

Use of Ozone for Disinfection and EDC Removal at CCWRD

Doug Drury, Ph.D.

Deputy General Manager

Clark County Water Reclamation District

Shane Snyder, Ph.D.

R&D Project Manager

Southern Nevada Water Authority



Objectives

- **Expansion of current facility**
 - **110 to 150 MGD**
 - **opportune time to utilize state of the art technology**
- **Investigate ozone for disinfection and emerging contaminant removal**
- **Use bench-scale evaluations for initial feasibility**
- **Engineering analysis to estimate capital and O&M costs**
 - **compare UV and ozone disinfection**

Why Ozone?

- **Powerful disinfectant**
- **No residual (compared to chlorine)**
- **Stronger oxidant (compared chlorine/UV)**
- **Three ozone plants in Southern Nevada**
 - **AMS 600 MGD drinking water**
 - **River Mountains 300 MGD drinking water**
 - **Big Bend (Laughlin) 20 MGD drinking water**
- **Ozone proven technology for disinfection & contaminant removal**

SNWA Treatment Studies



Emerging Contaminants

- **1994: Britain discovers fish below WWTP outfalls with symptoms of exposure to estrogenic compounds**
- **1996: USGS reports similar findings in carp from the Las Vegas Bay, Lake Mead**
- **1996: EPA reports endocrine disruption in fish from Minnesota near WWTPs**
- **1996: Amendment to SDWA mandates EPA develop a screening program for EDCs**
- **1997: SNWA initiates monitoring and fish studies for EDCs**

Sewage Altering Fish, Study Reports

Male bottom-dwellers with female sex characteristics are found near outfall pipes in waters off Los Angeles and Orange counties.

By Marla Cone
Times Staff Writer



November 14, 2005

Male fish with female characteristics have been discovered in ocean waters off Los Angeles and Orange counties, raising concerns that treated sewage released offshore contains hormone-disrupting compounds that are deforming the sex organs of marine life.

Scientists around the world have found sexual abnormalities in frogs, fish, alligators and other wild animals exposed to sewage effluent and industrial contaminants that mimic estrogens and other hormones. But the latest research in the waters off Southern California is among the first to find such effects in ocean creatures.

Eleven male bottom-dwelling fish out of 64 caught between Santa Monica and Huntington Beach had ovary tissue in their testes. No such sexual defects were found elsewhere off Southern California, even though fish were collected from Point Conception to the U.S.-Mexico border.

Two other studies found other signs of feminized fish in the same ocean areas. Two-thirds of male turbot and sole caught near Orange County's sewage outfall had egg-producing proteins. And when males were exposed in a laboratory to ocean sediment collected off the Palos Verdes Peninsula and Huntington Beach — where huge volumes of sewage effluent are pumped out to sea — all of them developed female egg proteins.

SNWA EDC Research

- **1997: Initial screening of LV Wash & Lake**
 - Estrogen compounds detected in Wash & Bay
 - No estrogens detected in drinking water
 - First detection of pharmaceuticals
- **1998: Fish caged in Lake Mead**
 - Subtle differences in fish from LV Bay, but not dramatic as seen in USGS studies
- **2000: DOD funded study of fish**
 - Small differences among LV Bay & Overton
 - Perchlorate not related to EDC effects in fish
- **2003-Current: Monitoring of Lake Mead**

SNWA Monitoring 1998

<u>Compound</u>	<u>Usage</u>	<u>ng / L</u>
Phenytoin (Dilantin)	seizure treatment	53 – 261
Phenobarbital (Luminal)	seizure treatment	11 - 39
Carbamazepine (Tegretol)	seizure treatment	14 – 35
Primidone (Myidone)	seizure treatment	11 – 130
Hydrocodone	pain medication	6 – 13
Codeine	pain medication	17 – 123
Diazepam (Valium)	depression	3 – 62
Guaifenesin (Robotusin)	expectorant	21 – 52
Pentoxifylline (Trental)	blood thinner	5 – 50

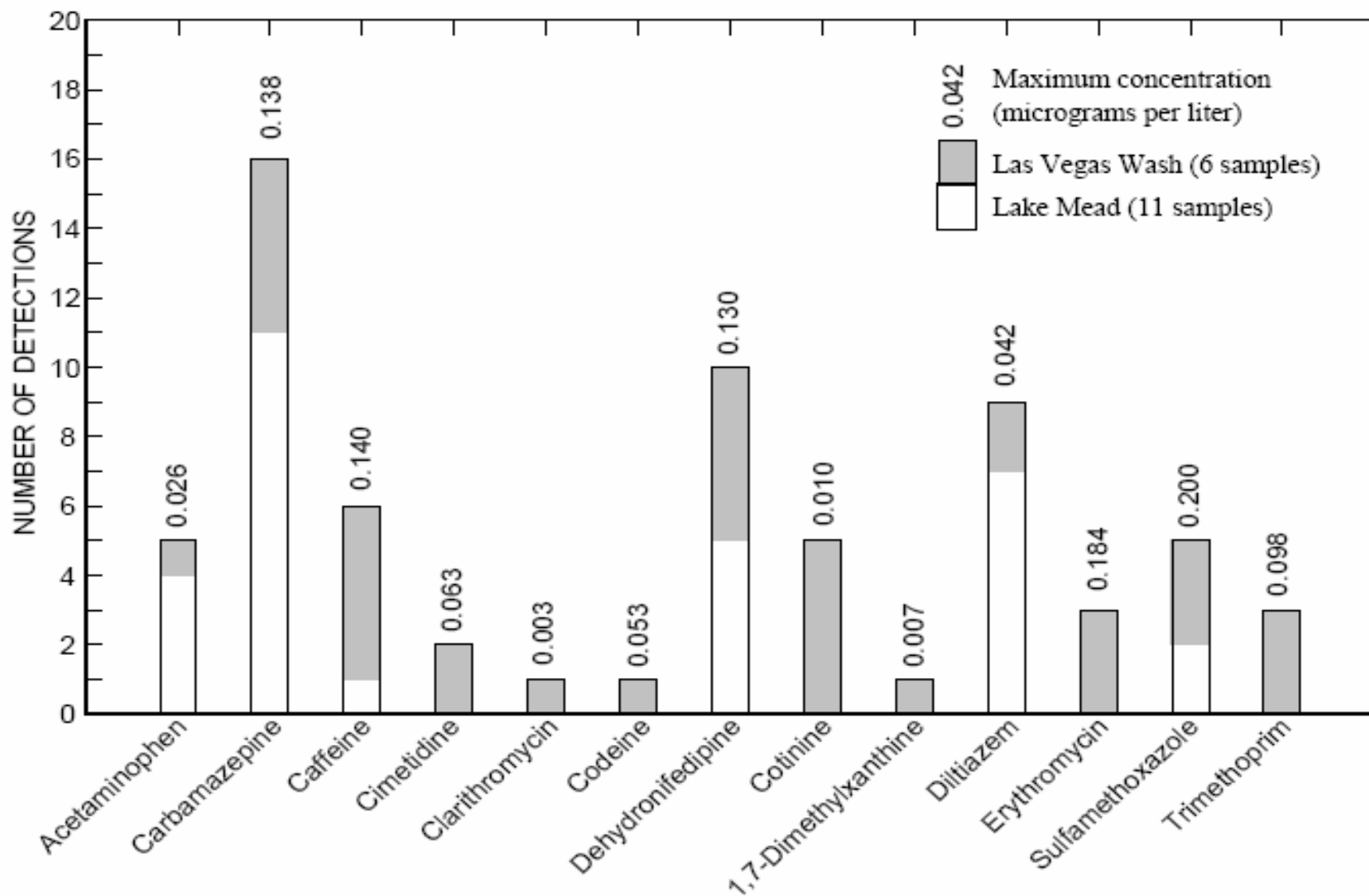


Figure 3. Summary of human-health pharmaceutical compounds detected in water samples collected from Lake Mead, Nevada and Arizona, and Las Vegas Wash, Nevada, October 2000–August 2001.

Adapted from USGS Report 02-385 *Boyd & Furlong*

2001-2002 USGS Monitoring of Lake Mead

Acetaminophen	Analgesic; anti-inflammatory
Amoxicillin	Antibiotic
Azithromycin	Antibiotic
Caffeine	Stimulant
Carbamazepine	Antiepileptic; analgesic
Cephalexin	Antibiotic
Cimetidine	Antiulcerant; stomach-acid reducer
Clarithromycin	Antibiotic
Codeine	Narcotic; analgesic
Cotinine	Metabolite of nicotine
Dehydronifedipine	Metabolite of Procardia (vasodilator)
Digoxigenin	Metabolite of Digoxin (antianginal)
Digoxin	Antianginal (cardiac stimulant)
Diltiazem	Antianginal
1,7-dimethylxanthine	Metabolite of caffeine
Diphenhydramine	Antihistamine
Enalaprilat	Antihypertensive
Erythromycin	Antibiotic
Fluoxetine	Antidepressant
Furosemide	Edema medication; diuretic
Gemfibrozil	Cholesterol regulator
Ibuprofen	Analgesic; anti-inflammatory
Lisinopril	Antihypertensive
Metformin	Antiglycemic
Miconazole	Antifungal
Paroxetine metabolite	Metabolite of Paroxetine (antianxiety)
Ranitidine	Antiulcerant; antacid
Salbutamol (albuterol)	Anti-inflammatory; bronchodilator
Sulfamethoxazole	Antibiotic
Thiabendazole	Anthelmintic (intestinal wormer)
Trimethoprim	Antibiotic
Urobilin	Metabolite of human excrement
Warfarin	Anticoagulant

Adapted from
USGS Report 02-385
Boyd & Furlong - 2002

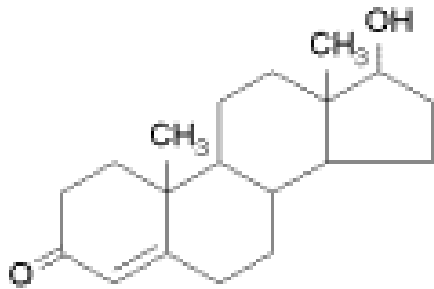
Southern Nevada WWTPs 2003 (ng/L)

Analyte	WWTP#1	WWTP#2	WWTP#3
	ppt	ppt	ppt
Hydrocodone	64	<1.0	44
Trimethoprim	24	<1.0	<10
Acetaminophen	<1.0	1.2	<10
Caffeine	39	64	38
Erythromycin	262	<1.0	507
Sulfamethoxazole	141	15	20
Fluoxetine	9.9	5.3	52
Pentoxifylline	<1.0	16	<10
Meprobamate	195	594	571
Dilantin	57	78	244
TCEP	122	187	155
Carbamazepine	91	86	67
DEET	279	269	<10
Atrazine	<1.0	<1.0	<10
Diazepam	2.0	1.9	<10
Oxybenzone	4.2	4.3	<10
Estriol	1.6	2.1	<100
Ethinylestradiol	<1.0	<1.0	<10
Estrone	<1.0	2.5	<25
Estradiol	<1.0	<1.0	<10
Testosterone	2.0	6.8	<10
Progesterone	<1.0	<1.0	<10
Androstenedione	<1.0	3.0	<10
Iopromide	82	29	101
Naproxen	5.0	<1.0	<10
Ibuprofen	6.1	7.0	110
Diclofenac	6.9	<1.0	<10
Triclosan	15	19	<10
Gemfibrozil	14	8.4	<10

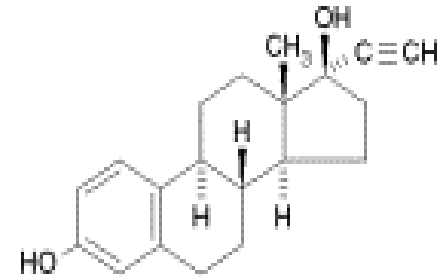
AwwaRF Treatment Study

- Evaluation of conventional and advanced water treatment for EDC removal
 - Disinfection: UV, chlorine, ozone
 - Membranes: RO, NF, UF, MF, EDR, MBR
 - Activated carbon
 - Biological
 - Ion exchange
- SNWA received \$350,000 from AwwaRF
- Project completed in early 2005

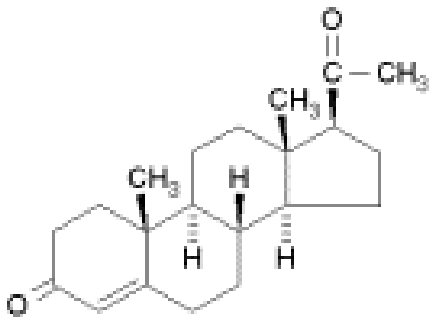
Steroids



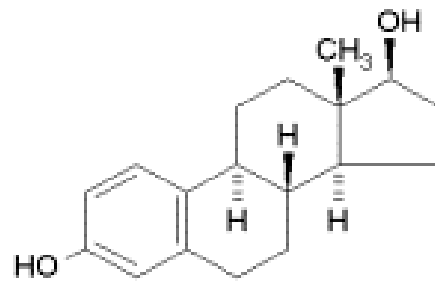
Testosterone



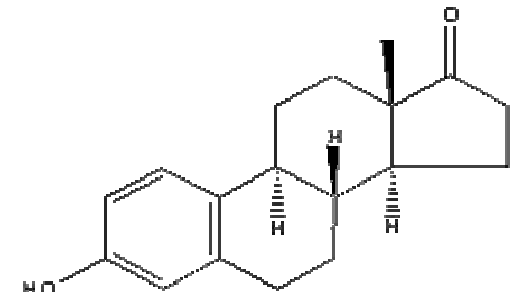
Ethinyl estradiol



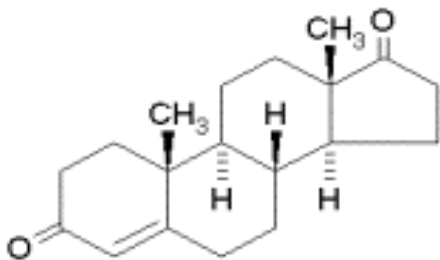
Progesterone



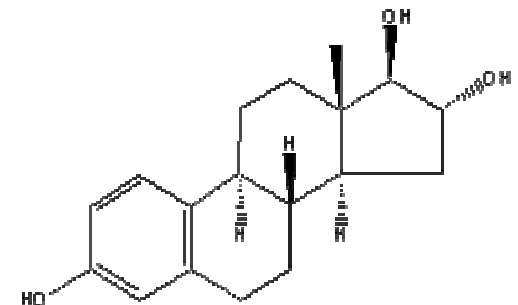
17β Estradiol



Estrone

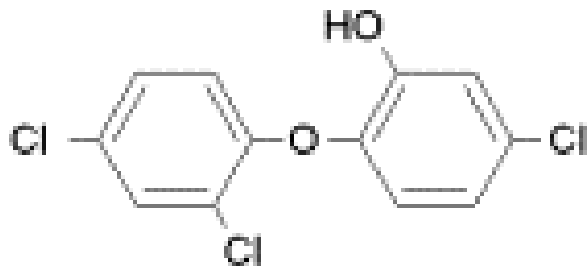


Androstenedione

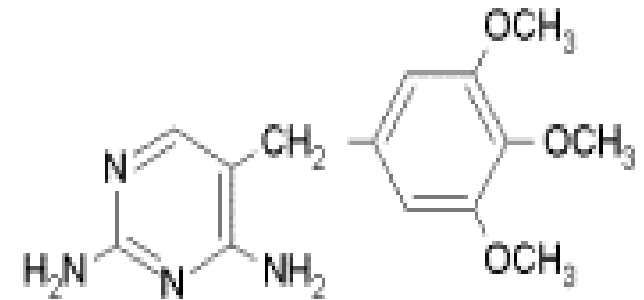


Estriol

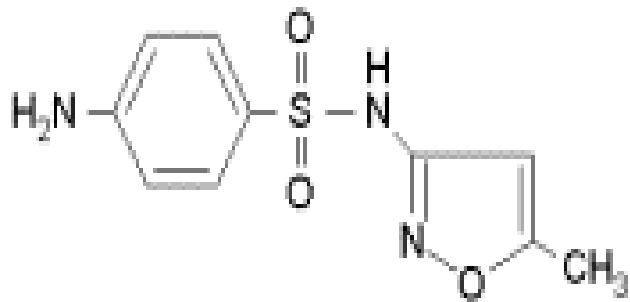
Antimicrobials



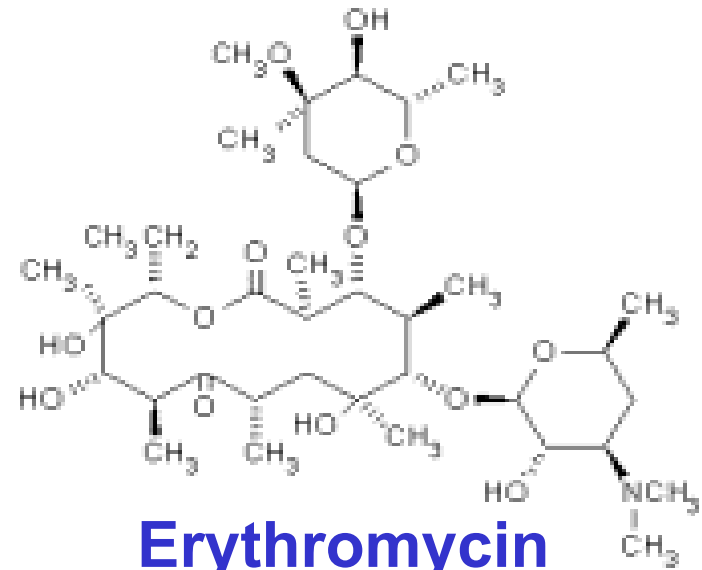
Triclosan



Trimethoprim

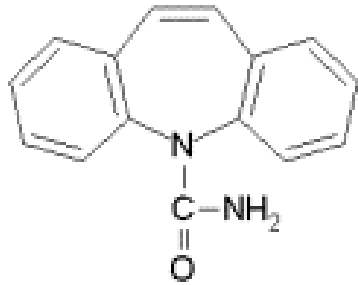


Sulfamethoxazole

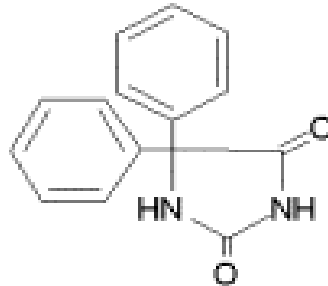


Erythromycin

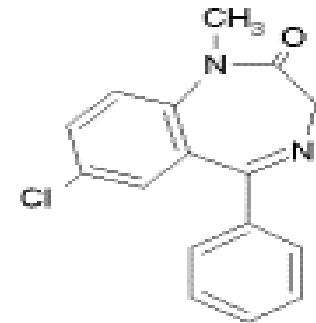
Psychoactive



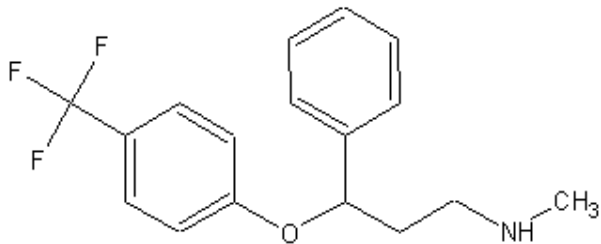
Carbamazepine



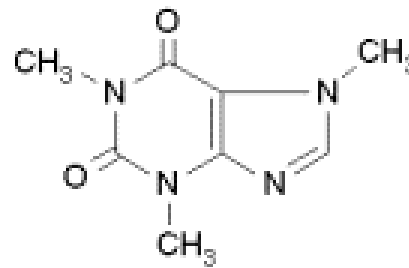
Dilantin



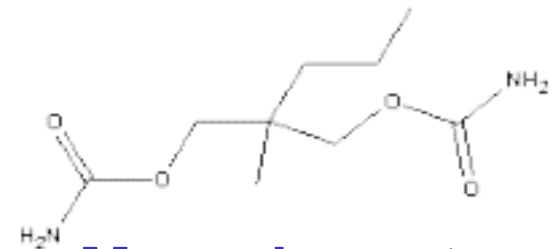
Diazepam



Fluoxetine

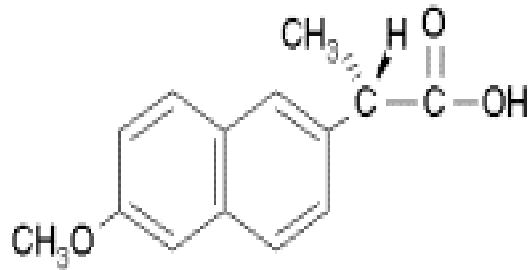


Caffeine

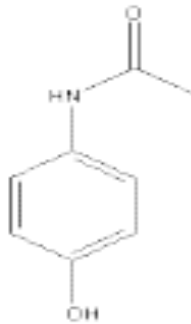


Meprobamate

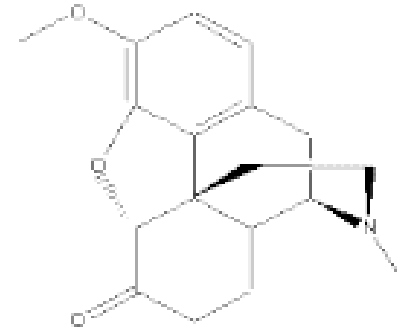
Analgesics



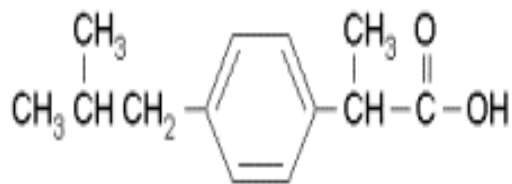
Naproxen



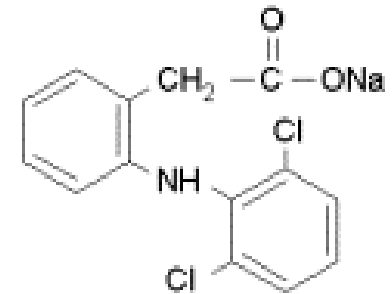
Acetaminophen



Hydrocodone

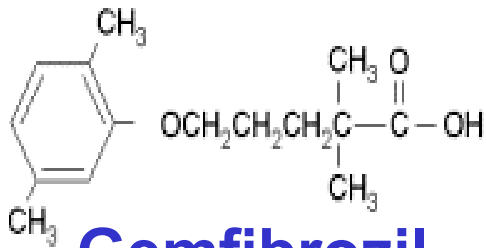


Ibuprofen

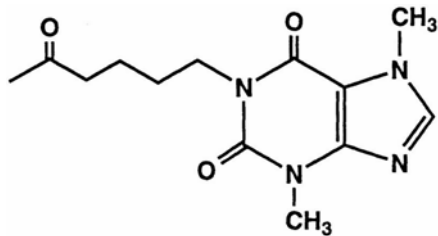


Diclofenac

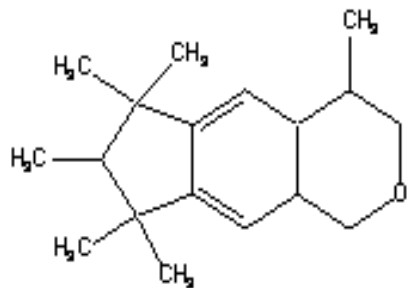
Others



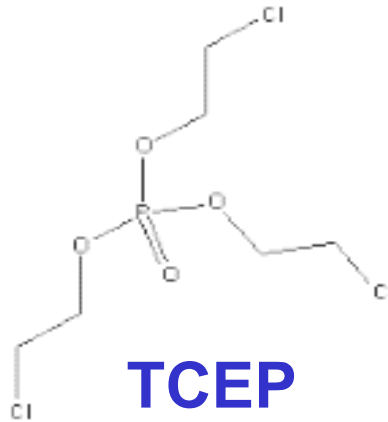
Gemfibrozil



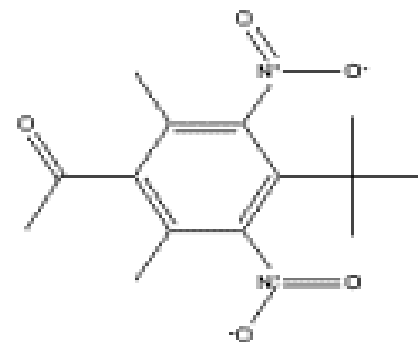
Pentoxifylline



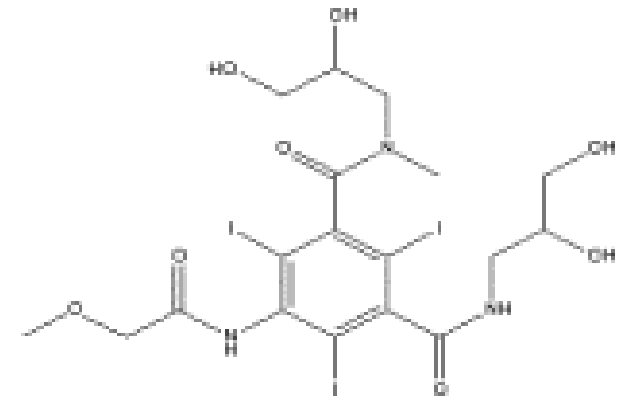
Galaxolide



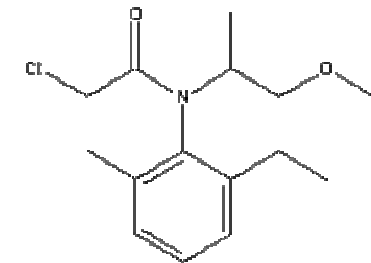
TCEP



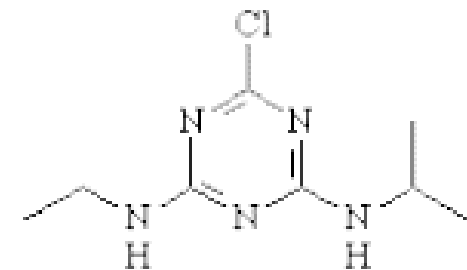
Musk Ketone



Iopromide



Metolachlor



Atrazine

<30% Removal**30-70% Removal****>70% Removal**

Testosterone	Sulfamethoxazole
Progesterone	Triclosan
Androstenedione	Diclofenac
Estriol	Acetaminophen
Ethinylestradiol	
Estrone	
Estradiol	
Erythromycin-H ₂ O	
Trimethoprim	
Naproxen	
Hydrocodone	
Ibuprofen	
Caffeine	
Fluoxetine	
Meprobamate	
Diazepam	
Dilantin	
Carbamazepine	
DEET	
Atrazine	
Galaxolide	
TCEP	
Iopromide	
Pentoxifylline	
Metolachlor	
Gemfibrozil	
Musk Ketone	

UV 40mJ/cm²

Chlorine 3.5 mg/L 24 hr

<30% Removal

Testosterone
Progesterone
Androstenedione
Caffeine
Fluoxetine
Meprobamate
Diazepam
Dilantin
Carbamazepine
DEET
Atrazine
Galaxolide
TCEP
Iopromide
Pentoxifylline

30-70% Removal

Ibuprofen
Metolachlor
Gemfibrozil

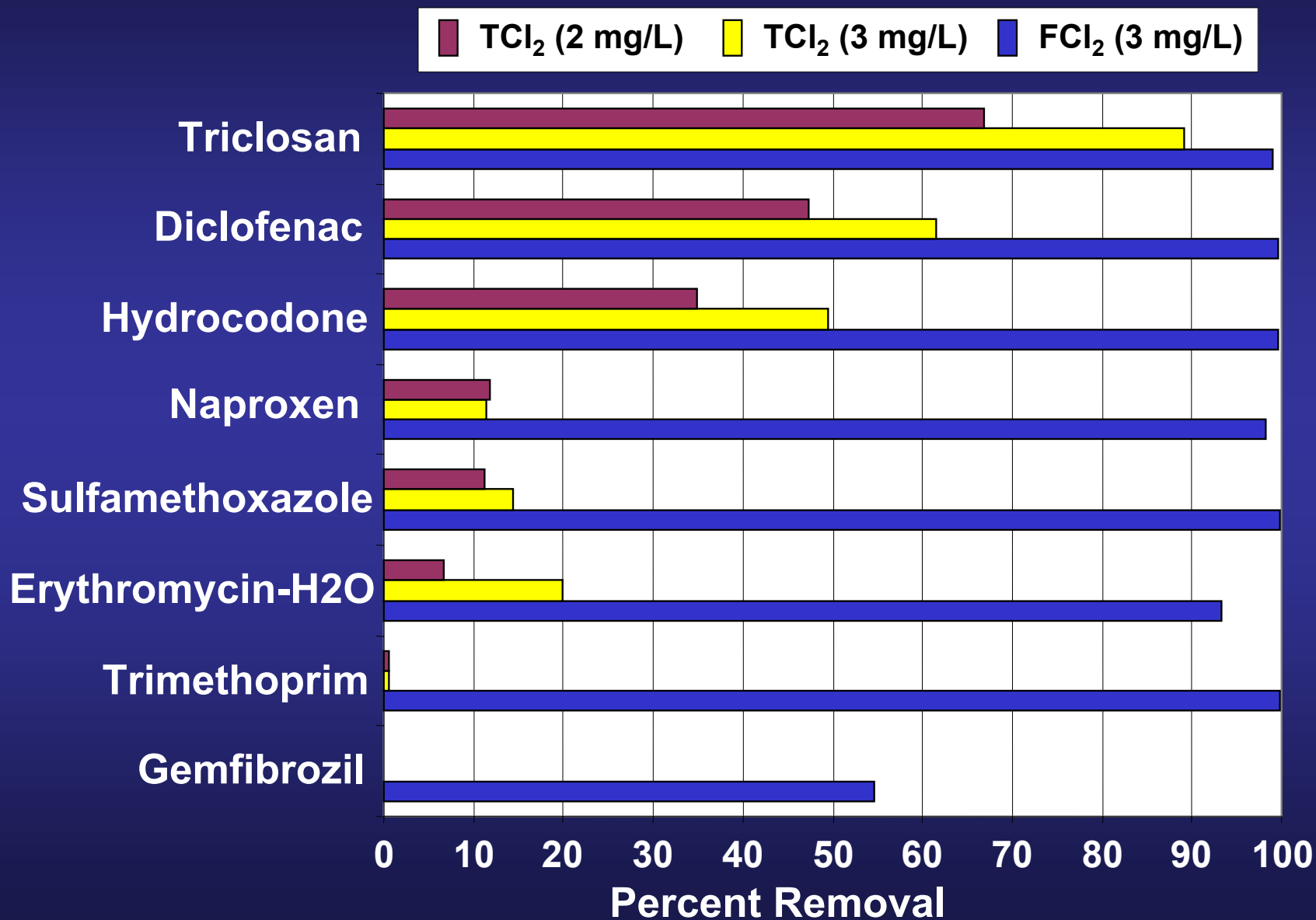
>70% Removal

Estriol
Ethinylestradiol
Estrone
Estradiol
Erythromycin-H ₂ O
Sulfamethoxazole
Triclosan
Trimethoprim
Naproxen
Diclofenac
Hydrocodone
Acetaminophen
Musk Ketone

<30% Removal	30-70% Removal	>70% Removal
Musk Ketone	Meprobamate	Testosterone
TCEP	Atrazine	Progesterone
	Iopromide	Androstenedione
		Estriol
		Ethinylestradiol
		Estrone
		Estradiol
		Erythromycin-H2O
		Sulfamethoxazole
		Triclosan
		Trimethoprim
		Naproxen
		Diclofenac
		Ibuprofen
		Hydrocodone
		Acetaminophen
		Carbamazepine
		Dilantin
		Diazepam
		Caffeine
		Fluoxetine
		DEET
		Metolachlor
		Galaxolide
		Pentoxifylline
		Gemfibrozil

Ozone 2.5 mg/L

Free Chlorine vs Chloramine

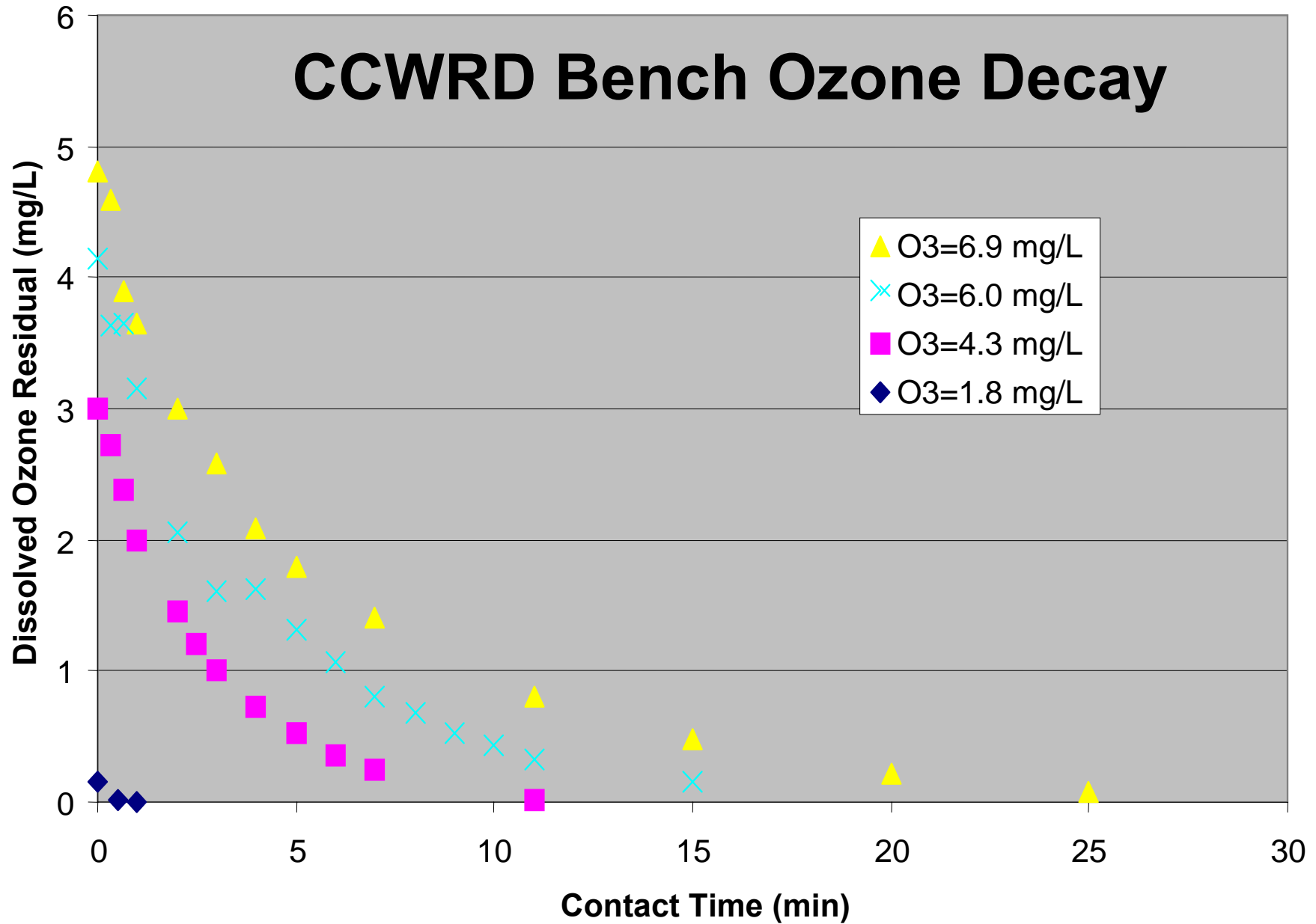


CCWRD Evaluation

- **200 L of tert. treated effluent collected prior to UV disinfection**
 - **June 2005**
 - **Ozone demand/decay determined**
 - **1-L/min flow through “micro-pilot”**
 - **12 contactors with 2 min. contact time each**
 - **Ozone injection in 1st contactor only**
 - **Organic contaminants, microbes, and estrogenicity (bioassay) monitoring**
 - **Samples collected at various contact times**



CCWRD Bench Ozone Decay



	Raw Sewage- AVE	Secondary Effluent AVE	O ₃ 3 mg/L	O ₃ 6 mg/L	O ₃ 8 mg/L
<i>Analyte</i>	<i>ng/L</i>	<i>ng/L</i>	<i>ng/L</i>	<i>ng/L</i>	<i>ng/L</i>
Hydrocodone	218	240	ND	ND	ND
Trimethoprim	319	35	ND	ND	ND
Acetaminophen	43750	ND	ND	ND	ND
Caffeine	97800	51	ND	ND	ND
Erythromycin-H ₂ O	285	133	ND	ND	ND
Sulfamethoxazole	590	841	3.1	ND	ND
Pentoxifylline	46	ND	ND	ND	ND
Meprobamate	739	332	140	63	42
Dilantin	94	154	17	3.4	ND
TCEP	453	373	427	352	334
Carbamazepine	99	210	ND	ND	ND
DEET	413	188	39	10	3.4
Atrazine	251	ND	ND	ND	ND
Oxybenzone	2925	6	8.2	ND	1.5

	Raw Sewage-AVE	Secondary Effluent AVE	3 mg/L	6 mg/L	8 mg/L
<i>Analyte</i>	<i>ng/L</i>	<i>ng/L</i>	<i>ng/L</i>	<i>ng/L</i>	<i>ng/L</i>
Iopromide	37	22	6	2	ND
Naproxen	13200	13	ND	ND	ND
Ibuprofen	11950	19	ND	ND	ND
Diclofenac	28	54	ND	ND	ND
Triclosan	1590	85	112	50	72
Gemfibrozil	1105	ND	ND	ND	ND
Galaxolide	1680	1169	46	ND	ND
Musk Ketone	225	133	83	72	42
EEq ng/mL	>40	0.626	ND	ND	ND
Total Coliform	>16,000,000	6750	<2	<2	<2
Fecal Coliform	>16,000,000	2675	<2	<2	<2

Before Ozonation



After Ozonation



Conclusions

- **Ozone is effective for disinfection and removal of emerging contaminants**
- **No perfect treatment**
 - **RO/NF membranes = brine and water loss**
 - **Activated carbon = disposal/regeneration**
 - **Disinfection = byproducts**
- **Ozone can remove cellular estrogenicity**
 - **Effects on fish should be evaluated**
 - **European scientists found same effect**

Implications for CCWRD



Conclusions

- **Southern Nevada has extensive history & expertise in ozone technology**
- **Costs for ozone and UV are comparable for disinfection in reuse application**
 - UV is not oxidative at disinfect dose
 - Ozone provides disinfection & oxidation
 - UV subject to regrowth post-disinfection
 - Neither UV nor ozone have residual issues
- **Contact times from pilot would be realistic**
 - \approx 8-20 min contact time for ozone
 - \approx 90 min contact time for chlorine

Future Efforts

- **Repeat study January 2006**
 - during winter season
 - peroxide addition for advanced oxidation
- **Plant expansion design decisions will occur in 2006**
 - membranes versus conventional filters
 - ozone versus UV
 - on-line by approximately 2009 (?)
- **Monitoring efforts of Lake Mead will continue**
 - SNWA analyses
 - F&W, USGS, BOR, NPS all have on-going efforts
 - CWC's SCOP adaptive management plan

Questions

Doug Drury, Ph.D.

ddrury@cleanwaterteam.com

Shane Snyder, Ph.D.

shane.snyder@snwa.com