Occurrence, Treatment, and Toxicological Relevance of Endocrine Disruptors and Pharmaceuticals in Drinking Water

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1. Introduction

Over the past decade a great amount of interest has arisen regarding the occurrence and fate of trace organic contaminants in the aquatic environment. Of particular concern are human hormones and pharmaceuticals, many of which are ubiquitous contaminants in conventional municipal wastewater treatment plant effluents when measured with ng/L detection limits. As analytical procedures and bioassay techniques become more readily available and increasingly sensitive, additional new contaminants will be discovered. The presence or absence of any chemical in commerce in a wastewater effluent is essentially a function of the analytical detection capability. This poses a unique challenge for water treatment processes intent on the removal of organic contaminants, as complete removal is merely a reflection of an analytical reporting limit. The projects described here sought to was designed to investigate the attenuation of a group of structurally diverse emerging contaminants in a variety of commonly utilized conventional and advanced water treatment processes and to determine the concentration of these compounds in drinking water that would be expected to invoke toxicological responses in humans.

This study shows that the majority of emerging contaminants can be readily removed using ozone or UV-advanced oxidation. However, some compounds are recalcitrant and difficult to oxidize using commonly employed oxidant doses. Magnetic ion-exchange (MIEX ®) provided minimal contaminant removal; however, contaminants that were negatively charged at ambient pH were well removed. Activated carbon, both in powdered and granular forms, was effective for contaminant absorption. Carbon type, contact time, and dose or regeneration are influential parameters in removal efficacy by activated carbon. No single treatment process was capable of removing all contaminants consistently to less than the analytical method reporting limits employed. Moreover, each treatment process provided advantages and disadvantages that will be discussed in this chapter. A multi-barrier approach would

provide the most comprehensive removal strategy for organic contaminant treatment.

The human health relevance of pharmaceuticals detected in full scale drinking water facilities in the US was investigated. A series of toxicological endpoints were evaluated, and the most sensitive endpoint chosen as a point of departure. In some cases, the most sensitive endpoint was not the therapeutic effect of the pharmaceutical. For all pharmaceuticals investigated, the drinking water equivalent level (DWEL) of concern was in μg/L, or larger, concentrations. Therefore, there appears to be no human health relevance at the levels detected in drinking water. A further component of this study sought to investigate endocrine disrupting impacts of select EDCs. The EDC component also included an investigation into the estrogenicity of common food items as compared to drinking and reuse water. The concentrations of selected chemicals to induce EDC effects occurred at concentrations far above those found in US drinking waters. Moreover, the concentrations of these chemicals in food/beverage items were often orders of magnitude greater than those find in water. Using an in vitro bioassay, it was determined that the estrogenicity of soy sauce, green tea, and milk were orders of magnitude greater than estrogenicity of water (even wastewater). It is unlikely the endocrine disruptive effects from trace organic chemicals are relevance in US drinking waters.

2. Overview

2.1 History

In 1965 Stumm-Zollinger and Fair of Harvard University published the first known report indicating that steroid hormones are not completely eliminated by wastewater treatment (Stumm-Zollinger and Fair 1965). In an article published in 1970, Tabak and Bunch investigated the fate of human hormones during wastewater treatment and stated “since they (hormones) are physiologically active in very small amounts, it is important to determine to what extent the steroids are biodegraded” (Tabak and Bunch 1970). As early as the 1940s, scientists were aware that certain chemicals had the ability to mimic endogenous estrogens and androgens (Schueler 1946; Sluczewski and Roth 1948). In 1977, researchers from the University of Kansas published the first known report specifically addressing the discharge of pharmaceuticals from a wastewater treatment plant (Hignite and Azarnoff 1977). Despite these early findings, the issue of steroids and pharmaceuticals in wastewater outfalls did not gain significant attention until the 1990s, when the occurrence of natural and synthetic steroid hormones in wastewater was linked to reproductive impacts in fish living downstream of outfalls (Purdom, Hardiman et al. 1994; Desbrow, Routledge et al. 1998; Routledge, Sheahan et al. 1998).

Since the initial link between trace contaminants (sub-μg/L) in wastewater

effluents and ecological impacts in receiving waters, many studies have focused on the occurrence of these contaminants (Halling-Sorensen, Nielsen et al. 1998; Ternes, Hirsch et al. 1998; Daughton and Ternes 1999; Snyder, Keith et al. 1999; Metcalfe, Koenig et al. 2000; Ternes and Hirsch 2000; Snyder, Kelly et al. 2001; Kolpin, Furlong et al. 2002; Vanderford, Pearson et al. 2003). As a result, pharmaceuticals and steroid hormones have been detected in many water bodies around the world (Kolpin, Furlong et al. 2002; Cargouet, Perdiz et al. 2004; Petrovic, Eljarrat et al. 2004). One major contributor of such widespread contamination is municipal wastewater discharge, which impacts surface water quality by contaminating receiving water bodies with chemicals not completely removed by current treatment processes. Indirect potable water reuse, either planned or unplanned, can occur when wastewater treatment plant discharge comprises a significant portion of the receiving stream's total flow. In some cases, effluent dominated surface waters are used as source waters for drinking water treatment facilities. Global water sustainability depends in part upon effective reuse of water. In particular, the reuse of municipal wastewater for irrigation and augmentation of potable water supplies is critical. Public perception and concern regarding trace hormones and pharmaceuticals is creating resistance to reuse projects. It is necessary to obtain accurate information on the attenuation or elimination of these contaminants from wastewater, the impact of wastewater discharge on surface water or groundwater supplies, and the removal efficiency of the remaining contaminants by drinking water treatment processes.

A significant number of articles have investigated the fate of trace hormones and pharmaceuticals in water treatment processes (Ternes, Kreckel et al. 1999; Ternes, Stumpf et al. 1999; Snyder, Westerhoff et al. 2003; Huber, Korhonen et al. 2005; Westerhoff, Yoon et al. 2005; Snyder, Adham et al. 2006; Snyder, Wert et al. 2006; Yoon, Westerhoff et al. 2006). The ability of a particular treatment process to remove organic contaminants depends mostly on the structure and concentration of the contaminant. In addition, the operational parameters of the process (e.g., oxidant dose and contact time) will also determine the degree of attenuation of a particular contaminant.

3. Results

The results from US drinking water testing for select EDCs and pharmaceuticals are shown in Table 1. The insect repellant N,N diethyl-*m*-toluamide (DEET), the suspected endocrine disrupting herbicide atrazine, and the anti-anxiety pharmaceutical meprobamate were the top three occurring contaminants, respectively, in this study. In raw waters, the profile was quite different. The greatest impact in most water treatment systems occurs during disinfection. Disinfection with ozone provided, by far, the greatest removal of contaminants, followed by free chlorine,

chloramine, and UV, respectively (Tables 2-5). In full scale plants, removal by disinfection was quite comparable to that predicted in bench and pilot scale testing. Removal by activated carbon and membranes can be highly efficient depending upon the operation parameters (Snyder, Adham et al. 2006); however, these processes are far less common in US drinking water treatment facilities. While ozone was found to be highly-efficient oxidizing selected contaminants in both drinking and reuse waters (Snyder, Wert et al. 2006), the formation of oxidation products must be considered.

The human health consideration of selected trace contaminants was evaluated. Table 6 provides the DWEL values for some of the contaminants considered. Using the MCF-7 *in vitro* bioassay, it was demonstrated that estrogenicity of recommended serving sizes of soy sauce, green tea, and cows milk provided far greater estrogenicity than did any wastewater or drinking water. These data show that using an *in vitro* measure of estrogenicity may not be suitable for extrapolation to health risk. Oxidation by ozone and chlorine readily degraded any observed estrogenicity, and subsequent byproducts were no longer estrogenic.

4. Conclusions

Trace levels of hormones and pharmaceuticals are ubiquitous contaminants of municipal wastewater effluents. The detection of these chemicals is a direct function of analytical detection limits. Therefore, more and more trace contaminants will continue to be discovered. Water treatment processes have various levels of efficacy in the attenuation of these contaminants. In drinking water, oxidation provides a cost-effective means for disinfection and simultaneous contaminant removal. Those compounds which are resilient to oxidation are often detected in finished US drinking waters. However, the concentration at which these occur is extremely small, and far below the concentrations that would be expected to be of human health concern. In an evaluation of estrogenicity as a class of toxicity, the estrogenicity of common food items is far beyond that of any wastewater or drinking water evaluated. The relative risk factors of common exposure to EDCs through foods and beverages appears to be far greater than the exposure through drinking water. More research is needed to adequately address human health relevance of EDCs and pharmaceuticals, but it is likely that most drinking waters do not provide a substantial exposure and the concentrations expected to have human health detriment.

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Table 1. Occurrence of EDCs and Pharmaceuticals in 20 US Drinking Waters

Compound	Hits	% Freq	Min (ng/L)	Max (ng/L)	Median (ng/L)	Ave (ng/L)
DEET	**18**	**90**	**2.1**	**30**	**5.1**	**8.2**
Atrazine	**15**	**75**	**1.4**	**430**	**29**	**74**
Meprobamate	**15**	**75**	**1.6**	**13**	**3.8**	**6.1**
Dilantin	**14**	**70**	**1.1**	**6.7**	**2.3**	**2.7**
Ibuprofen	**13**	**65**	**1**	**32**	**3.8**	**7.9**
Iopromide	**13**	**65**	**1.1**	**31**	**6.5**	**8.5**
Caffeine	**12**	**60**	**2.6**	**83**	**23**	**25**
Carbamazepine	**11**	**55**	**1.1**	**5.7**	**2.8**	**2.8**
TCEP	**7**	**35**	**3**	**19**	**5.5**	**10.1**
Gemfibrozil	**5**	**25**	**1.3**	**6.5**	**4.2**	**3.9**
Metalochlor	**4**	**20**	**14**	**160**	**86**	**86**
Estrone	**2**	**10**	**1.1**	**2.3**	**1.7**	**1.7**
Progesterone	**2**	**10**	**1.1**	**1.1**	**1.1**	**1.1**
Erythromycin	**1**	**5**	**1.3**	**1.3**	**1.3**	**1.3**
Musk Ketone	**1**	**5**	**17**	**17**	**17**	**17**
Naproxen	**1**	**5**	**8**	**8**	**8**	**8.0**
Sulfamethoxazole	**1**	**5**	**20**	**20**	**20**	**20**
Triclosan	**1**	**5**	**43**	**43**	**43**	**43**
Trimethoprim	**1**	**5**	**1.3**	**1.3**	**1.3**	**1.3**

Table 2. Summary of Removal by Ozone Disinfection

24 Minutes Contact Time			
> 80% Removal	50-80% Removal	20-50% Removal	< 20% Removal
Acetaminophen	DEET	Atrazine	TCEP
Androstenedione	Diazepam	Iopromide	
Caffeine	Dilantin	Meprobamate	
Carbamazepine	Ibuprofen		
Diclofenac			
Erythromycin			
Estradiol			
Estriol			
Estrone			
Ethynylestradiol			
Fluoxetine			
Gemfibrozil			
Hydrocodone			
Naproxen			
Oxybenzone			
Pentoxifylline			
Progesterone			
Sulfamethoxazole			
Triclosan			
Trimethoprim			
Testosterone			

Table 3. Summary of Removal by Free Chlorine

Chlorine Dose = 3 mg/L, Contact Time = 24 hours, pH=7.9-8.5			
> 80% Removal	50-80% Removal	20-50% Removal	< 20% Removal
Acetaminophen	Gemfibrozil	Diazepam	Androstenedione
Benzo(a)pyrene		Galaxolide	Atrazine
Diclofenac		Pentoxifylline	Caffeine
Erythromycin			Carbamazepine
Estradiol			DDT
Estriol			DEET
Estrone			Dilantin
Ethynylestradiol			Fluorene
Hydrocodone			Fluoxetine
Musk Ketone			g-BHC
Naproxen			Ibuprofen
Oxybenzone			Iopromide
Sulfamethoxazole			Meprobamate
Triclosan			Metolachlor
Trimethoprim			Progesterone
			TCEP
			Testosterone

Table 4. Summary of Removal by Chloramine

Chloramine Dose = 3 mg/L, Contact Time = 24 hours			
> 80% Removal	50-80% Removal	20-50% Removal	< 20% Removal
Acetaminophen	Benzo(a)pyrene	Hydrocodone	Androstenedione
Estradiol	Diclofenac	Galaxolide	Atrazine
Estriol	Oxybenzone		Caffeine
Estrone			Carbamazepine
Ethynylestradiol			DDT
Triclosan			DEET
			Diazepam
			Dilantin
			Erythromycin
			Fluorene
			Fluoxetine
			g-BHC
			Gemfibrozil
			Ibuprofen
			Iopromide
			Meprobamate
			Metolachlor
			Musk Ketone
			Naproxen
			Pentoxifylline
			Progesterone
			Sulfamethoxazole
			TCEP
			Testosterone
			Trimethoprim

Table 5. Summary of Removal by UV disinfection (40 mJ/cm^2)

> 80% Removal	50-80% Removal	20-50% Removal	< 20% Removal
	Diclofenac	Acetaminophen	Androstenedione
	Sulfamethoxazole		Atrazine
	Triclosan		Caffeine
			Carbamazepine
			DEET
			Diazepam
			Dilantin
			Erythromycin-H_2O
			Estradiol
			Estriol
			Estrone
			Ethynylestradiol
			Fluoxetine
			Gemfibrozil
			Hydrocodone
			Ibuprofen
			Iopromide
			Meprobamate
			Naproxen
			Oxybenzone
			Pentoxifylline
			Progesterone
			TCEP
			Testosterone
			Trimethoprim

Table 6. Human Health Evaluation of Select Contaminants

Drug	Composite Safety Factor	DWEL (ng/L)	Max Finished Water Conc. (ng/L)	Margin of Safety
Atenolol	300	81,000	20	4,100
Atorvastatin	1,000	96,000	<0.25	380,000
o-hydroxy atorvastatin			<0.50	190,000
o-hydroxy atorvastatin			<0.50	190,000
Carbamazepine	3,000	330,000	18	18,000
Diazepam	1,000	4,800	<0.25	19,000
Diclofenac	300	66,000	<0.25	260,000
Enalapril	300	33,000	<0.25	130,000
Fluoxetine	1,000	36,000	<0.50	66,000
Gemfibrozil	1,000	450,000	2.1	210,000
Meprobamate	1,000	480,000	43	11,000
Naproxen	300	330,000	<0.50	960,000
Phenytoin	1,000	2,400,000	15	160,000
Risperidone	1,000	780	0.34	2,300
Simvastatin	3,000	57,000	<0.25	230,000
Simvastatin hydroxy acid			<0.25	230,000
Sulfamethoxazole	300	3,900,000	3	1,300,000
Triclosan	1,000	29,000	1.2	24,000
Trimethoprim	300	1,100,000	<0.25	4,400,000

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SNWA

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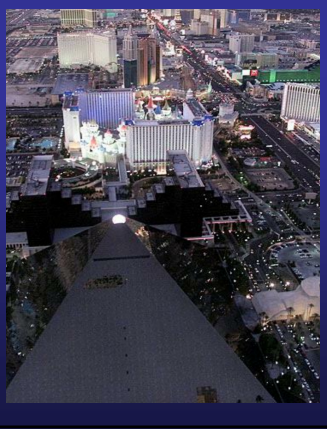
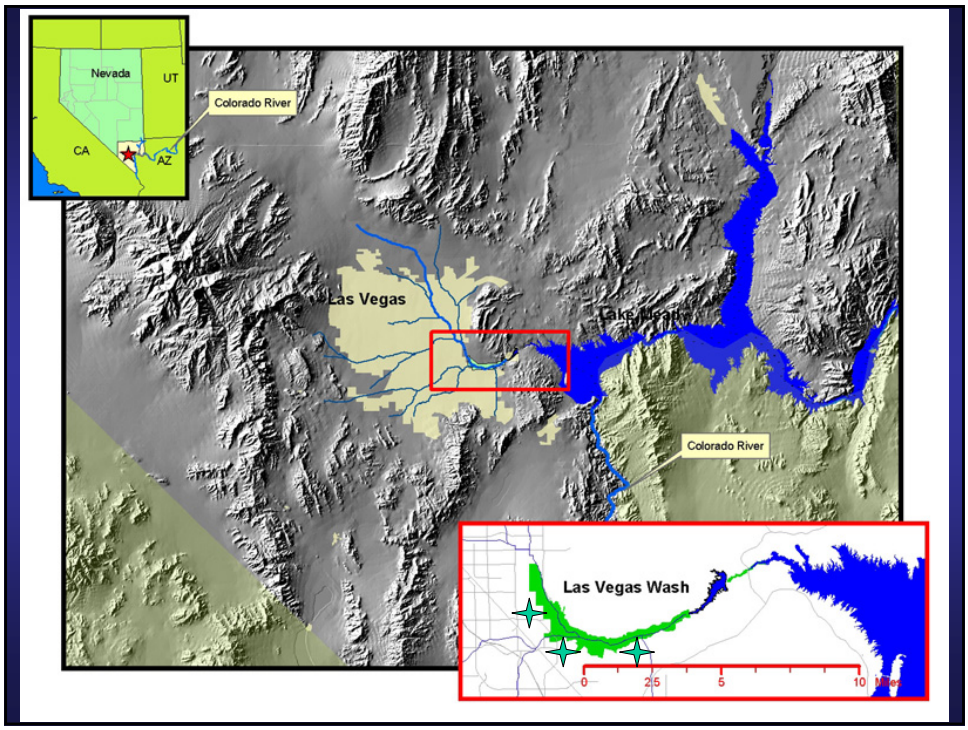
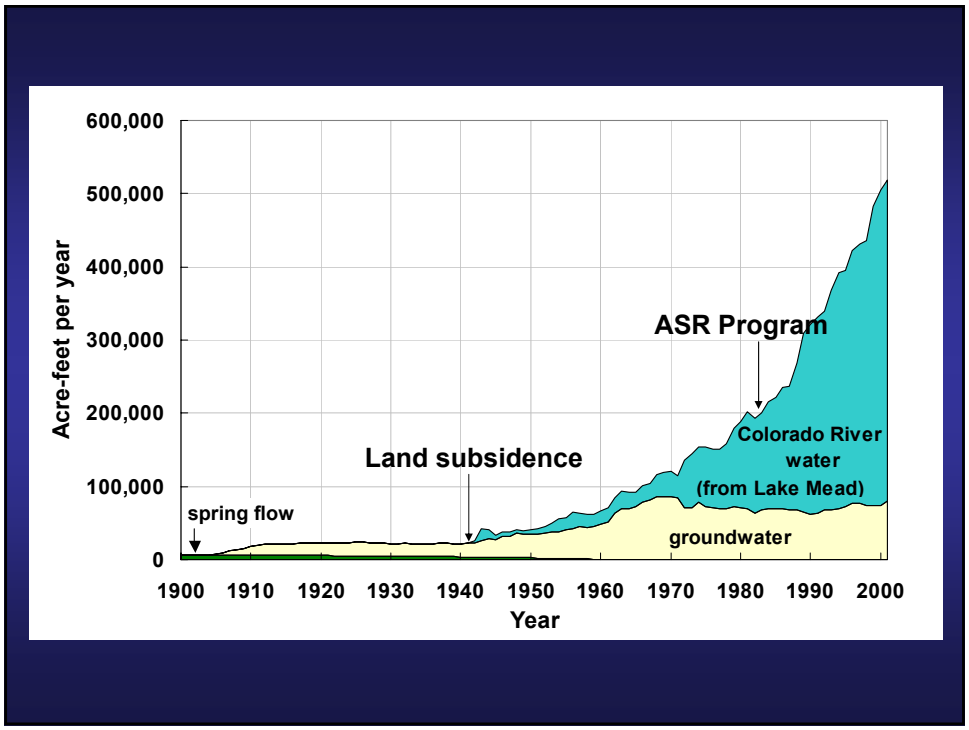
EDCs: A Tale of Sin City or EDC-CSI Las Vegas

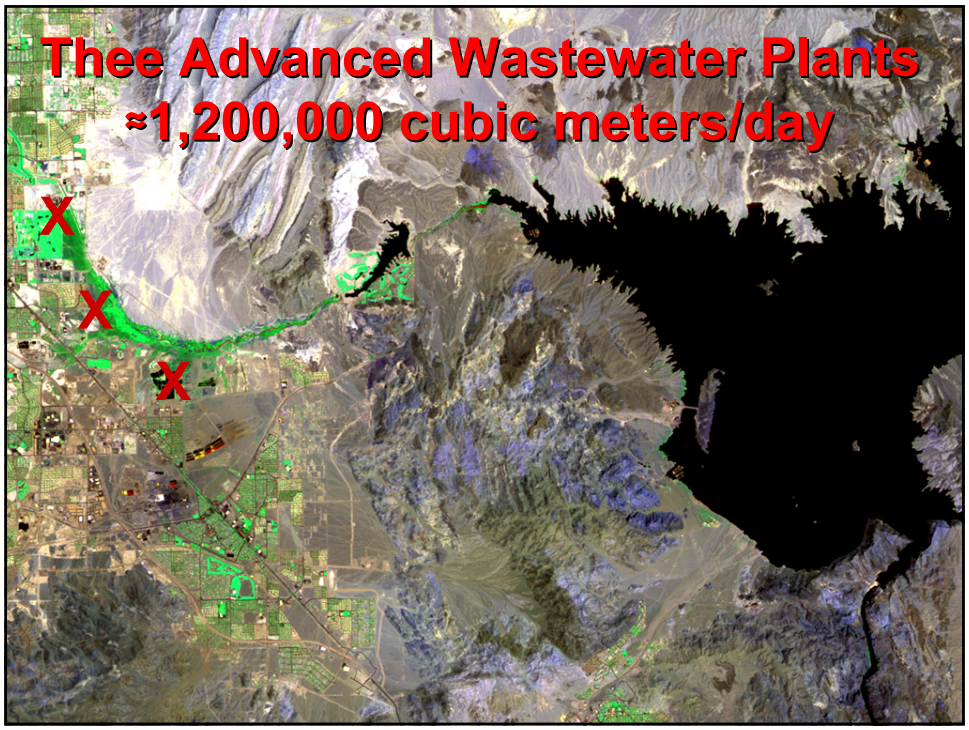




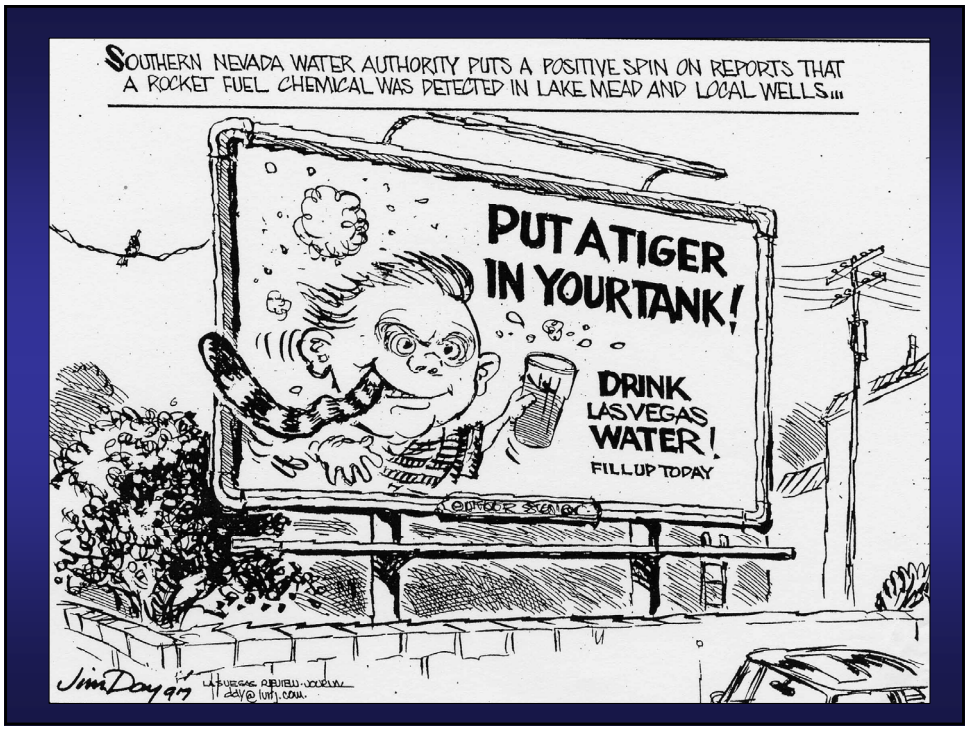
- Las Vegas, Nevada – pop. ≈2,000,000
- ≈35,000,000 visitors per year
- VERY DRY - <7 cm rain & >2 M evap.
- Water reuse critical for sustainability

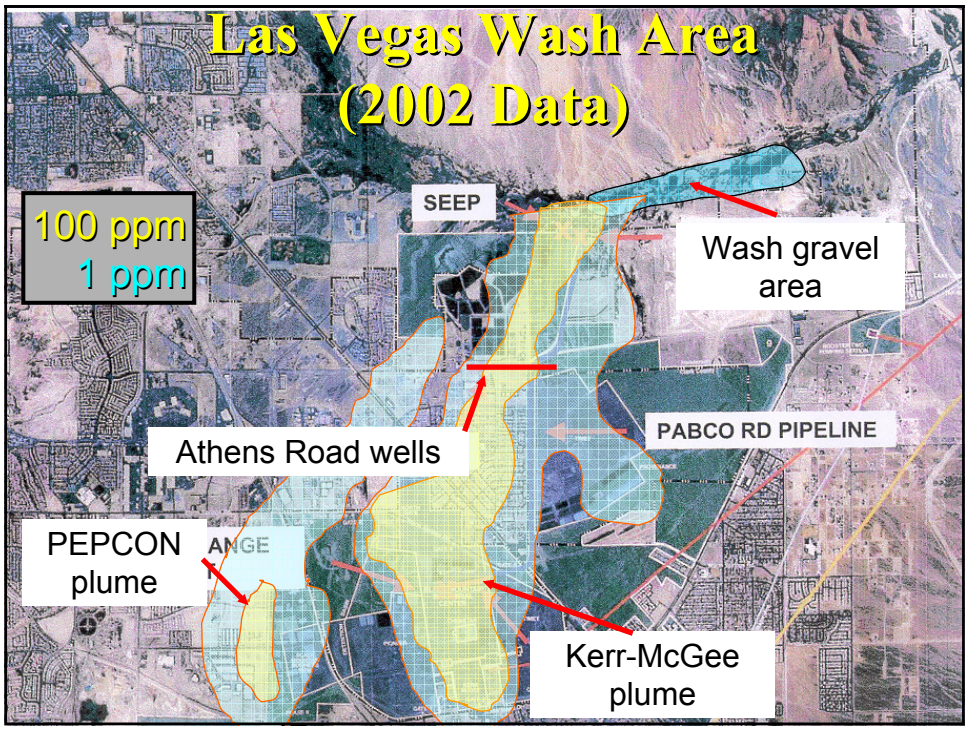

≈ 5,500 new people/month
≈ 1,200 new homes/month
≈ 1 new school/month
≈ 100 teachers/month
> $3,000,000,000 in water projects
≈ $5,000,000,000 expected projects
WATER CONTROLS LAS VEGEAS!


600,000
500,000
400,000
300,000
200,000
100,000
0
Acre-feet per year
1900
1910
1920
1930
1940
1950
1960
1970
1980
1990
2000
Year
ASR Program
Land subsidence
Colorado River water (from Lake Mead)
spring flow
groundwater


Thee Advanced Wastewater Plants
≈1,200,000 cubic meters/day
X
X
X


Lake Mead and the Lower
Colorado River provide water for
More than 22,000,000 people


SOUTHERN NEVADA WATER AUTHORITY PUTS A POSITIVE SPIN ON REPORTS THAT A ROCKET FUEL CHEMICAL WAS DETECTED IN LAKE MEAD AND LOCAL WELLS...
PUT A TIGER IN YOUR TANK!
DRINK LAS VEGAS WATER!
FILL UP TODAY
Jim Day '97


Las Vegas Wash Area
(2002 Data)
100 ppm
1 ppm
SEEP
Wash gravel area
Athens Road wells
PABCO RD PIPELINE
PEPCON plume
Kerr-McGee plume


FREMONT
APACH

U.S. Department of the Interior—U.S. Geological Survey

SYNTHETIC ORGANIC COMPOUNDS AND CARP ENDOCRINOLOGY AND HISTOLOGY IN LAS VEGAS WASH AND LAS VEGAS AND CALLVILLE BAYS OF LAKE MEAD, NEVADA, 1992 AND 1995

Water-Resources Investigations Report 96-4266

Nevada Basin and Range Study Unit
National Water-Quality Assessment Program

By Hugh E. Bevans[1], Steven L. Goodbred[2], John F. Miesner[3], Sharon A. Watkins[1], Timothy S. Gross[4], Nancy D. Denslow[4], *and* Trenton Schoeb[4]

ABSTRACT

The Nevada Basin and Range study unit of the National Water-Quality Assessment Program, U.S. Geological Survey, in cooperation with the National Park Service, National Biological Service, and U.S. Fish and Wildlife Service, investigated the occurrence of organochlorines and semivolatile industrial compounds in the water column, bottom sediment, and carp (*Cyprinus carpio*) tissue at five sites in Las Vegas Wash and Lake Mead. Endocrine systems of carp were assessed by analyzing concentrations of female and male sex-steroid hormones, 17β-estradiol and 11-ketotestosterone, and vitellogenin (an estrogen-controlled egg protein) in blood-plasma samples. The histology of carp gonads, hepatopancreas, kidney, gill, and lower intestine were analyzed for effects that can result from endocrine disruption or exposure to toxicants.

Organochlorines (pesticides and industrial compounds) and semivolatile industrial compounds were detected in semipermeable membrane devices and bottom-sediment samples; only organochlorines were detected in carp-tissue samples. Concentrations of organochlorines were higher in Las Vegas Wash and Bay than in Callville Bay (the reference site) for the three media that were sampled. Results of a carp-tissue bioassay indicated the presence of dioxins or furans with low toxic-equivalent factors relative to 2,3,7,8-tetrachlorodibenzo-*p*-dioxin in Las Vegas Wash and Las Vegas and Callville Bays. Patterns of necrosis observed in hepatopancreas and kidney samples from carp are consistent with long-term subchronic exposure to toxicants. Polycyclic aromatic hydrocarbons, phthalates, and phenols also were detected at higher concentrations in bottom-sediment samples from Las Vegas Bay than in a comparable sample from Callville Bay. Polycyclic aromatic hydrocarbons were detected in samples from semipermeable membrane devices from all sites.

Endocrine disruption in carp from Las Vegas Wash and Bay, as compared to Callville Bay, is evidenced by high concentrations of 11-ketotestosterone levels in blood-plasma samples of female carp in Las Vegas Wash, low concentrations in male carp from Las Vegas Bay, and low 17β-estradiol concentrations in male carp from Las Vegas Bay. The most compelling evidence of endocrine disruption is the presence of vitellogenin in blood-plasma samples of male carp from Las Vegas Wash and Bay and elevated concentrations in female carp from Las Vegas Bay.

Many of the organochlorines and semivolatile industrial compounds detected in semipermeable membrane devices, bottom sediment, and carp tissue from Las Vegas Wash and Bay have been linked to endocrine disruption in fish by previous investigations of other areas. The endocrine disruption observed in carp from Las Vegas Wash and Bay could be due to the presence of these compounds.

Aerial view of lower Las Vegas Wash and Las Vegas Bay of Lake Mead. View to the northwest, Oct. 12, 1995. Photograph by A.S. VanDenburgh.

November 19, 1996

Chemicals polluting

Lake Mead

Biological studies find deformities in carp

By Mary Manning
LAS VEGAS SUN

Federal and state agencies announced increased pollution monitoring in Lake Mead, the primary drinking water supply for Las Vegas, after two studies released today showed deformed carp in the lake's waters.

Organic chemicals from treated and untreated wastewater, pesticides and chemicals were discovered in the water, bottom sediment and the fish in the Las Vegas Wash and Las Vegas Bay where 125 million gallons a day of treated sewage flow from the Las Vegas Valley.

U.S. Geological Survey officials, who conducted the studies, cautioned that while the findings are important, they can't begin to answer questions about human health.

"These findings suggest the potential for a significant problem," USGS chief biologist Dennis Fenn said.

But Alan O'Neill, superintendent of the Lake Mead National Recreation Area, said, "We want to stress that Lake Mead has outstanding water quality."

"What these results show is that we will need to do additional studies with the participation of other entities in the Las Vegas Valley to determine when and where deterioration occurred or is presently occurring and what actions are needed to improve water quality in Las Vegas Wash before it enters Lake Mead."

LAS VEGAS REVIEW-JOURNAL
reviewjournal.com

November 20, 1996

Park Service to step up water monitoring at Lake Mead

Keith Rogers

Park service to monitor **Lake Mead** water more

Despite a study's findings about **Lake Mead** pollution, the drinking water is safe, the water authority says.

By Keith Rogers Review-Journal

The National Park Service said Tuesday it will increase monitoring of **Lake Mead**'s water quality in the wake of a new federal study that claims a potential link between pollution and problems with carp reproductive systems.

'We're concerned. We all feel we need to find out more,' said Bill Dickinson, assistant superintendent at **Lake Mead** National Recreation Area.

February 01, 1997

Scientists fear mystery plume could affect LV water quality

By Mary Manning <manning@lasvegassun.com>
LAS VEGAS SUN

Like a mythical monster, a river of salty and polluted water drains from the Las Vegas Valley into Lake Mead, passing the pipe from which Southern Nevada draws its drinking water.

For more than five years, federal scientist James LaBounty has tracked this polluted plume.

Month after month, LaBounty worries as the contaminated plume streams past Saddle Island, site of the pipeline that delivers drinking water to a million Las Vegas residents and more than 31 million visitors a year.

Part of the problem is Southern Nevada's rapid growth, creating 10 times the sewage flow into Lake Mead of 20 years ago. Once, diluting the polluted waters took care of the problem. Today, dilution isn't enough.

"The major source of drinking water for the Las Vegas Valley is at risk," LaBounty stated in a preliminary report on the plume.

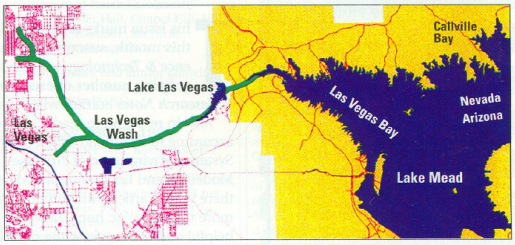
ENVIRONMENTAL NEWS

8 A ■ JAN. 1, 1998 / ENVIRONMENTAL SCIENCE & TECHNOLOGY / NEWS

Human estrogens linked to endocrine disruption

For the first time in North America, high levels of natural and synthetic hormones in municipal wastewater treatment plant effluent have been linked with endocrine disruption in fish. The study by researchers at Michigan State University's Department of Zoology indicates that human hormones, not industrial chemicals, in the effluent caused male fish to produce vitellogenin, a well-accepted indicator of endocrine disruption.

"This is a significant, if not a surprising, result," commented Gary Ankley, an EPA toxicologist who studies endocrine disrupters. The results were similar to findings published last year by U.K. researchers that identified hormones secreted in women's urine as the cause of vitellogenesis in caged fish exposed to sewage effluent in U.K. waters.



High levels of a female protein in male fish found in Lake Mead, Nev., led to a search for the cause in the effluent-dominated waters of the Las Vegas Wash. (Courtesy Shane Snyder, Michigan State University)

the compounds that were likely to act like estrogens in the fish. They also used an innovative method that involves solid-phase extraction and in vitro cellular bioassays to detect endocrine-modulating compounds in complex aqueous mixtures. Of the

the highest level of estrogenic activity in effluent downstream from a small plant (55,000 gal/day) with relatively few treatment processes.

Results from a companion Michigan State study, in which caged fish were exposed to Michigan wastewater effluent, suggest

Resource

PUBLISHED BY ASAE – THE SOCIETY FOR ENGINEERING IN AGRICULTURAL, FOOD, AND BIOLOGICAL S

MAY 1999

• *Bad Medicine*
• *Grease Relief*
• *Giving Barn Waste the Treat*
• *Biotrickling Filter*
• *1999 ASAE/CSAE-SCGR Annu International Meeting*

ENGINEERING & TECHNOLOGY FOR A SUSTAINABLE W

Bad Medicine

Pharmaceuticals taken by humans and animals can end up in waterways

Shane Snyder and Erin Snyder

Pharmaceuticals have improved human health and lengthened the human life span.

But new research is showing that although most medicine taken into the body is absorbed, some of the non-degraded or biologically activated drugs may be excreted as waste. These human-passed drugs ultimately end up in wastewater treatment plants (WWTPs) where they are processed and often released into waterways.

The degree to which these drugs are eliminated by WWTPs depends on the treatment method. Some percentage of the pharmaceuticals passes through WWTPs unaffected and is discharged into lakes or rivers.

Concerns about pharmaceuticals entering natural U.S. waters have surfaced in the past. In 1970, Henry H. Tabak of the U.S. Environmental Protection Agency (EPA) investigated synthetic ovulation-inhibiting hormones in wastewater. He found significant levels of natural and synthetic hormones in WWTP effluent.

"Although a prediction of possible future danger from the accumulation of synthetic steroid compounds in treated wastewater is not possible at present," Tabak said in 1970, "it is certain that if treatment processes are not modified in the future to encourage high conversion rates of these compounds into safe end products, one might predict their accumulation in water courses."

Pinpointing the problem

European scientists recently detected clofibric acid, a drug used to lower blood cholesterol, in high concentrations in lakes and rivers in their countries. As early as 1976, clofibric acid and salicylic acid were discovered in wastewater effluents in the United States.

Pharmaceuticals discharged into U.S. natural waters are at low levels, generally a few parts per trillion (ppt) or less. The U.S. Food and Drug Administration (FDA) suggests that a drug or bioactivated metabolite enter the aquatic environment at levels no greater than 1 part per billion (ppb).

Reports of pharmaceuticals in natural U.S. waters are rare. There have been no reports of pharmaceuticals in drinking water.

But antibiotic-resistant bacteria strains have been detected in Michigan's Detroit River by R.C. Campeau of the University of Detroit Mercy. He believes the bacteria pose "a potential health risk." Similar strains have been reported in Asia and Europe. The problem is magnified by large concentrations of antibiotics used in raising livestock.

Endocrine disruption in the aquatic environment has brought the issue of pharmaceuticals in wastewater effluents to the forefront. Much of the current interest in endocrine disrupting chemicals in wastewater was generated by a finding in the United Kingdom that fish living in water influenced by wastewater effluents showed reproductive abnormalities. These abnormalities were seen infrequently in fish not exposed to wastewater.

In 1996, Hugh Bevans of the U.S. Geological Survey (USGS) in Carson City, Nevada, reported that feral carp captured in a bay of Nevada's Lake Mead, which received large amounts of treated wastewater, showed reproductive abnormalities. No cause has been established for these effects.

In spring 1997, the National Park Service and the Southern Nevada Water Authority (SNWA) contacted the Aquatic Toxicology Laboratory (ATL) at Michigan State University (MSU) regarding the USGS report of endocrine disruption in feral carp. At the time, MSU researchers were developing the Toxicity Identification and Evaluation (TIE) method to screen for estrogenic and anti-estrogenic compounds in effluents and rivers in Michigan.

The method involved extracting 5.3 qt. (5 L) of water *in situ* using solid-phase extraction (SPE) disks. The chemicals trapped on the disks were eluted in the laboratory and the resulting extract was fractionated and tested using analytical techniques.

Michigan State University researchers used this equipment to take samples of waste water effluents.

LAS VEGAS SUN

MONDAY, OCTOBER 16, 2000

Traces of drugs found in LV Wash

Effects on area's water supply unknown

By Mary Manning
LAS VEGAS SUN

Pill-popping, sun screen-smearing people living in and visiting Southern Nevada are leaving traces of drugs, detergents and DDT in the Las Vegas Wash.

The good news is that the contaminant levels discovered in the wash and the Las Vegas Bay are so low they might not disrupt human health. But scientists are still concerned over what they don't know about the new discovery — how it might affect the environment and water supplies.

The Las Vegas Wash runs into Lake Mead, where Southern Nevada draws most of its drinking water.

Scientists had found pesticides and detergents in the wash before, but this is the first time the presence of prescription and nonprescription drugs — as well as one pesticide previously only suspected, lindane — has been confirmed.

The Southern Nevada Water Authority first guessed drugs may be finding their way into the Las Vegas Valley's wastewater after German and British studies found evidence of prescription and over-the-counter drugs in the water supplies of their countries.

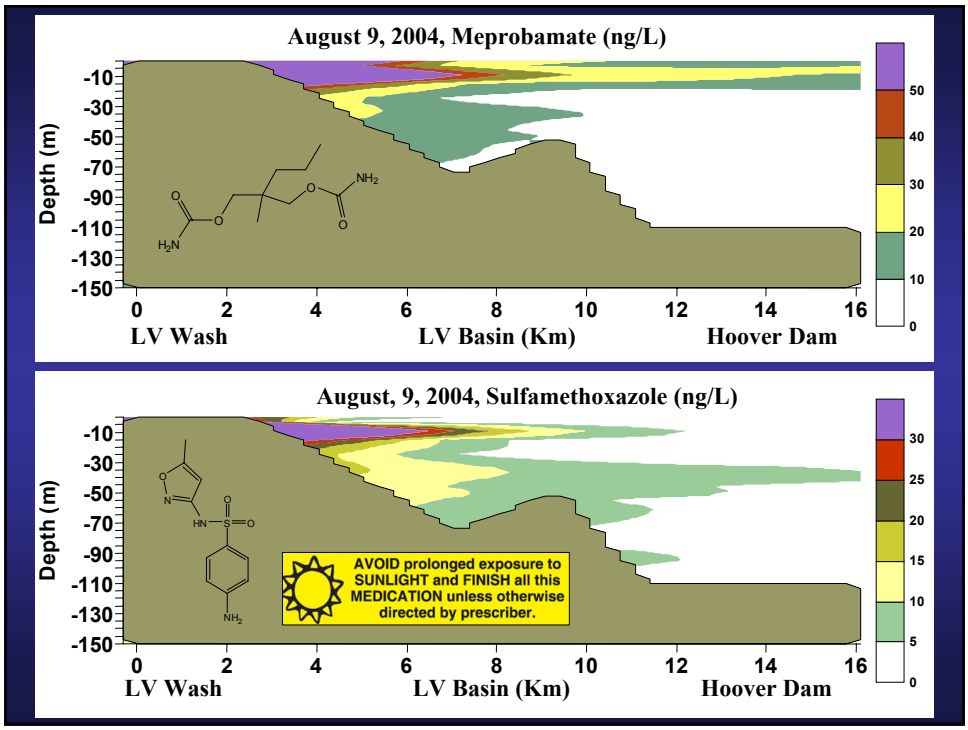
But now research by University of Michigan toxicologist Shane Snyder, hired by the water authority to test

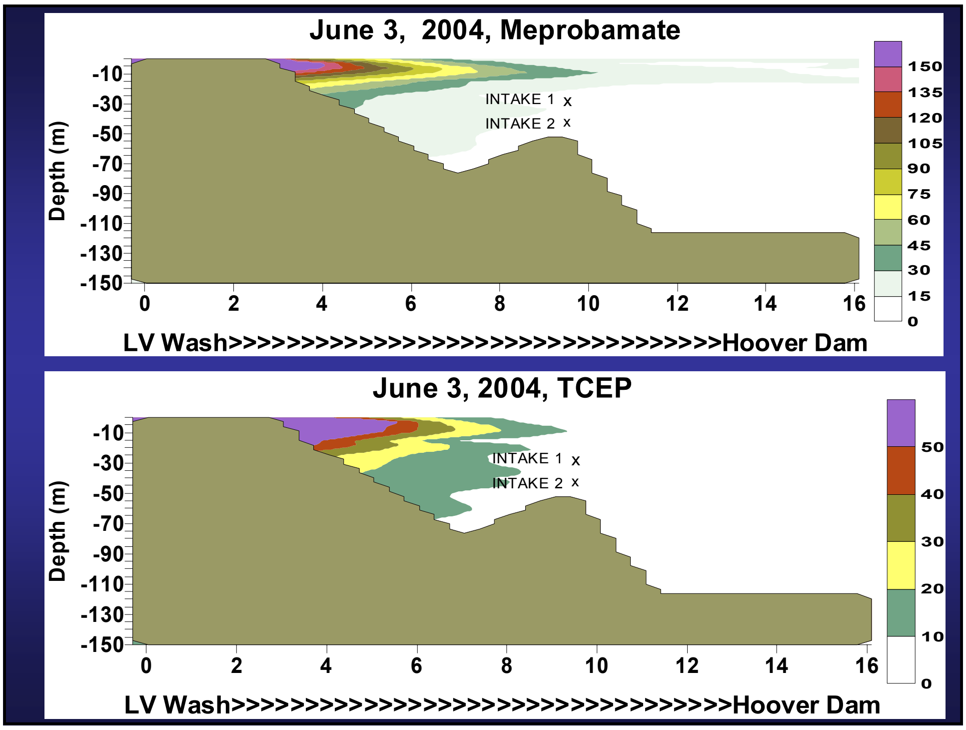
See Drugs, 4A

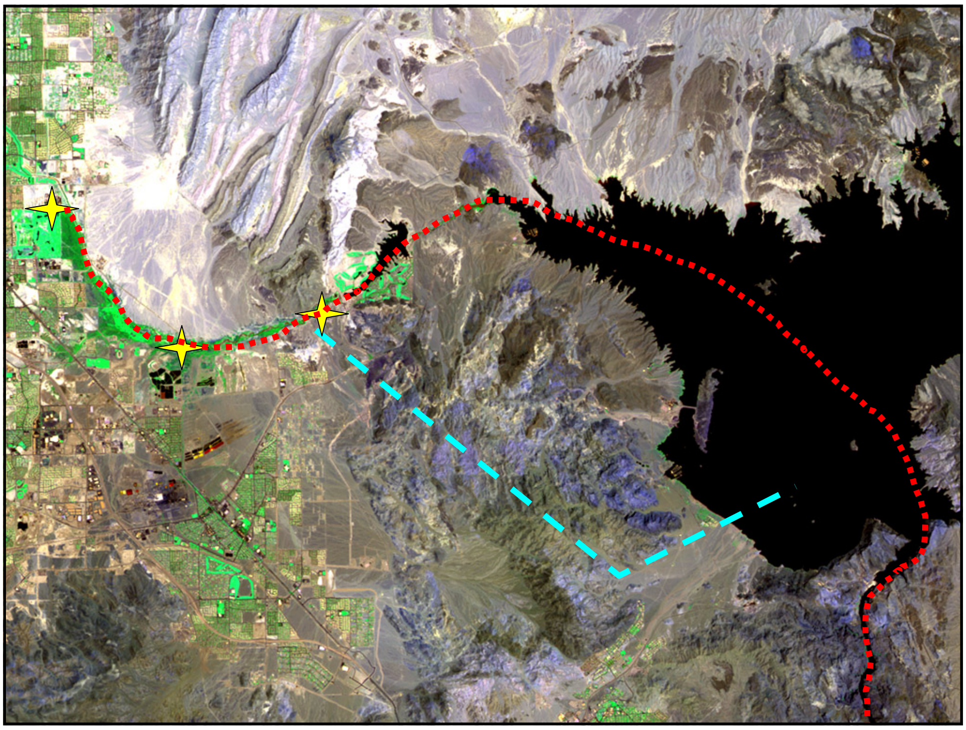
CONTAMINANTS

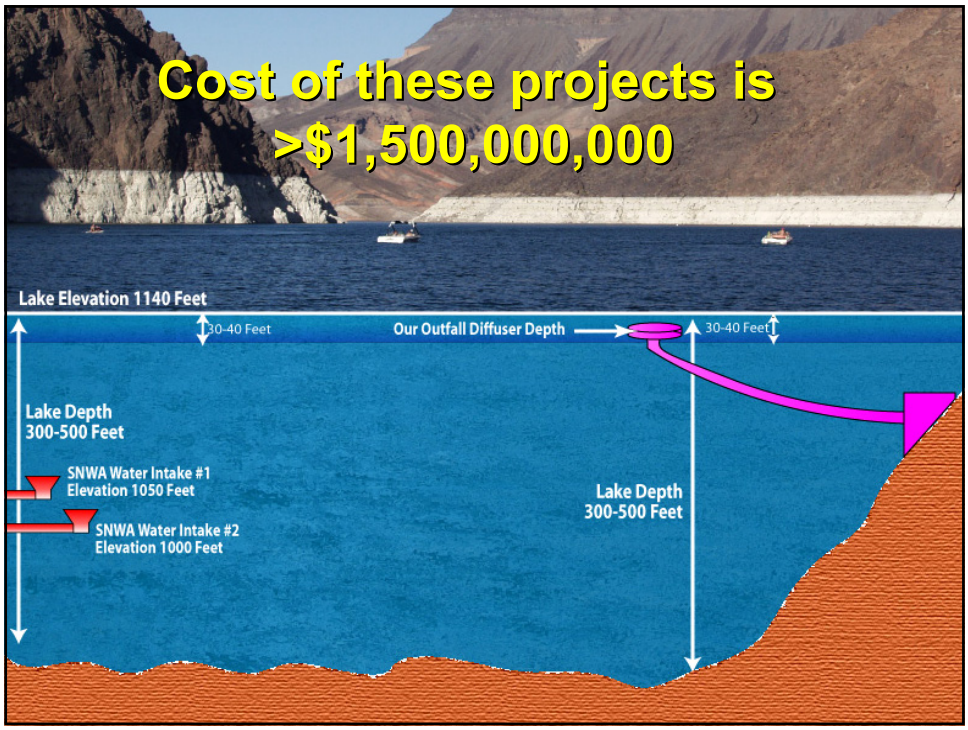
Toxicology studies of the Las Vegas Wash and the Las Vegas Bay have revealed traces of:

- Pesticides such as DDT and lindane
- Boat fuel compounds
- Oral contraceptives
- Seizure drugs such as Dilantin
- Pain medication such as hydrocodone and codeine
- Valium
- Robitussin
- Blood thinner such as Trental


August 9, 2004, Meprobamate (ng/L)
Depth (m)
-10
-30
-50
-70
-90
-110
-130
-150
0
2
4
6
8
10
12
14
16
LV Wash
LV Basin (Km)
Hoover Dam
50
40
30
20
10
0
August, 9, 2004, Sulfamethoxazole (ng/L)
Depth (m)
-10
-30
-50
-70
-90
-110
-130
-150
0
2
4
6
8
10
12
14
16
LV Wash
LV Basin (Km)
Hoover Dam
30
25
20
15
10
5
0
AVOID prolonged exposure to SUNLIGHT and FINISH all this MEDICATION unless otherwise directed by prescriber.


June 3, 2004, Meprobamate
Depth (m)
-10
-30
-50
-70
-90
-110
-130
-150
0
2
4
6
8
10
12
14
16
LV Wash>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>Hoover Dam
INTAKE 1 x
INTAKE 2 x
150
135
120
105
90
75
60
45
30
15
0
June 3, 2004, TCEP
Depth (m)
-10
-30
-50
-70
-90
-110
-130
-150
0
2
4
6
8
10
12
14
16
LV Wash>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>>Hoover Dam
INTAKE 1 x
INTAKE 2 x
50
40
30
20
10
0

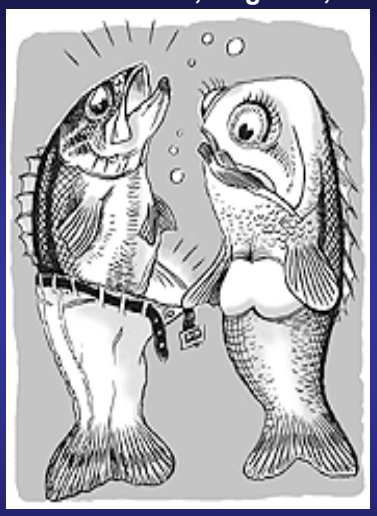




On Tap Winter 2003

"They're in the Water... They Make Fish Change Sex...
Endocrine Disruptors-What are they doing to you?"

Phoenix New Times, August 9, 2001



"Nevada's wastewater is causing sex problems in fish.
But will Arizona get screwed by the solution?"

The US Fish & Wildlife Service is requesting a flow-through fish exposure study to compare our current wastewater to wastewater after advanced treatment processes (i.e., membranes, ozone, UV-AOP)

EDCs and Pharmaceuticals Pose Major Threats to Water Sustainability!

Treatment Processes (>60 EDCs/PPCPs) AwwaRF #2758

Awwa Research Foundation
Advancing the Science of Water®

Treatment Processes

- Coagulation and Softening
- Activated Carbon (GAC and PAC)
- Membranes (UF, NF, RO, MBR, e-dialysis)
- Magnetic Ion-Exchange (MIEX)
- Biological Processes
  - Biologically active filtration (carbon and anthracite)
  - River Bank Filtration
  - MBR
  - ASR/SAT
- Chlorination (ambient and pH 5.5)
- Ozonation (and AOP with peroxide)
- UV (and AOP with peroxide)

Anal. Chem. **2003,** *75,* 6265–6274

Analysis of Endocrine Disruptors, Pharmaceuticals, and Personal Care Products in Water Using Liquid Chromatography/Tandem Mass Spectrometry

Brett J. Vanderford,* Rebecca A. Pearson, David J. Rexing, and Shane A. Snyder

Southern Nevada Water Authority, 243 Lakeshore Road, Boulder City, Nevada 89005

Environ. Sci. Technol. **2006,** *40,* 7312–7320

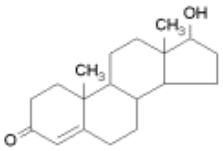
Analysis of Pharmaceuticals in Water by Isotope Dilution Liquid Chromatography/Tandem Mass Spectrometry†

BRETT J. VANDERFORD* AND SHANE A. SNYDER

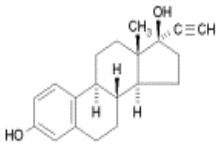
Southern Nevada Water Authority, 1350 Richard Bunker Avenue, Henderson, Nevada 89015

pensate for matrix effects by using different calibration techniques, including standard addition (*13, 17, 22*), surrogate monitoring (*15, 20*), and various forms of internal calibration (*14–16, 19, 23*). Still more have been developed to minimize matrix effects using different extraction, cleanup and elution techniques, including size-exclusion chromatography (*18, 24*), solid-phase extraction (*22*), LC chromatographic procedures (*14, 22*), ultra performance liquid chromatography (*25*), hollow fiber liquid-phase microextraction (*26*), flow-splitting and reduced eluent flow rates (*24, 27*). However, most become problematic when applied to the simultaneous analysis of a broad range of compounds that encompass many different classes and structures in matrices having varying degrees of suppression and enhancement.

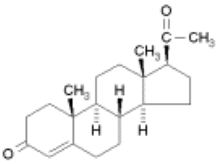
Steroids



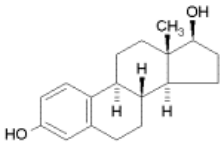
Testosterone



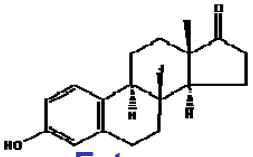
Ethinyl estradiol



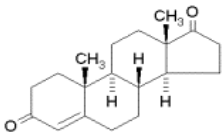
Progesterone



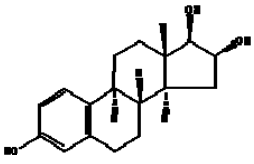
17β Estradiol



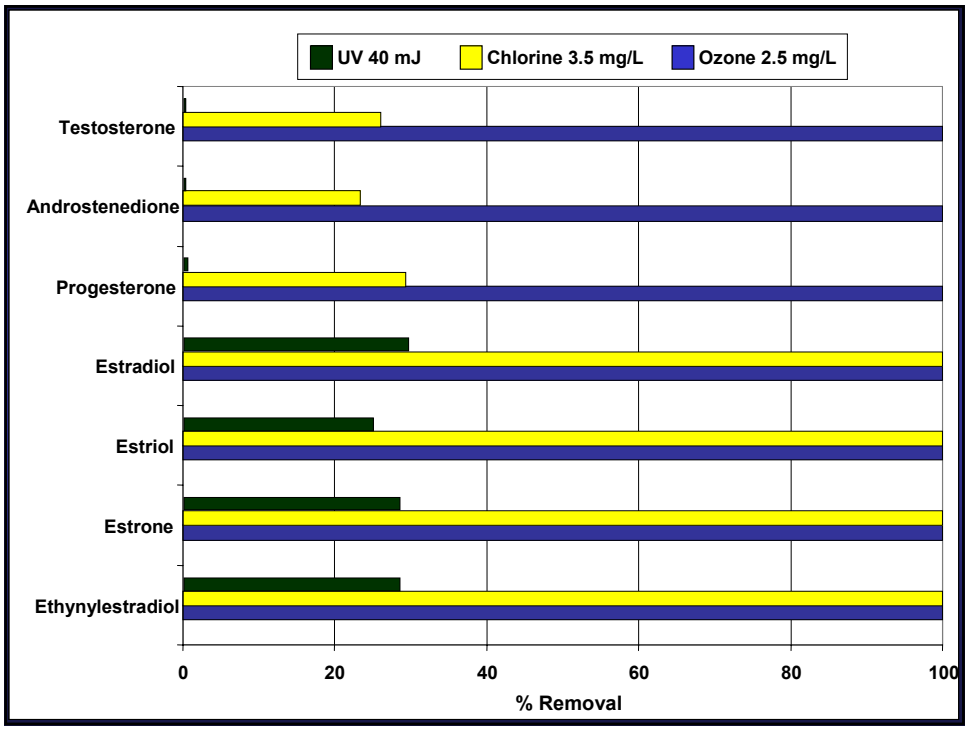
Estrone

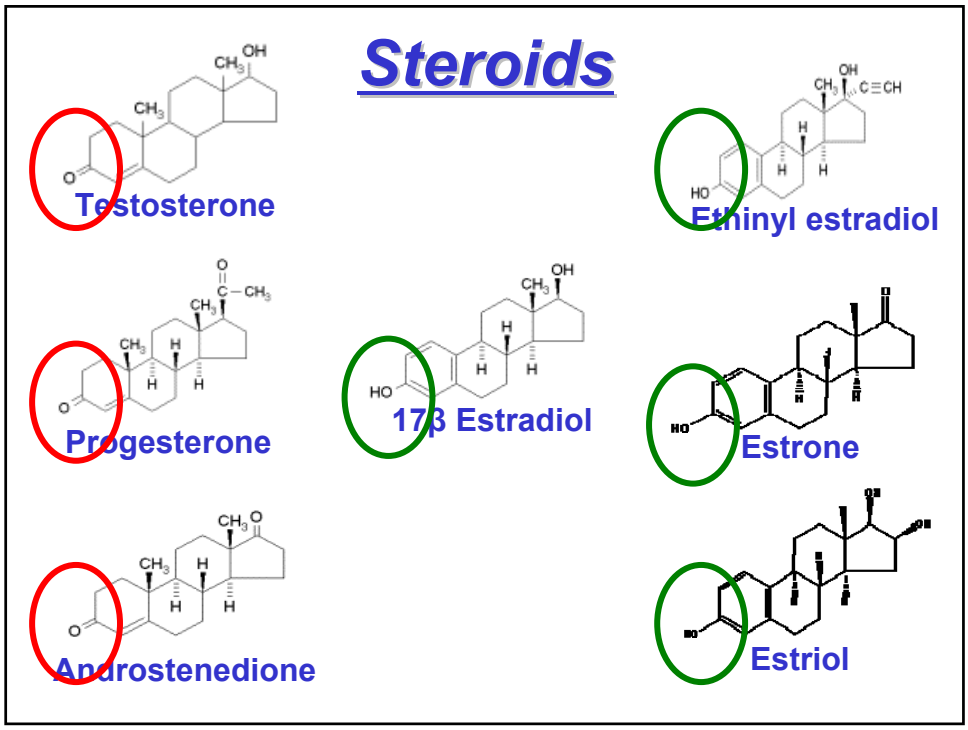


Androstenedione

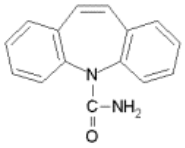


Estriol

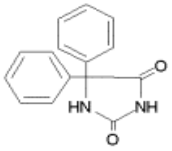

UV 40 mJ
Chlorine 3.5 mg/L
Ozone 2.5 mg/L
Testosterone
Androstenedione
Progesterone
Estradiol
Estriol
Estrone
Ethynylestradiol
0
20
40
60
80
100
% Removal


Steroids
Testosterone
Ethinyl estradiol
Progesterone
17β Estradiol
Estrone
Androstenedione
Estriol

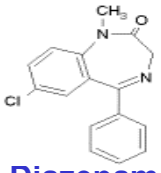
Psychoactive



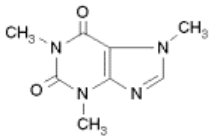
Carbamazepine



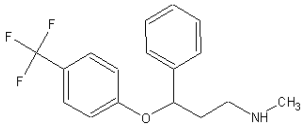
Dilantin



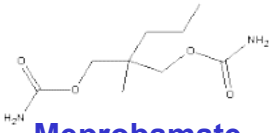
Diazepam



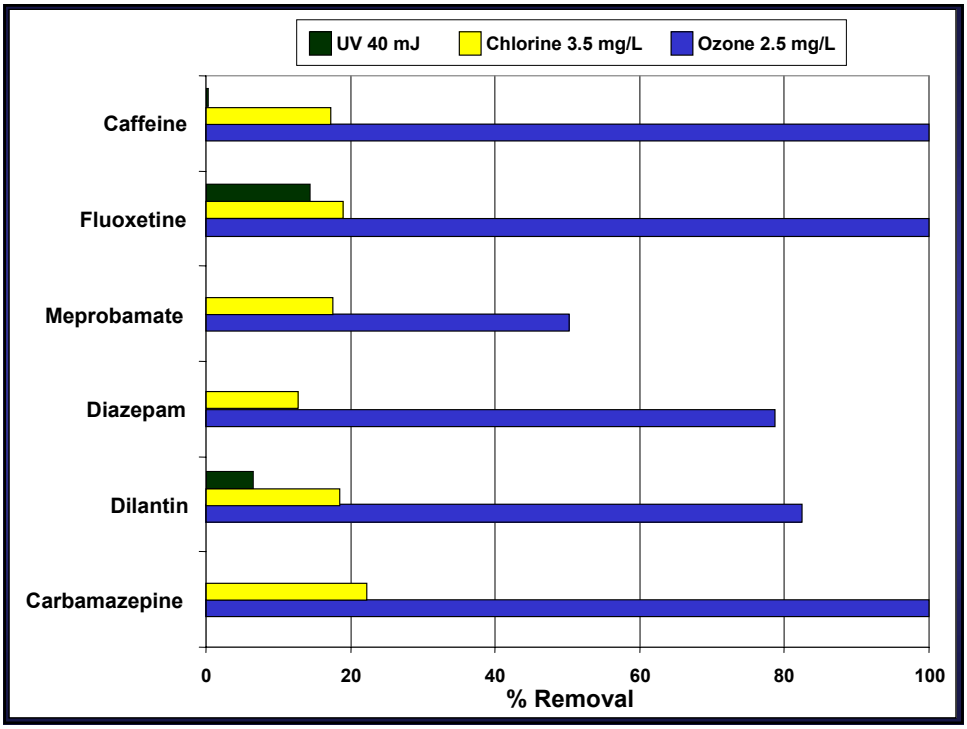
Caffeine



Fluoxetine



Meprobamate



<30% Removal	30-70% Removal	>70% Removal
Testosterone	Sulfamethoxazole	
Progesterone	Triclosan	
Androstenedione	Diclofenac	
Estriol	Acetaminophen	
Ethynylestradiol		
Estrone		
Estradiol		
Erythromycin-H_2O		
Trimethoprim		
Naproxen		
Hydrocodone		
Ibuprofen		
Caffeine		
Fluoxetine		
Meprobamate		
Diazepam		
Dilantin		
Carbamazepine		
DEET		
Atrazine		
Galaxolide		
TCEP		
Iopromide		
Pentoxifylline		
Metolachlor		
Gemfibrozil		
Musk Ketone		

UV 40mJ/cm^2

Chlorine 3.5 mg/L 24 hr

<30% Removal	30-70% Removal	>70% Removal
Testosterone	Ibuprofen	Estriol
Progesterone	Metolachlor	Ethynylestradiol
Androstenedione	Gemfibrozil	Estrone
Caffeine		Estradiol
Fluoxetine		Erythromycin-H_2O
Meprobamate		Sulfamethoxazole
Diazepam		Triclosan
Dilantin		Trimethoprim
Carbamazepine		Naproxen
DEET		Diclofenac
Atrazine		Hydrocodone
Galaxolide		Acetaminophen
TCEP		Musk Ketone
Iopromide		
Pentoxifylline		

<30% Removal	30-70% Removal	>70% Removal
Musk Ketone	Meprobamate	Testosterone
TCEP	Atrazine	Progesterone
	Iopromide	Androstenedione
		Estriol
		Ethynylestradiol
		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

Environ. Sci. Technol. **2005**, *39*, 6649–6663

Fate of Endocrine-Disruptor, Pharmaceutical, and Personal Care Product Chemicals during Simulated Drinking Water Treatment Processes

PAUL WESTERHOFF,*,† YEOMIN YOON,‡ SHANE SNYDER,§ AND ERIC WERT§

three general groups: (1) compounds easily oxidized (>80% reacted) by chlorine are always oxidized at least as efficiently by ozone; (2) 6 of the ~60 compounds (TCEP, BHC, chlordane, dieldrin, heptachlor epoxide, musk ketone) were poorly oxidized (<20% reacted) by chlorine or ozone; (3) compounds (24 of 60) reacting preferentially (higher removals) with ozone rather than chlorine. Conventional treatment (coagulation plus chlorination) would have low removal of many EDC/PPCPs, while addition of PAC and/or ozone could substantially improve their removals. Existing strategies that predict relative removals

Ozone: Science and Engineering, 28: 445–460

ISSN: 0191-9512 print / 1547-6545 online
DOI: 10.1080/01919510601039726

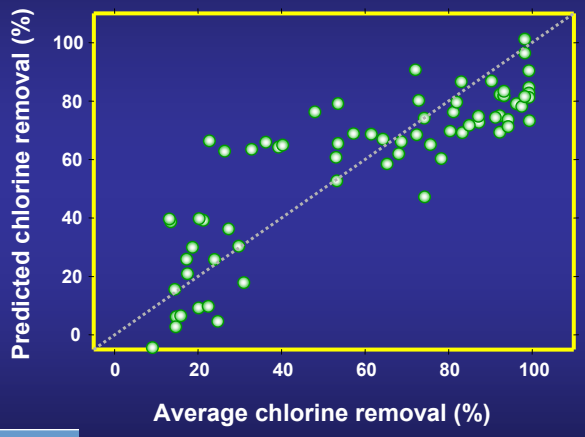
Taylor & Francis
Taylor & Francis Group

Ozone Oxidation of Endocrine Disruptors and Pharmaceuticals in Surface Water and Wastewater

Shane A. Snyder,[1] Eric C. Wert,[1] David J. Rexing,[1] Ronald E. Zegers,[1] and Douglas D. Drury[2]

[1]Southern Nevada Water Authority, Henderson, Nevada, USA
[2]Clark County Water Reclamation District, Las Vegas, Nevada, USA

Chlorine Model QSAR

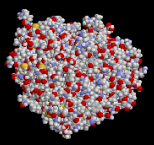


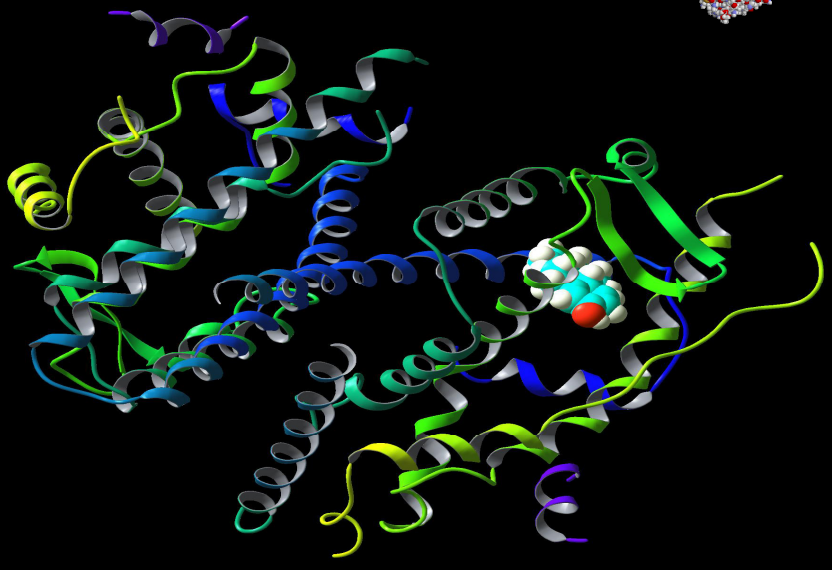
WERF
Water Environment Research Foundation

Project 03-CTS-21UR "*Household Chemical Fate*"

Glide

– Estradiol dock with 1GWR





Wastewater Ozonation

WATEREUSE FOUNDATION

Projects 04-007 & 06-012 "*Advanced Oxidation*"

Las Vegas WWTP Ave Conc.

Target Compound	Jun-05 ng L^{-1}	Jan-06 ng L^{-1}	Jan-06 ng L^{-1}	Target Compound	Jun-05 ng L^{-1}	Jan-06 ng L^{-1}	Jan-06 ng L^{-1}
Androstenedione	<1	1.6	2.4	Ibuprofen	19	5.6	15
Caffeine	51	21	31	Iopromide	22	139	45
Carbamazepine	210	139	139	Meprobamate	332	796	737
DEET	188	133	123	Musk Ketone	133	NM	NM
Diclofenac	54	73	71	Naproxen	13	25	71
Dilantin	154	143	110	Oxybenzone	6	<1	3.0
Erythromycin	133	162	149	Sulfamethoxazole	841	669	695
Estriol	<5	5.7	<5	TCEP	373	235	187
Estrone	<1	5.4	20	Testosterone	<1	1.8	<1
Fluoxetine	<1	14	11	Triclosan	<10	35	58
Galaxolide	1170	NM	NM	Trimethoprim	35	191	229
Gemfibrozil	<1	16	567				
Hydrocodone	240	199	161	EEq*	0.63	1.00	3.17

Las Vegas WWTP:

shade = <MRL @ 3 mg/L O_3

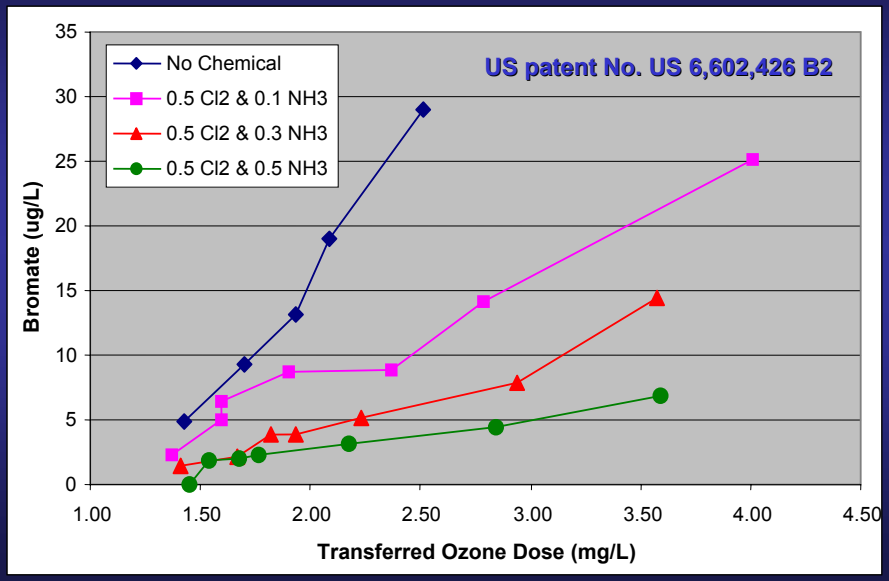
Target Compound	Jun-05 ng L^{-1}	Jan-06 ng L^{-1}	Jan-06 ng L^{-1}
Androstenedione	<1	1.6	2.4
Caffeine	51	21	31
Carbamazepine	210	139	139
DEET	188	133	123
Diclofenac	54	73	71
Dilantin	154	143	110
Erythromycin	133	162	149
Estriol	<5	5.7	<5
Estrone	<1	5.4	20
Fluoxetine	<1	14	11
Galaxolide	1170	NM	NM
Gemfibrozil	<1	16	567
Hydrocodone	240	199	161

Target Compound	Jun-05 ng L^{-1}	Jan-06 ng L^{-1}	Jan-06 ng L^{-1}
Ibuprofen	19	5.6	15
Iopromide	22	139	45
Meprobamate	332	796	737
Musk Ketone	133	NM	NM
Naproxen	13	25	71
Oxybenzone	6	<1	3.0
Sulfamethoxazole	841	669	695
TCEP	373	235	187
Testosterone	<1	1.8	<1
Triclosan	<10	35	58
Trimethoprim	35	191	229
EEq*	0.63	1.00	3.17

Before Ozonation

After Ozonation

Bromate Formation/Mitigation



Environ. Sci. Technol. **2005**, *39*, 4586–4593

Trace Analysis of Bromate, Chlorate, Iodate, and Perchlorate in Natural and Bottled Waters

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are the perchlorate and bromate anions, which have become focal issues for regulatory agencies. The U.S. EPA originally published a reference dose for perchlorate, which would suggest a drinking water equivalent level of approximately 1 μg/L (*1*). More recently, the National Academy of Sciences and the U.S. EPA have suggested reference doses with a drinking water equivalent level of 24.5 μg/L (*2*, *3*). However, the state of Massachusetts requires public notification of drinking water containing perchlorate at 1 μg/L or greater (*4*), while California has established a public health goal of 6.0 μg/L (*5*). Bromate, a disinfection byproduct, is currently regulated in U.S. drinking waters with a maximum contaminant limit (MCL) of 10 μg/L in drinking water (*6*). Chlorate and iodate are not currently regulated in drinking water;

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Toxicology 221 (2006) 229–234
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Analysis of bromate and bromide in blood

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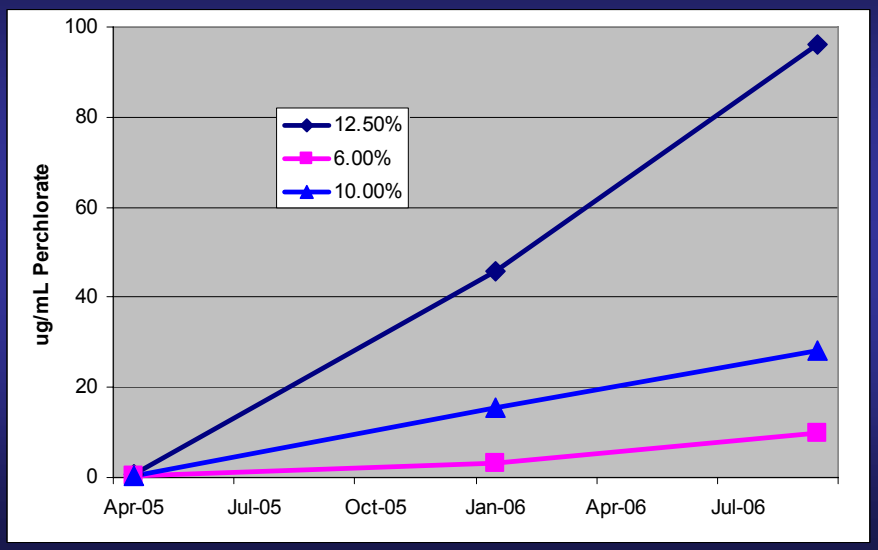
Received 15 November 2005; received in revised form 5 January 2006; accepted 12 January 2006
Available online 14 February 2006

Perchlorate in Commercial Bleach – Sodium Hypochlorite



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DESALINATION

Desalination 202 (2006) 156–181

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Role of membranes and activated carbon in the removal of endocrine disruptors and pharmaceuticals

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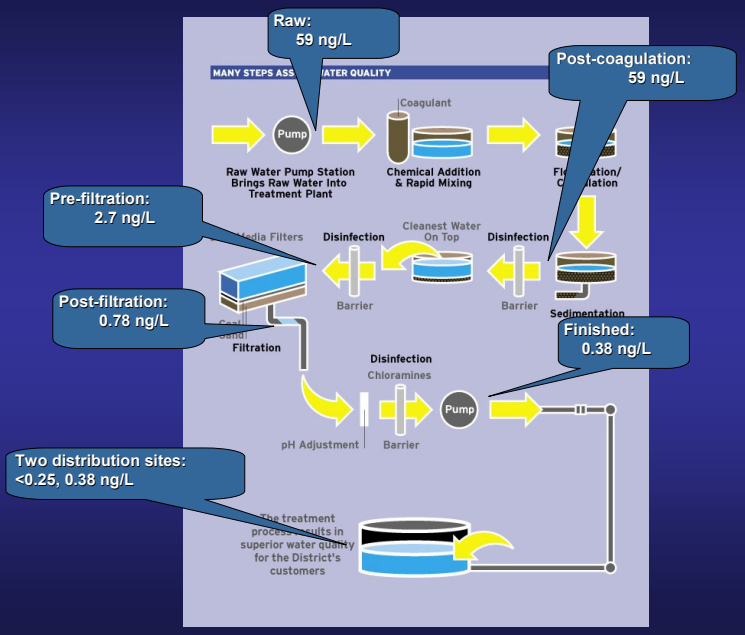
Received 31 July 2005; accepted 23 December 2005

Toxicological Relevance
AwwaRF #3085 & WRF 04-003

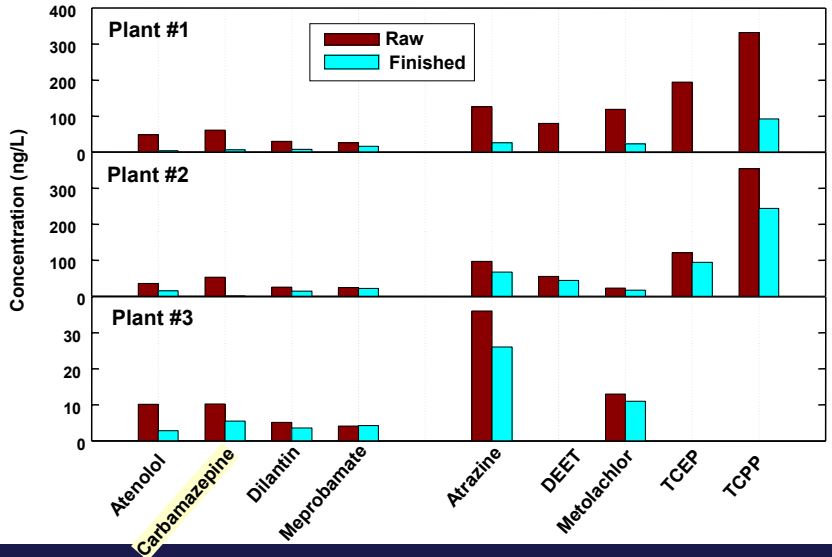
Emerging Contaminants in US Drinking Waters (n=20)

Compound	Hits	% Freq	Min (ng/L)	Max (ng/L)	Median (ng/L)	Ave (ng/L)
DEET	18	90	2.1	30	5.1	8.2
Atrazine	15	75	1.4	430	29	74
Meprobamate	15	75	1.6	13	3.8	6.1
Dilantin	14	70	1.1	6.7	2.3	2.7
Ibuprofen	13	65	1	32	3.8	7.9
Iopromide	13	65	1.1	31	6.5	8.5
Caffeine	12	60	2.6	83	23	25
Carbamazepine	11	55	1.1	5.7	2.8	2.8
TCEP	7	35	3	19	5.5	10.1
Gemfibrozil	5	25	1.3	6.5	4.2	3.9
Metalochlor	4	20	14	160	86	86
Estrone	2	10	1.1	2.3	1.7	1.7
Progesterone	2	10	1.1	1.1	1.1	1.1
Erythromycin	1	5	1.3	1.3	1.3	1.3
Musk Ketone	1	5	17	17	17	17
Naproxen	1	5	8	8	8	8.0
Sulfamethoxazole	1	5	20	20	20	20
Triclosan	1	5	43	43	43	43
Trimethoprim	1	5	1.3	1.3	1.3	1.3

Sulfamethoxazole – Chlorine/Chloramine



Three Example US Drinking Water Facilities



Relevance to Human Health

Drug	Effect Dose (mg/kg-d)	Effect	Human Equiv. Dose (mg/kg-d)	UF	RfD (mg/kg-d)	DWEL (ppb)
Atenolol	0.8 (LOAEL)	Developmental, human	0.8	300	0.0027	81
Atorvastatin	20 (LOAEL)	Developmental, rat	3.2	1,000	0.0032	96
Carbamazepine	200 (LOAEL)	Developmental, rat	32	3,000	0.011	330
Diazepam	1 (LOAEL)	Developmental, rat	0.16	1,000	0.00016	5
Diclofenac	4 (NOAEL)	Reproductive, rat	0.65	300	0.0022	66
Enalapril	0.3 (LOAEL)	Developmental, baboon	0.3	300	0.001	30
Fluoxetine	7.5 (LOAEL)	Developmental, rat	1.2	1,000	0.0012	36
Gemfibrozil	92 (NOAEL)	Reproductive, rat	15	1,000	0.015	450
Meprobamate	No data	No data	---	---	---	No data
Naproxen	20 (NOAEL)	Developmental, rat	3.2	300	0.011	330
Phenytoin	17.5 (NOAEL)	Developmental, mouse	1.4	1,000	0.08	2,400
Risperidone	0.16 (LOAEL)	Reproductive, rat	0.026	1,000	0.000026	0.8
Simvastatin	10 (NOAEL)	Developmental, rabbit	3.2	300	0.011	330
Sulfamethoxazole	250 (NOAEL)	Reproductive, rat	40	300	0.13	3,900
Triclosan	3 (NOAEL)	Systemic, rabbit	0.97	1,000	0.00097	29
Trimethoprim	70 (NOAEL)	Reproductive, rat	11	300	0.037	1,100

Intentional vs. Unintentional

	Drinking Water (ng/L)			Reuse Water (ng/L)		
Sulfamethoxazole	<0.25	<0.25	0.38	<0.25	<0.25	<0.25
Atenolol	20	0.42	0.35	1.7	2.6	2.1
Trimethoprim	<0.25	<0.25	<0.25	0.41	0.60	0.50
Meprobamate	12	24	35	0.58	<0.25	0.34
Dilantin	13	7.4	11	<1.0	<1.0	<1.0
Carbamazepine	8.2	10	9.9	<0.50	<0.50	<0.50
Atrazine	76	138	1080	<0.25	<0.25	<0.25
Linuron	8.1	<0.50	<0.50	<0.50	<0.50	<0.50
Gemfibrozil	0.48	0.51	0.33	0.62	<0.25	0.53

Soy Sauce vs. Wastewater Estrogenicity (EEq)

SOY SAUCE

Kikkoman	147
Tabasco	257
Kimlan	70
La Choy	14

WASTEWATER EFFLUENT

WWTP-1	4.6
WWTP-2	0.05
WWTP-3	0.61

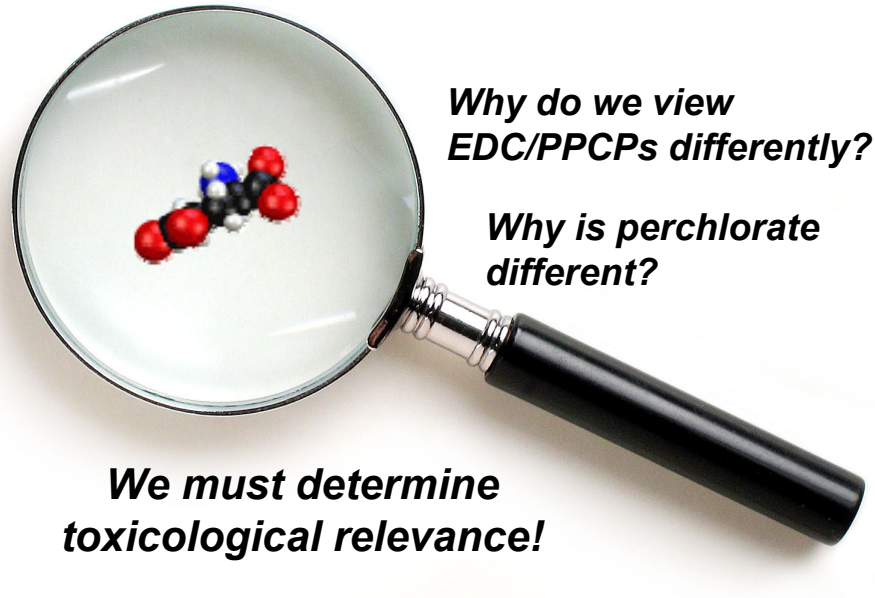
RAW WASTEWATER

WWTP-1	70
WWTP-2	41
WWTP-3	53

DRINKING WATER

Utility-1	<0.03
Utility-2	<0.03
Utility-3	0.07

What will we find at pg/L, fg/L, åg/L?



Why do we view EDC/PPCPs differently?

Why is perchlorate different?

We must determine toxicological relevance!

The public has difficulty with the concept of relative concentrations

- Instead, they apply the "present/absent" litmus test

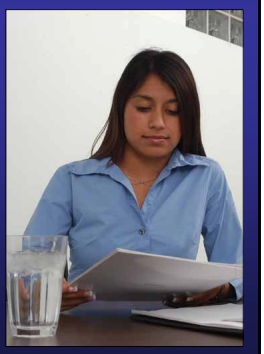
- Adverse health effects are presumed if present

Micrograms per liter ?

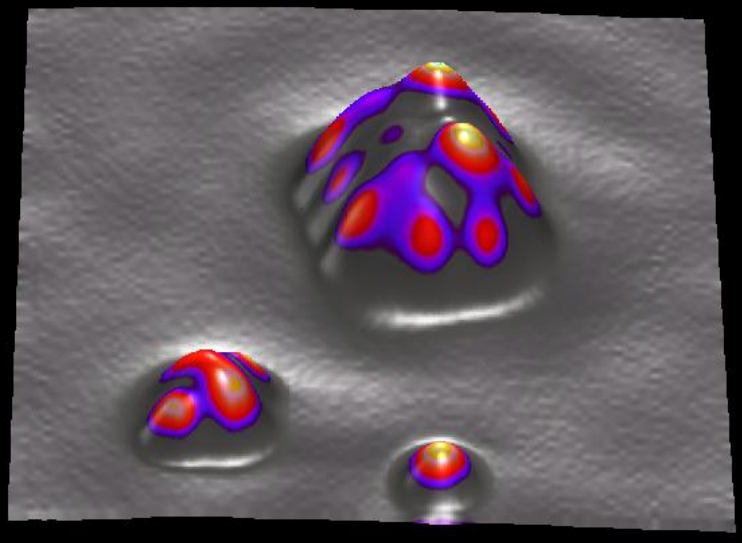
Nanograms per liter ?

Picograms per liter ?

Zeptograms per liter ?



How Low can We Go?



Sodium and Iodine Atoms on Copper

Conclusions

- **EDCs and Pharmaceuticals are ubiquitous**
- **Removal related to structure (and dose)**
  - Chlorine good for phenolics, less effective for ketones
  - Ozone more effective than chlorine
  - UV ineffective at disinfection doses
    - Effective with high-energy UV & AOP using peroxide
- **Ozone eliminates *in vitro* estrogenicity**
- **Surface water under influence of conventional WWTPs will have more trace contaminants than IPR system**

Take Home Thoughts…

- Non-detect ≠ Safe
- Safe ≠ Non-detect
- Non-detect ≠ Zero
- Consider public perception
- Consider public dollars
  - The public will pay for monitoring programs
  - The public will pay for additional treatment
- There is NO silver bullet
  - Oxidation = Byproducts
  - Membranes = Brines
  - Activated Carbon = Disposal/Regeneration
  - ALL processes use energy = air quality issues

2007 – SNWA opened a new Laboratory & Applied R&D Center

Las Vegas will…

- Leaders in sustainability
- Model City for conservation
- Model City for research
- Explore cutting-edge conservation practices
- International destination "water tourism/science"
- Establish collaborations globally

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WATER RESEARCH

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Occurrence and removal of pharmaceuticals and endocrine disruptors in South Korean surface, drinking, and waste waters

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Perchlorate Assessment of the Nakdong and Yeongsan Watersheds, South Korea

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