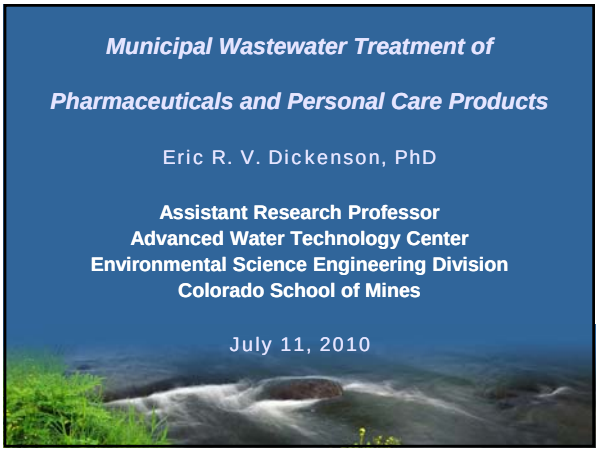
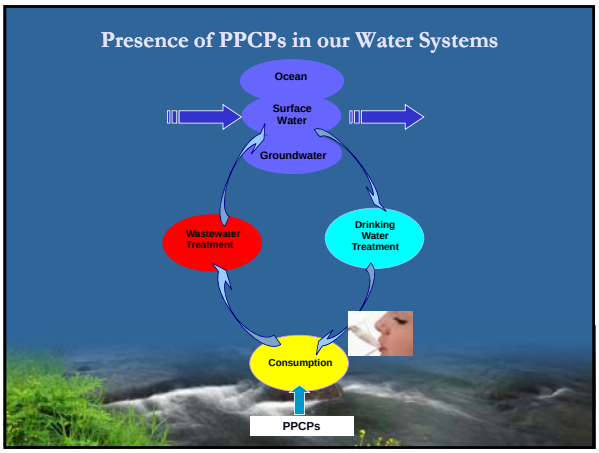

Expanding Our Horizons
2010 AACP Annual Meeting and Seminars
American Association of Colleges of Pharmacy
AACP
July 10–14 | Seattle

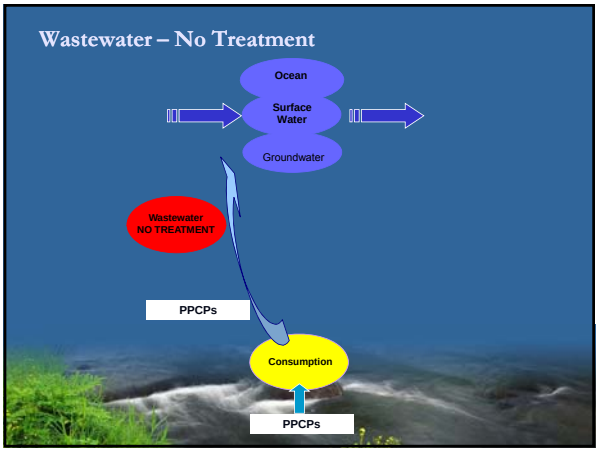

Municipal Wastewater Treatment of
Pharmaceuticals and Personal Care Products
Eric R. V. Dickenson, PhD
Assistant Research Professor
Advanced Water Technology Center
Environmental Science Engineering Division
Colorado School of Mines
July 11, 2010


Pharmaceuticals and Personal Care Products (PPCPs)
Pharmaceutically-Active Compounds
Personal Care Products
Household Chemicals
Endocrine-Disrupting Compounds

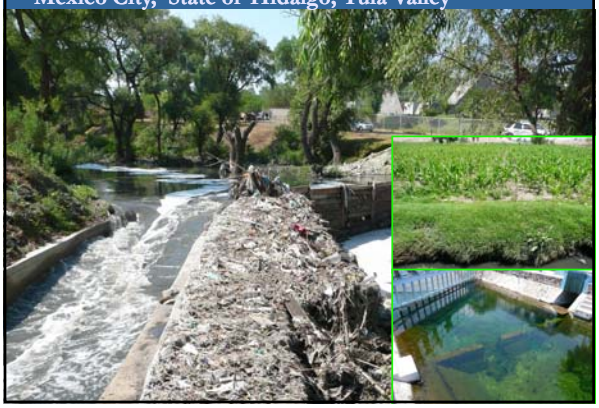
Presence of PPCPs in our Water Systems



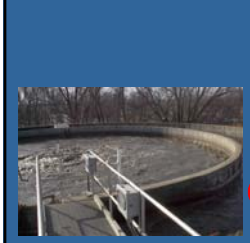
Wastewater – No Treatment

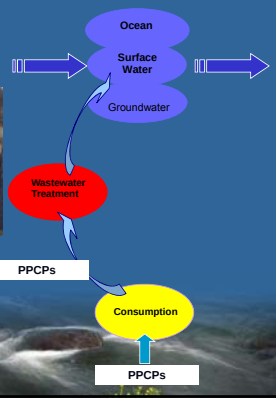


Mexico City, State of Hidalgo, Tula Valley

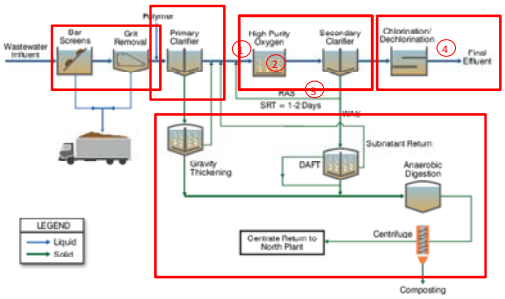


Wastewater Treatment



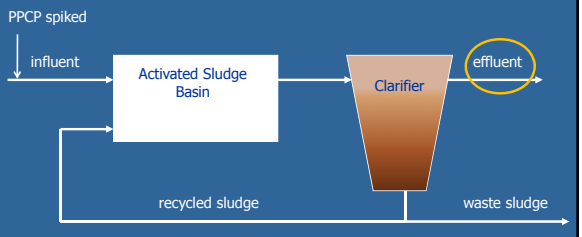


Wastewater Treatment - Solids and Nutrient Removal

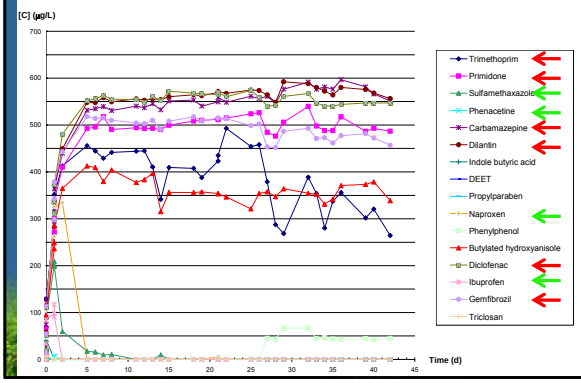


Not designed to remove PPCPs!

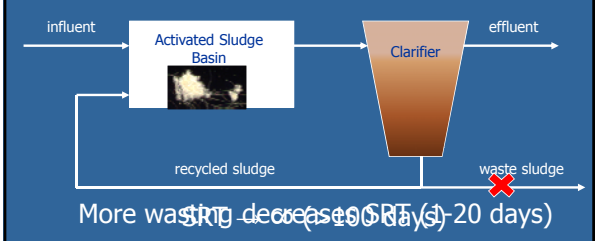
Activated-Sludge Treatment – Laboratory Scale



Activated-Sludge Treatment – Effluent Concentrations



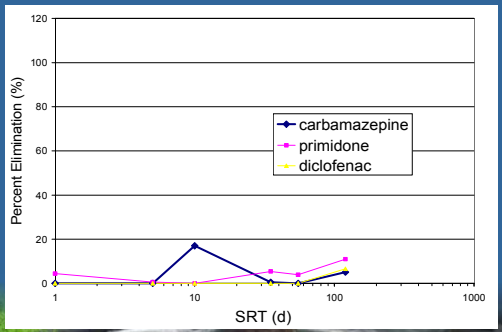
Sludge Age – Sludge Retention Rate or SRT (days)



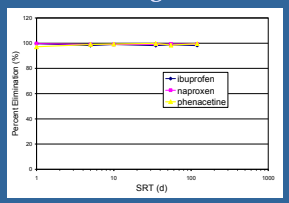
More wasting ~~decreases~~ increases SRT (1-20 days)

- With increasing SRT the bacterial population becomes more diversified
- Bacteria start to compete for compounds that are more complex and harder to degrade with increasing SRT

Activated-Sludge Treatment - Effect of SRT

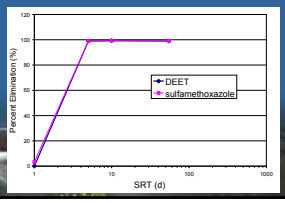


Activated-Sludge Treatment - Effect of SRT

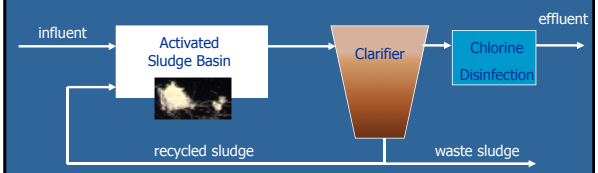


Critical SRT > 1 day

Critical SRT > 5 days



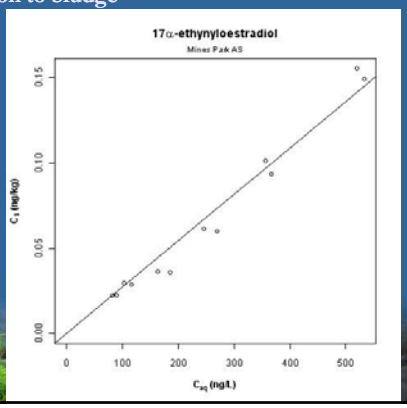
Fate and Transport of PPCPs



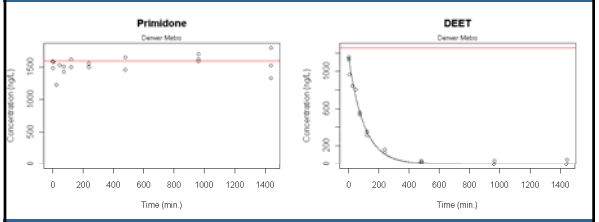
- No removal
- Sorption to Sludge Solids
- Biodegradation
- Volatilization
- Chlorine Oxidation

Sorption to Sludge

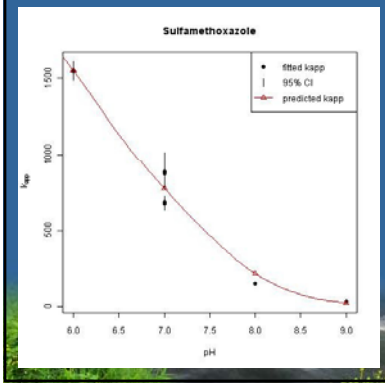
Sorption to Sludge



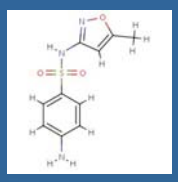
Biotransformation by Activated-Sludge



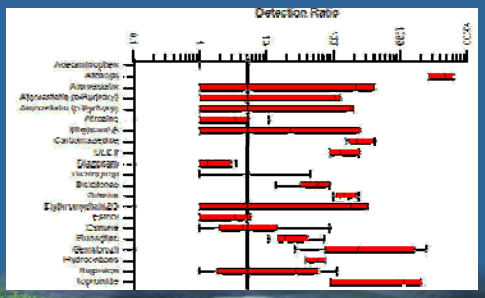
Chlorine Transformation



Hypochlorous Acid



Occurrence in Treated Effluent

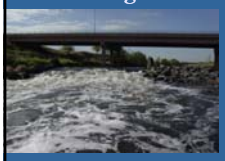


Detection Ratio (DR):
DR = Median/MDL

Advanced Treatment – *Planned* Indirect Potable Reuse

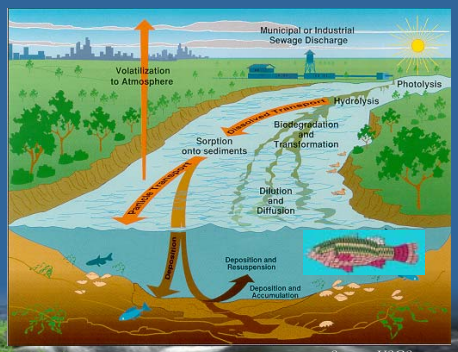
Ocean
Surface Water
Groundwater
Advanced Treatment
PPCP
Wastewater Treatment
Consumption
PPCP

Receiving Waters

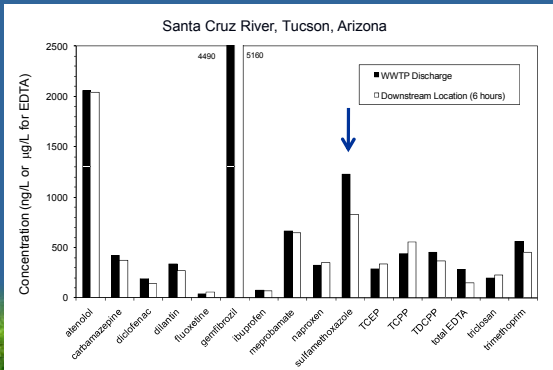


Ocean
Surface Water
PPCP
Groundwater
Wastewater Treatment
Consumption
PPCP

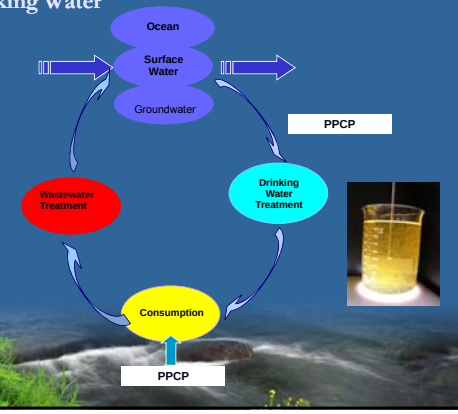
Fate and Transport in Receiving Waters



PPCPs in a Receiving Water

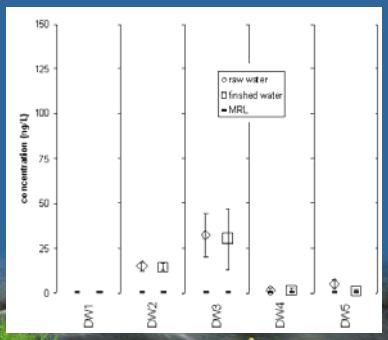


Drinking Water

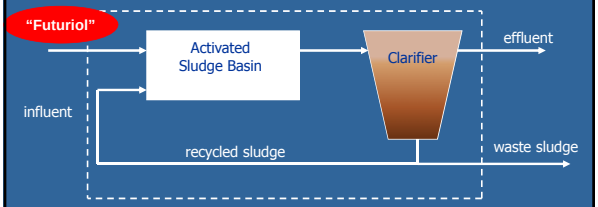


Conventional Drinking Water Treatment

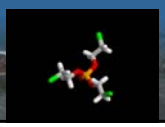
Primidone



Screening Mass Balance Models



Quantitative Structure Property Relationships



Indicator Compound for Monitoring

- **Ozonation of Treated Wastewater**

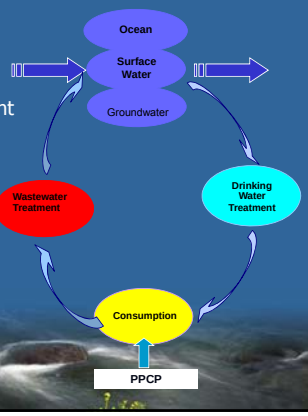
Good Removal >90%	Intermediate Removal 90-50%	50-25%	Poor Removal <25%
hydroxy aromatic acyl/amino aromatic alkoxy aromatic nonaromatic alkene deprotonated amines		nitro aromatic nitrosamine	halogenated aliphatic

alkyl aromatic

saturated aliphatic

Summary

- Water Reuse
- Multiple Barrier Treatment Strategy
- Byproduct Formation
- Fate from Biosolids
- Indicator Monitoring
- Screening Models
- Health Effects



Acknowledgements

- Colorado School of Mines, Advanced Water Technology Center
- University of California-Berkeley
- University of New South Wales, Australia
- Carollo Engineers
- Southern Nevada Water Authority
- Other U.S. Public Water Treatment Facilities
- Water Research Foundation
- Water Environment Research Foundation
- WateReuse Research Foundation

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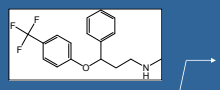
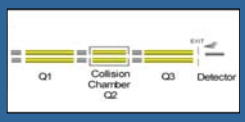
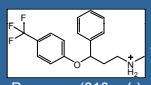
Tandem Mass Spectrometry (MS/MS) – quantify ppt levels

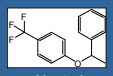


Fluoxetine (Prozac)
MW: 309





Precursor (310 *m/z*)
(From source)



Neutral

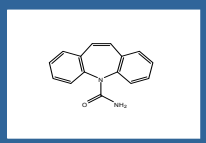
+

Product (44 *m/z*)

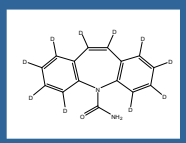
Precursor/product ion transition (310 → 44) – very selective!

Isotope Dilution Strategy

- Add isotopically labeled versions of target compounds to all samples
  - Corrects for extraction losses
  - Corrects for matrix effects

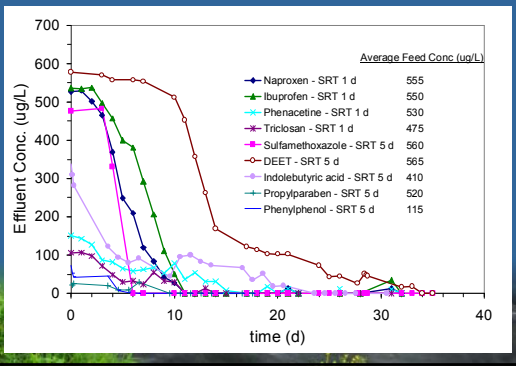


Carbamazepine
Anti-epileptic

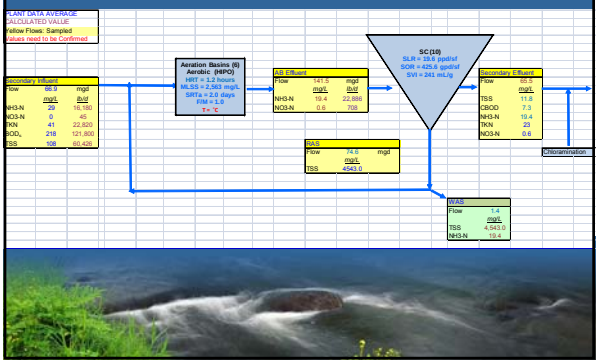


Carbamazepine-d10
Non-radioactive isotope label
Low probability of natural occurrence
Chemically similar

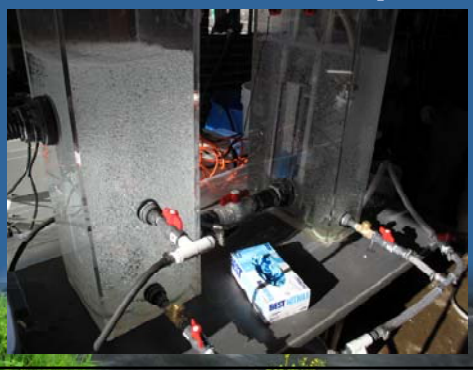
Activated-Sludge Treatment: Acclimation



Solids and Nutrient Removal

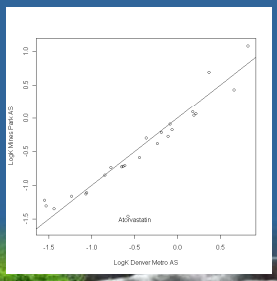


Activated-Sludge Treatment – Effect of Operational Parameters/Conditions: SRT, Redox, Temperature

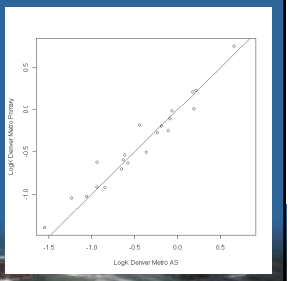


Sorption to Sludge

Comparison of Two Activated Sludges



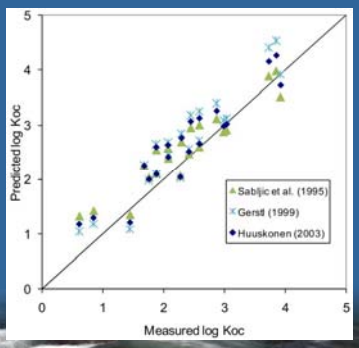
Comparison of Activated and Primary Sludges



Stevens-Garmon et al., In Review, *Water Research*

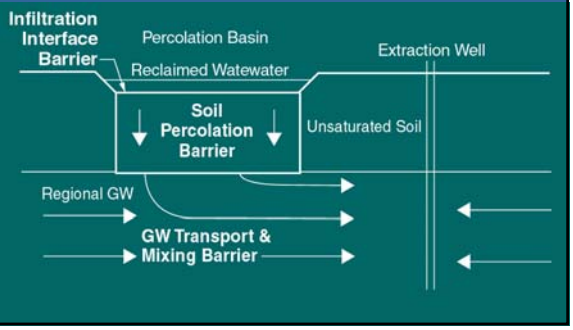
Sorption QSPRs

- Kd= Koc x foc
- log Koc = alog Kow + b
- Soil-based systems
- Neutral Compounds



Advanced Treatment - Managed Aquifer Recharge

Soil Aquifer Treatment (SAT)



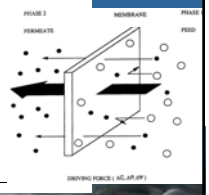
Managed Aquifer Recharge

Good Removal (>90%)		Intermediate Removal (90–50%)	(50–25%)	Poor Removal (<25%)
Acetyl cedrene[a]	Indolebutyric acid[c]	TCEP[1]		Carbamazepine[1]
Atenolol[c,1]	Iopromide[1]	TCPP[1]		Primidone[1]
Atorvastatin[c,1]	Isobornyl acetate[a]	TDCPP[1]		
Benzophenone[1]	Meprobamate[1]		Dilantin[1]	
Benzyl acetate[c]	Methyl dihydrojasmonate[c]			
Benzyl salicylate[d]	Methyl ionine[c]			
Bisphenol A[c]	Methyl salicylate[c]			
BHA[1]	Metoprolol			
Bucinal[d]	Musk ketone[a]			
Caffeine[1]	Musk xylene[a]			
DEET[1]	Naproxen[1]			
Diclofenac[1]	NDMA			
EDTA	Nonylphenol			
Erythromycin[1]	OTNE[a]			
Estrone	Propranolol			
Fluoxetine[1]	Propylparaben[c]			
Galaxolide[a,1]	Sulfamethoxazole[1]			
Gemfibrozil[1]	Terpineol[a]			
Hexyl salicylate[d]	Tonalide[a]			
Hexylcinnamaldehyde[a]	Triclocarban[a]			
Hydrocodone[1]	Triclosan[1]			
Ibuprofen[1]	Trimethoprim[1]			

Partially nitrified treated wastewater, extensive vadose zone (>100'); subsurface travel time: > 2 weeks
Nitrified/denitrified treated wastewater, shallow vadose zone (<10'); subsurface travel time: > 2 months

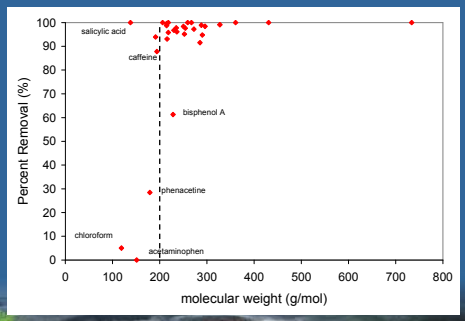
Reverse Osmosis

Good Removal (>90%)				Intermediate Removal (90–50%)	(50–25%)	Poor Removal (<25%)
Indolebutyric acid[a]	Dichlorprop	Isobutylparaben[c]	Propranolol		Chloro-form	
Acetaminophen	Diclofenac	Ketoprofen	Propylparabe		NDMA	
Acetyl cedrene[a]	Dilantin	Mecoprop	Salicylic acid		NDEA	
Atenolol	EDTA	Meprobamate	Simvastatin hydroxy acid			
Atorvastatin	Erythromycin-H2O	Methyl dihydrojasmonate[a]	Sulfamethoxazole			
Atorvastatin (o-hydroxy)	Estriol	Methyl ionine[a]	TCEP			
Atorvastatin (p-hydroxy)	Estrone	Methyl salicylate[a]	TCPP			
Benzyl acetate[a]	Fluoxetine	Metoprolol	TDCPP			
Benzyl salicylate[a]	Galaxolide	Musk ketone	Terpineol[a]			
Bisphenol A	Gemfibrozil	Musk xylene[a]	Tonalide[a]			
Bucinal[a]	Hexyl salicylate[a]	Naproxen	Triclocarban[a]			
Butylated hydroxyanisole[a]	Hexylcinnam-aldehyde[a]	Nonylphenol	Triclosan			
Caffeine	Hydrocodone	Norfluoxetine	Trimethoprim			
Carbamazepine	Ibuprofen	OTNE				
Ciprofloxacin[a]	Iopromide	Phenylphenol[a]				
DEET	Isobornyl acetate[a]	Primidone				



Operating conditions: ESPA membrane; 85% recovery; permeate flux: ~12 gfd; pH = 6.5

Nanofiltration



NF-4040 (Dow/Filmtec), 82% recovery and permeate flux of 12 gfd

Activated Carbon Adsorption

- Log D (pH 7) > 3
- Positively Charged Compounds

Good Removal (>90%)	Intermediate Removal (90–50%)	Intermediate Removal (50–25%)	Poor Removal (<25%)
Acetyl cedrene[c]	Acetaminophen[b]	Atenolol[b]	Ciprofloxacin[r]
Benzyl salicylate[c]	Caffeine[a]	Atorvastatin (o-hydroxy)[r]	Dichlorprop[r]
Bisphenol A[c]	Carbamazepine[a]	Atorvastatin (p-hydroxy)[r]	EDTA[r]
Bucinal[c]	Erythromycin-H_2O[c]	Atorvastatin[r]	Iopromide[a]
Butylated hydroxyanisole[c]	Estriol[a]	Benzyl acetate[c]	Mecoprop[r]
Estrone[a]	Hydrocodone[a]	Chloroform[a]	Meprobamate[a]
Fluoxetine[a]	Methyl dihydrojasmonate[c]	DEET[a]	NDMA[r]
Galaxolide[c]	Methyl salicylate[c]	Diclofenac[a]	Ofloxacin[r]
Hexyl salicylate[c]	Naproxen[a]	Dilantin[a]	Primidone[r]
Hexylcinnamaldehyde[c]	Phenylphenol[c]	Gemfibrozil[a]	Salicylic acid[r]
Isobornyl acetate[c]	Propranolol[a]	Ibuprofen[a]	Sulfamethoxazole[a]
Isobutylparaben[c]	Propylparaben[c]	Indolebutyric acid[r]	TCEP[a]
Methyl ionine[c]	Trimethoprim[a]	Ketoprofen[r]	
Musk ketone[c]		Metoprolol[a]	
Musk xylene[c]		TCPP[a]	
Nonylphenol[c]		TDCPP[a]	
Norfluoxetine			
OTNE[c]			
Simvastatin hydroxy acid[c]			
Terpineol[c]			
Tonalide[c]			
Triclocarban[c]			
Triclosan[a]			

DOC < 3 mg/L; Norit HD4000, Norit Superdarco; EBCT = 7.5 min

Ozonation of Treated Wastewater

Before Ozonation **After Ozonation**

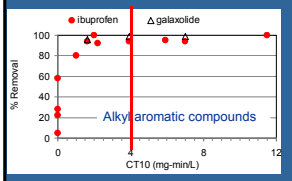
Ozonation

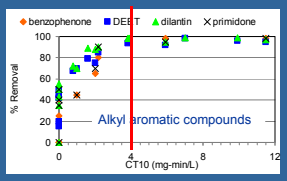
Good Removal > 90%			Intermediate Removal 90-50%	Intermediate Removal 50-25%	Poor Removal < 25%
Hydroxy Aromatic:	*Nonaromatic C=C:*	*Alkoxy Polyaromatic:*	*Saturated Aliphatic:*	*Nitrosamine:*	*Halogenated Aliphatic:*
Acetaminophen	Acetyl cedrene	Naproxen[a,8,15,A(3)]	Iopromide[a,1,3,4,15,D(7)]	NDMA[D(8)]	Chloroform[D(3,5)]
Atorvastatin (o-hydroxy)	Carbamazepine[a,1,4,15,A(4)]	Propranolol[A(<72),A(24)]	Isobornyl acetate		TCEP[a,1,15]
Atorvastatin (p-hydroxy)	Hexylcinnamaldehyde		Meprobamate[a,1,15]	*Nitro Aromatic:*	TCPP[a,15]
Benzyl salicylate	Methyl ionine	*Alkoxy Aromatic:*	Methyl dihydrojasmonate	Musk ketone[1]	TDCPP[a]
Bisphenol A[a,15,A(0.2)]	OTNE	Dichlorprop		Musk xylene	
Butylated hydroxyanisole[a]	Simvastatin hydroxy	Gemfibrozil[a,15]			
Estriol[A(12)]	Terpineol	Hydrocodone[a,1]			
Estrone[A(<77),A(>80),8,15,A(12)]		Mecoprop			
Hexyl salicylate	*Deprotonated Amine:*				
Isobutylparaben[2]	Atenolol[15,B(14)]	*Alkyl Aromatic:*			
Methyl salicylate	Caffeine[15]	Benzophenone[D(<60),15]			
Nonylphenol[A(12)]	Ciprofloxacin[5,B(5)]	Benzyl acetate			
Phenylphenol	Diclofenac[a,1,3,4,15,A(7,13)]	Bucinal			
Propylparaben[2]	EDTA[A(11)]	DEET[a,1,15]			
Salicylic acid[B(10)]	Erythromycin-H_2O[a,1,3,4]	Dilantin[a,1,15]			
Triclosan[a,6,15,A(9)]	Fluoxetine[a,1,15]	Galaxolide[c,4]			
Vanillin	Metoprolol[B(14)]	Ibuprofen[a(<62),1,15,C(7)]			
	Norfluoxetine	Indolebutyric acid[a(80),2(85)]			
Amino/Acylamino Aromatic:	Ofloxacin	Ketoprofen			
Sulfamethoxazole[a,1,3,4,5,15,A(7.5)]	Trimethoprim[a,4(<45),5,6,15,A(5)]	Primidone[15]			
Atorvastatin		Tonalide[a(<50)]			
Triclocarban[a,2]					

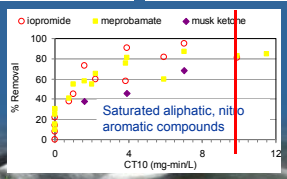
Operational Conditions: secondary/tertiary treated wastewater, O3:TOC = 0.6-1 mg/mg, ozone exposure CT_{10} = 4-11 mg min/L, pH 7-8, ~20°C, Alkalinity <300 mg/L as CaCO3

Dickenson et al., 2009, *Environ. Sci. Technol.* 43, 6242–6247

Indicator Compound Coupled with Operational Parameter







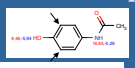
Dickenson et al., 2009, *Environ. Sci. Technol.* 43, 6242–6247

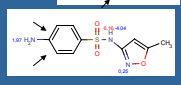
Disinfection Treatment Technologies

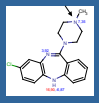
- UV is not effective
- Chloramines are not effective
- Chlorine transforms some compounds
- Ozone transforms many compounds

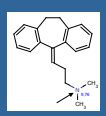
Dickenson et al., 2009, *Environ. Sci. Technol.* 43, 6242–6247
Drewes, Dickenson, et al. 2009. *WateReuse Foundation*

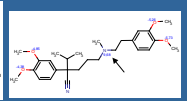
Chlorine Reactive Compounds









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Pharmaceuticals fouling U.S. drinking water
A five-month study finds a variety of drugs in water supplies - and growing concern among experts.
By Jeff Donn, Martha Mendoza and Justin Pritchard
The Associated Press
Article Last Updated: 03/10/2008 01:15:50 AM MDT
A vast array of pharmaceuticals — including antibiotics, anti-convulsants, mood stabilizers and sex hormones — has been found in the drinking-water supplies of at least 41 million Americans, an Associated Press investigation shows.
To be sure, the concentrations of these pharmaceuticals are tiny, measured in parts per billion or trillion, far below the levels of a medical dose. Also, utilities insist their water is safe.
But the presence of so many prescription drugs — and over-the- counter medicines like acetaminophen and ibuprofen — in our drinking water is heightening worries among scientists of long-term consequences to human health.
Comprehensive Utility Guide for Endocrine Disrupting Chemicals, Pharmaceuticals, and Personal Care Products in Drinking Water (Water Research Foundation)