

Trace Organic Microconstituents Bringing Antimicrobials and Nano-particles into Focus

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National Association Clean Water Agencies

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Presentation Outline

- Trace Organic Microconstituent Overview
- Water Quality Trends
- Treatment Effectiveness
- Yes, Microconstituents are Present in Our Lives
- Health Concerns
- Sustainable Implementation
- What Can We Do? What Can You Do?

Magnitude of Microconstituent Chemicals

American Chemical Society -Chemical Abstract Service

- Organic and inorganic compounds: 44,142,652
- Commercially available: 30,240,845
- Inventoried or regulated: 247,755
- New: 10,000 Synthetic Organic Chemical / year

<http://www.cas.org/cgi-bin/cas/regreport.pl>

- Additional considerations:
 - Reactions and interactions that occur between chemicals
 - Matrix effects of compounds combined

<http://mail.chemicosystems.com/myweb/Chemicals.jpg>



Trace Organic Microconstituents

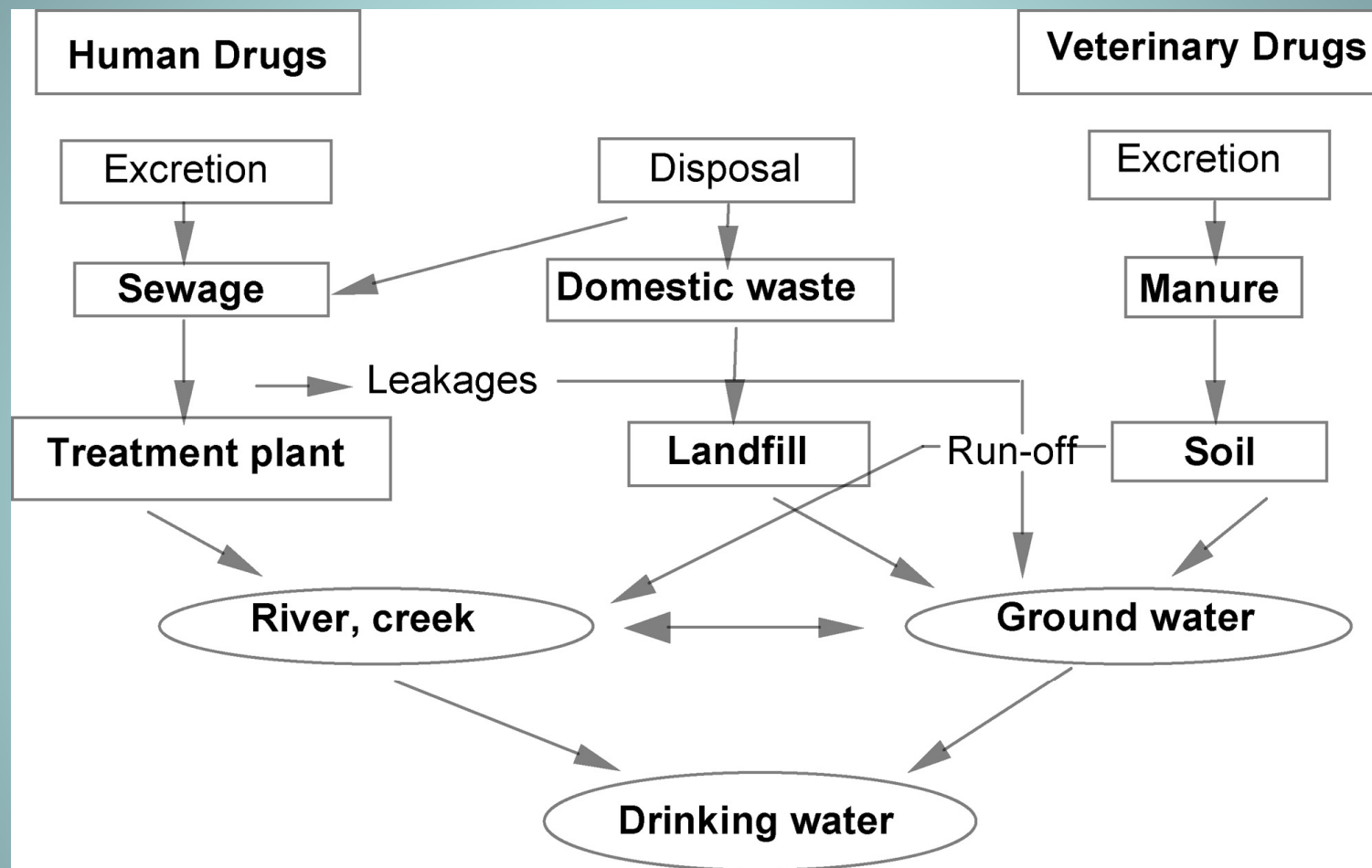
- Pharmaceuticals
 - Antibiotics
 - Anti-inflammatories
 - Antidepressants
 - X-ray contrast media
 - Contraceptives
 - Steroids
- Personal Care Product
 - Antibacterial Soap
 - Hair Care
 - Cosmetics
 - Cleaning Products
 - Flame retardants
- Household Chemicals
- Industrial Chemicals
- Agricultural
 - Pesticides
 - Herbicides
- Disinfection byproducts
- Synthetic and Naturally occurring hormones
- Metals



<http://matbeny.com/images/Phamaceuticals.png>

http://www.dtsc.ca.gov/HazardousWaste/images/PillsSpilledShadowy_1.jpg

Pathways to the Environment



Published in: Sushil K. Khetan; Terrence J. Collins; *Chem. Rev.* **2007**, 107, 2319-2364. DOI: 10.1021/cr020441w
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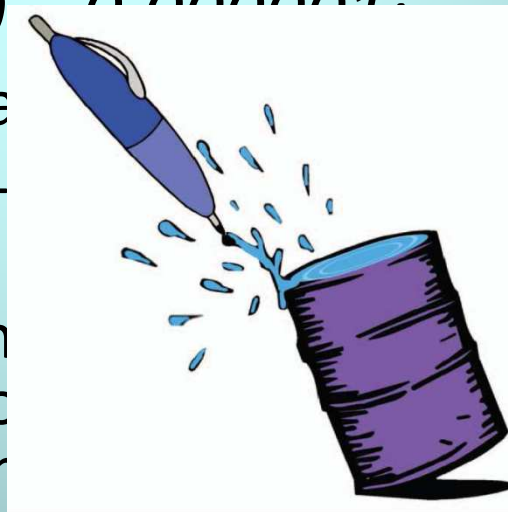
Understanding Concentration

- One *ppb* is $1/1,000,000,000 = 0.000001$
 - 1 ppb of one year is 1/32 of a second, or 32 years
 - 1 cent in \$10 million
 - 1 sheet of toilet paper in a roll stretching from NY to London



One *ppm* is $1/1,000,000 = 0.000001$

- Half a person in Alaska
- One car in bumper-to-bumper traffic from Cleveland to San Francisco
- Four drops of ink in one million gallons of water (mixed thoroughly) would be a concentration of 1 ppm



from Cleveland

of water

Water Quality Trends from USGS Studies

- Untreated Drinking Water Sources
 - 25 ground and 49 surface in 25 states and Puerto Rico
 - More common in surface than groundwater
 - 60% of the 36 pharmaceuticals only slightly above detection limits
- Ground Water
 - 47 wellheads in 18 states tested for 65 chemicals
 - 35% of sites had detectable
 - 87% of the 137 detections were less than 1µg/L

Compounds in the Environment

USGS Research Results

- Five most frequently detected chemicals - surface water
 - cholesterol (59%, natural sterol)
 - metolachlor (53%, herbicide)
 - cotinine (51%, nicotine metabolite)
 - β -sitosterol (37%, natural plant sterol)
 - 1,7-dimethylxanthine (27%, caffeine metabolite)
- Five most frequently detected chemicals - ground water
 - tetrachloroethylene (24%, solvent)
 - carbamazepine (20%, pharmaceutical)
 - bisphenol-A (20%, plasticizer)
 - 1,7-dimethylxanthine (16%, caffeine metabolite)
 - tri (2-chloroethyl) phosphate (12%, fire retardant).

http://www.sciencedirect.com/science?_ob=ArticleURL&_udi=B6V78-4SBRTJ2-3&_user=628632&_rdoc=1&_fmt=&_orig=search&_sort=d&view=c&_acct=C000033138&_version=1&_urlVersion=0&_userid=628632&md5=c2226e5db8d79a45313ee77d7be8e799

Ubiquitous Compounds

From WaterReuse Research

- Pharmaceuticals
 - DEET
 - Caffeine
 - Triclosan
 - Bisphenol A
- Human Steroids
 - Cholesterol
 - Coprostanol
- Nutrients
 - N & P
- Volatile Organics
 - Chloroform
- Semi Volatile Organic
 - Dichloroacetic Acid
 - THAs
 - Dibromoacetic Acid
 - Trichloroacetic Acid
- Microbiologicals
 - Coliphage, general
 - Fecal Coliforms
- Synthetic Organics
 - Atrazine
 - Diethylatrazine

Fate and Transport

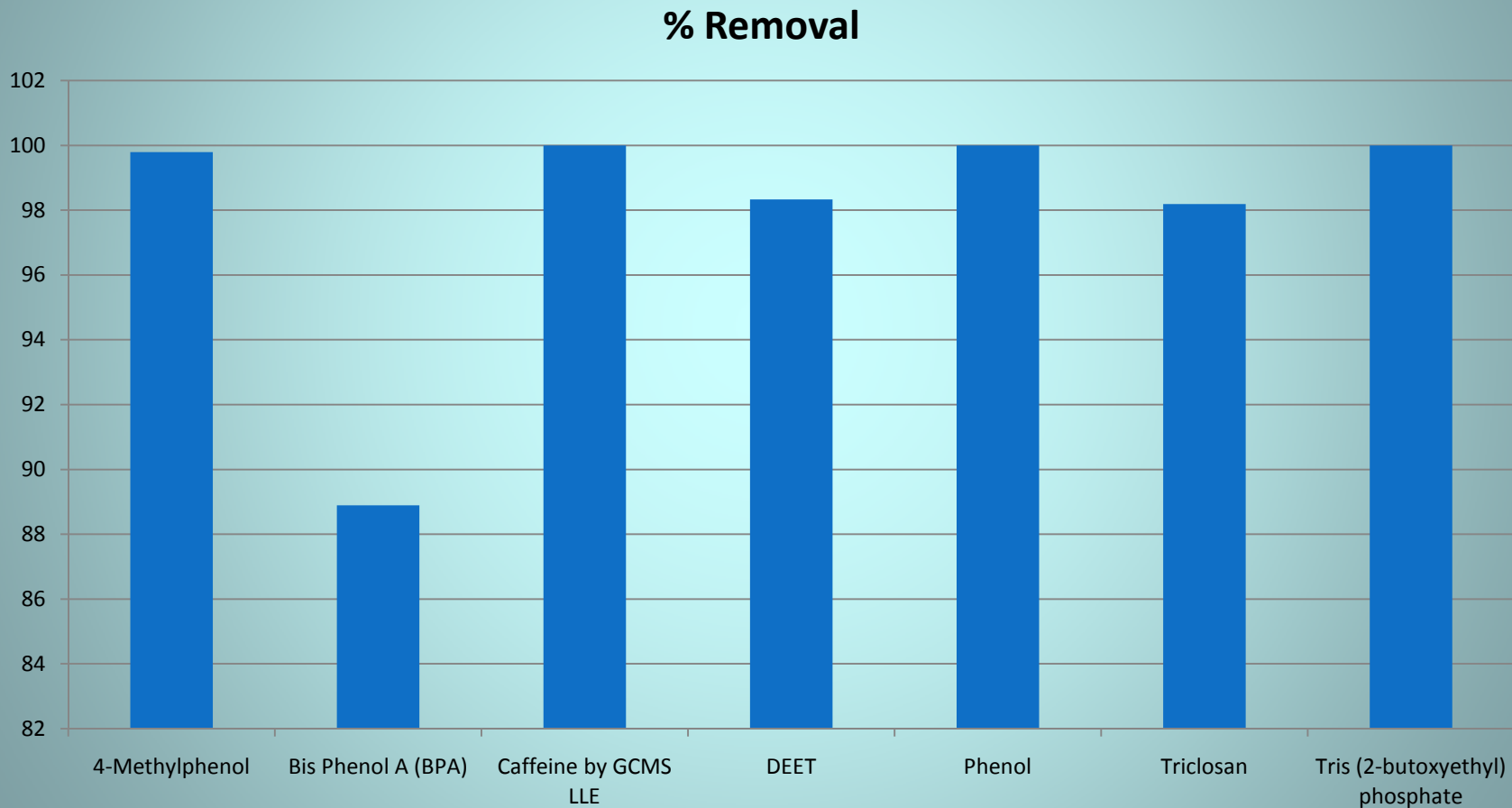
- Understanding needed for the dynamics and persistence within our environment
- Mechanisms for transformations and removal
 - Chemical reactions
 - Adsorption
 - Biodegradation
 - Physical separation
 - Volatilization

Treatment Methods

- Activated Sludge
 - Biodegradation and removal of organics
- Membrane – Micro, Ultra, Nano, and RO
 - Physical separation and adsorption
- Membrane Bioreactors
 - Combination Activated Sludge and Membranes
- Disinfection – UV, Chlorine, Ozone
- Advanced Oxidation
 - Ozone with H_2O_2
 - Chemical breakdown with oxidation
- Multiple Barrier Mechanisms Needed

Treatment Plant Removal Efficiency

UNC Charlotte – MWH Research



PPCP Occurrence & Treatment Bins

Aeration Basin Treatment Research by MWH

Oppenheimer, J., R. Stephenson, et al. (2007).

Treatment Occurrence	Bin T1 Good Removal	Bin T2 Moderate Removal	Bin T3 Poor Removal
Bin O1 Infrequent	<ul style="list-style-type: none"> •Caffeine •Ibuprofen •Oxybenzone •Chloroxylenol •Methylparaben •Benzyl salicylate •3-phenylpropionate •Butylbenzylphthalate •Octylmethoxycinnamate $SRT_{80} \leq 5$ Days		
Bin O2 Intermediate			
Bin O3 Frequent			

Analytes	Biological Dissolved Organic Carbons	Aquifer Storage and Recovery	Field Sites (Golf Course and WWTF Infiltration Pond)	QSAR Modeling
Hydrocodone	M	R	ND	NP
Trimethoprim	M	R	M	M
Acetaminophen	R	R	AMB	R
Caffeine	R	R	AMB	NP
Erythromycin-H2O	S	AMB	S	S
Sulfamethoxazole	S	S	AMB	M
Fluoxetine	S	R	M	M
Dilantin	S	M	M	R
Carbamazepine	S	M	M	M
DEET	M	M	M	R
Atrazine	S	R	ND	M
Diazepam	S	R	ND	R
Estriol	M	R	AMB	R
Estrone	R	R	ND	M
Estradiol	R	R	ND	R
Testosterone	M	R	ND	M
Naproxen	M	R	ND	NP
Ibuprofen	R	R	AMB	R
Triclosan	AMB	AMB	M	S
Gemfibrozil	R	R	R	R

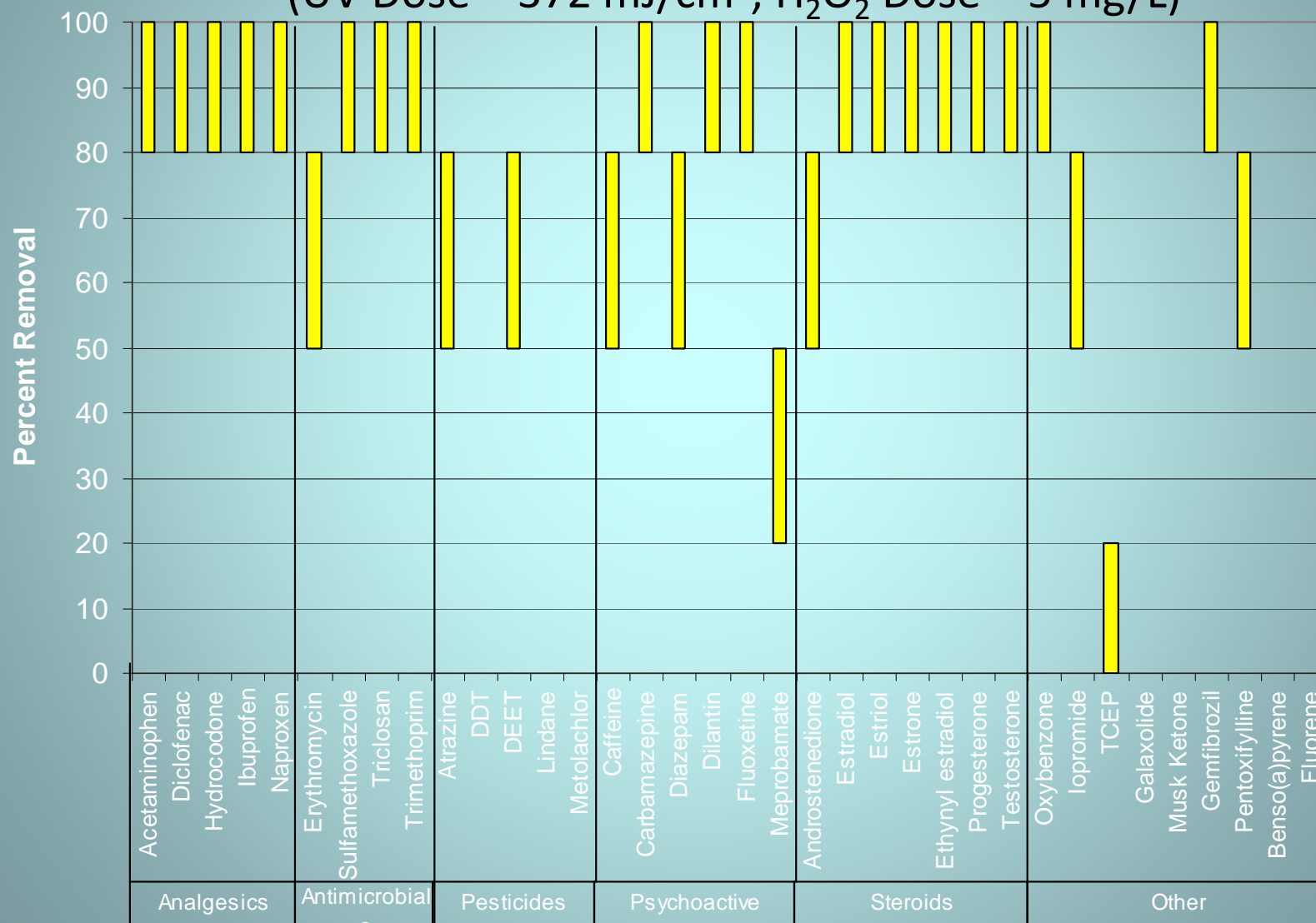
KEY: R = Rapid degraded/adsorbed
M = Moderately degraded/adsorbed
S = Slowly degraded/ adsorbed
ND = Non Detected
AMB = Ambiguous
NP = Not Predicted

Removal Rates for Biological Degradation, Soil Adsorption, and Model

Southern Nevada Water Authority
Snyder, Shane A., et. al.

Ultraviolet/Hydrogen Peroxide Oxidation – AWWARF Report

(UV Dose = 372 mJ/cm², H₂O₂ Dose = 5 mg/L)



Treatment Effectiveness for Removal from AWWARF Report

Excellent

- ◆ PAC (e.g. Cary)
- ◆ GAC (e.g. NRWASA)
- ◆ Nanofiltration
& Reverse Osmosis
(e.g. Dare County)
- ◆ Ozone (e.g.
Wilmington)
- ◆ Ozone/H₂O₂
- ◆ UV/H₂O₂

Moderate

- ◆ Chlorine
- ◆ Ultrafiltration*
- ◆ UV (439 mJ/cm²)

Ineffective

- ◆ Coag/Floc
- ◆ Microfiltration
- ◆ MIEX
- ◆ Chloramines
- ◆ UV (40 mJ/cm²)

Trace Organics Are Present

"This concentration is roughly equivalent to $\frac{1}{2}$ of an inch in the distance between the earth and the moon..."



Significance as A Health Concern

- Widespread Usage
- Continually Released
- Potential for Health Effects
 - Toxicological
 - Wildlife - Aquatic Life
 - Human Health
- Detectable does not mean harmful to humans.
- Trace substances detected at very low levels in source waters.
- Higher concentrations through medicines, food, beverage and other sources.

Mechanisms of Endocrine Disruptors



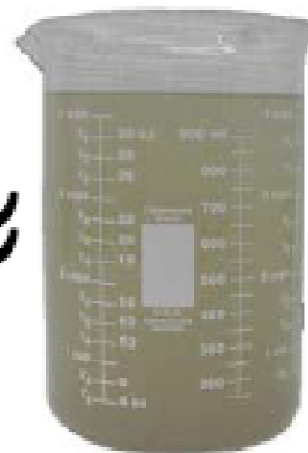
Personal Risk and Choices

EEq Comparison ("Worst" WWTP)

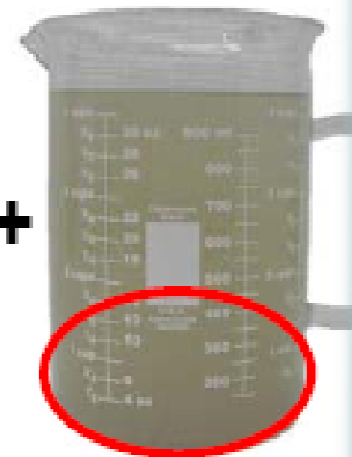


Mug of Beer
(6 ng/L, 500 mL)

≈



+



1.4 L Wastewater
(4.6 ng/L)

Sustainable Implementation

- Determine health risks to justify advanced treatment needs
- Design treatment strategies to a new criteria:
 - Minimize energy requirements
 - Lower carbon footprints
 - Use resources wisely
 - Decrease environmental impacts
- Set up a matrix to judge the sustainability of design

Air Quality Impacts Magnified

- **WWTF Energy Demand**
 - WWTF with Activated Sludge: 166 kWh/Day
 - Reverse Osmosis and Electro-deionization : 7,777 kWh/Day
 - High Efficiency Reverse Osmosis: 5,068 kWh/Day

Impacts	Emission Factor*	WWTF	RO/EDI	HERO
• CO₂ (lbs/day)	1.46	243	11355	5068
• NO_x (lbs/day)	0.0017	0.28	13	9
• VOC (g/day)	0.025	4.26	194	127
• PM (g/day)	0.061	10.15	474	309

*Charlotte Area

What's To Be Done?



<http://blogs.townonline.com/newton/wp-content/uploads/2008/03/head-in-sand.JPG>

Environmental Management

- Water₂Water
- Science Based Decisions
- Source Reduction – Individual Level /Industrial
- On-going Treatment Reduction at the Focus Point (WWTF)
- Site Specific Treatment and Remediation
- Implement Strategies Balanced with Sustainable Practices
- Long-Term and Large Scale Monitoring
- Regulations for Reduction
- Determination of Health Effects
- Limiting Exposure of Vulnerable Populations

You are one in a
million making a
difference in a part
per billion!

The struggle to save the global environment is in one way much more difficult than the struggle to vanquish Hitler, for this time the war is with ourselves. We are the enemy, just as we have only ourselves as allies.

~Al Gore



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- Helgeson, T.J., Mc Neal, M., Slitfko, T.R., (2007) "Reclaimed, Surface, and Groundwater Quality, What's the Difference?" WaterReuse Foundation Project.
- Current Literature Status: There are 7,094 literature articles noted with EPA
<http://www.epa.gov/ppcp/citations.pdf>

Website Resources

- US Department of Health and Human Services – Household Database:

<http://hpd.nlm.nih.gov/cgi-bin/household/list?tbl=TblChemicals&alpha=A>

- AWWA – Endocrine Disruptors:

<http://www.awwa.org/Resources/topicspecific.cfm?ItemNumber=3647&navItemNumber=32969>

- USGS New research: Occurrence of Organic Wastewater Compounds in Selected Surface-Water Supplies, Triangle Area of North Carolina, 2002–2005

<http://pubs.usgs.gov/sir/2007/5054/pdf/SIR2007-5054.pdf>