Emerging Contaminants Pharmaceuticals and Personal Care Products (PPCPs)

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Outline

- Definition of Emerging Contaminants
- Review of previous studies
- Fate & transport
- Exposure pathways
- Monitoring
- Detection
- Dispersal in environment
- Potential for harm to organisms

Emerging Contaminants

- Pesticides
- Pharmaceuticals (prescription and non-prescription)
- Antibiotics/Antibacterial soaps
- Plastics
- Industrial chemicals
- Cosmetics
- Detergents
- Natural and synthetic hormones
- Ordinary household products

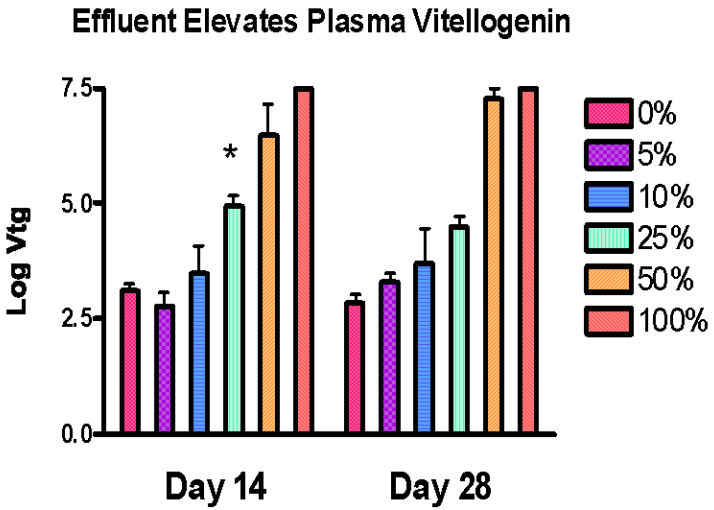
What is an endocrine disruptor?

- **An endocrine disruptor is a synthetic chemical that when absorbed into the body either mimics or blocks hormones and disrupts the body's normal functions. This disruption can happen through altering normal hormone levels, halting or stimulating the production of hormones, or changing the way hormones travel through the body, thus affecting the functions that these hormones control.**

Endocrine Disruption: Elevated Plasma Vitellogenin, Nuptial Tubercle Expression, Intersex: Fathead Minnows

Reference
NT

Treatment



Estrogens → Liver → Vitellogenin
Reference
Vajda et al., 2008 Complex Mixtures and Potential Ecological Effects Treatment

Examples

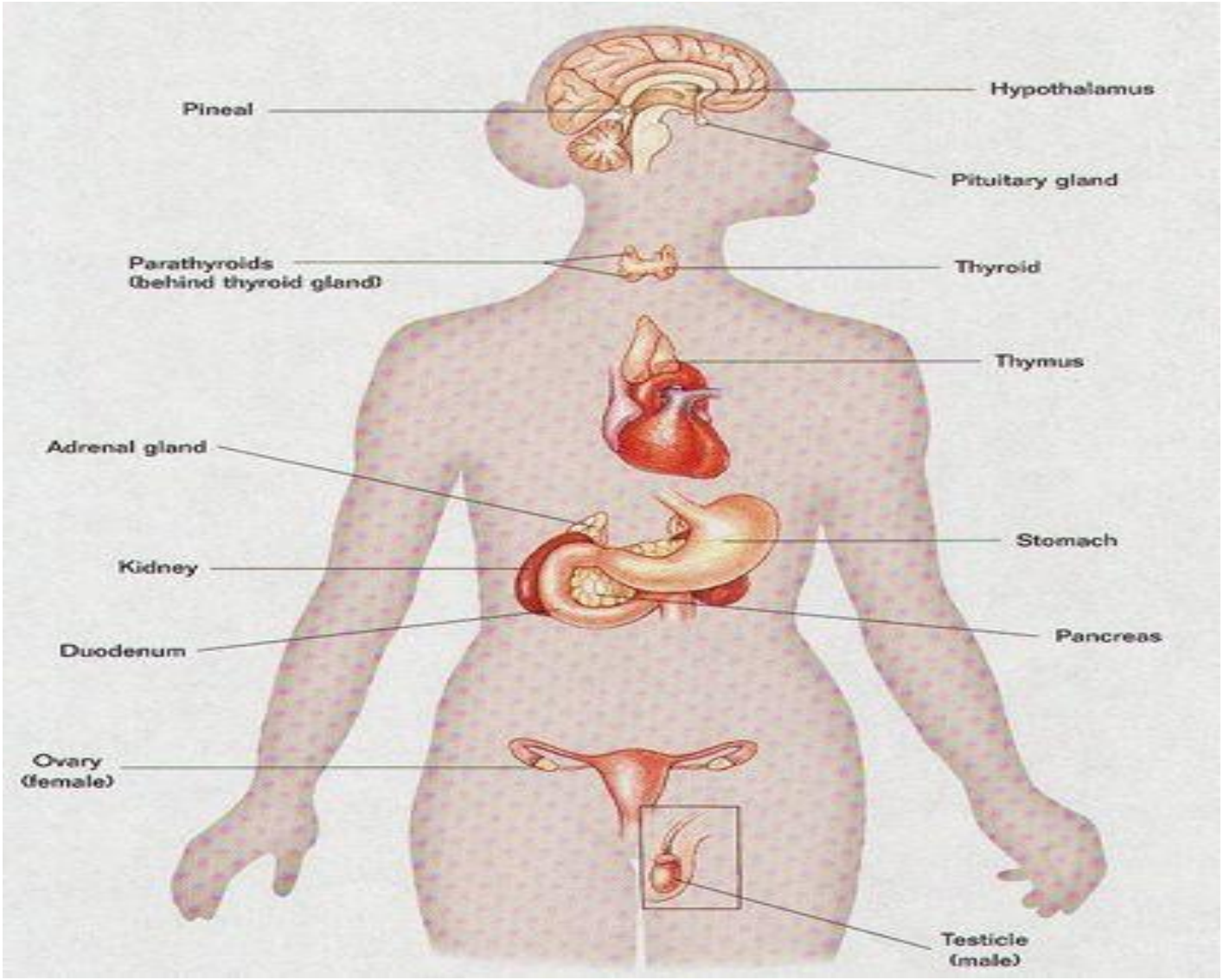
Chemicals that are known human endocrine disruptors include diethylstilbesterol (the drug DES), dioxin, PCBs, DDT, and some other pesticides. Many chemicals, particularly pesticides and plasticizers, are suspected endocrine disruptors based on limited animal studies.

Endocrine Disrupting Compounds

- A subgroup of Emerging Contaminants
- Natural or synthetic chemicals that interfere with normal hormonal functions
  - Some mimic or block natural hormones
  - Others directly stimulate or inhibit the endocrine system
  - Can cause over or under-production of hormones
- Shown to cause adverse health effects in many species
- Shown to have significant effects at very low levels of exposure

What is the endocrine system?

- The endocrine system is a complex network of glands and hormones that regulates many of the body's functions, including growth, development and maturation, as well as the way various organs operate. The endocrine glands -- including the pituitary, thyroid, adrenal, thymus, pancreas, ovaries, and testes -- release carefully-measured amounts of hormones that act as chemical messengers.



From Biology: Principles and Explorations,
Teaching Transparencies.

Kolpin U.S. Stream Study (USGS)

- 139 streams across the US were screened for 95 ECs.
- 82 of 95 were detected at least once.
- 80% of the 139 streams studied had detectable amounts of ECs in them.
- Concentrations ranged from low parts per trillion to parts per billion.

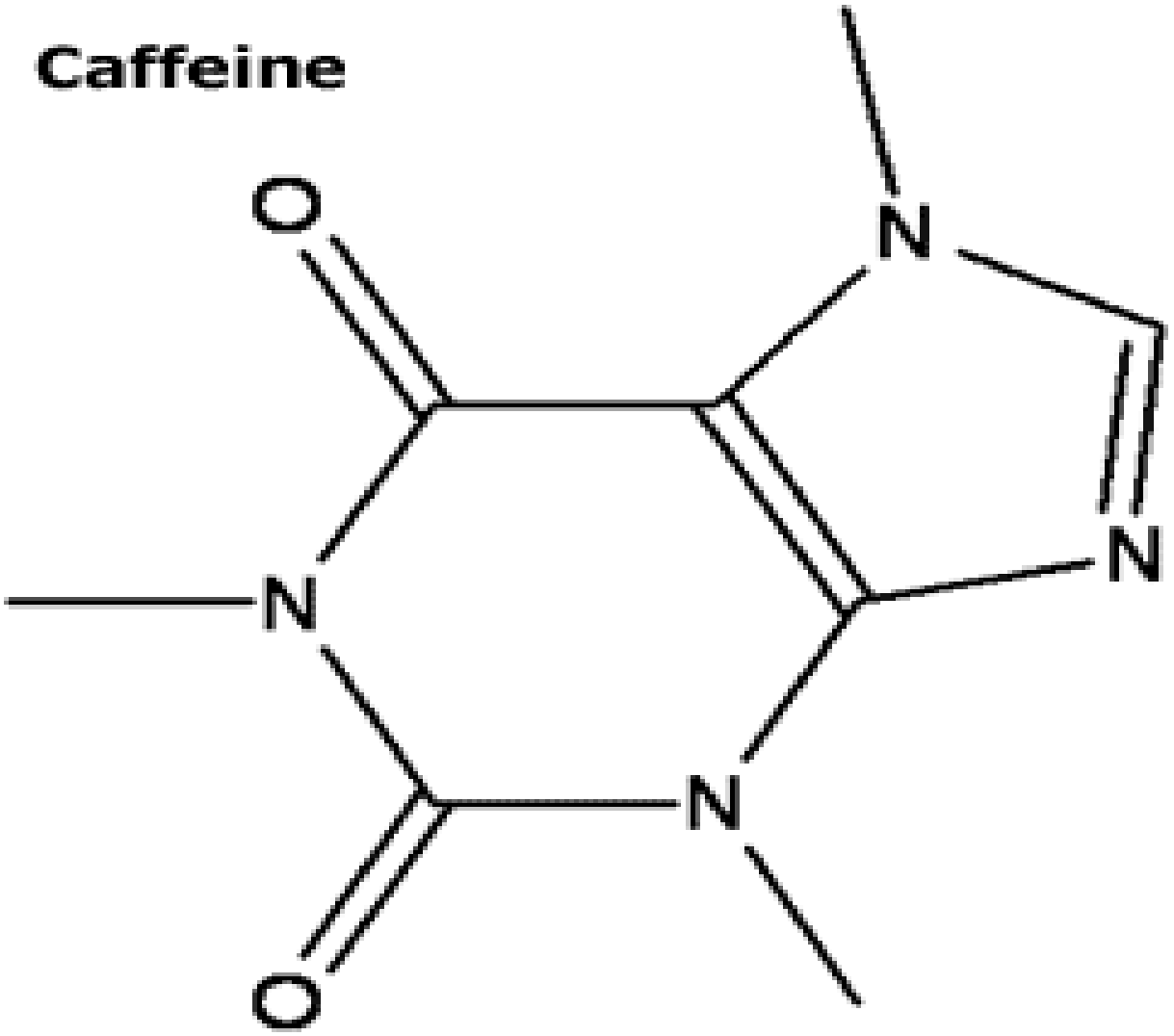
Stream Monitoring Network (1999-2000)

139 streams in 30 states

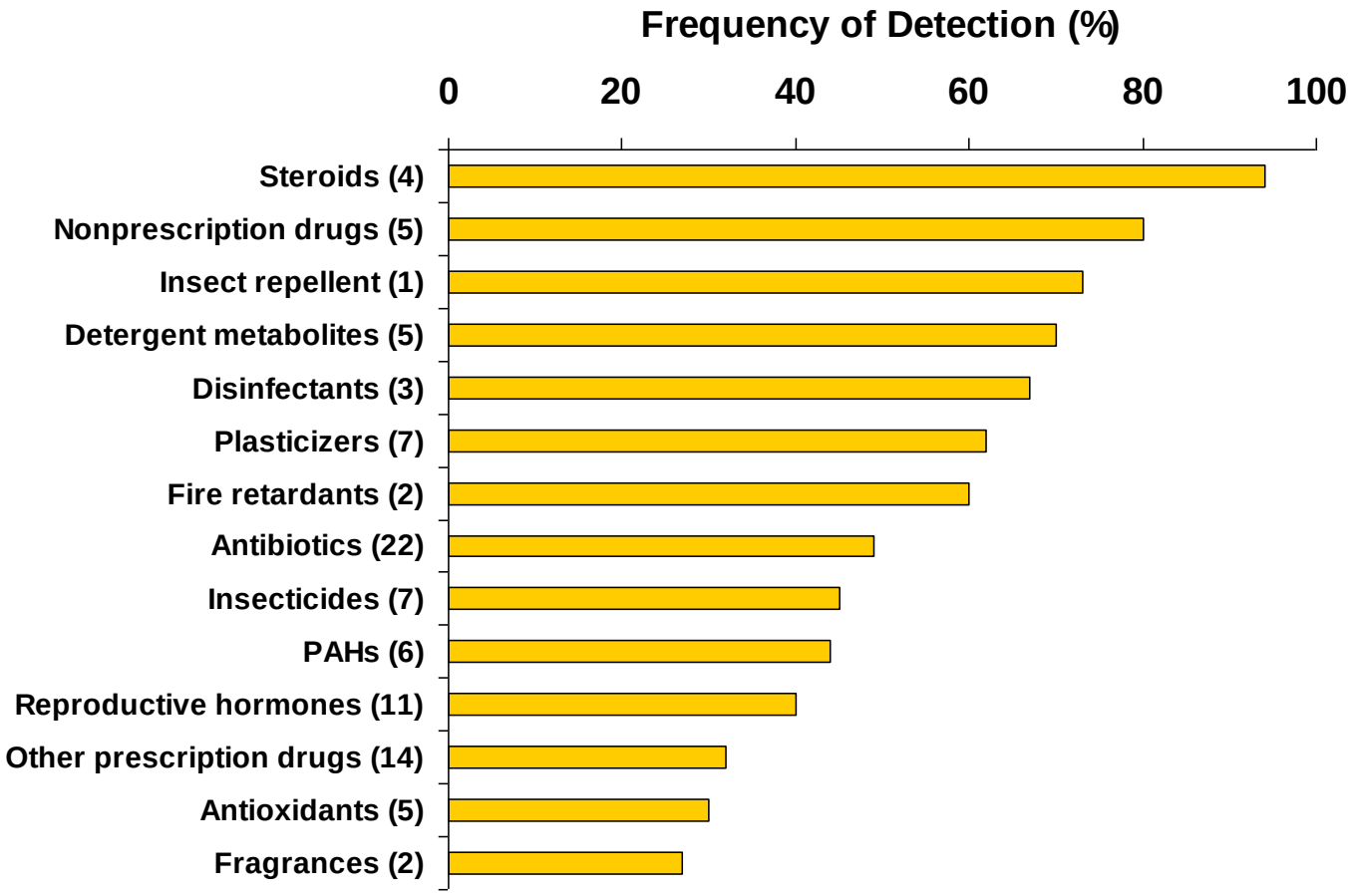
- 52 Urbanized.
- 62 Animal Production.
- 17 Mixed Land Use.
- 8 Minimally Developed.

USGS

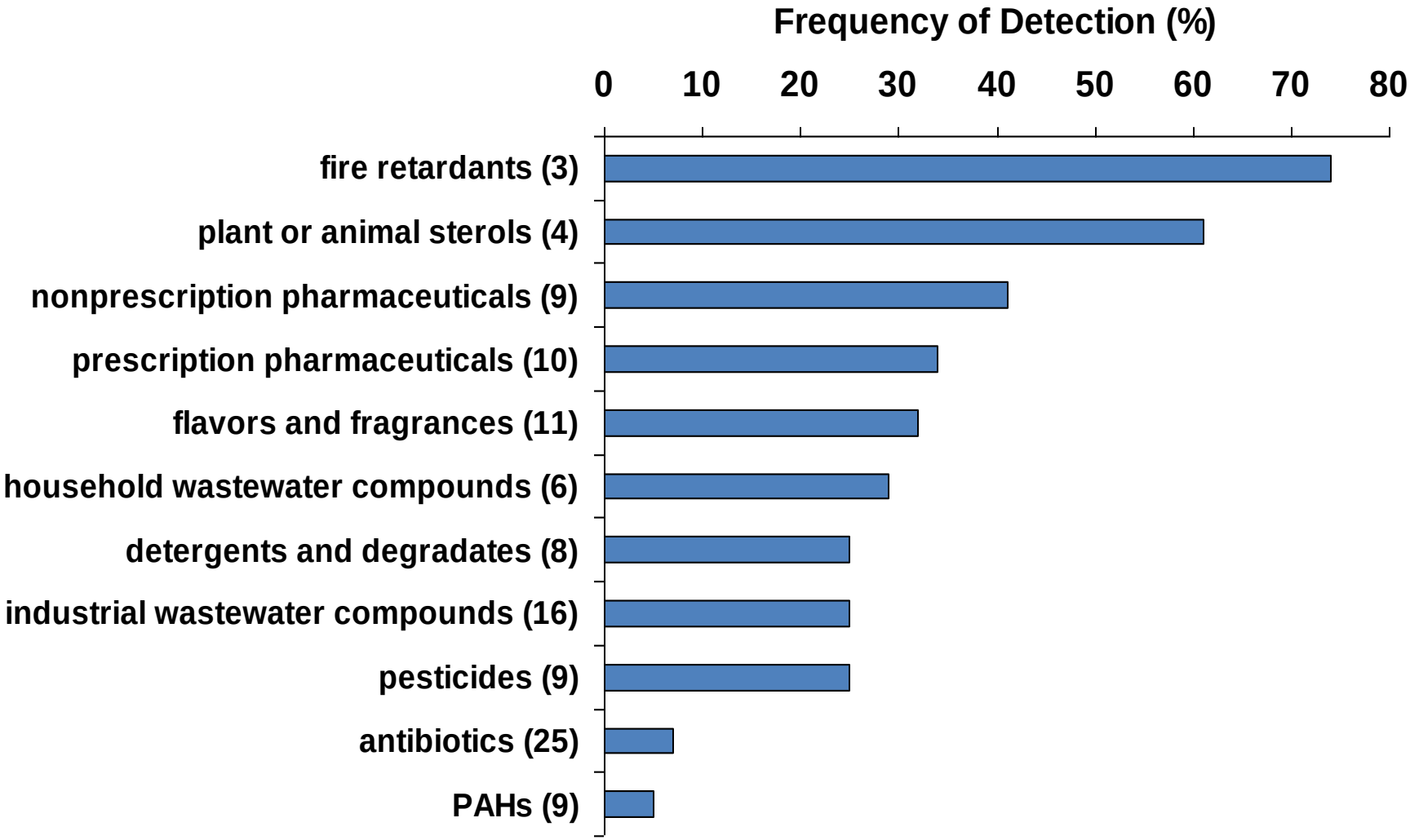
Caffeine is commonly found in many other products but is also found in several over the counter (OTC) medications.



Kolpin USGS Study results



USGS Effluent Study



Research names top 11 compounds in tap Water

- Monday, January 12, 2009 LAS VEGAS — New research has identified the 11 most frequently detected pharmaceutical and hormonally active chemical compounds in the drinking water of 19 US water utilities, a January 12 NewScientist.com article reported.
- Researchers Shane Snyder and colleagues at the Southern Nevada Water Authority in Las Vegas screened tap water from 19 US water utilities for 51 different compounds. The research, which is scheduled to appear in the next issue of the journal *Environmental Science & Technology*, indicates that all of the 11 most frequently detected compounds were found at extremely low concentrations.

According to the NewScientist.com article, the 11 most frequently detected compounds were:

- ● Atenolol, a beta-blocker used to treat cardiovascular disease
- ● Atrazine, an organic herbicide banned in the European Union but still used in the United States, which has been implicated in the decline of fish stocks and in changes in animal behavior
- ● Carbamazepine, a mood-stabilizing drug used to treat bipolar disorder, among other things
- ● Estrone, an estrogen hormone secreted by the ovaries and blamed for causing gender-bending changes in fish
- ● Gemfibrozil, an anti-cholesterol drug
- ● Meprobamate, a tranquilizer used in psychiatric treatment
- ● Naproxen, a painkiller and anti-inflammatory linked to increases in asthma incidence
- ● Phenytoin, an anticonvulsant that has been used to treat epilepsy
- ● Sulfamethoxazole, an antibiotic used against the *Streptococcus* bacteria, which is responsible for tonsillitis and other diseases
- ● TCEP, a reducing agent used in molecular biology
- ● Trimethoprim, an antibiotic.

- Christian Daughton, Ph.D., of the US Environmental Protection Agency's (EPA) National Exposure Research Laboratory, said in the report that neither this nor other recent water assessments give cause for health concern. He added, "But several point to the potential for risk — especially for the fetus and those with severely compromised health."

San Marcos Study Design

- Collected multiple water samples from different sample sites in the San Marcos, Tx area
  - seven locations at the Wastewater Treatment Plant (WWTP)
  - upstream and downstream of the WWTP effluent discharge into the San Marcos River
  - two discharge ports at the hospital
  - influent and effluent of the San Marcos Water Treatment Plant (WTP)
- USGS Solid phase extraction methods
- Gas Chromatography-Mass Spectrometry and Liquid Chromatography-Mass Spectrometry to determine concentrations

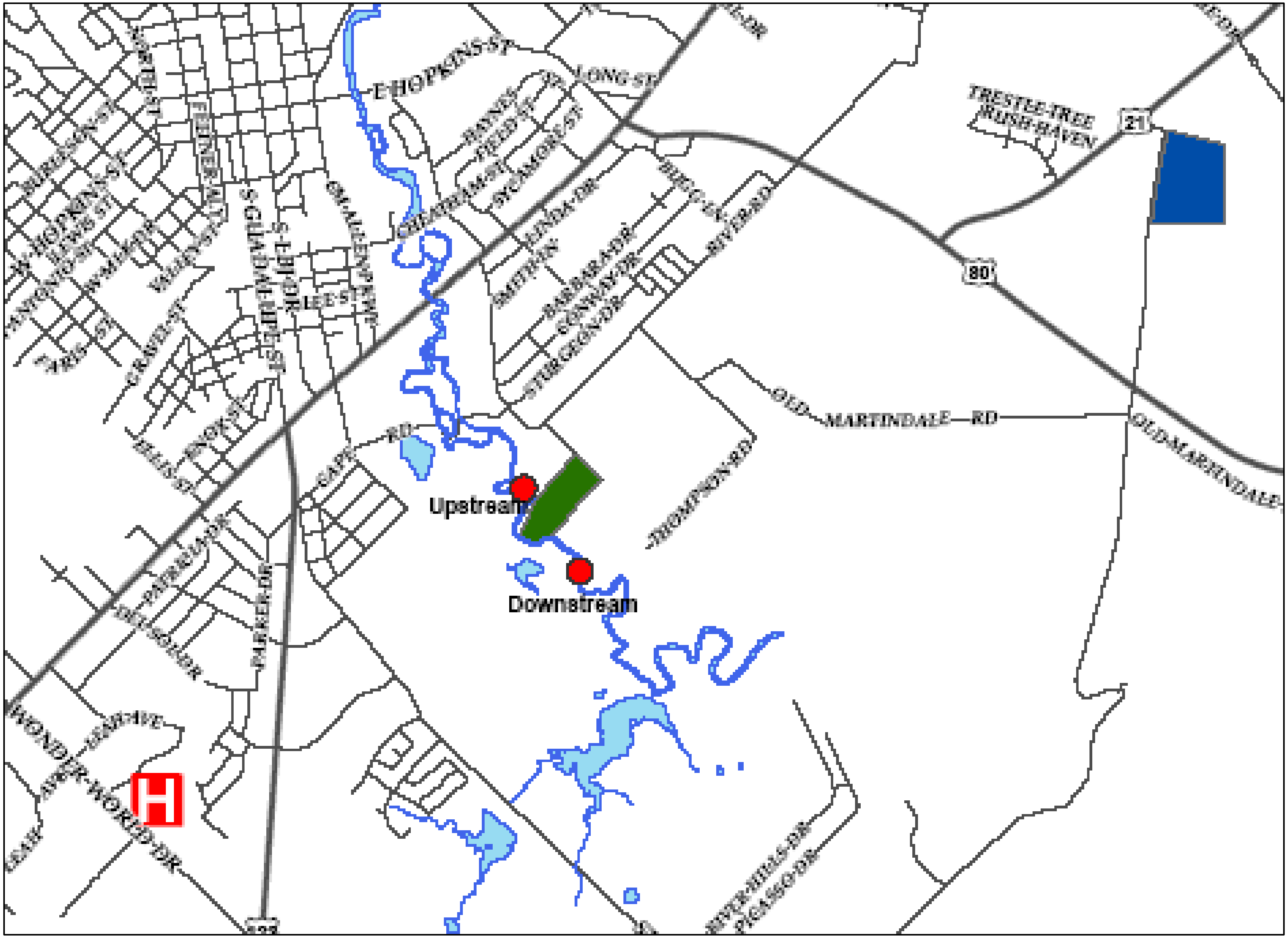
Purpose

Determine…

- efficiency of the WWTP in removing the 23 EDCs
- which treatment step is the most effective
- if the WWTP effluent is affecting the concentration of these compounds in the San Marcos river
- if the hospital is contributing any of these compounds to the WW collection system
- the occurrence of these compounds in the water supply

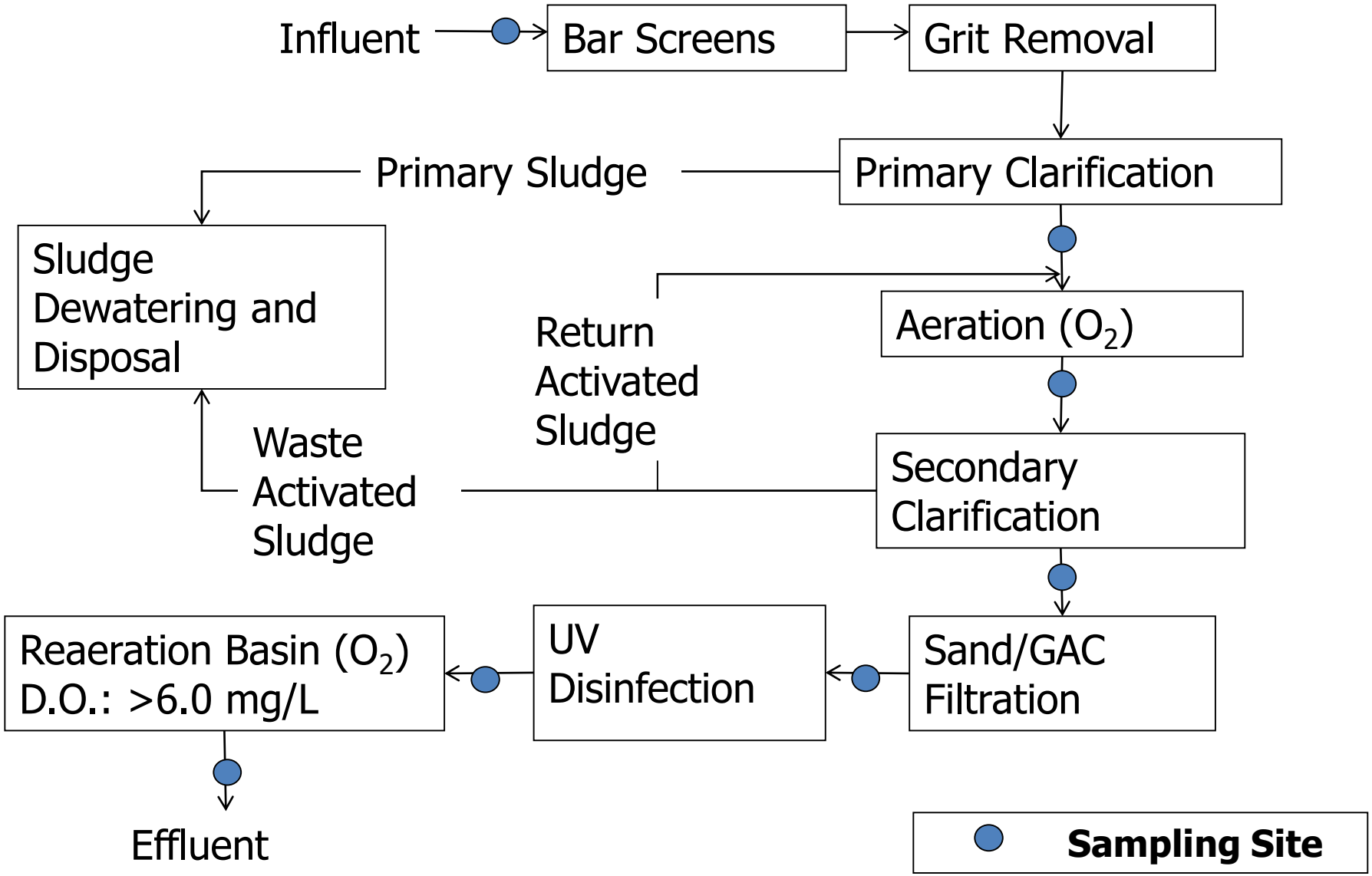
Compounds Investigated

- Hormones: Ethynylestradiol, coprostanol, estradiol
- Detergent metabolites: Nonylphenol, octylphenol
- Pharmaceuticals: Carbamazepine (Carbatrol®), codeine, diltiazem (Cardizem®), fluoxetine (Prozac®)
- Antibiotics: Sulfamethoxazole, trimethoprim
- Fire retardants: Tributylphosphate, Tris(2-chloroethyl)phosphate (TCEP)
- Pesticides: Diazinon
- Nonprescription Drugs: Acetaminophen, cotinine, caffeine
- Poly-Aromatic Hydrocarbons: Fluoranthene
- Flavors and fragrances: Benzophenone, triethyl citrate
- Household wastewater compounds: DEET, triclosan
- Industrial wastewater compounds: Bisphenol A



Upstream
Downstream
E-HOPKINS-ST
LONG-ST
TRESTLE-TREE
BRUSH-HAVEN
21
80
CHEATHAM-ST
SYCAMORE-ST
LINDA-DR
BARBARA-DR
CONWAY-DR
STURGEON-DR
RIVER-RD
LEE-ST
KNOX-ST
ELLIS-ST
CAPE-RD
PARKER-DR
OLD-MARTINDALE-RD
OLD-MARTINDALE
THOMPSON-RD
WONDER-WORLD-DR
RIVER-HILLS-DR
PICASSO-DR
H

San Marcos WWTP



Results

Of the 23 compounds investigated…

- 18 of those were detected in at least one sample (Cotinine, diazinon, ethynylestradiol, trimethoprim, and Prozac® were not detected in any samples)
- 14 were detected each sampling event
- One was detected at trace amounts in the San Marcos water drinking supply (TCEP @ 8 ng/L)

Hospital Results

Compound	Detection Frequency (%)			Mean Concentration (ng/L)		
	#1	#2	Total	#1	#2	Average
Acetaminophen	100	100	100	110,000	180,000	140,000
Caffeine	100	100	100	61,000	86,000	73,000
Triclosan	100	100	100	77,000	36,000	57,000
Coprostanol	100	83	92	11,000	14,000	12,000
DEET	67	67	67	110	110	110
TCEP	50	83	67	43	63	53
Benzophenone	67	50	58	380	600	490
Diltiazem	50	50	50	710	1,600	1,100
Triethyl citrate	67	33	50	230	300	260
Nonylphenol	33	33	33	29,000	8,900	19,000
Tributylphosphate	0	67	33	<80	190	190
Codeine	25	0	13	50,000	<200	50,000

WWTP Influent Concentrations (ng/L)

Compound	Detection Frequency (%)	Mean Concentration (ng/L)	Minimum Concentration (ng/L)	Maximum Concentration (ng/L)
Acetaminophen	100	44,000	16,000	80,000
Nonylphenol	100	31,000	9,000	63,000
Coprostanol	100	30,000	12,000	39,000
Caffeine	100	17,000	7,600	29,000
Benzophenone	100	2,500	630	6,200
Triethyl citrate	100	2,300	960	5,300
Triclosan	100	2,200	840	3,000
DEET	100	1,700	500	3,000
Bisphenol A	100	280	160	360
TCEP	100	260	33*	590
Diltiazem	50	1,600	1,200	1,900
Carbamazepine	50	590	550	620
Octylphenol	33	4,100	3,900	4,300
Estradiol	33	3,000	3,000	3,000
Fluoranthene	33	360	290	430
Tributylphosphate	33	260	100	410
Codeine	25	35,000	35,000	35,000

WWTP Removal Efficiencies

	% Removal		% Removal
Acetaminophen	100.0	Benzophenone	99.4
Bisphenol A	100.0	Triclosan	99.3
Codeine	100.0	DEET	99.2
Fluoranthene	100.0	Triethyl citrate	98.8
Octylphenol	100.0	Estradiol	97.0
Tributylphosphate	100.0	Diltiazem	91.9
Caffeine	99.8		
Nonylphenol	99.7	TCEP	33.0
Coprostanol	99.5	Carbamazepine	24.8

$$\text{Removal Efficiency} = 100 - \left(\frac{\text{effluent concentration}}{\text{influent concentration}} \right) * 100$$

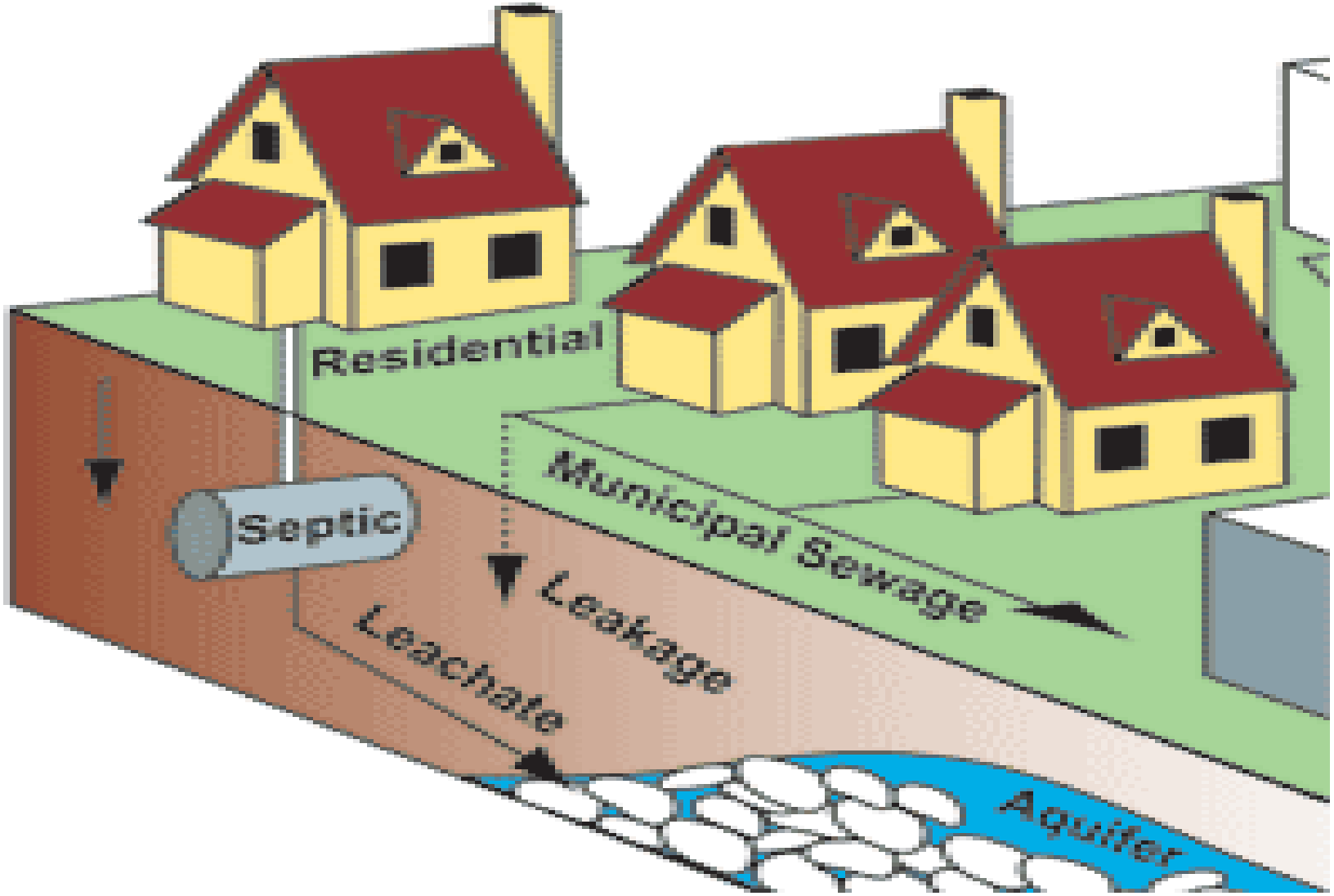
Effluent Results

Compound	Detection Frequency (%)			Mean Concentration (ng/L)		
	US	Effluent	DS	US	Effluent	DS
TCEP	0	100	100	<20	140	130
Caffeine	67	100	83	7*	22*	15*
Triethyl citrate	0	100	83	<20	16*	12*
Triclosan	0	83	0	<20	15*	<20
Carbamazepine	0	75	75	<50	330	290
Sulfamethoxazole	0	50	50	<50	560	1,200
Diltiazem	0	50	50	<50	130	100
Coprostanol	0	50	33	<20	110	84
Nonylphenol	0	33	33	<40	180	210
DEET	0	33	33	<20	23	9*
Estradiol	0	17	0	<20	89	<80
Benzophenone	0	17	33	<20	11*	11*
Bisphenol A	33	0	0	7*	<20	<20

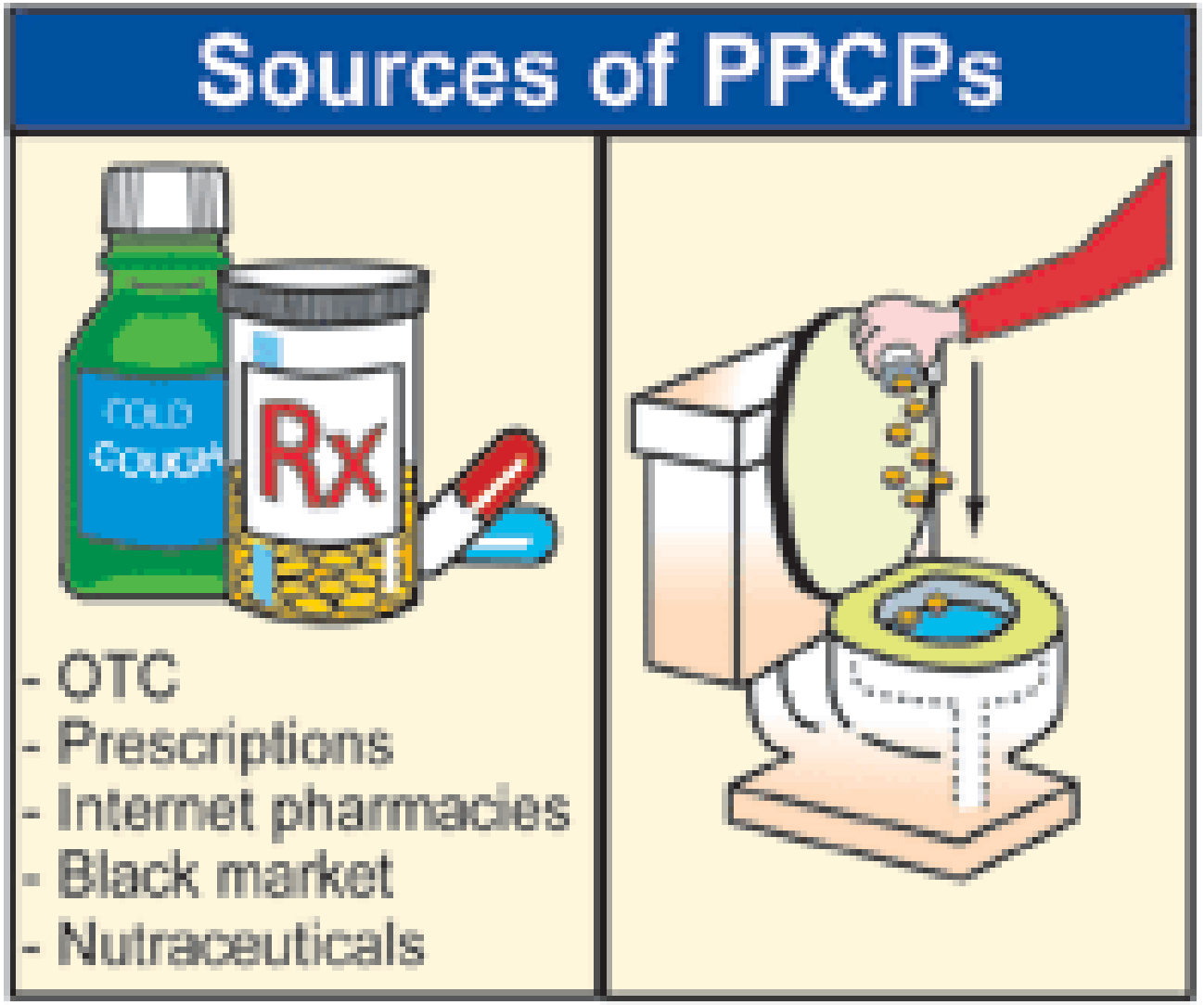
Conclusions

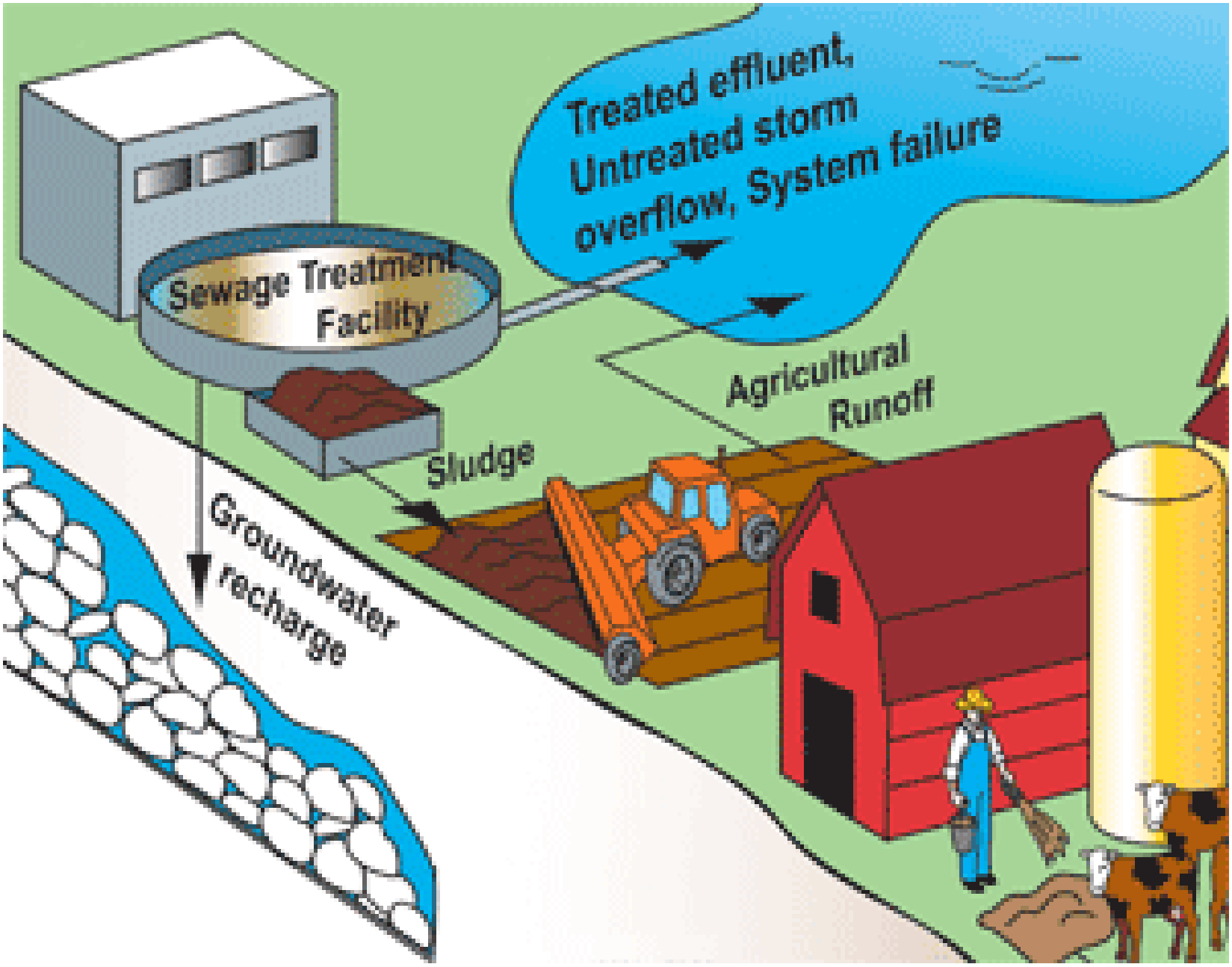
- The San Marcos WWTP removed >99.9% of the 23 EDCs (by mass)
- The aeration process was the most effective at removal of these compounds
- The WWTP effluent was increasing the concentrations of 12 compounds downstream from the plant discharge.
- The hospital was contributing 12 compounds to the WW collection system (22 – 370,000 ng/L).

Pathways to WWTPs



Improper disposal of PPCPs




Treated effluent,
Untreated storm
overflow, System failure
Sewage Treatment
Facility
Agricultural
Runoff
Sludge
Groundwater
recharge

Emerging contaminants can originate from a variety of animal- and human-waste sources such as this hog production facility

References

Barnes, K.K., Kolpin, D.W., Furlong, E.T., Zaugg, S.D., Meyer, M.T., and Barber, L.B., 2008, A national reconnaissance of pharmaceuticals and other organic wastewater contaminants in the United States--I. Groundwater: Science of the Total Environment, doi:10.1016/j.scitotenv.2008.04.028.

Focazio, M.J., Kolpin, D.W., Barnes, K.K., Furlong, E.T., Meyer, M.T., Zaugg, S.D., Barber, L.B., and Thurman, E.M., 2008, A national reconnaissance for pharmaceuticals and other organic wastewater contaminants in the United States--II. Untreated drinking water sources: Science of the Total Environment, doi:10.1016/j.scitotenv.2008.02.021.

Barnes, K.K., Kolpin, D.W., Focazio, M.J., Furlong, E.T., Meyer, M.T., Zaugg, S.D., Haack, S.K., Barber, L.B., and Thurman, E.M., 2008, Water-quality data for pharmaceuticals and other organic wastewater contaminants in ground water and in untreated drinking water sources in the United States, 2000-01: U.S. Geological Survey Open-File Report 2008-1293, 6 p. plus tables.

Questions?

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