EPA Biosolids Program Update - PPCPs



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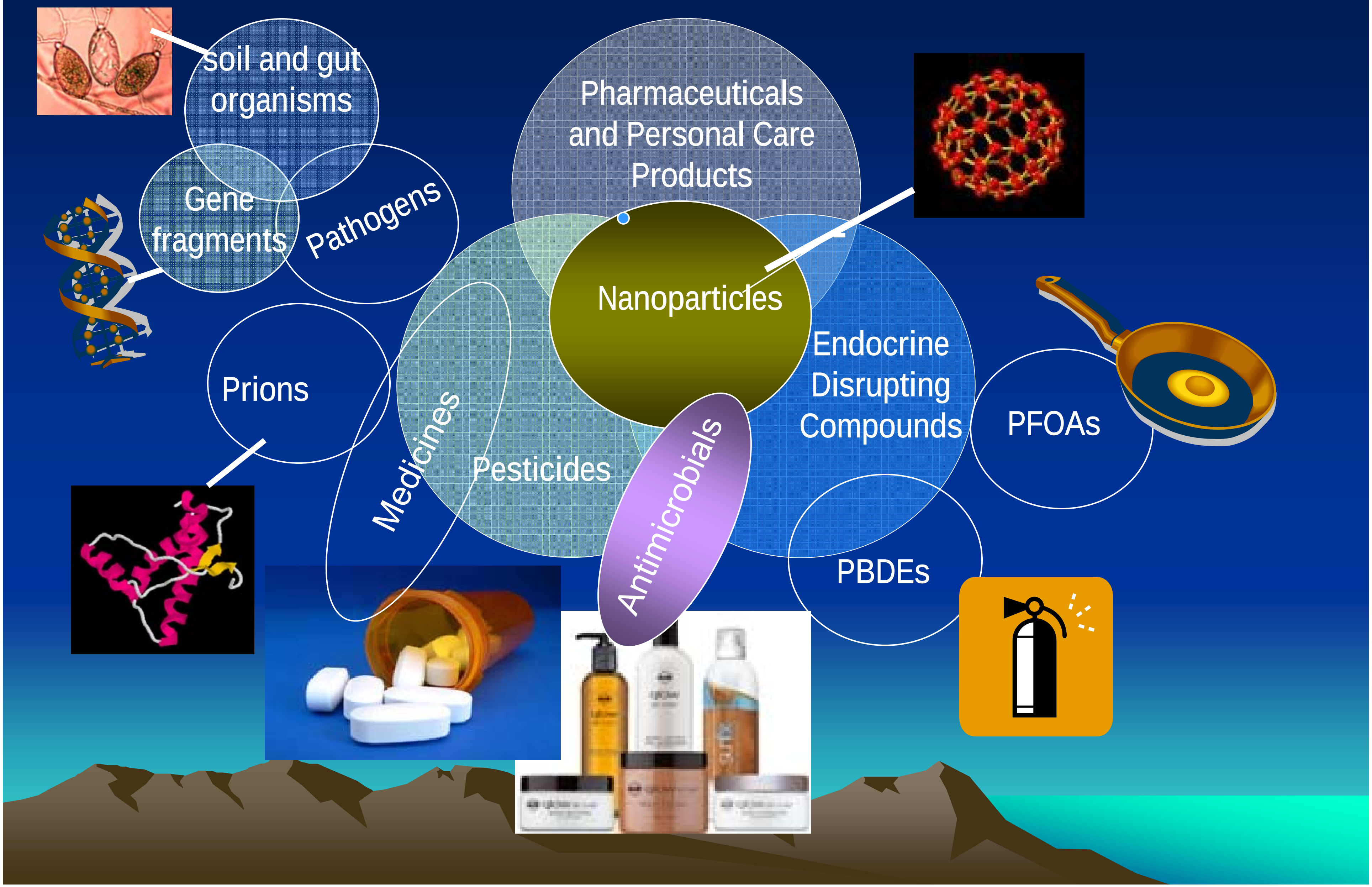
Region 8

May 12, 2009

Emerging Contaminants



Estimating the ECs Universe
Chemicals

CAS Registry*

- 31 million organic and inorganic substances
- Updated daily with ~4000 new substance records

**American Chemical Society's Chemical Abstracts Service*

Estimating ECs Universe
Pathogens

- Known
  - Viruses
    - Hepatitis
    - Adenovirus 12
    - Norovirus
  - Bacteria
    - *Salmonella* spp. (to include *S. enterica*)
    - *Escherichia coli*
    - *Enterococcus* spp.
  - Parasites
    - *Giardia*
    - *Cryptosporidium*
- Emerging
  - *E. coli* strains:
    - *Escherichia coli* O157:H7 [enterohemorrhagic/Shiga-toxin producing; EHEC or STEC]
    - Antibiotic-resistant (focus on vancomycin- and methicillin-)
  - Analogous *Salmonella typhimurium* strains

Emerging Contaminants (ECs)
What are they?

EU Definition:

- New chemicals produced to offer improvements in industry, agriculture, medicine, and common conveniences.
- New reasons for concern for existing contaminants.
- New capabilities enabling improved examination of contaminants.

What's in a Name

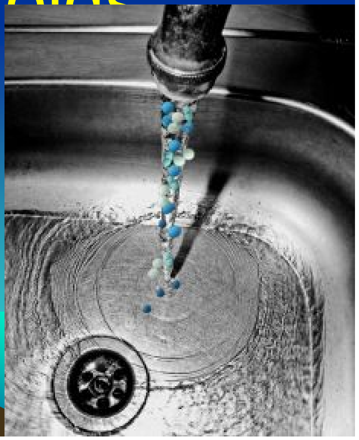
What to call these 'compounds' without negatively branding them as "worry" or "concern"

- Emerging Contaminants of Concern
- Compounds of Emerging Concern
- Emerging Contaminants
- Organic Wastewater Contaminants
- Emerging = Emergency

Microconstituents (WEF 2007)

Reasons for concern:

- Large quantities of PPCP can enter the environment after use by individuals or domestic animals.
- Sewage systems are not fully equipped for PPCP removal.
- The risks are uncertain. The risks posed to aquatic organisms, and to humans are unknown, largely because the concentrations are so low.
- Current major concerns have been antibiotics resistance and disruption of aquatic endocrine systems by natural and synthetic sex steroids.



So Why the Interest?

PPCPs illustrate the connection of individuals' activities have with their environment (Our Society uses PPCPs)

- Chemicals are getting into the environment
- Reports of intersex fish and other findings
- Congressional and public interest

- No evidence of adverse human health effects

- As our analytical capabilities increase our detection of these chemicals is also likely to increase – but will our understanding increasing at the same rate?

Future Concerns

Are biosolids a human health or environmental concern? Or not?

Do we understand all the risks?

Do we have all the needed risk assessment tools? Or information?

Do we fully understand how well sewage treatment mitigates health and environmental risks?

Targeted National Sewage Sludge Survey (TNSSS)

Development and Application of Analytical Methods for Detecting Pharmaceutical and Personal Care Products in Sewage Sludge

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TNSSS

Why conduct the TNSSS

- Response to the 2002 NRC report
- Update source concentrations
- Last Survey 1988

What we did

- Randomly selected POTWs
- Three flow groups with at least secondary treatment
- Sampled August 2006 through March 2007
- Collected 84 samples at 74 facilities in 36 states
- U.S. EPA Region 8
  - Colorado - 1
  - Utah -1

Figure 2. Geographic Distribution of 80 POTWs Originally Selected for Sampling

Targeted National Sewage Sludge Survey

145 Analytes

- PPCPs
- Metals
- PAHs
- Semi-volatiles
- Inorganic ions
- PBDEs

2006 Biosolids Data

	CO 2006 mg/Kg[1]	R8 2006 mg/Kg[1]	National 2006 mg/Kg[2]	Typical Soils Conc. mg/Kg	503 Table 3 mg/Kg[5]
As	4	8	7	5.5[3]	41
Cd	2.5	3	3	0.27[4]	39
Cr	25	30	83	40[4]	N.R.
Cu	550	525	569	16.3[4]	1500
Pb	34	45	80	11.8[4]	300
Hg	0.8	2.3	1.3	0.05[3]	17
Mo	11	12	17	1-2	(75)[6]
Ni	18	24	53	15[4]	420
Se	8	10	7	0.29[3]	100
Zn	599	645	1029	54.3[4]	2800

Notes: [1]2006 Annual Reports summarized in US EPA Region 8 BDMS,[2] US EPA 2007, [3] As, Hg, Se are median values from Shacklette and Boerngen 1984; [4] Cd, Pb, Zn, Cu and Ni are background Great Plains means from Holmgren et al 1993; [5] US EPA 1993: [6]Table 1 Requirement; N.R. Not Required

PPCPs - EPA Methods 1694, 1698, and 1699

Single lab validated / Peer reviewed

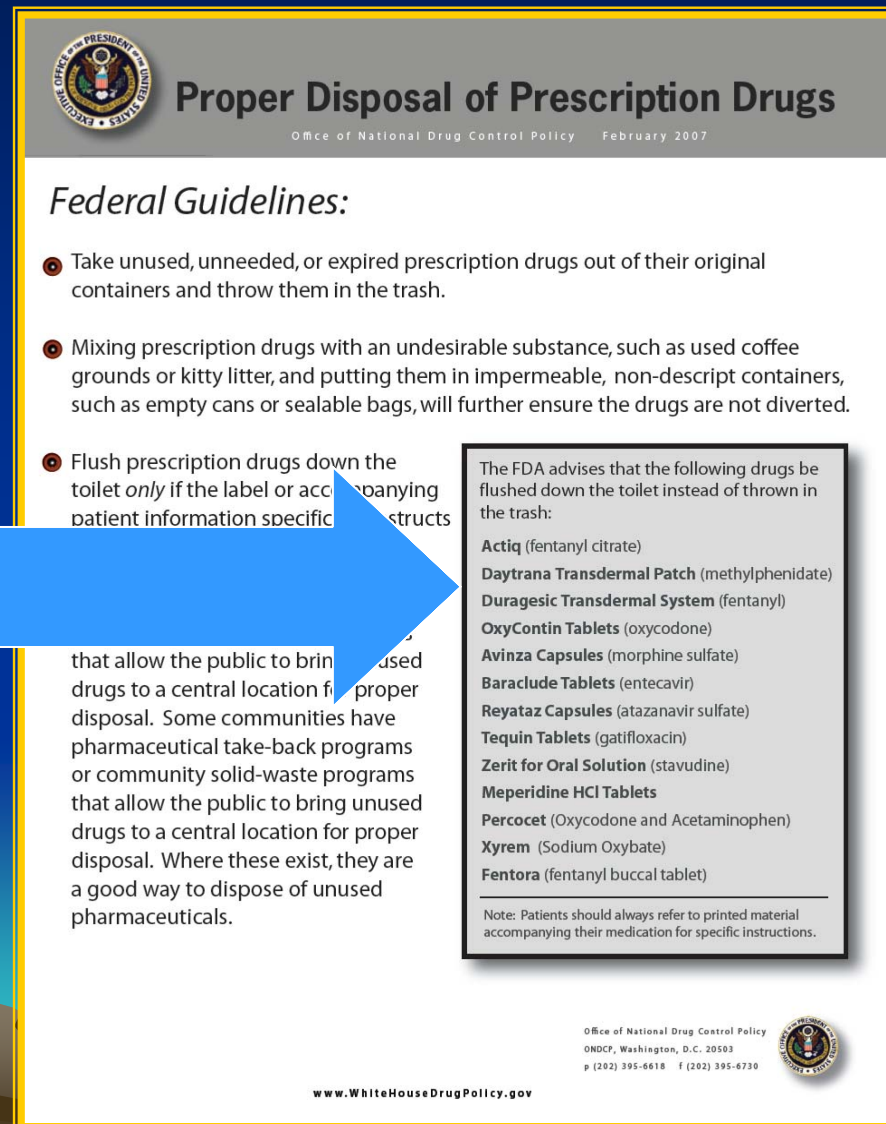
208 analytes

Posted to EPA's Waterscience Methods web site and EPA's PPCP web site:

- http://www.epa.gov/waterscience/methods/method/other.html
- http://www.epa.gov/ppcp/

White House Office of National Drug Control Policy

Prescription Drug Abuse Guidance



Proper Disposal of Prescription Drugs

Office of National Drug Control Policy February 2007

Federal Guidelines:

- Take unused, unneeded, or expired prescription drugs out of their original containers and throw them in the trash.
- Mixing prescription drugs with an undesirable substance, such as used coffee grounds or kitty litter, and putting them in impermeable, non-descript containers, such as empty cans or sealable bags, will further ensure the drugs are not diverted.
- Flush prescription drugs down the toilet *only* if the label or acc[...]panying patient information specific[...]structs

that allow the public to brin[...]used drugs to a central location f[...] proper disposal. Some communities have pharmaceutical take-back programs or community solid-waste programs that allow the public to bring unused drugs to a central location for proper disposal. Where these exist, they are a good way to dispose of unused pharmaceuticals.

The FDA advises that the following drugs be flushed down the toilet instead of thrown in the trash:

Actiq (fentanyl citrate)
Daytrana Transdermal Patch (methylphenidate)
Duragesic Transdermal System (fentanyl)
OxyContin Tablets (oxycodone)
Avinza Capsules (morphine sulfate)
Baraclude Tablets (entecavir)
Reyataz Capsules (atazanavir sulfate)
Tequin Tablets (gatifloxacin)
Zerit for Oral Solution (stavudine)
Meperidine HCl Tablets
Percocet (Oxycodone and Acetaminophen)
Xyrem (Sodium Oxybate)
Fentora (fentanyl buccal tablet)

Note: Patients should always refer to printed material accompanying their medication for specific instructions.

Office of National Drug Control Policy
ONDCP, Washington, D.C. 20503
p (202) 395-6618 f (202) 395-6730

www.WhiteHouseDrugPolicy.gov

Table 5. Target Analytes for the 2006 National Sewage Sludge Survey, by Analyte Class

Analyte Class	Analyte			
Metals	*Aluminum*		**Manganese**	
	Antimony		*Mercury**	
	*Arsenic**		*Molybdenum**	
	Barium		*Nickel*	
	Beryllium		*Phosphorus*	
	Boron		*Selenium**	
	*Cadmium**		**Silver**	
	Calcium		*Sodium*	
	*Chromium**		*Thallium*	
	Cobalt		*Tin*	
	*Copper**		*Titanium*	
	Iron		*Vanadium*	
	*Lead**		*Yttrium*	
	Magnesium		*Zinc**	
Polycyclic Aromatic Hydrocarbons (PAHs)	*Benzo(a)pyrene*		*2-Methylnaphthalene*	
	Fluoranthene		**Pyrene**	
Semivolatiles	*bis (2-Ethylhexyl) phthalate*		**4-Chloroaniline**	
Inorganic Anions	*Fluoride*		*Water-extractable phosphorus*	
	Nitrate/Nitrite			
Polybrominated diphenyl ethers (PBDEs) - focusing on the following congeners of potential environmental and public health significance	*2,4,4'-TrBDE*	*BDE-28*	*2,2',3,4,4',5'-HxBDE*	*BDE-138*
	2,2',4,4'-TeBDE	*BDE-47*	*2,2',4,4',5,5'-HxBDE*	*BDE-153*
	2,3',4,4'-TeBDE	*BDE-66*	*2,2',4,4',5',6-HxBDE*	*BDE-154*
	2,2',3,4,4'-PeBDE	*BDE-85*	*2,2',3,4,4',5',6-HpBDE*	*BDE-183*
	2,2',4,4',5-PeBDE	*BDE-99*	*DeBDE*	*BDE-209*
	2,2',4,4',6-PeBDE	*BDE-100*		

* Metals currently regulated at 40 CFR 503

PPCP Analytes – Drugs, Antibiotics and antimicrobials

Analyte

1,7-Dimethylxanthine
Acetaminophen
Albuterol
Azithromycin
Caffeine
Carbadox
Chlortetracycline
Cimetidine
Ciprofloxacin
Cotinine
Digoxigenin
Digoxin
Diltiazem
Doxycycline
Enrofloxacin
Erythromycin hydrate
Fluoxetine
Gemfibrozil
Ibuprofen
Lincomycin
Metformin
Norfloxacin
Norgestimate
Oxytetracyclin
Ranitidine
Roxithromycin
Sarafloxacin

Analyte

Sulfachloropyridazine
Sulfadimethoxine
Sulfamerazine
Sulfamethazine
Sulfamethizole
Sulfamethoxazole
Sulfanilamide
Sulfathiazole
Tetracycline
Trimethoprim
Tylosin
Virginiamycin
Warfarin
4-Epianhydrochlortetracycline
4-Epianhydrotetracycline
4-Epichlortetracycline
4-Epioxytetracycline
4-Epitetracycline
Anhydrochlortetracycline
Anhydrotetracycline
Carbamazepine
Cefotaxime
Clarithromycin

Analyte

Clinafloxacin
Cloxacillin
Codeine
Dehydronifedipine
Demeclocycline
Diphenhydramine
Flumequine
Isochlortetracycline
Lomefloxacin
Miconazole
Minocycline
Naproxen
Ormetoprim
Oxacillin
Oxolinic Acid
Penicillin G
Penicillin V
Sulfadiazine
Thiabendazole
Triclocarban
Triclosan

PPCP Analytes – Steroids and Hormones

Analyte

Cholestanol
Cholesterol
Coprostanol
Desmosterol
17-alpha-Dihydroequilin
17-alpha-Estradiol
17-alpha-Ethinyl-Estradiol
17-beta-Estradiol
beta-Estradiol-3-benzoate
Epicoprostanol
Equilin
Ergosterol
Estrone
Mestranol
Norethindrone
Norgestrel
beta-Sitosterol
Stigmasterol
Testosterone

Analyte

Androstenedione
Androsterone
Campesterol
Desogestrel
Equilenin
Estriol
Progesterone
beta-Stigmastanol

Analytes Selected for In-Depth Statistical Analysis

Metals	Barium Beryllium	Manganese Silver
Organics	4-Chloroaniline Fluoranthene	Pyrene
Classicals	Nitrate/Nitrite	

Analyte
Azithromycin
Beta Stigmastanol
Campesterol
Carbamazepine
Cholestanol
Cholesterol
Cimetidine
Ciprofloxacin
Coprostanol
Diphenhydramine

Analyte
Doxycycline
4-Epitetracycline (ETC)
Epicoprostanol
Erythromycin-Total
Fluoxetine
Miconazole
Ofloxacin
Stigmasterol
Tetracycline (TC)
Triclocarban
Triclosan

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Preliminary Observations

Of the 72 pharmaceuticals:

- 3 in all 84 samples
- 9 in at least 80 of the samples
- 15 not in any sample
- 29 were found in fewer than 3 samples

Preliminary Observations

Of the 25 steroids and hormones

- 3 steroids in all 84 samples
- 6 steroids in at least 80 of the samples
- 5 hormones in fewer than 6 samples
- 1 hormone not in any sample

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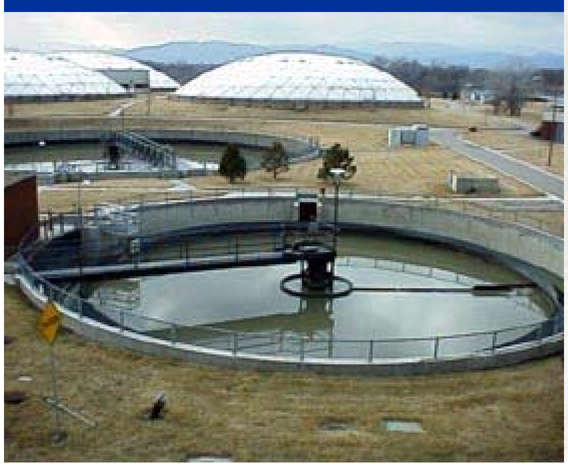
Summary of Survey Results for Pharmaceuticals (drugs and antibiotics)

Analyte	Units	# Detects	Observed Dry-weight Concentration	
			Minimum	Maximum
% Solids	%	84	0.14	94.9
Acetaminophen	µg/kg	2	1,120	1,300
Albuterol		1	23.2	23.2
Azithromycin		80	10.2	6,530
Caffeine		39	65.1	1,110
Carbamazepine		80	8.74	6,030
Cimetidine		74	7.59	9,780
Ciprofloxacin		84	74.5	47,500
Codeine		20	9.59	328
Diphenhydramine		84	36.7	5,730
Doxycycline		76	50.8	5,090
Erythromycin-total		77	3.1	180
Fluoxetine	µg/kg	79	12.4	3,130
Ibuprofen		54	99.5	11,900
Miconazole		80	14.2	9,210
Tetracycline		81	38.3	5,270
Triclocarban		84	187	441,000
Triclosan		79	430	133,000

Summary of Survey Results for Steroids and Hormones				
			Observed Dry-weight Concentration	
Analyte	**Units**	**# Detects**	**Minimum**	**Maximum**
% Solids	%	84	0.14	94.9
Cholestanol	ug/kg	84	3,860	4,590,000
Cholesterol		81	18,700	5,390,000
Coprostanol		84	7,720	43,700,000
Ergosterol	ug/kg	53	4,530	91,900
17 α-Estradiol		5	16.1	48.8
17 β-Estradiol		11	22	355
β-Estradiol 3-benzoate		18	30.2	1850
17 α-Ethinyl-Estradiol		0	NA	NA
Estriol		18	7.56	232
Estrone		60	26.7	965
Norethindrone		5	21	1,360
Norgestrel		4	43.8	1,300
Progesterone		19	143	1,290
β-Sitosterol		73	24,400	1,640,000
β-Stigmastanol		83	3,440	1,330,000
Stigmasterol		76	11,000	806,000
Testosterone		17	30.8	2,040

PPCP Removal in Wastewater Treatment



ert W. Hite Treatment Facility

Overview of Today's Discussion

- Review effectiveness of biological treatment
  - EU Poseidon Project
  - Meta-Analysis of Mass Balance Studies on WWT
  - Other studies
- Land Application of Wastewater and Biosolids
- Recommended Approaches in information gathering

Objectives

- To provided information that indicated that these compounds ARE treated in a WWTP
- Discuss the need to distinguish between results and mechanisms and their meanings and applicability to environmental fate
- Discuss possibility of using WWTPs are a model of treatment for the environment
- Discuss ways we can modify existing WWTPs to improve removal efficiencies
- Discuss the need for proper sample planning to assure relevant results.

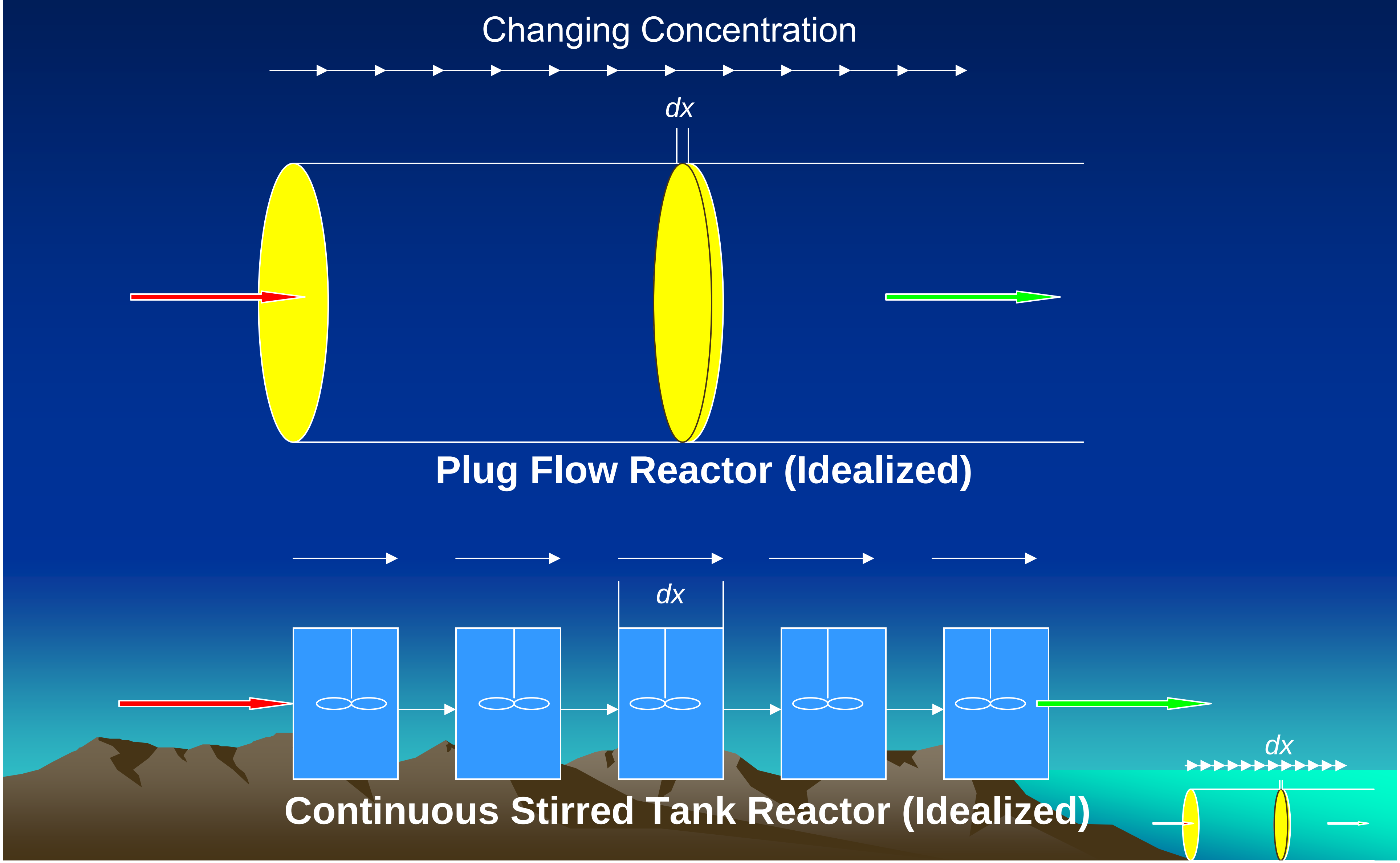
Why are we looking at WW Treatment

- Biological wastewater plants can remove significant % of PPCP
- Partitioning of the PPCP (Water vs Solids)
- Limited Success with Voluntary Programs (give/buy back etc.) therefore treatment is much more important
- To better understand mechanisms of environmental removal

Biological Treatment

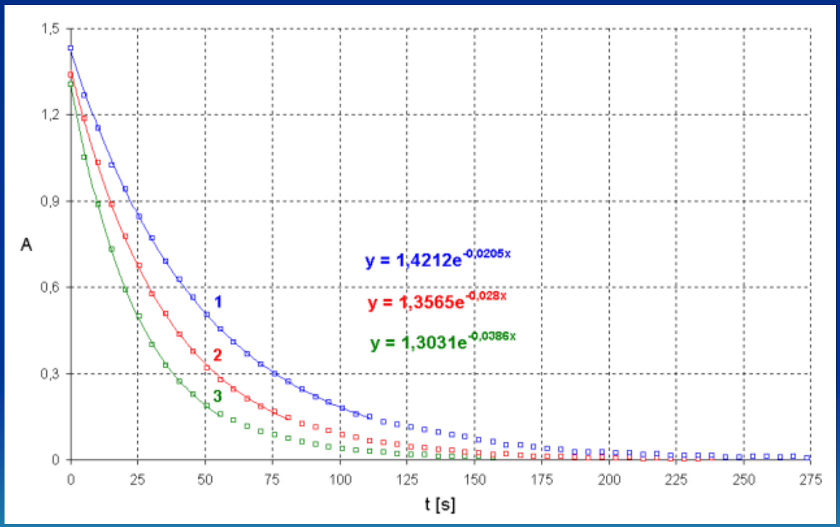
- HRT and SRT
  - HRT = effluent/influent flowrate
  - **(SRT)** = average time the activated-sludge solids are in the system. (also SRT, Sludge age, MCRT, θ_c)
- Absorption/ Adsorption
  - **Absorption** - Hydrophobic interactions of aliphatic and aromatic groups with lipophilic cell membrane and lipid fraction of sludge
  - **Adsorption** – Electrostatic interaction of the *positively* charged chemical groups with *negatively* charged surfaces of microorganisms

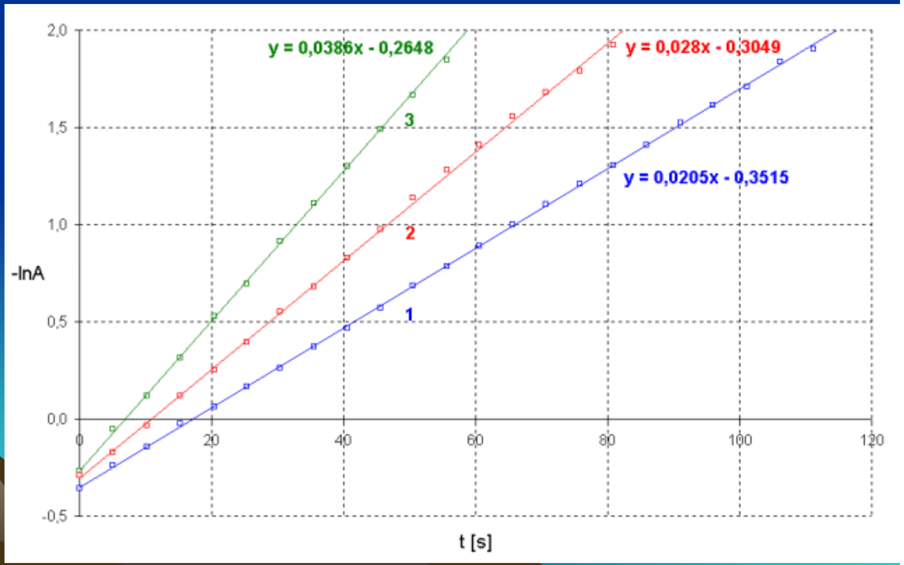
Idealized Treatment Schematic Diagram



Reaction Rates

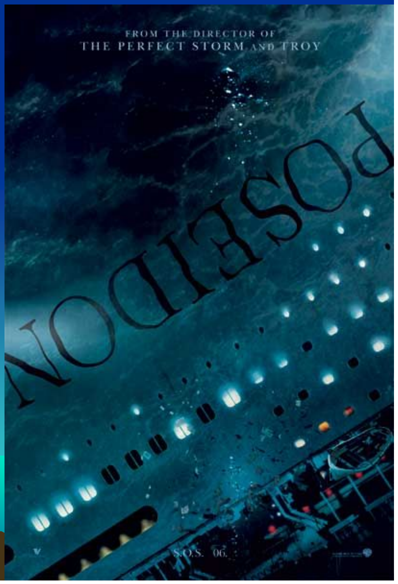
- Pseudo First Order Reaction





EU - Poseidon Project

- **Assessed Removal of Pharmaceuticals and Personal Care Products in Sewage and Drinking Water Facilities**
- **Began in 2001**



EU Poseidon Project Findings Study 1

- Sludge Age
  - Increased age increased Biodiversity
    - Research has shown a significant increase removals when comparing Sludge Age ≤ 4d and Sludge Age ≥ 10-15d
    - > 15d removal increases removal - but less prominent
  - Inert Sludge Content
    - Increase sludge age – increase rise in inert (non-volatile) faction relative to total mass
  - Sludge Production
    - Increase sludge age – decreased sludge production per WW volume -

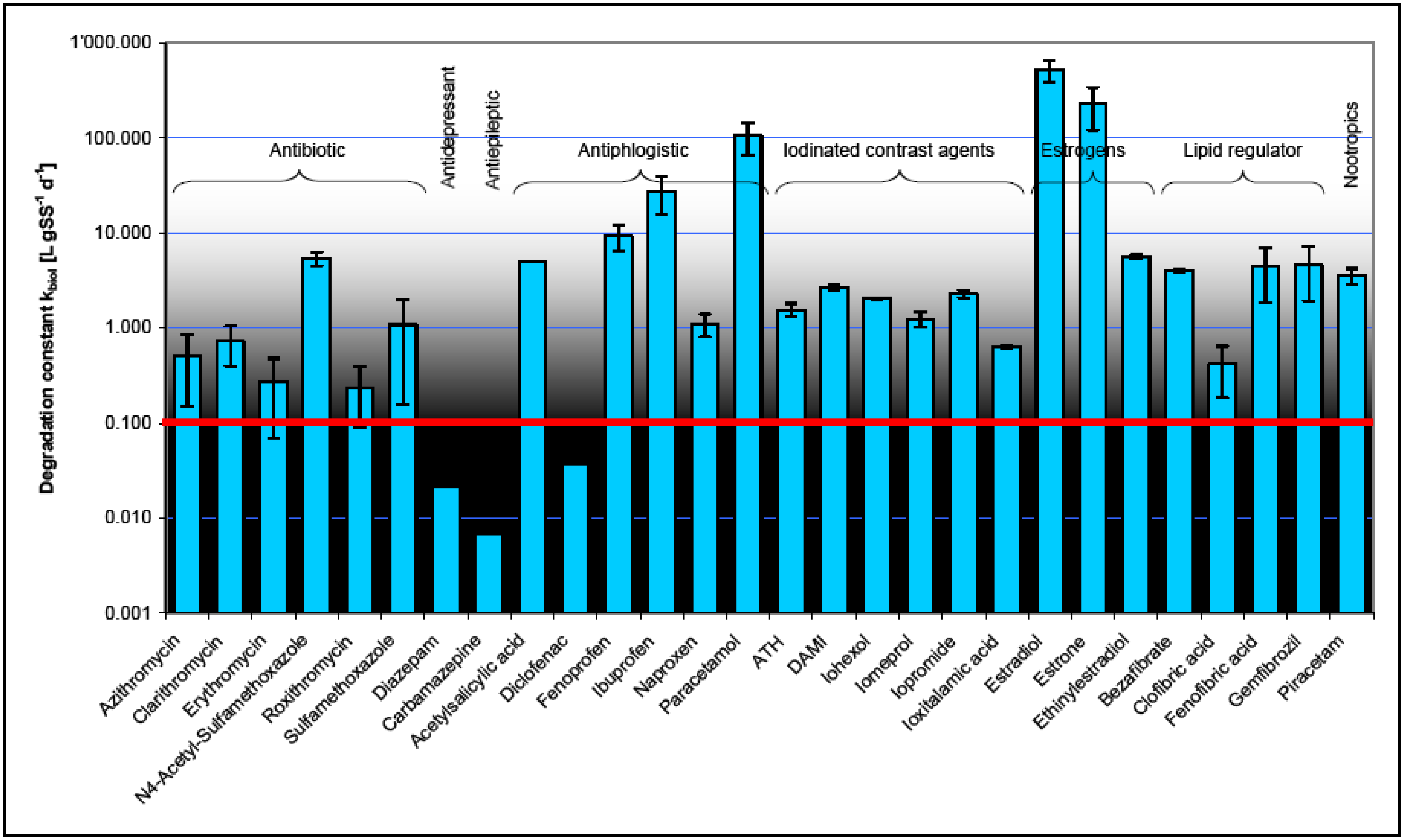
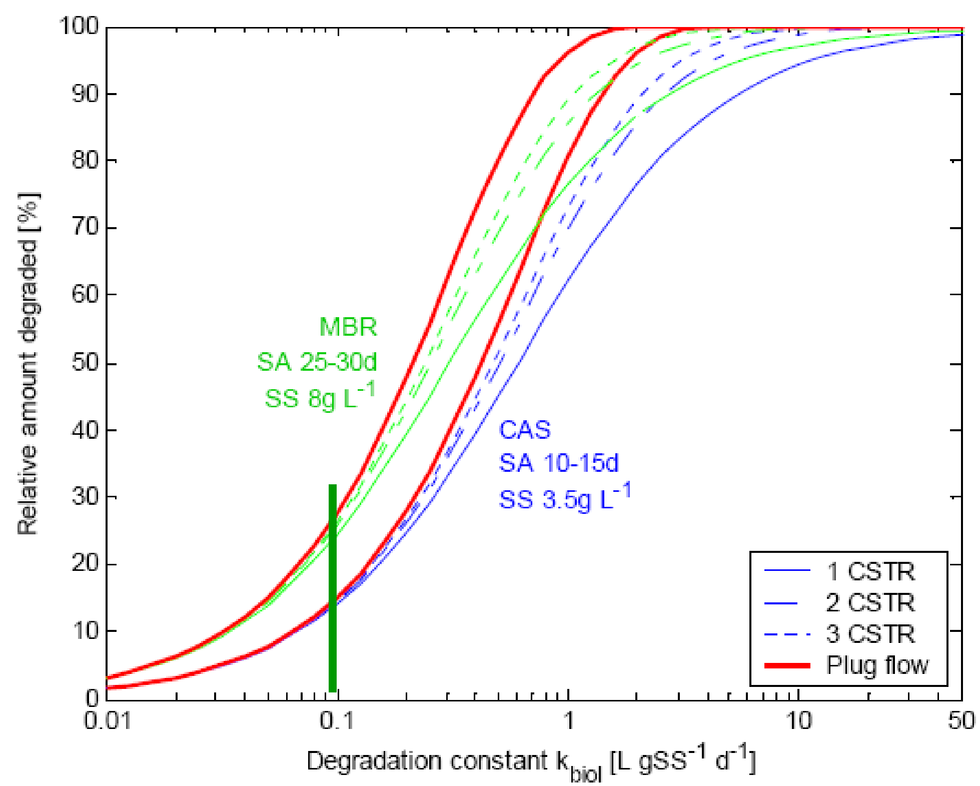


Figure 1.2: Biological pseudo first order degradation rate constants k_{biol} observed in aerobic batch experiments run with activated sludge from plants with a sludge age ≥ 8d. In the case of several observations being available, error bars indicate variation range (minimum and maximum). The red line at k_{biol} 0.1 L gSS^{-1} d^{-1} indicates the limit below which no significant degradation can be expected in typical municipal wastewater treatment plants (Figure 1.3).

Relative Amount Degraded in Various Reactor Configurations

Figure 1.3 Relative amount degraded in reactor configurations typical for municipal wastewater treatment: 8 h hydraulic retention time, reactor divided in one two or three cascaded completely stirred compartments (CSTR; eq. 1.2 and 1.4). Suspended solids concentration of 3.5 gSS L^{-1} is typical for conventional activated sludge systems (CAS, SA=10-15d), while membrane bioreactors (MBR, SA=25-30d) often run with up to 10 gSS L^{-1}. A high degree of removal can be expected for compounds with k_{biol} values ≥ 1 L gSS^{-1} d^{-1}.



Equation **1.2**

$$\frac{C_{i,out}}{C_{i,in}} = e^{-k_{i,biol} \cdot SS \cdot HRT} = e^{-k_{i,biol} \cdot SP \cdot SA}$$

Equation **1.3**

$$\frac{C_{i,out}}{C_{i,in}} = \left(\frac{1}{1 + k_{i,biol} \cdot \frac{SS \cdot HRT}{n}} \right)^n = \left(\frac{1}{1 + k_{i,biol} \cdot \frac{SP \cdot SA}{n}} \right)^n$$

Reactor Configurations EU Poseidon Project Findings

- Hydraulic Retention
  - Max % Removal thru Biological Treatment is completed at highest possible PPCP concentrations.
    - Minimize I and I (Stormwater and GW inputs)
- Cascades
  - The number of tanks in series increases removal (approach idealized Plug Flow)
  - MBR
    - Similar to activated Sludge

Reactor Configurations EU Poseidon Project Findings

- Most significant factors in removal of PPCP in biological treatment (Activated Sludge)
  - Sludge Age (10-15d)
  - Number of Cascaded Compartments (Plug Flow)
  - Dilution of Wastewater (Minimize I and I)

Reactor Configurations EU Poseidon Project Findings

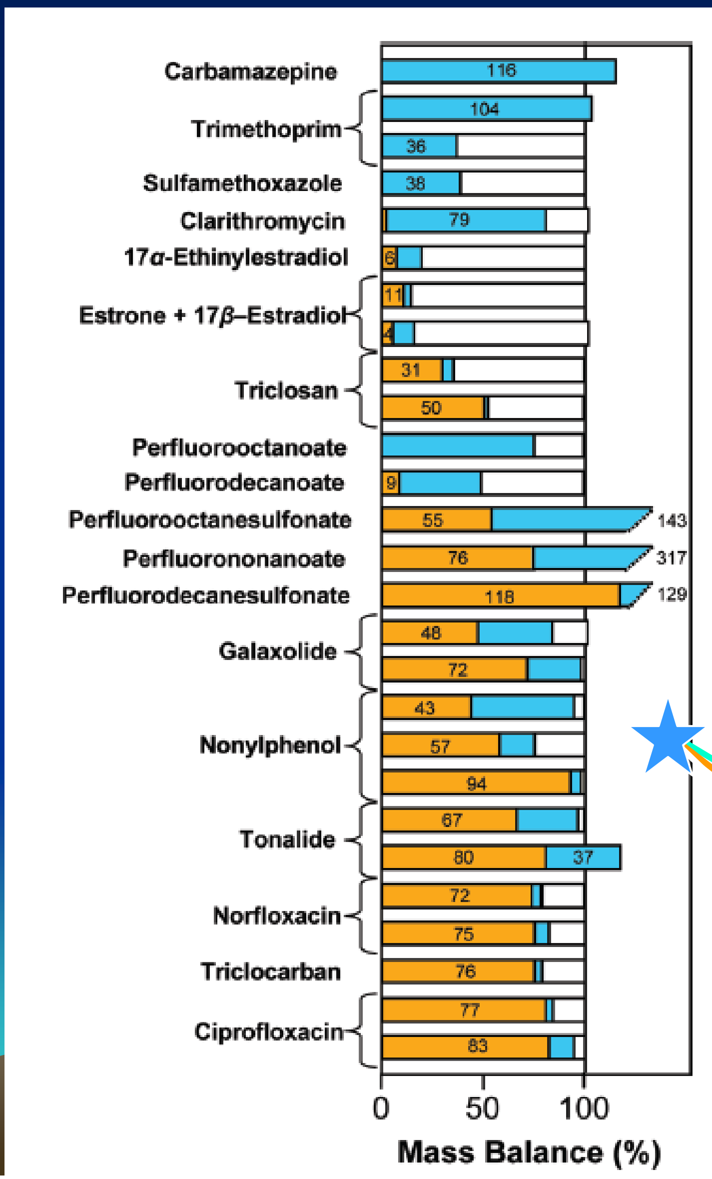
- Other removal mechanisms
  - Air stripping removal is not relevant in PPCP removal.
  - Ozonation of treated effluent can substantially reduces PPCPs
  - Anaerobic digestion can significantly reduce selected PPCPs others better degrade in aerobic conditions
  - uV has shown promise

Mass Balance Removal Meta-Analysis

Study 2

- Meta Analysis of 12+ Studies
- Reported as Mass Balance
  - With partitioning to water or solids
- Challenges to use of data

Mass Balance Removal Meta-Analysis



- Removal Efficiencies vary by treatment and by chemical properties

- Validity of results complicated by treatment schemes, θ_c, sampling issues, day of week, analytical recovery

% mass balance - Water

% mass balance - Solids

% mass balance - Treated

The role of Sorption in WWTP

- Upon entry hydrophobic and hydrophilic compounds enter
  - Quickly separate
  - Receive different treatment
    - Water pathway
    - Solids pathway

Mass Balance Removal Meta-Analysis

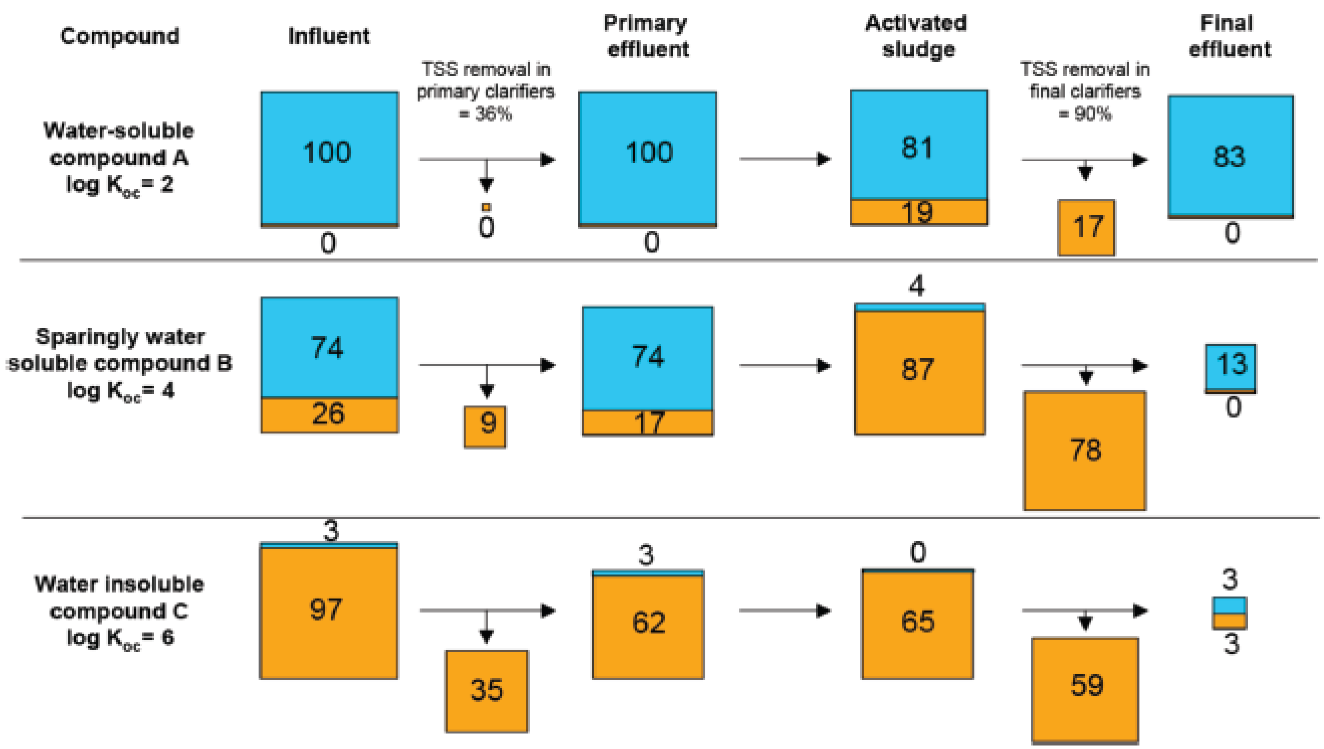


FIGURE 2. Schematic illustrating the role of sorption in the fate of organic wastewater compounds during their hypothetical passage through a conventional activated sludge wastewater treatment plant assuming a lack of both transformation and loss processes. The partitioning of compounds between the dissolved phase (blue) and wastewater solids (orange) is shown for three organic wastewater compounds featuring logarithmic organic carbon normalized sorption coefficients (log K_{OC}) of 2, 4, and 6 (top, middle, and bottom panels, respectively).

Assuming TSS $_{inf}$ 119 mgkg^{-1} Primary $_{slg}$ 78 mgKg^{-1}Primary$_{slg}$ 2000 mgKg^{-1} MLSS 8000 mgKg^{-1} TSS 30% OM by mass

Information derived from the mass-balance – meta data

- K_{ow}/K_{oc} appears to be the combined master variable
  - Measuring partitioning, accumulation, persistence
  - Including transformation, removal processes
    - Biotic
    - Abiotic

Issues raised in WWTP studies

- Day of week issues
- Time of day issues
- Sampling frequency
- Sampling locations
- Sample handling
- Various Treatment affects and effectiveness
- Use of isotope dilution
- Breakdown products
- Screening – what chemicals to use
- Sorting out options give PPCP response in WWTP

Water Reuse and Biosolids Land Application

- Snyder et al 2004 found that (reuse)
  - Attenuation for at least some compounds
    - Occurs in Soil and GW
    - Complete may take hundreds of days
- Lapen et al 2008 found that (biosolids)
  - Soil temp, Oxygen content and moisture can impact persistence

Proposed WWTP Projects

- Proposal for Studies --ideas
  - Selecting WWTPs based on treatment detail and conducting evaluations
  - Studying treatment detail vs stream - targeted locational studies
  - What info do we need to make informed decisions- currently much incomplete data
  - Use WWTPs as a model for the environment

Selecting WWTPs based on treatment details and conducting evaluations

- Little information of the details exist – looking at only removals

- If details of operation are included - Models can be developed allowing predictions across WWTPs

Studying treatment detail vs. stream

- Targeted studies would allow for regional / seasonal differences

- Would allow for external environmental factors to be taken into account.

What info do we need to make informed decisions- currently much of the data are incomplete?

- Having analytical values is nice but
  - Sampling, sample timing, analytical recoveries, etc. difficulties still remain
- Having mechanisms allows for understanding
- LOOK for mechanisms

Use WWTPs as a model for the environment

- WWTPs are controled models of the world
- Experiments could utilize WWTP concepts then verify attenuation in the environment

Proposed Land-based Projects Needs

- The need to do sorption – desorption studies (SOM)
- Proper design of sampling programs
  - Soil sampling ? Groundwater ?
  - Biological Sampling
    - Flora
    - Fauna
  - Chemical
    - pH, SOC, DOC, Metal interactions,
  - Physical
    - Temp, O2, Texture, Structural components

Conclusions

- There is information that indicated that these compounds ARE treated in a WWTP
  - If we understand mechanisms we can improve treatment
- Distinguish between results and mechanisms and their meanings and applicability to environmental fate
  - Mechanisms will speed understanding in various environs
- WWTPs are a model of treatment for the environment
- We can modify existing WWTPs to improve removal efficiencies
- We must begin to look for mechanisms in the environment, whether a WWTP, water or soil

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