

CEE 697z

Organic Compounds in Water and Wastewater

PPCPs: Key Examples & Sources

Lecture #17

For Background see:

<http://www.ecs.umass.edu/eve/background/chemicals/PPCPs/PPCP%20intro.html>

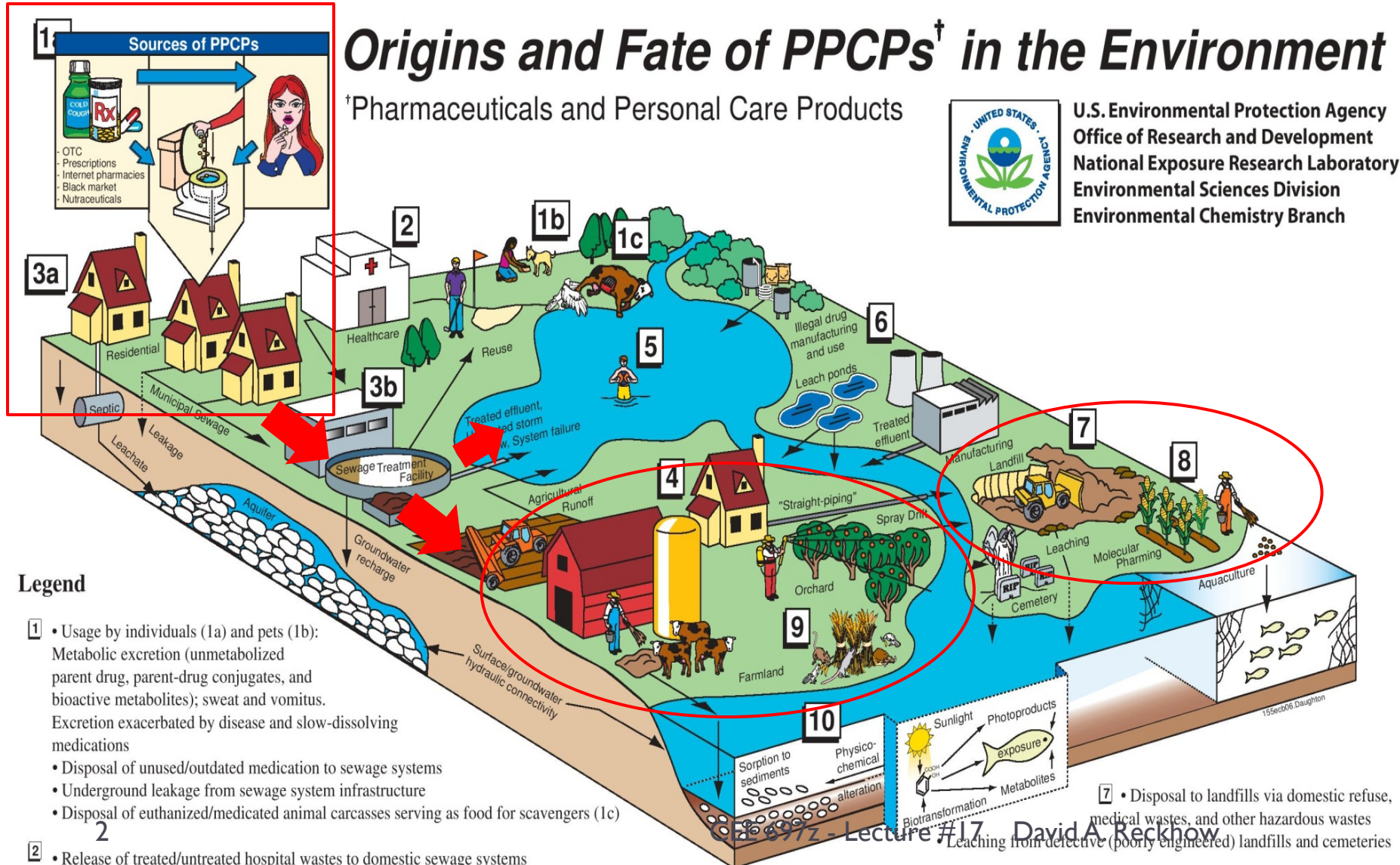
EDC/PPCP Sources

Origins and Fate of PPCPs[†] in the Environment

[†]Pharmaceuticals and Personal Care Products



U.S. Environmental Protection Agency
Office of Research and Development
National Exposure Research Laboratory
Environmental Sciences Division
Environmental Chemistry Branch

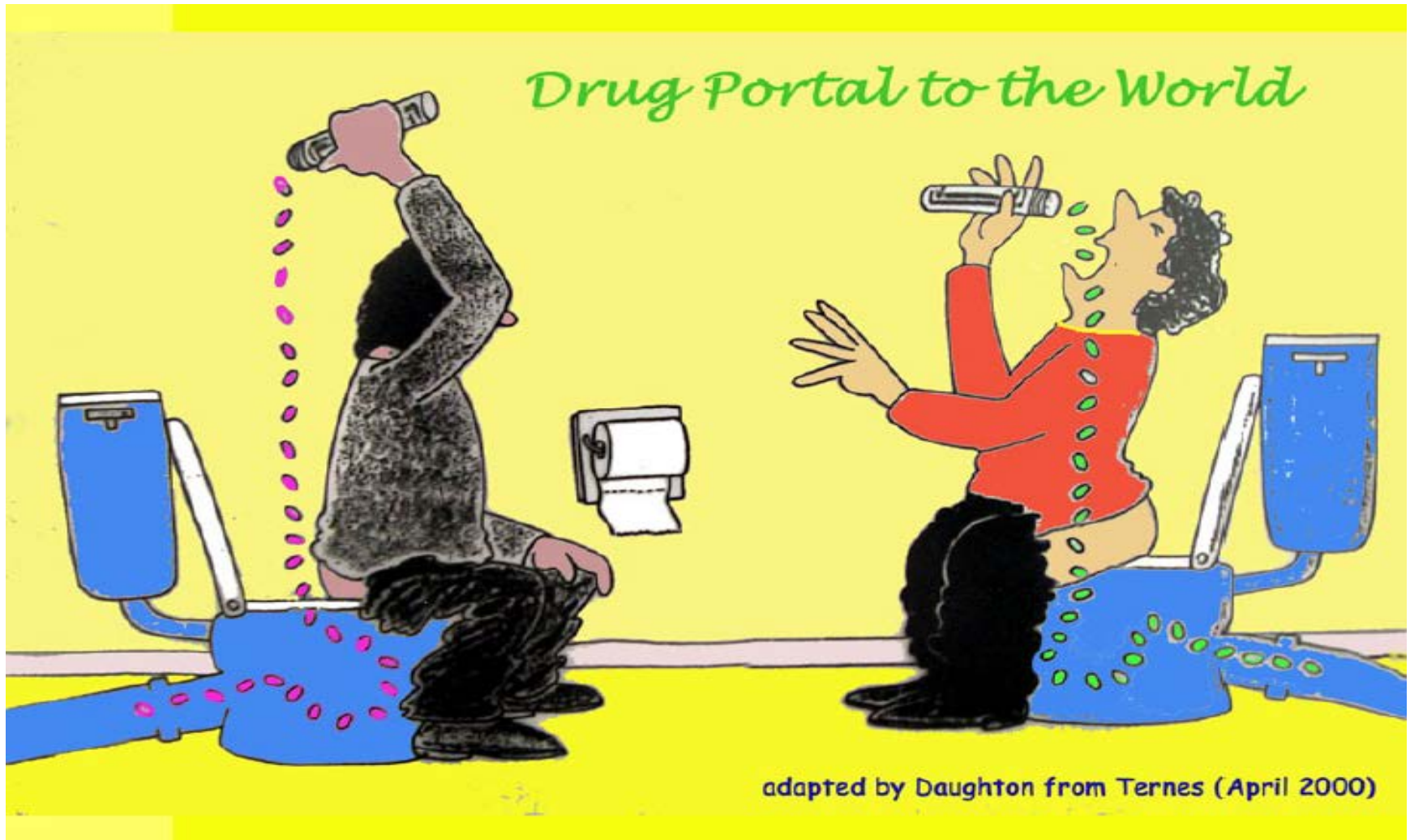


Urban Sources

- ▶ How do they get into the aquatic environment?
 - ▶ Credit: Time Magazine



Sources (2)



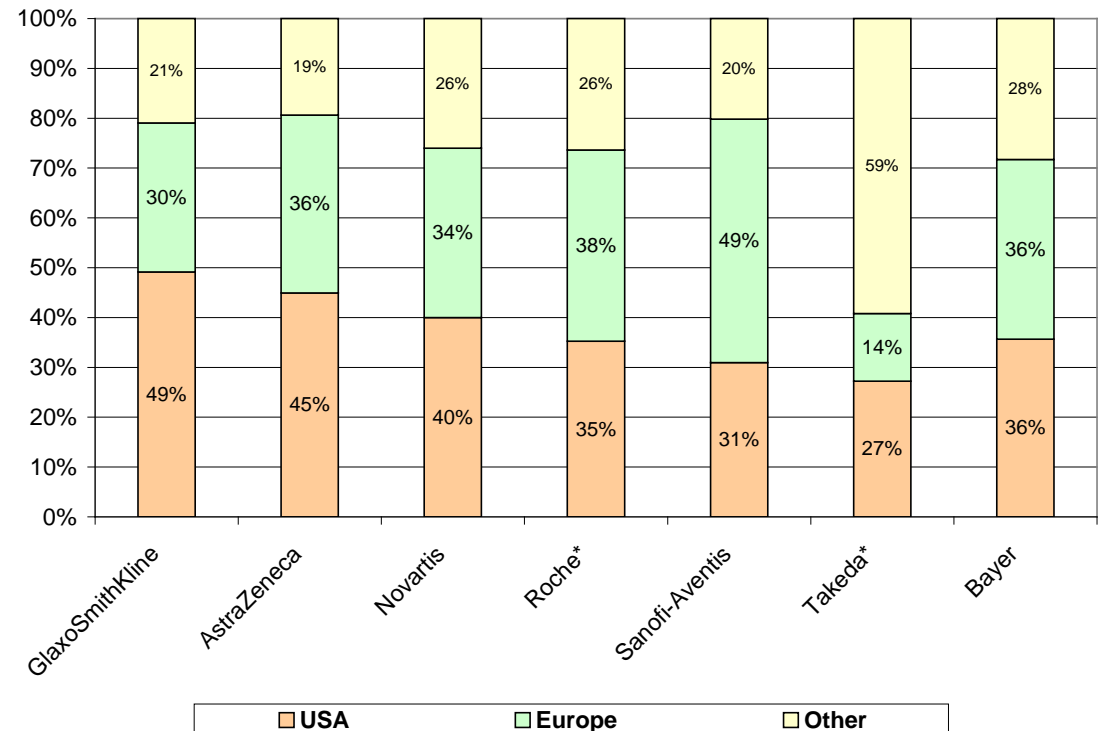
Major pharmaceutical companies

- ▶ From: **The Pharmaceutical industry in the Global Economy**
 - ▶ Summer 2005
 - ▶ Larry Davidson and Gennadiy Greblov

Company	HQ location	Revenue of pharmaceutical segment, mln USD	Total sales, mln USD	Share of pharmaceutical segment, %
Pfizer	NY, U.S.	46,133	52,516	87.85%
GlaxoSmithKline	UK	31,434	37,324	84.22%
Johnson & Johnson	NJ, U.S.	22,190	47,348	46.87%
Merck	NJ, U.S.	21,494	22,939	93.70%
AstraZeneca	UK	21,426	21,426	100.00%
Novartis	Switzerland	18,497	28,247	65.48%
Sanofi-Aventis	France	17,861	18,711	95.46%
Roche	Switzerland	17,460	25,168	69.37%
Bristol-Myers Squibb	NY, U.S.	15,482	19,380	79.89%
Wyeth	NJ, U.S.	13,964	17,358	80.45%
Abbott	IL, U.S.	13,600	19,680	69.11%
Eli Lilly	IN, U.S.	13,059	13,858	94.23%
Takeda	Japan	8,648	10,046	86.09%
Schering-Plough	NJ, U.S.	6,417	8,272	77.57%
Bayer	Germany	5,458	37,013	14.75%

Source: 2004 Annual Reports of the companies

Geographical distribution of sales, 2004



Top 5 pharmaceutical products based on the sales in 2004

GlaxoSmithKline	Sales, mln GBP	% of total sales	Sales, mln USD
Seretide / Advair	£2,461	12.1%	\$4,512
Avandia / Avandamet	£1,116	5.5%	\$2,046
Paxil	£1,063	5.2%	\$1,949
Zofran	£763	3.7%	\$1,399
Wellbutrin	£751	3.7%	\$1,377
AstraZeneca	Sales, mln USD	% of total sales	
Nexium	\$3,883	18.1%	
Seroquel	\$2,027	9.5%	
Losec / Prilosec	\$1,947	9.1%	
Seloken	\$1,387	6.5%	
Pulmicort	\$1,050	4.9%	
Novartis	Sales, mln USD	% of total sales	
Diovan / Co-Diovan	\$3,093	10.9%	
Gleevec/Glivec	\$1,634	5.8%	
Lamisil	\$1,162	4.1%	
Zometa	\$1,078	3.8%	
Neoral / Sandimmun	\$1,011	3.6%	

Roche	Sales, mln CHF	% of total sales	Sales, mln USD
MabThera / Rituxan	CHF 3,378	10.8%	\$2,719
NeoRecormon, Epogin	CHF 2,082	6.7%	\$1,676
Pegasys + Copegus	CHF 1,562	5.0%	\$1,257
Herceptin	CHF 1,435	4.6%	\$1,155
CellCept	CHF 1,403	4.5%	\$1,129
Sanofi-Aventis	Sales, mln EUR	% of total sales	Sales, mln USD
Lovenox	€1,904	12.7%	\$2,368
Plavix	€1,694	11.3%	\$2,107
Allegra	€1,502	10.0%	\$1,868
Taxotere	€1,436	9.5%	\$1,786
Stilnox	€1,423	9.5%	\$1,770
Bayer	Sales, mln EUR	% of total sales	Sales, mln USD
Ciprobay / Cipro	€837	2.8%	\$1,041
Adalat	€670	2.3%	\$833
Ascensia	€627	2.1%	\$780
Aspirin	€615	2.1%	\$765
Kogenate	€563	1.9%	\$700

Source: Financial reports of the companies

Sales are provided in the currency of financial reports; conversion of sales into USD was made for comparison purposes

Recent acquisitions by major non-US pharmaceutical companies

Company	Company acquired*	Core business of target	Purchase price
GlaxoSmithKline	Merger of Glaxo Wellcome and SmithKline Beecham	Megrer of two major pharmaceutical companies (registered in 2000)	-
	Block Drug	Oral care and over-the-counter medicines	843 mln GBP
AstraZeneca	Merger of Astra and Zeneca	Megrer of two major pharmaceutical companies (registered in 1999)	-
Novartis	Sabex	Generic manufacturer with a leading position in generic injectables	565 mln USD
	Mead Johnson's adult nutrition business	Global adult medical nutrition	385 mln USD
	Idenix Pharmaceuticals Inc	Biotechnology	255 mln USD + up to 357 mln USD in possible additional payments
Roche	Igen International	Human in-vitro diagnostics	1,823 mln CHF
	Disetronic	Insulin pumps and injection systems for the treatment of diabetes.	1,132 mln CHF
Sanofi-Aventis	Merger of Sanofi-Synthelabo and Aventis	Merger of two major pharmaceutical companies (registered in 2004)	-
Bayer	Roche's over-the-counter business	Over-the-counter medicines	206 mln EUR
	Gustafson	Seed treatment	100 mln EUR

Source: Annual Reports of the companies

*Acquisition of patents is not included in this table

Major areas of focus of non-US pharmaceutical companies

	GlaxoSmithKline	AstraZeneca	Novartis	Roche	Sanofi-Aventis	Takeda	Bayer
Anti-bacterial / anti-fungal / infections	X	X	X	X	X		X
Anti-inflammatory / anagletics	X	X		X			
Cardiovascular diseases	X	X	X	X	X	X	X
Dermatology	X		X	X			
Eye diseases			X				
Gastrointestinal	X	X	X			X	
Hematology			X				
Immunology			X				
Metabolic diseases	X		X	X	X		
Neurology / psychiatric disorders	X	X	X	X	X	X	
Oncology	X	X	X	X	X	X	X
Respiratory diseases	X	X	X		X		
Urogenital conditions	X		X		X	X	X
Virology (including HIV)	X			X			

Source: Annual Reports of the companies

Recent acquisitions by major U.S. pharmaceutical companies

	Company acquired*	Core business of target	Purchase price, bln. USD
Pfizer	Pharmacia	Prescription pharmaceutical products, consumer healthcare products and animal healthcare products	\$56.0
	Esperion Therapeutics	Biopharmaceutical company with no approved products	\$1.3
Johnson & Johnson	Guidant	Treatment of cardiac and vascular disease	\$25.4
	Consumer Pharmaceuticals	Non-prescription pharmaceutical products (former JV of J&J and Merck)	\$0.6
	Egea Biosciences	R&D in synthesis of DNA sequences, gene assembly and construction of large synthetic gene libraries	
	Biopharm SAS	Skin care products	
	Micomed	Spinal implants	
Merck	Aton Pharma	Development of novel treatments for cancer and other diseases	\$0.1
	Banyu Pharmaceutical	R&D, manufacturing and sales of drugs for cardiovascular diseases and antibiotics	\$1.5
Bristol-Myers Squibb	Acordis	Materials for Wound Therapies products	\$0.2
Eli Lilly	Applied Molecular Evolution	Treatment of non-Hodgkin's lymphoma and rheumatoid arthritis	\$0.4
Abbott	TheraSense	Advanced diabetes management technology	\$2.3
	i-Stat	Diagnostic testing	
	Spine Next SA	Spine-care business	

Source: Annual Reports of the companies

*Acquisitions of patents only is not included in this table

Major area of focus of U.S. pharmaceutical companies

	Pfizer	J&J	Merck	BMS	Wyeth	Lilly	Abbott	Schering-Plough
Allergies	X							X
Anti-bacterial / anti-fungal / infections	X	X	X	X	X	X	X	X
Anti-inflammatory / analgesics	X	X	X		X		X	X
Cardiovascular diseases	X	X	X	X	X	X		X
Dermatology		X						
Endocrine disorders	X					X		
Eye diseases	X		X					
Gastrointestinal		X			X			
Hematology		X						
Immunology		X	X		X		X	
Metabolic diseases	X		X	X			X	
Neurology / psychiatric disorders	X	X		X	X	X	X	X
Oncology	X	X	X	X	X	X	X	X
Respiratory diseases	X		X					X
Urogenital conditions	X	X	X					
Virology (including HIV)			X	X	X			

Source: Annual Reports of the companies

Getting rid of unused drugs

- ▶ Which is best?



Landfill Liners

- ▶ Modern composite liner systems
 - ▶ 2 feet clay & 60 mil HDPE liner
 - ▶ includes leachate collection & disposal
- ▶ Expectation: >99.9% of leachate captured
 - ▶ to WWTP?
- ▶ <0.1% lost to groundwater via holes in liner system



Current Regulations

▶ **State of California**

- ▶ California Department of Public Health(CDPH) developed criteria for use of **reclaimed municipal wastewater** to recharge **groundwater basins** that are **sources of drinking water** supply.
- ▶ Uses **TOC limits** as means of ensuring lowest possible concentrations of unregulated WW-derived organic contaminants.
- ▶ Additional monitoring of **38 organic contaminants**.

Source: CDPH 2003;CDPH 2007; Drewes et al 2008

EDCs and PPCPs

- ▶ Why study these?
 - ▶ Direct impacts on human health
 - ▶ Maybe not the most important?
 - ▶ Public perception
 - ▶ Becoming a very sensitive issue
 - ▶ Direct impacts on ecological health
 - ▶ Well documented: feminization of fish, etc.
 - ▶ Tracers of wastewater contamination
 - ▶ Indicators & promoters of antibiotic resistance
 - ▶ Precursors to more Hazardous DBPs

WW Tracers

- ▶ **WW contributions: Near conservative PPCP tracers**
 - ▶ Primidone
 - ▶ Others? Carbamazepine, caffeine, etc.
- ▶ **Raw vs Treated: Chiral PPCPs**
 - ▶ Racemic mixtures that undergo enantioselective biodegradation
 - ▶ Analysis of enantiomeric fractions may permit discrimination between raw and treated WW contributions
 - ▶ Propranolol example: Fono & Sedlak, 2005 [ES&T]

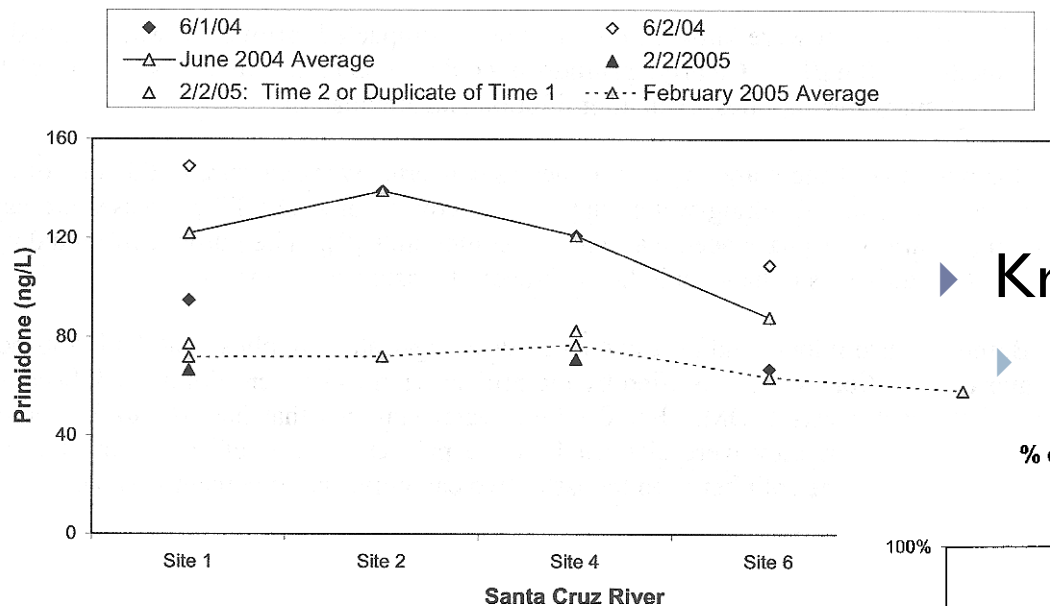
Antibiotic Resistance

- ▶ One of the most critical human health challenges of the 21st century (WHO report)
 - ▶ 2,000,000 Americans infected each year
 - ▶ 23,000 deaths annually
- ▶ Cause: antibiotics are everywhere
 - ▶ Up to 95% of antibiotics in US are excreted in an unaltered state
 - ▶ Over prescription in humans
 - ▶ Heavy use in agriculture
- ▶ Result: Antibiotic resistant genes (ARGs) are ubiquitous in the aquatic environment
 - ▶ e.g., Pruden et al., 2006 [ES&T]

C&E News
Oct 6, 2014

Primidone

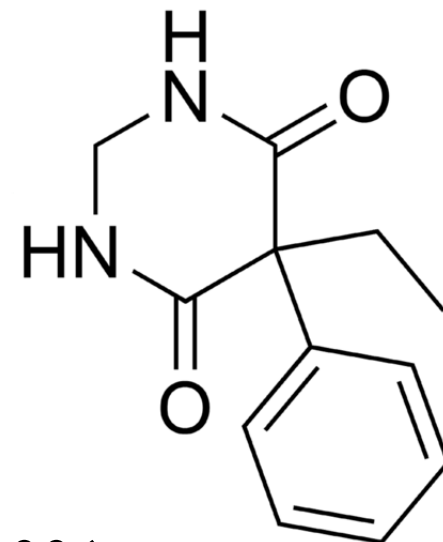
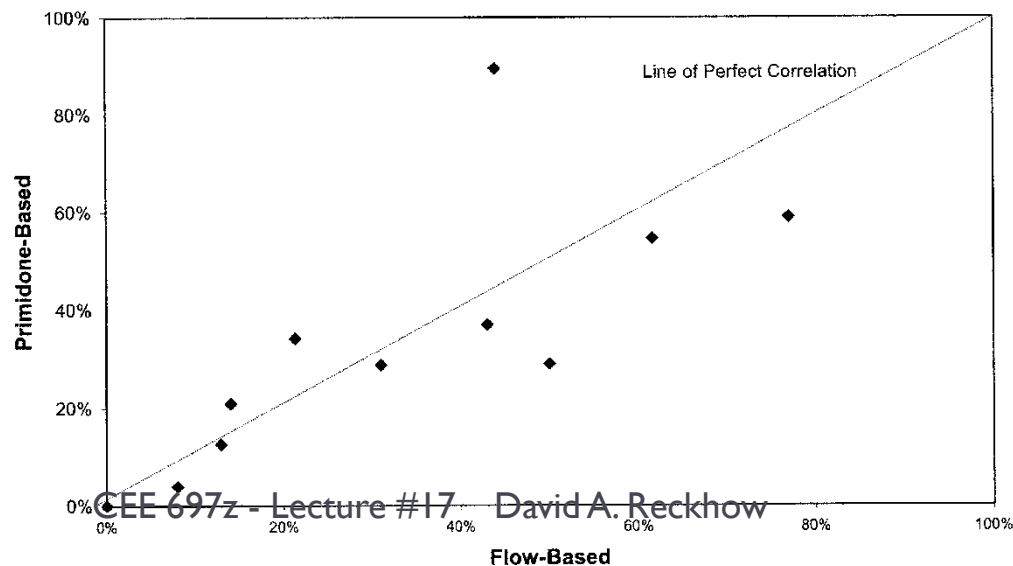
Variability in Primidone Over Time and Space at Nogales WWTP (Site 1) and in Santa Cruz River (Sites 2-10): 2 Sample Events



► Krasner et al., 2006

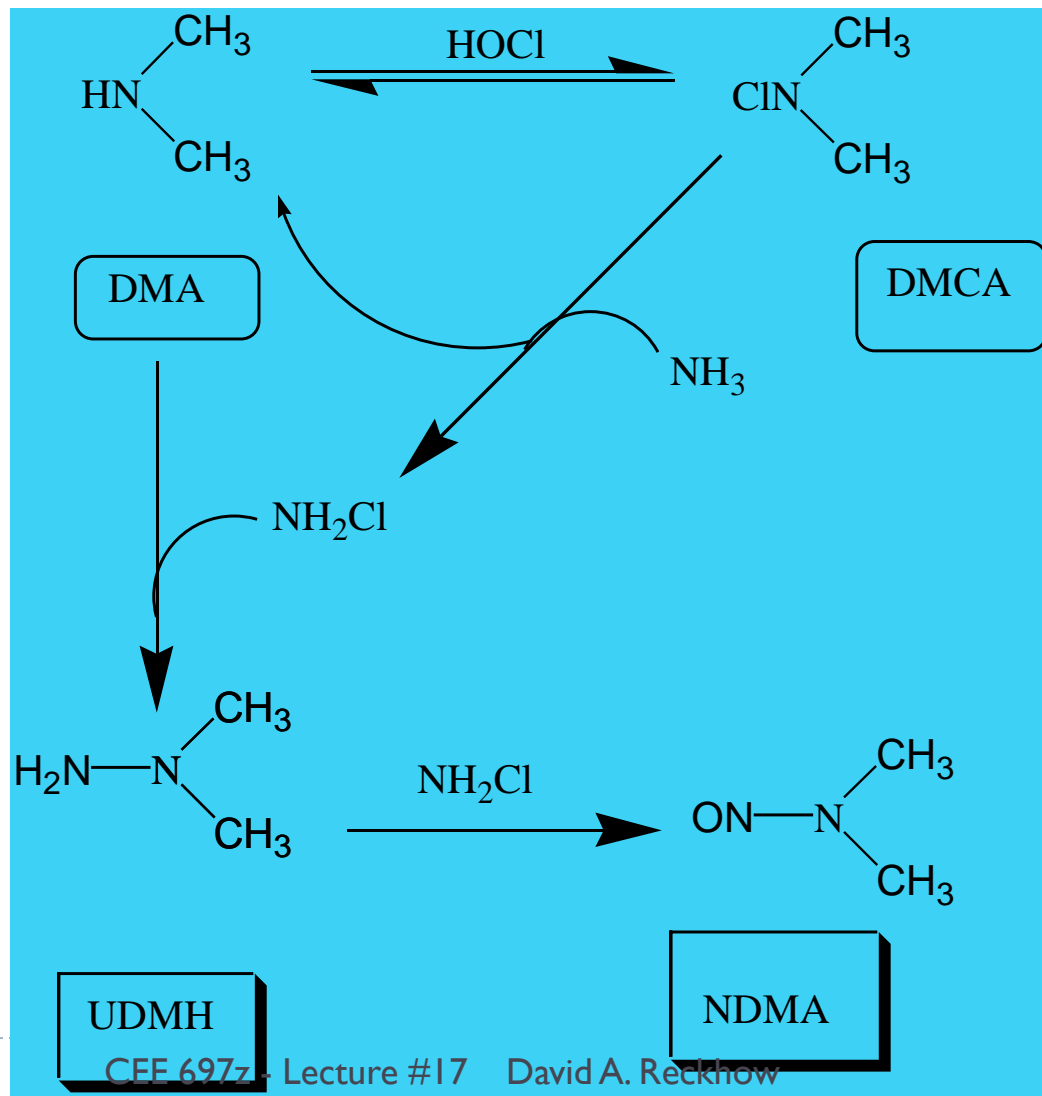
► WQTC

**% of South Platte River Flow Due to Treated Wastewater:
Flow-Based versus Primidone-Based**

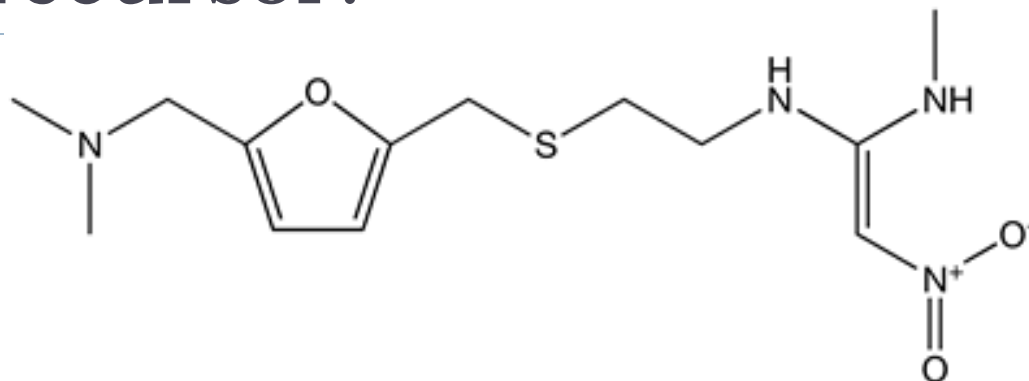


Precursors to NDMA??

- ▶ NDMA (nitrosodimethylamine) is a very potent probable human carcinogen
- ▶ Formation of NDMA from chloramination of dimethylamine (DMA)
 - ▶ Not enough DMA to account for anything much
- ▶ NDMA formation is **much** higher in municipal WW than in pristine natural waters
- ▶ Major precursor is not natural???



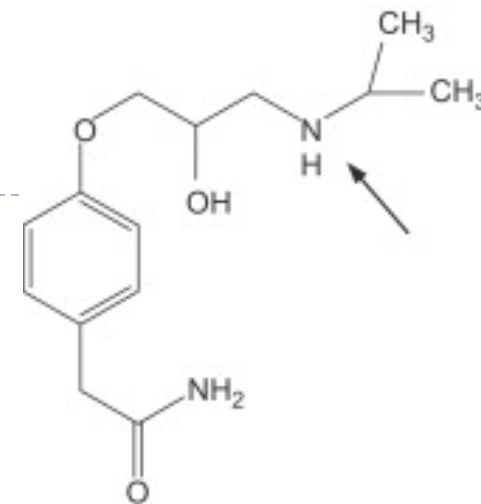
The Unnatural Precursor?



▶ Ranitidine (Zantac)

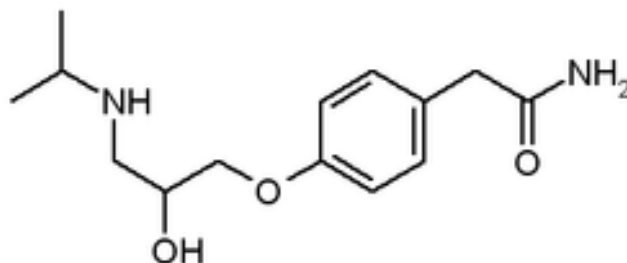
- ▶ 63% conversion to NDMA
 - ▶ Schmidt et al., 2006 [WQTC]
- ▶ Introduced in 1981, largest selling prescription drug by 1988
 - ▶ Stomach ulcers and esophageal reflux
- ▶ Mean concentration of 3000 ng/L estimated for raw municipal WW (national average)
 - ▶ Sedlak 2005 AWWARF report
- ▶ 450 ng/L formation in raw WW expected
- ▶ Unknowns: how much does this persist in treatment and in the environment?

Beta-Blockers: Atenolol



- ▶ Atenolol is a representative of the group of Beta-blockers, for treating cardiovascular disease (also known as Tenormin).
 - ▶ In use since 1976.
 - ▶ Sedlak and co-workers (2005) estimate a nationwide average raw municipal wastewater concentration of about 1500 ng/L.
- ▶ This compound is rather unreactive with free chlorine, as it lacks activated aromatic structures as well as reactive nitrogen sites.
 - ▶ reactivity with ozone is low, but may be significant in some cases
- ▶ May be used as an indicator of treated vs raw WW as propranolol was by Fono & Sedlak

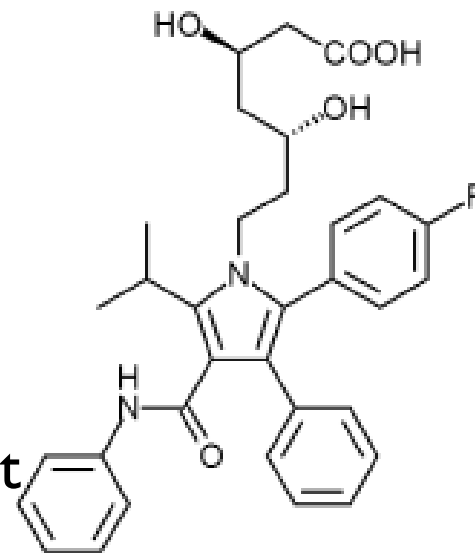
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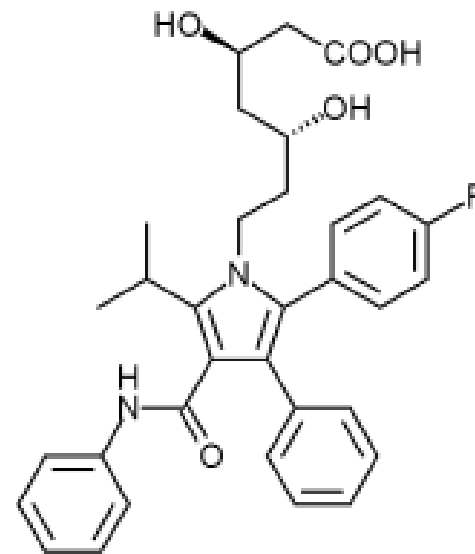
Statins: Atorvastatin

- ▶ This compound is more commonly known as Lipitor®, and it is representative of a larger group of cholesterol-reducing drugs called statins.
- ▶ It does not appear to have been tested for removal by coagulation or reaction with either chlorine or ozone.
- ▶ Based on its structure, we would expect it to be slightly reactive with ozone, but little affected by the other treatments



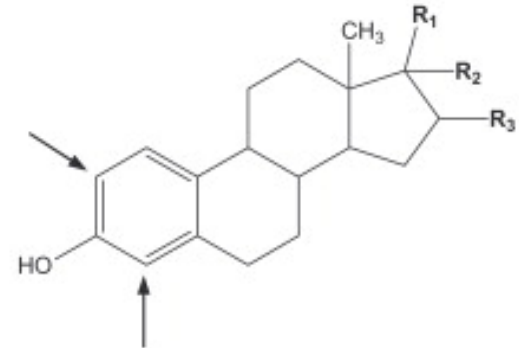
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Reproductive Hormones:

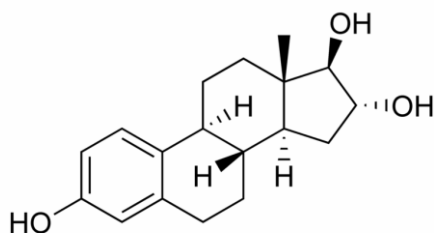
17b-estradiol, 17a-ethinylestradiol, Estrone, Estriol



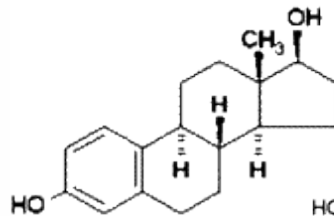
Estradiol:	R ₁ = OH,	R ₂ = H	R ₃ = H
Estrone:	R ₁ = ketone,	R ₂ = H	R ₃ = H
Estriol :	R ₁ = OH,	R ₂ = H	R ₃ = OH
Ethinylestradiol:	R ₁ = OH,	R ₂ = C≡H	R ₃ = H

- ▶ Three of these four (17b-estradiol, Estrone, Estriol) are naturally occurring human estrogens. Ethinylestradiol is the estrogen component of oral contraceptives.
 - ▶ All four of these compounds have the fundamental steroid skeleton, with many similarities in positioning of the functional groups.
- ▶ All of these compounds are rapidly destroyed by free chlorine
 - ▶ (Westerhoff et al., 2005; Deborde et al., 2004). Reaction with chlorine should result in large fragments that are partially oxygenated or even halogenated.
 - ▶ Estradiol has been found to produce at least 7 daughter products that persist in treated waters (Irmak et al., 2005; Hu et al., 2003)

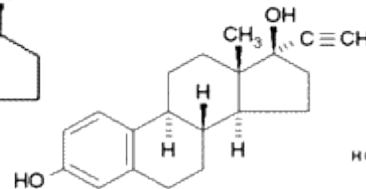
Reproductive Hormones: 17b-estradiol, 17a-ethinylestradiol, Estrone, Estriol



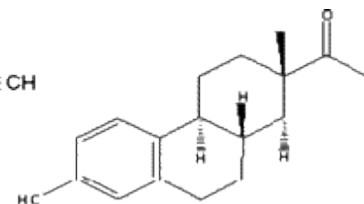
Estriol



17β-Estradiol



Ethinylestradiol



Estrone

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 - ▶ All four of these compounds have the fundamental steroid skeleton, with many similarities in positioning of the functional groups.
- ▶ All of these compounds are rapidly destroyed by free chlorine
 - ▶ (Westerhoff et al., 2005; Deborde et al., 2004). It's quite likely that the phenolic "A" ring is the initial site of attack and the most reactive structure within each of these compounds.
- ▶ Reaction with chlorine should result in large fragments that are partially oxygenated or even halogenated.
 - ▶ Estradiol has been found to produce at least 7 daughter products that persist in treated waters (Irmak et al., 2005; Hu et al., 2003)

Structure is reactivity

► Steroidal estrogens

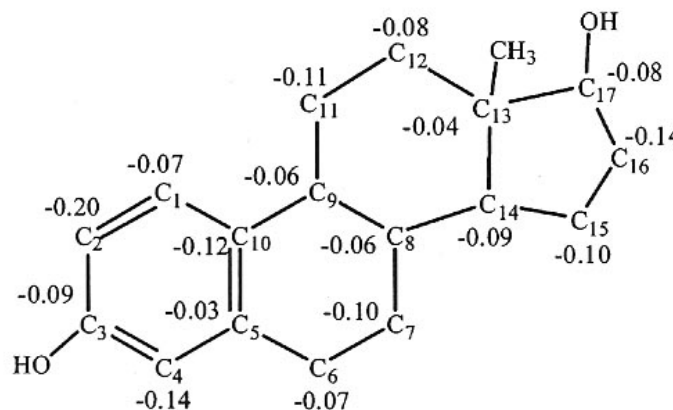
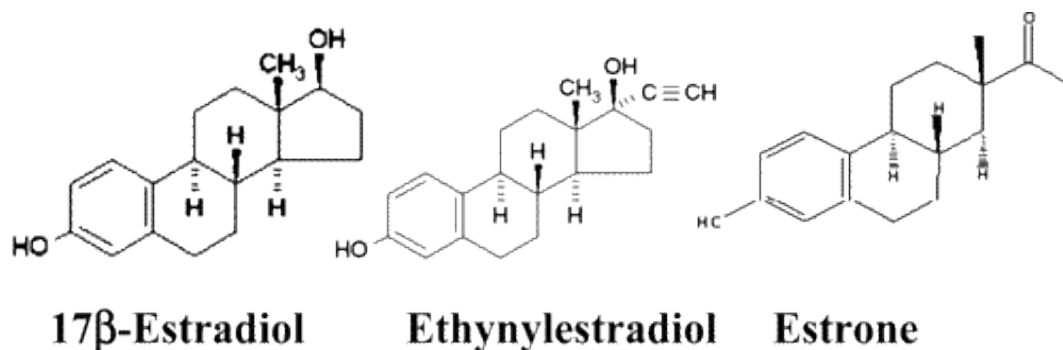
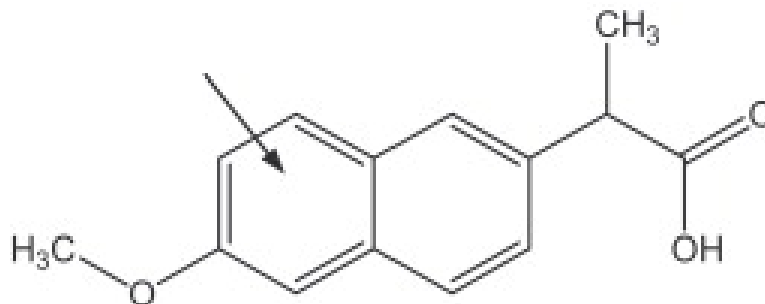


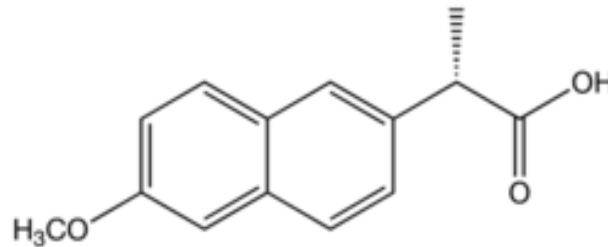
FIGURE 3. Atom partial charge of 17β-estradiol.

Non-steroidal anti-inflammatory: Naproxen



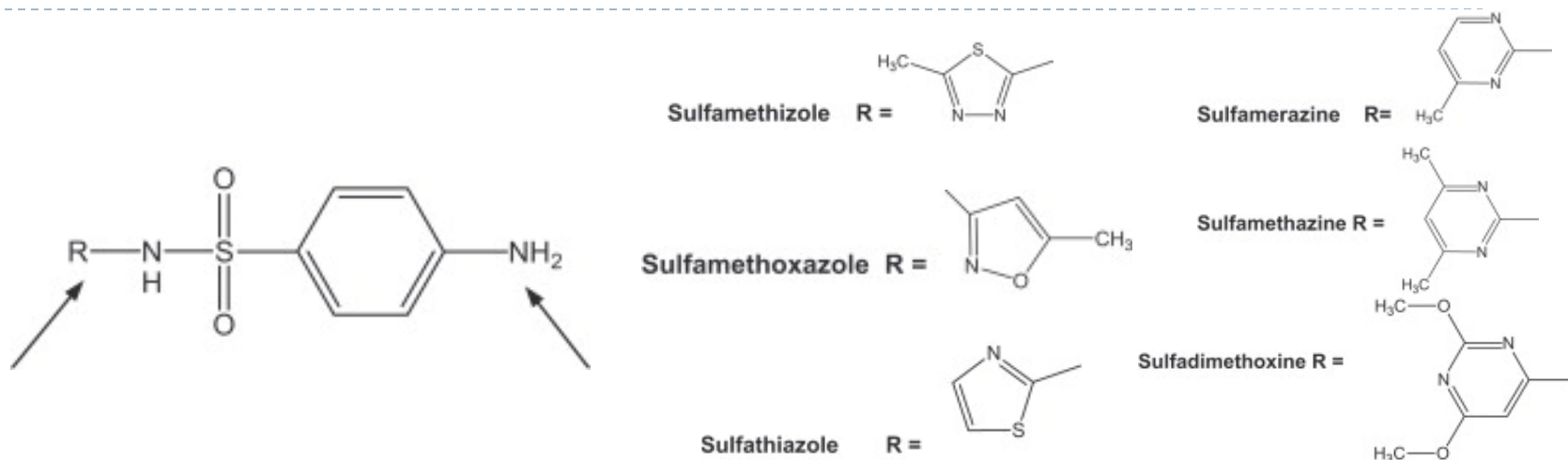
- ▶ Naproxen (also known as Aleve®) is a common arthritis treatment, intended to reduce pain and inflammation.
- ▶ Its mean concentration in US wastewaters has been estimated to be about 2400 ng/L (Sedlak et al., 2006). Limited occurrence data has centered around 300 ng/L in US wastewaters
- ▶ It is quite reactive with ozone, and surprisingly reactive with chlorine too.
- ▶ Probably many daughter products

Non-steroidal anti-inflammatory: Naproxen



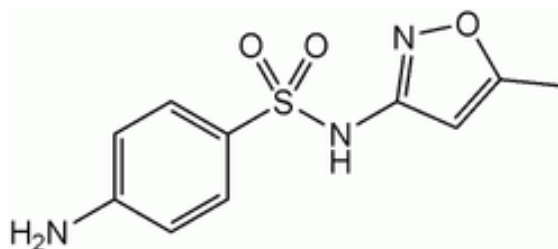
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- ▶ Probably many daughter products

Sulfa Antibiotic: Sulfamethoxazole



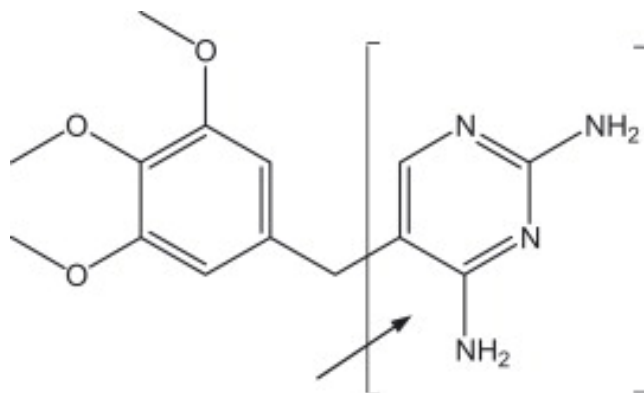
- ▶ This antibiotic is a major component of Bactrim®.
 - ▶ Commonly used for sinus infections
- ▶ Its median concentration in treated wastewaters has been measured at 1400 ng/L, a value quite close to its nationwide estimated level of 3200 ng/L.
- ▶ This compound is moderately reactive with free chlorine and ozone

Sulfonamide Antibiotic: Sulfamethoxazole



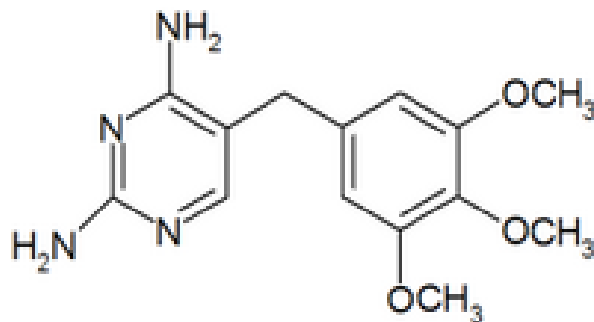
- ▶ This antibiotic is a major component of Bactrim.
- ▶ Its median concentration in treated wastewaters has been measured at 1400 ng/L, a value quite close to its nationwide estimated level of 3200 ng/L.
- ▶ This compound is moderately reactive with free chlorine and ozone

Antibiotic: Trimethoprim



- ▶ This particular antibiotic is widely used for treatment of urinary tract infections. It is also known as: Proloprim®, Monotrim® and Triprim®
- ▶ It is quite prevalent in US wastewaters (500 ng/L median; 1500 ng/L estimated nationwide).
- ▶ It is extremely reactive with free chlorine, as would be expected from its structure. It is quite likely that the molecule is extensively degraded and oxidized by chlorine or ozone treatments.

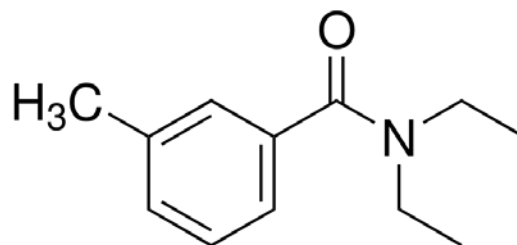
Bacteriostatic Antibiotic: Trimethoprim



- ▶ This particular antibiotic is widely used for treatment of urinary tract infections. It is also a member of the group of dihydrofolate reductase inhibitors.
- ▶ It is quite prevalent in US wastewaters (500 ng/L median; 1500 ng/L estimated nationwide).
- ▶ It is extremely reactive with free chlorine, as would be expected from its structure. It is quite likely that the molecule is extensively degraded and oxidized by chlorine or ozone treatments.

Insecticide: DEET

- ▶ N,N, Diethyl-m-toluamide
- ▶ Most common active ingredient in most insect repellents



- ▶ Little or no human toxicity?

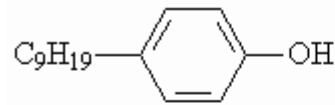
Surfactants: Nonylphenols & Ethoxylates

► Nonylphenols (NP)

- ▶ Used in the manufacture of detergents and other products.
- ▶ Breakdown products of the nonlyphenol ethoxylates
- ▶ Displace estrogen from its receptor in rainbow trout (due to their stronger affinity to the E2 receptor) and cause feminization

- ▶ **Nonylphenol ethoxylates (NPE)**

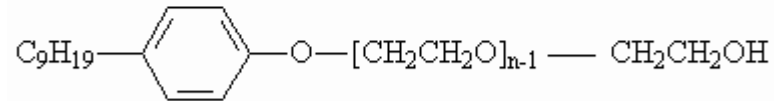
- ▶ Surfactants used for 50 years
- ▶ produced from NP and degrade to NP.



Nonylphenol

▶ Regulatory Action

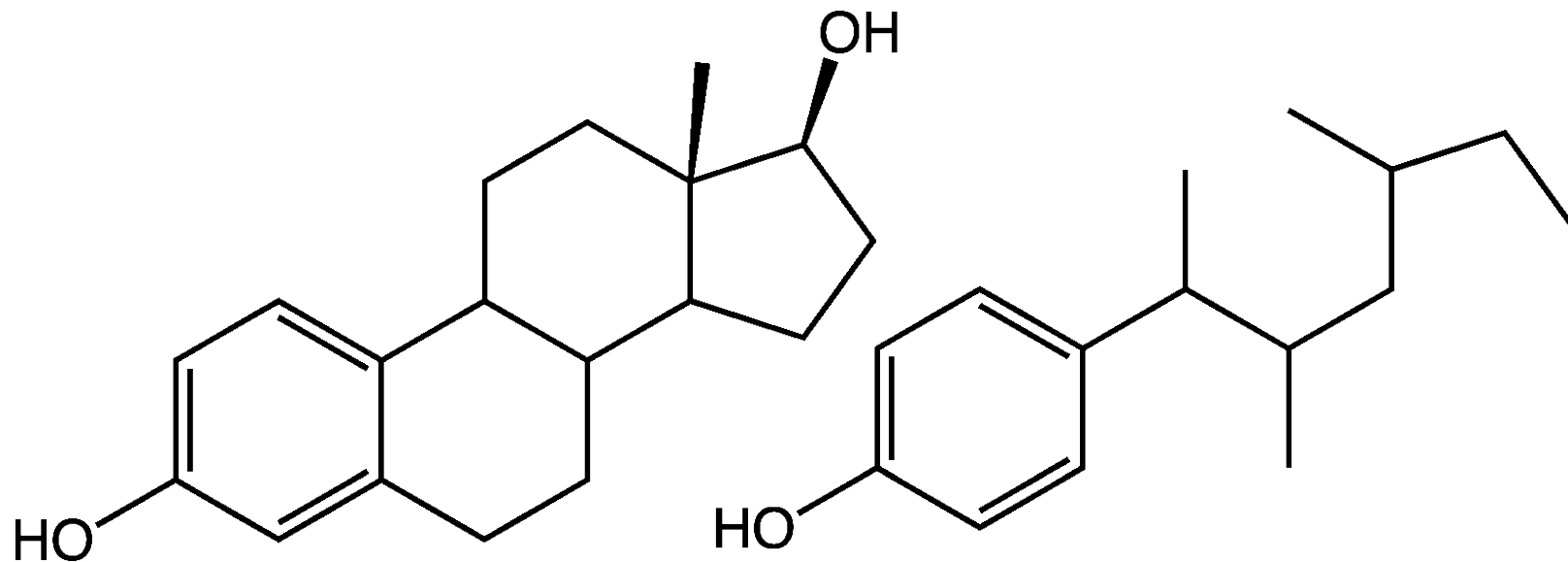
- ▶ **Toxics Release Inventory**
 - ▶ Deemed “highly toxic” to aquatic life
 - ▶ Published: Sept 30, 2014
 - ▶ <http://www2.epa.gov/toxics-release-inventory/nonylphenol-category-final-rule>



Nonylphenol ethoxylate, generalised formula
n = number of ethyle oxide units

Estrogen mimics

► Compare structure



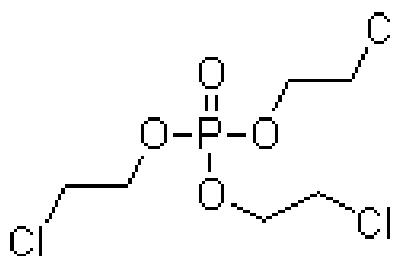
Estradiol

and a

Nonylphenol

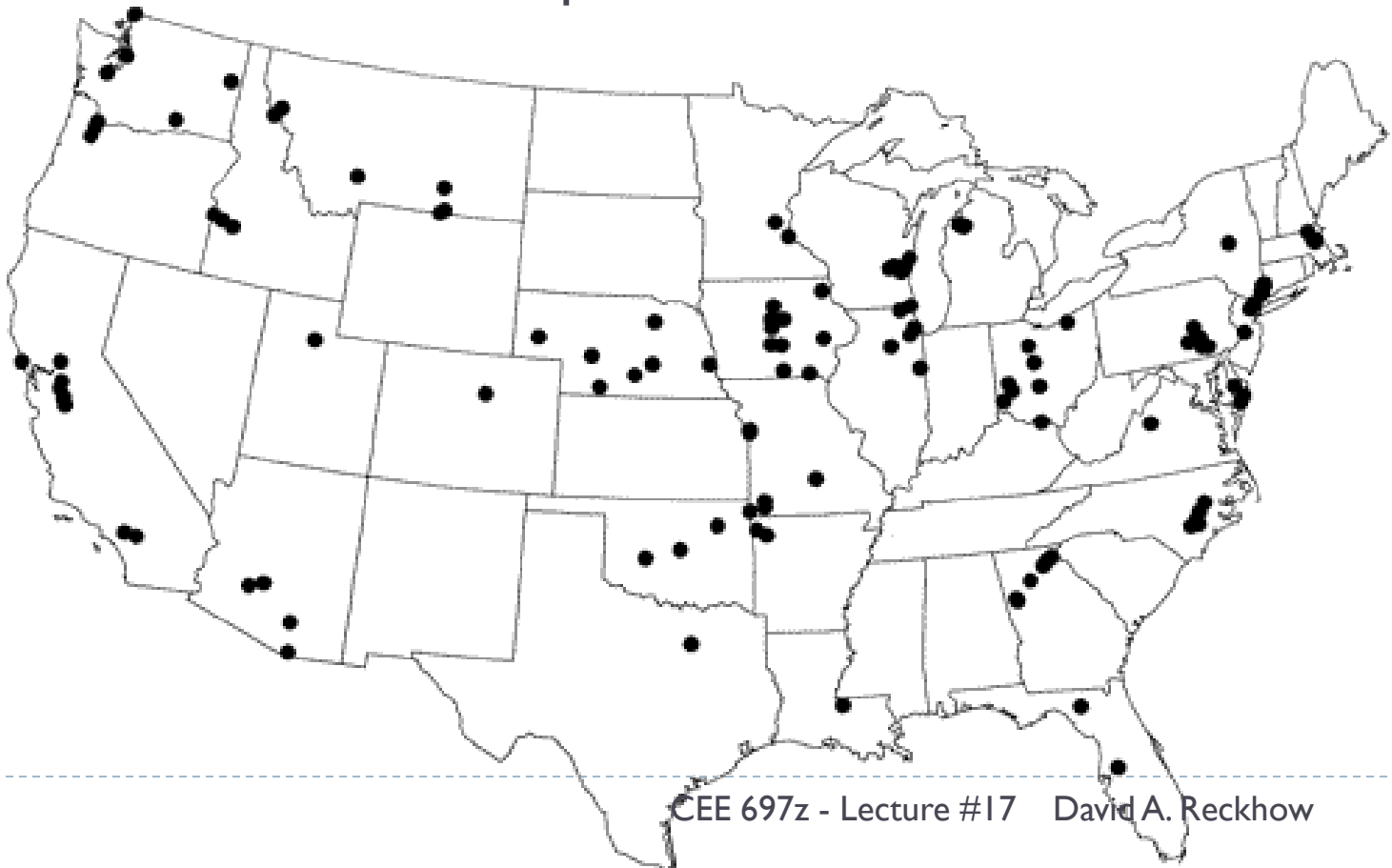
Flame Retardant: TCEP

- ▶ Tris(2-chloroethyl)phosphate



USGS Survey

- ▶ 138 stream sampling sites
- ▶ Kolpin et al., 2002



First to study PPCPs?

- ▶ Who are these people?



Werner Stumm



Dana Kolpin



Thomas Ternes

J. WPCF, Nov 1965

► Elizabeth Stumm-Zollinger

BIODEGRADATION OF STEROID HORMONES

Elisabeth Stumm-Zollinger and Gordon M. Fair

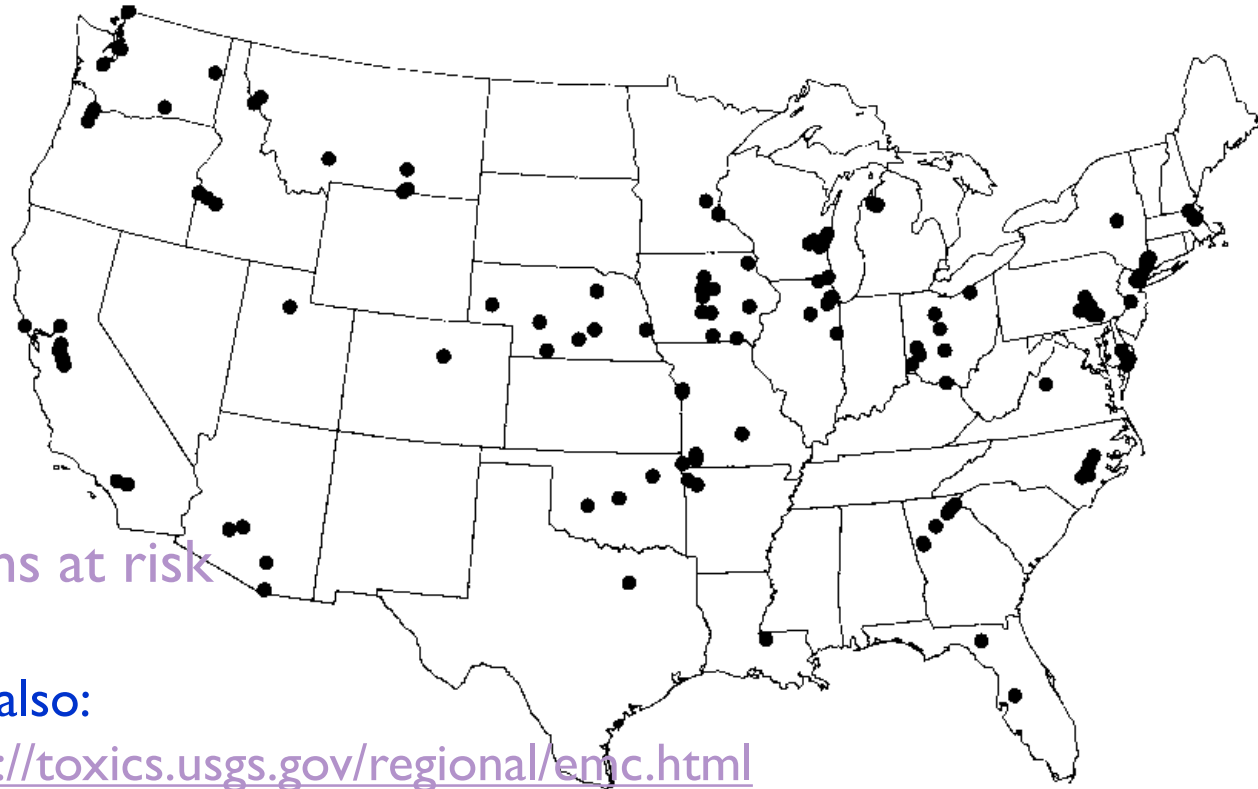
This brief and preliminary report on the biodegradation of steroid hormones responds specifically to a question asked by the senior author almost four years ago (1961) but not studied experimentally until late 1963. In broader terms, however, the report exemplifies the kind of inquiry that water engineers and water scientists conceivably will make in increasing number and rising intensity if the available water resource is allowed to become heavily contaminated with the waste products of man and with the expanding complex of chemicals synthesized by him for agricultural and

to be small—a few tenths of a mg/l and probably seldom in excess of one to two mg/l. However, this is not so where water use is less extravagant. Under periurban and advanced rural conditions, for example, concentrations well may be doubled. In more primitive rural situations (pit privies and shallow wells) concentrations indeed may become relatively high. To the fundamental amounts will be added, if present indications prove correct, increasing amounts of hormones used for medical purposes. Examples are the ovulation-inhibiting steroids. So long as dosages remain in line with



US National Reconnaissance

- ▶ USGS Study
 - ▶ 1999-2000
 - ▶ 95 compounds
 - ▶ 139 streams
 - ▶ Focus on systems at risk

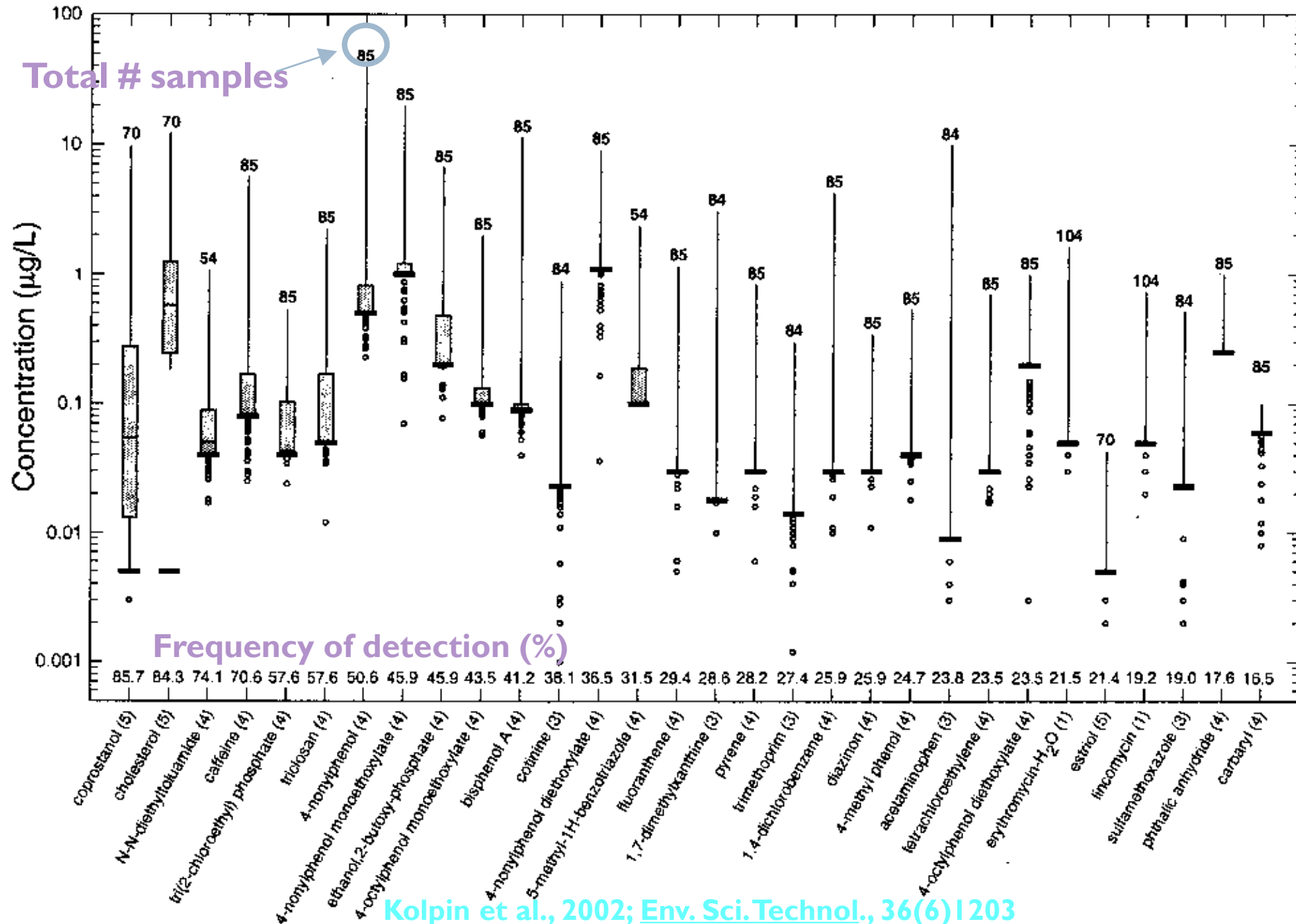


See also:

<http://toxics.usgs.gov/regional/emc.html>

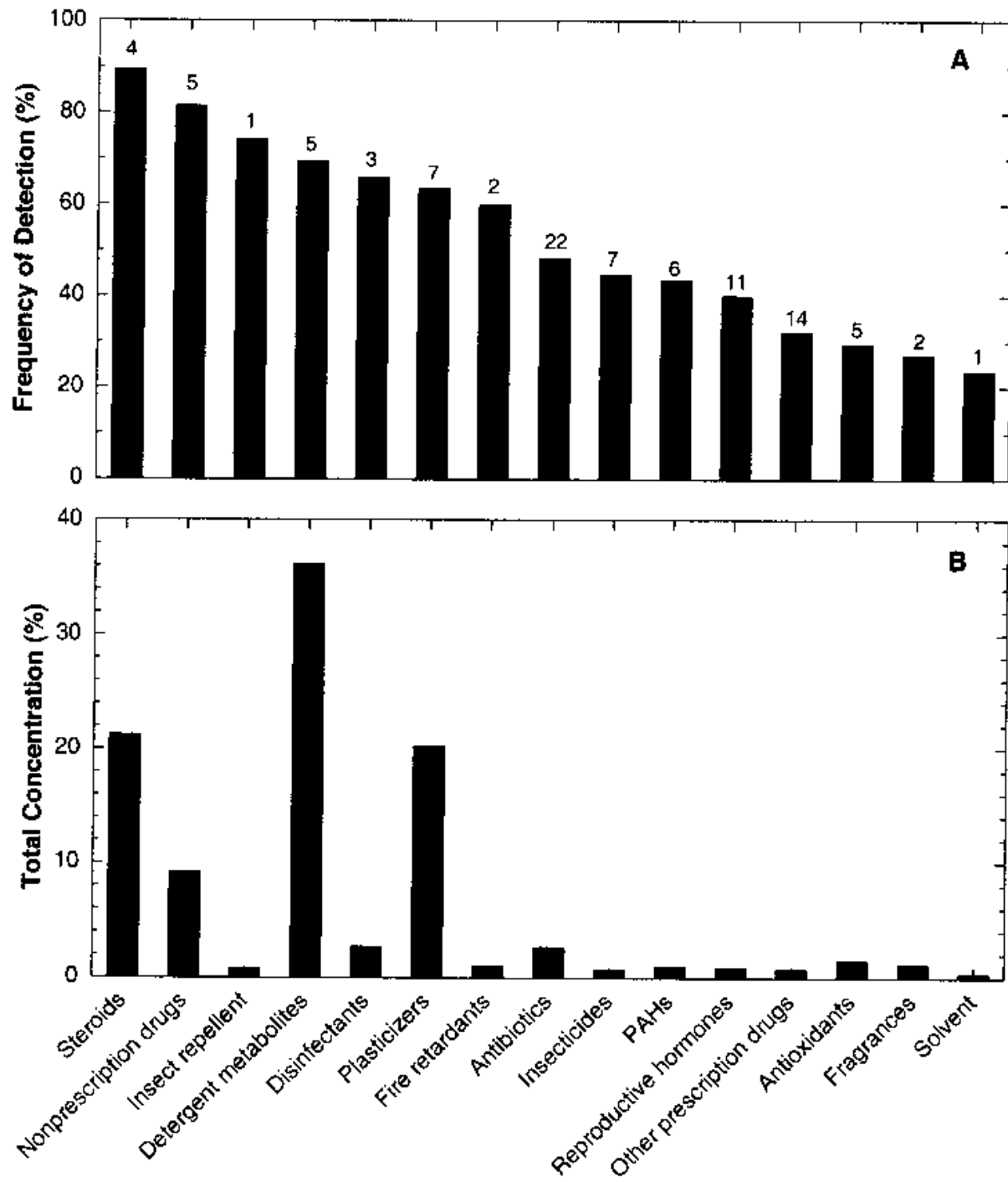
FIGURE 1. Location of 139 stream sampling sites.

Kolpin et al., 2002; *Env. Sci. Technol.*, 36(6) 1203



Kolpin et al., 2002; [Env. Sci. Technol.](#), 36(6) 1203

► Detection by category



urgency about climate change even within groups that once dismissed assertions of an overheating planet as a liberal ruse. The president of the Southern Baptist Convention was among the signers. (AP)

MICHIGAN

Paper ties mayor's friend to contracts

DETROIT — Companies headed by a friend of Mayor Kwame Kilpatrick won millions of dollars in city contracts while the friend secretly consulted with the mayor's chief of staff about bidding strategies, the Detroit Free Press reported yesterday. The paper said Bobby Ferguson and companies he partnered collected at least \$45 million. Ferguson, the city, and a lawyer for former chief of staff Christine Beatty denied wrongdoing. (AP)

FLORIDA

Shuttle cleared for launch with new lab

CAPE CANAVERAL — NASA cleared the space shuttle Endeavour yesterday for launch early tomorrow to begin attaching a Japanese laboratory to the International Space Station and install Canadian-built robot arms. Liftoff from the Kennedy Space Center is scheduled for 2:28 a.m. Meteorologists predicted a 90 percent chance that weather conditions would be suitable for the rare night launch. (Reuters)

Bus, pickup collide, killing woman

FORT LAUDERDALE — A tour

Pharmaceuticals found in US drinking water

Trace quantities could endanger wildlife, humans

By Jeff Donn
ASSOCIATED PRESS

NEW YORK — An array of pharmaceuticals — including antibiotics, anticonvulsants, mood stabilizers, and sex hormones — have been found in the drinking water supplies of at least 41 million Americans, an Associated Press investigation found.

The concentrations of these pharmaceuticals are tiny, measured in quantities of parts per billion or trillion, far below the levels of a medical dose. And utilities insist that their water is safe.

But the presence of so many prescription drugs — and over-the-counter medicines like acetaminophen and ibuprofen — in so much of our drinking water is heightening worries among scientists of long-term consequences to human health.

In the course of a five-month inquiry, the AP discovered that drugs have been detected in the drinking water supplies of 24 major metropolitan areas — from southern California to northern



EPA ADDRESSING THE ISSUE

'We recognize it is a growing concern, and we're taking it very seriously,' said Benjamin Grumbles, assistant administrator for water at the federal EPA.

New Jersey, from Detroit to Louisville, Ky.

Water providers rarely disclose results of pharmaceutical screenings, unless pressed, the Associated Press found.

For example, the head of a group representing major California suppliers said the public "doesn't know how to interpret the information" and might be unduly alarmed.

When people take pills, their bodies absorb some of the medication, but the rest of it passes through and is flushed down the toilet. The wastewater is treated before it is discharged into reservoirs, rivers, or lakes.

Then, some of the water is cleaned again at drinking water treatment plants and piped to consumers. But most treatments do not remove all drug residue.

While researchers do not yet understand the exact risks from decades of persistent exposure to

random combinations of low levels of pharmaceuticals, recent studies, which have gone virtually unnoticed by the public, have found alarming effects on human cells and wildlife.

"We recognize it is a growing concern, and we're taking it very seriously," said Benjamin H. Grumbles, assistant administrator for water at the US Environmental Protection Agency.

The Associated Press reviewed hundreds of scientific reports, analyzed federal drinking water databases, visited environmental study sites, and treatment plants and interviewed more than 230 officials, academics, and scientists.

They also surveyed the nation's 50 largest cities and a dozen other major water providers, as well as smaller community water providers in all 50 states.

Here are some of the key test results:

■ Officials in Philadelphia said testing discovered 56 pharmaceu-

ticals or byproducts in treated drinking water, including medicines for pain, infection, high cholesterol, asthma, epilepsy, mental illness, and heart problems. Sixty-three pharmaceuticals or byproducts were found in the city's watersheds.

■ Antiepileptic and antianxiety medications were detected in a portion of the treated drinking water for 18.5 million people in southern California.

■ Researchers at the US Geological Survey analyzed a Passaic Valley Water Commission drinking water treatment plant, which serves 850,000 people in northern New Jersey, and found a metabolized angina medicine and the mood-stabilizing carbamazepine in drinking water.

■ A sex hormone was detected in San Francisco's drinking water.

■ The drinking water for Washington, D.C., and surrounding areas tested positive for six pharmaceuticals.

The federal government doesn't require any testing and hasn't set safety limits for drugs in water. Some providers screen only for one or two pharmaceuticals, leaving open the possibility that others are present.

Of the 62 major water providers contacted, the drinking water for 28 was tested. Boston is among the 34 that haven't been tested, along with Baltimore, Chicago, Houston, Miami, New York, and Phoenix.

The investigation also indicates that watersheds, the natural sources of most of the nation's water supply, also are contaminated. Tests were conducted in the watersheds of 35 of the 62 major providers surveyed by the Associated Press and pharmaceuticals were detected in 28.

Yet officials in six of those 28 metropolitan areas said they did not go on to test their drinking water: Fairfax, Va.; Montgomery County in Maryland; Omaha; Oklahoma City; Santa Clara, Calif.; and New York City.

Of the 28 major metropolitan areas where tests were performed on drinking water supplies, only Albuquerque; Austin, Texas; and Virginia Beach, Va., said tests were negative.

Calif. dunes lure off-road enthusiasts, smugglers

By Richard Marosi
LOS ANGELES TIMES

of fortification that they hope will cut down on incursions.

CEE 697z - Lecture #17 David A. Reckhow

the Department of Homeland Security seems willing to flex its

Tests find water supply is drug-free

► Boston Globe
► Apr 27, 2008

Two reservoirs that serve city, region checked

By John C. Drake
GLOBE STAFF

As New York, Chicago, and other US cities struggle over how to respond to reports that traces of pharmaceuticals exist in their drinking water, a first-ever test of the reservoirs that serve Greater Boston makes one thing crystal-clear: The water supply is drug-free.

The testing by an independent laboratory of the water pumped to the city and surrounding communities found no detectable levels of more than two dozen pharmaceutical products that have tainted water supplies elsewhere.

"We were guardedly optimistic, but you never say never," said Fred Laskey, executive director of the Massachusetts Water Resources Authority, which commissioned the study. "We wanted to do the test just to reassure the public, and ourselves, what we were convinced of — that our water is pristine at the source."

While the MWRA routinely tests the water supply for more than 100 contaminants including lead, chlorine, and disinfectant by-products, state and federal governments do not require tests for pharmaceuticals such as acetaminophen, progesterone, and the insect repellent DEET.

A five-month Associated Press investigation, released in March, found that water supplies for at least 41 million Americans contained trace amounts of antibiotics, mood stabilizers, and other drugs, raising concerns about what impact the substances, even in minuscule amounts, might have on consumers' health.

The news service did not include in its investigation the MWRA, which provides drinking water from the Wachusett and Quabbin watersheds in Central Massachusetts to 2 million users in Boston and all the communities inside Interstate 95/Route 128 except Cambridge, along with a few other communities such as Framingham and Chicopee.

The MWRA decided to conduct its own tests, given the recent public concern over the issue, Laskey said.

Boston residents should be happy to hear the test results, said Amy Pruden, a professor of environmental engineering at Colorado State University who has studied the effects of antibiotics in drinking water.

"It sounds like, at least with respect to that particular water quality issue, they can rest fairly easy," she said. "It sounds like Boston's in good shape, especially for such a big city."

Unlike most of the water systems found to contain trace amounts of pharmaceutical products, Boston's water supply does not have a wastewater treatment plant upstream, Laskey said. The

MWRA's two reservoirs are mostly protected from nearby development, which limits the introduction of human and industrial waste into the water supply.

"That certainly lowers the level of concern if there's no known sources," said Pruden.

The MWRA paid California-based MWH Laboratories \$23,250 to test 31 samples of raw and treated water drawn on March 14 from testing sites at its reservoirs.

The only compound picked up in the testing was a softener commonly used for rubber gaskets, washers, and food containers called tris (2-butoxyethyl) phosphate, or TBEP. It was found in a test of untreated water, and Laskey said officials believe the "minute trace amounts" of the compound actually came from the plant's testing spigot. The effects on humans of exposure to the chemical are unclear, but are believed to be minimal, according to data from the National Library of Medicine. Results of a follow-up test of water extracted directly from the reservoir, without contact with plumbing, should be available within three weeks, the MWRA said.

Given the small amount detected, and the fact it came from untreated water, officials are not concerned about it, Laskey said.

The tests of treated water came from a separate testing spigot at an MWRA plant, and not from the faucets from which residents ultimately collect their water. But an MWRA representative said that

Substance list

The MWRA tested Boston's drinking water supply for more than two dozen pharmaceuticals. The water was tested for substances such as:

- Acetaminophen
- Caffeine
- Ibuprofen
- Progesterone
- Testosterone
- BisPhenol A
- DEET
- Phenol

Source: Massachusetts Water Resources Authority

water "never sees the light of day" between the reservoir and the tap, so there would be no opportunity for foreign substances to enter the stream before it reaches consumers' homes.

Laskey said there are no immediate plans to institute regular screening of drinking water for pharmaceutical products, but he said it appears federal regulators may be moving toward requiring such testing. Advocacy groups and congressional committees have been demanding stricter federal monitoring of drinking water since the reports of the presence of pharmaceutical products surfaced.

John C. Drake can be reached at jdrake@globe.com.

► To next lecture

