$
0.8	iopromide	$3.3 \cdot 10^9$
$2.5 \cdot 10^6$	sulfamethoxazole	$5.5 \cdot 10^9$
$3 \cdot 10^5$	carbamezapine	$8.8 \cdot 10^9$

Taken from von Gunten, Janex-Habibi, Ternes, Weber (2006) "Removal of PPCP During Drinking Water Treatment in Human Pharmaceuticals Hormones and Fragrances, Edited by Ternes and Joss, IWA Publishing, London · Seattle

MWH

MIAMI-DADE COUNTY

ACE San Diego
June 15, 2009

Ensuring High Pressure Membrane Performance for the Removal of EDCs, Pharmaceuticals, and Personal Care Products from Potable Supplies

Joan Oppenheimer

ACE 2009, San Diego
June 15, 2009

Study Objectives & Approach

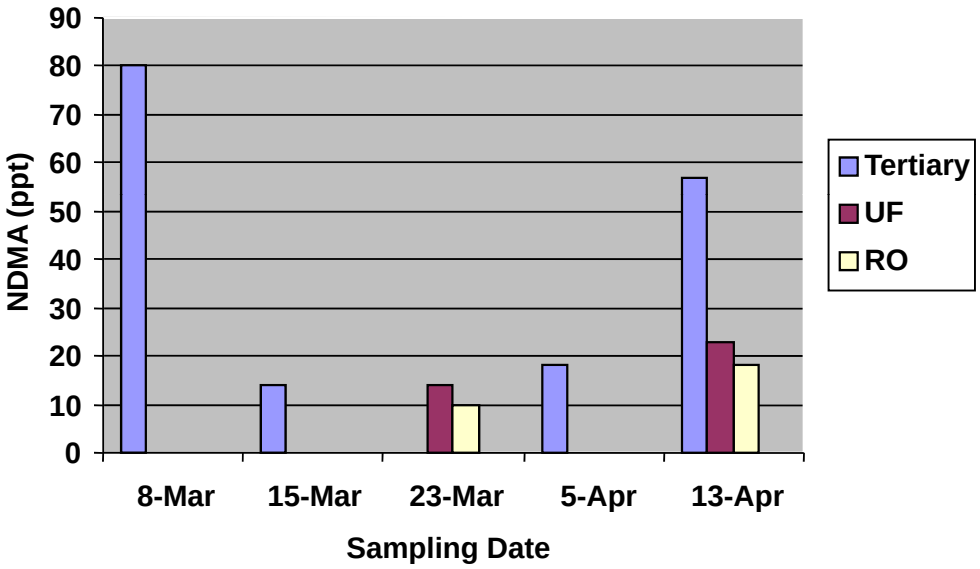
- Impact of UV @ NDMA control dose:
  - to reduce EDC and PPCP compounds
  - with and without addition of peroxide
  - utilizing IMS effluent

  - Review of published EEO values
  - Pilot-scale Testing to Assess EEO
  - Bench-scale CB to Relate EEO to Dose

MWH

MIAMI-DADE COUNTY

NDMA at Treatment Locations



MWH

MIAMI-DADE COUNTY

NDMA Regulatory Status

- Known animal carcinogen
- USEPA probable human carcinogen
- California list of cancer causing chemicals
- No federal or state MCL
- Listed in UCMR2
- California Notification Level = 10 ppt
- OEHHA proposed PHG in DW = 3 ppt
- USEPA ambient water criterion = 1.4 ppt

MWH

MIAMI-DADE COUNTY

EDC & PPCP Compounds

In RO Effluent:

- Trimethoprim
- Sulfamethoxazole
- Dilantin
- Meprobamate
- Carbomezapine
- Naproxen
- Gemfibrozil
- Iopromide
- Triclosan

Spiked:

- Iopromide
- Estrone
- Triclosan
- DEET
- Oxybenzone
- Ibuprofen
- Caffeine
- TCEP

MWH

MIAMI-DADE COUNTY

UV Pilot System

- Trojan UV Logic 8AL30
- 8 LPHO Lamps
- Parallel to flow
- 250 watts per lamp
- 6.35 cm radius spacing
- 30 cm ID reactor

- Test Flow = 106 gpm
- Lamp Power ~ 1200 W
- Lamp Intensity ~ 7.5 mW/cm^2
- Hydrogen Peroxide Dose = 5 mg/L

MWH

MIAMI-DADE COUNTY

Log Reduction Achieved

Compound	No Peroxide	With Peroxide
Caffeine	0.10	1.86
TCEP	0.02	0.19
DEET	0.16	2.28
Oxybenzone	-1.77	>2.51
Estrone	-0.99	>1.95
Iopromide	1.17	2.09
Ibuprofen	0.13	2.55
Triclosan	-0.06	2.39

Comparison with Full-Scale Reuse Data*

Approximately 400 mJ/cm^2 and 3 mg/L hydrogen peroxide

- Caffeine – 1.5 log reduction (1.9)
- DEET – 1.7 log reduction (2.2)
- Oxybenzone – 1.8 log reduction (>2.5)
- TCEP – >1.7 log reduction (0.19)

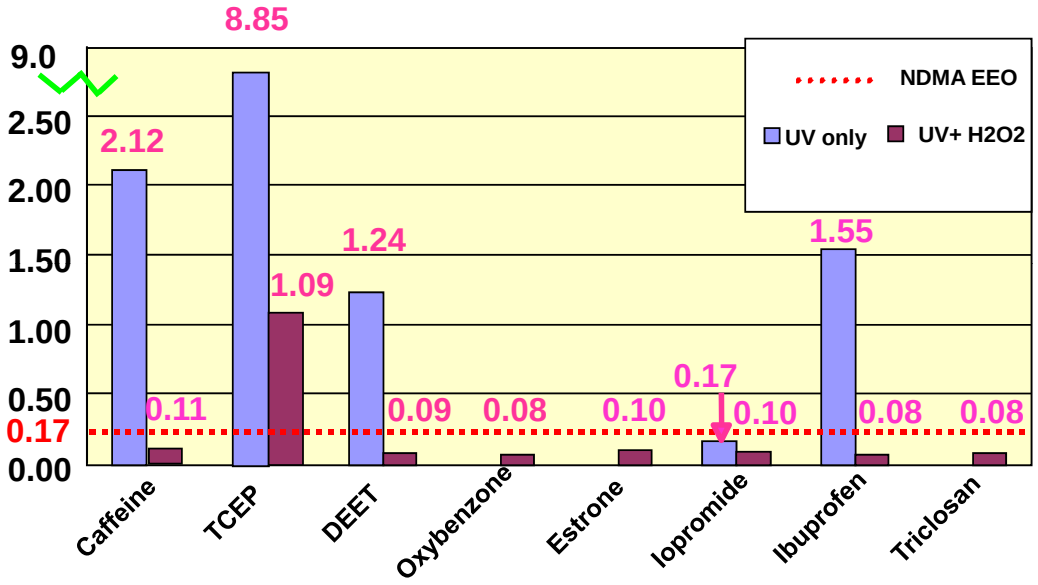
Values from previous slide denoted in (parenthesis)

***Synder et al. (2007) Removal of EDCs and Pharmaceuticals in Drinking And Reuse Treatment Processes", AwwaRf Publication, Denver, CO**

MWH

MIAMI-DADE COUNTY

UV/Peroxide Performance



MWH

MIAMI-DADE COUNTY

Study Conclusions

Peroxide : no impact on NDMA reduction
Peroxide : big impact on EDC/PPCP's
EDC/PPCP EEO range 0.17-8.85 (no H2O2)
EDC/PPCP EEO range 0.08-1.09 (with H2O2)
Only TCEP EEO greater than NDMA EEO
At least 1.5 log TCEP removal through RO

MWH

MIAMI-DADE COUNTY

Predominant mechanisms

- Nitrification/Denitrification:
  - biodegradation, sorption, volatilization
- Low Pressure Membranes
  - sieving effect, surface effects
- High Pressure Membranes:
  - diffusion barrier, surface effects
- Chem P:
  - coagulation
- AOP:
  - free radical oxidation

MWH

MIAMI-DADE COUNTY

47

Multiple-Barrier Approach

- Nit/Denit — Low Kbio, low Kow, low KH
- Chem P — Little additional removal
- MF — Removal of some additional compounds
- RO — Majority of remaining compounds removed
- AOP — Indiscriminate oxidation of remaining compounds

MWH

MIAMI-DADE COUNTY

48