Emerging Contaminants in Wet Weather Flows: Sources and Treatability

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Material in this presentation mostly summarized from the PhD dissertation by Kenya Goodson (2013)
http://unix.eng.ua.edu/~rpitt/Publications/11_Theses_and_Dissertations/Kenya_dissertation.pdf

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History of Emerging Contaminants (EC)

- Pharmaceuticals were first reported in waterways in the 1970s
- Antibiotics have been found in groundwater, surface waters, wastewaters and landfill leachates
- The pharmaceuticals are not under regulations as legacy pollutants in the US

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Sources of Emerging Contaminants

- Wastewater effluent is an important source of EC contamination.
- Wastewater treatment systems are not designed to treat xenobiotic compounds (chemicals not produced in the body)
- Wastewater treatment removal of pharmaceutical and personal care products (PPCP) generally range from 60% to 90%, but some much less.

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Frequency of PPCP Detection in US Streams

(USGS: Kolpin, *et al.* 2002)

Detection Frequency	Category of Contaminant	Representative Substances and Median Concentration (µg/L)
89%	Steroids	Cholesterol (0.83), Coprostanol (0.89)
81%	OTC Drugs	Acetaminophen (0.11), Caffeine (0.081), Ibuprofen (0.2), Cotinine (nicotine metabolite) (0.05)
74%	Insect Repellant	DEET (0.06)
68%	Disinfectants	Phenol (0.04), Triclosan (0.14)
48%	Antibiotics	Erythromycin metabolite (0.1), Ciproflaxin (0.02), Sulfamethoxazole (0.15)
37%	Reproductive Hormones	17α-ethynyl estradiol (0.073) (birth control), estrone (0.027)
32%	Other Prescription Drugs	Codeine (0.012), dehydronifedipine (antianginal) (0.012), diltiazem (0.021) (antihypertensive), fluoxetine (0.012) (antidepressant)
27%	Fragrances	Acetophenone (0.15)

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Chemical/Element	Common Usage	Example Hormone Target	Organism Type Impacted
Polybrominated Diphenyl Ethers (PBDEs)	Flame retardants	Thyroid	Mammals, Birds, Reptiles, Fish
DDT	Insecticide	Estrogen	Mammals, Birds, Reptiles, Amphibians, Fish, Invertebrates
PCBs	Industrial	Cortisol	Mammals, Birds, Reptiles, Amphibians, Fish, Invertebrates
Cadmium	Batteries	Adrenaline	Mammals, Birds, Fish
Fenoxycarb	Insecticide	Juvenile	Invertebrates
Bisphenol A	Plasticizer	Estrogen	Mammals, Birds, Amphibians, Fish, Invertebrates
Nonylphenol	Plasticizer	Estrogen	Mammals, Birds, Amphibians, Fish, Invertebrates

Southern California Coastal Water Resources Project (accessed 5/23/10)

Dog Feces are a Potentially Underestimated Source of ECs in the Urban Environment and Especially in Stormwater Runoff

http://www.fidosflushables.com/files/puppy_butt.jpg

http://www.treehugger.com/doggie-doo-flag-photo.jpg

Commonly-prescribed drugs in pet care (particularly for dogs)

Dr. Virginia Loder, DVM, Personal Communication to Dr. Shirley Clark

- Heartworm medications (parasiticides): ivermectin, selamectin, milbemycin. May contain dewormers, primarily pyrantel pamoate.
- Flea/tick (minimal systemic adsorption to pass to feces – washoff?) fipronil or imidacloprid. New product: metaflumizone. Over-the-counter contain various pyrethrins and permethrins.
- Common antibiotics: amoxicillin, ampicillin, amoxicillin/clavulanic acid (augmentin in the human world), enrofloxacin (some converted to ciprofloxacin), cephalexin, doxycycline. Fairly common: clindamycin, trimethoprim/sulfadiazine (or sulfamethoxazole), others from the cephalosporin group (cefazolin, cefpodoxime), other fluroquinolones (ciprofloxacin, marbofloxacin, orbifloxacin, difloxacin). Most human drugs are used in animals to some degree.
- Chemotherapeutic drugs
- Increased use of cyclosporine, as an immunosuppressant and allergy medication.

Commonly-prescribed drugs in pet care (particularly for dogs) (cont.)

Dr. Virginia Loder, DVM, Personal Communication

- Azathioprine commonly used in immune related disorders
- Mitotane acts against the adrenal gland
- Prednisone/prednisolone (other corticosteroids: betamethasone, dexamethasone are most common)
- Antihistamines (diphenhydramine, hydroxyzine, etc.),
- Thyroid supplements (L-thyroxine),
- Anti-inflammatories (carprofen, meloxicam, etodolac, deracoxib, tepoxalin, aspirin, tylenol/acetaminophen)
- Glucosamine and chondroitin supplements
- Other pain medications (tramadol and fentanyl are being increasingly used for long term pain managament)
- Psychoactive drugs (clomipramine, amitriptyline, fluoxetine), phenobarbital, diazepam (valium), alprazolam
- Heart medications (such as lasix and enalapril)

Physical and Chemical Properties of ECs

- Physical and chemical properties of emerging contaminant are important factors in predicting their treatability in wastewater
- There are many physical and chemical properties for emerging contaminants, but certain properties are important when estimating their behavior in treatment systems (Mauricio 2006).
  - Pharmaceuticals
    - Pka (disassociation constant, indicates breakdown of larger molecules. The logarithm of the ionization constant (K) of an acid, the pH of a solution in which half of the acid molecules are ionized.)
    - Log k_{ow} (octanol water coefficient, indicates attraction to organics. It represents the tendency of the chemical to partition itself between an organic phase (e.g., a fish, a soil) and an aqueous phase. Chemicals with low K_{ow} values may be considered relatively hydrophilic and tend to have high water solubilities, small soil/sediment adsorption coefficients, and small bioconcentration factors for aquatic life. Chemicals with high K_{ow} values are very hydrophobic.
    - Solubility (how much of the compound "dissolves" in water)

However, literature reports indicate a high level of variability in treatment performance even for compounds with similar solubilities and log k_{ow} values.

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Physical and Chemical Properties of ECs (cont.)

- PAHs
  - Log k_{ow}
  - Volativity atm^{-3}/mol (a measure of the tendency of a substance to vaporize)
  - Solubility
- Pesticides
  - Log k_{ow}
  - Solubility

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Polycyclic Aromatic Hydrocarbon Compounds (PAHs)

- Polycyclic aromatic hydrocarbon compounds are compounds derived from petroleum byproducts such as tar, oil and coal.
- They are ubiquitous environmental pollutants with carcinogenic and mutagenic properties
- Two kinds of PAHs
  - Low molecular weight PAH compounds (Low molecular weight PAHs are less toxic and less persistent than high molecular weight PAHs, and more likely to dissolve in water.) Low molecular weight PAHs are more likely to enter the environment from incidental spills of gasoline and diesel fuel.
  - High molecular weight PAH compounds (containing four or more fused benzene rings and are generally resistant to microbial attack; considered a persistent organic pollutant, POP); high temperature industrial processes tend to produce HMW PAHs. High molecular weight PAHs enter rivers and streams through atmospheric deposition and stormwater runoff.
- Increase of hydrophobicity with increase molecular weight
- High log octanol-water coefficient ~3.37-6.04

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Low Molecular Weight PAHs	High Molecular Weight PAHs
Naphthalene	Benzo(a)anthracene
Acenaphthene	Pyrene
Acenaphthylene	Benzo(a)pyrene
Fluorene	Chrysene
Phenanthrene	Benzo(b)flouranthene
Anthracene	Fluoranthene

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PAH Compound	Molecular weight (g/mol)	Solubility (water)(mg/L)	Log Kow	Volatility atm-3/mol	Toxicity **
Naphthalene (LMW)	128.2	31.7*	3.37*	$4.6x10^{-4}$ *	LC50 Pimephales promelas 7.76 mg/L
Acenaphthylene (LMW)	152.2	3.93*	3.89**	1.45×10^{-3} *	
Acenaphthene (LMW)	154.2	1.93*	4.02**	7.91×10^{-5} *	LC50 Salmo gairdneri 1,570 µg/L
Fluorene (LMW)	166.2	1.68-1.98 *	4.12**	1.0×10^{-4} *	EC50 V. fischeri 4.10 µg/mL
Anthracene (LMW)	178.2	0.076 *	4.53**	1.77×10^{-5} *	D.magna EC50 = 211 µg/L

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PAH Compound (cont.)	Molecular weight (g/mol)	Solubility (water)(mg/L)	Log Kow	Volatility atm-3/mol	Toxicity **
Phenanthrene (LMW)	178.2	1.20 *	4.48**	2.56×10^{-5} *	EC50; Daphnia magna 678 µg/L
Pyrene (HMW)	202.2	0.077 *	5.12**	1.14×10^{-5} *	D. magna EC50 = 67,000 µg/L
Fluoranthene (HMW)	202.2	0.20-0.26 *	5.14**	6.5×10^{-6} *	S. capricornutum EC50 = 54,400 µg/L
Benzo[a]anthracene (HMW)	228.3	0.010*	5.61*	n/a	
Chrysene (HMW)	228.3	2.8×10^{-3} *	5.16*	n/a	LC50 Daphnia magna 1.9 mg/L
Benzo[b]fluoranthene (HMW)	252.3	0.0012	6.04*	n/a	
Benzo[a]pyrene (HMW)	252.3	1.6×10^{-3}	6.06*	n/a	EC50 Daphnia magna 40 µg/L

*ATSDR; **Crunkilton 1997

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Pharmaceuticals

- Pharmaceuticals are chemicals that are used in the treatment and prevention of diseases
- They are a growing concern because they are being introduced in the wastewater stream in large amounts
- Some pharmaceuticals are highly reactive and can affect receptors in the environment
- Some pharmaceuticals enter the environment as metabolites
- Pharmaceuticals are relatively soluble in water and are less likely to sorb onto particulates.

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Pharmaceutical	Log k_{ow}	Solubility (mg/L)	pKa	Toxicity (µg/L)	Chemical Group
Carbamazepine	2.45	17.7	13.9	LC_{50} D. magna >100 mg/L	Carboxide
Fluoxetine	4.05	38.4	9.5	P. subcapitata LC_{50} 24 µg/L	Amine
Gemfibrozil	4.78	5.0	4.7	D. Magna. EC_{50} 23 mg/L	Valeric Acid/Pentoic Acid
Ibuprofen	3.5-4.0	41.5	4.9	Daphnia. EC_{50} 108 mg/L	Propanoic acid
Sulfamethoxazole	0.9	600	1.7/5.7	P. subcapitata. IC_{50} 1.5 mg/L	Sulfonamide
Triclosan	4.8-5.4	2-4.6	7.8-8.1	P. subcapitata. IC_{50} 1.4 µg/L	Phenol
Trimethoprim	0.79	400	7.2	P. subcapitata. IC_{50} 80- 130 mg/L	Diamine

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Pesticides

- Pesticides and herbicides are used to reduce pests that can have a negative impact on agriculture or public health.
- Chemical pesticides have contributed to increase yields of agriculture by controlling pests and diseases Ahmad (2010), however, excessive amounts of pesticides can have adverse effects on wildlife and human populations.
- Persistent organic pollutants (POPs) tend to have (Katsoyiannis 2004):
  - Low water solubility
  - Stability during degradation processes.
  - Persistent in the environment.
  - Very high sorption

Pesticide	Log k_{ow} *	Solubility (mg/L)*	Toxicity (LC_{50}) ***	Biodegradation (half-life) ***
Methoxychlor	4.68-5.08	0.1	D. magna (EC50) 16 µg/L	7 to 29 days; >100 days
Aldrin	6.5	0.027	Salmo gairdneri (rainbow trout) 2.6 µg/L	20 to 100 days
Dieldrin	6.2	0.1	Salmo gairdneri (rainbow trout) 1.2 µg/L	Did not find
Chlordane	~5.54	Insoluble	Chironomus plummosus (10 µg/L	10 to 20 yrs**
Arochlor Σ	5.6-6.8	Insoluble	P. subcapitata 182 nmol/L	volatilization half-life from a model pond is 82 days to 58 years
Lindane	3.8	17	D. magna (EC50) 1.64 mg/L	70 hours to 15 months
Heptachlor	6.10	0.056	S. capricornutum 26.7 µg/L	6 months to 3.5 years
Heptachlor-epoxide	5.40	Not found	Not found	Not found

*ATSDR; **Bondy 2000; ***HSDB

Endocrine Disruptor Chemicals

- U.S. EPA defines an EDC as “an exogenous agent that interferes with the synthesis, secretion, transport, binding, action, or elimination of natural hormones of natural hormones in the body that are responsible for the maintenance of homeostatis, reproduction, development, and/or behavior (Campbell 2006).
- Some personal care products, pharmaceuticals, and pesticides have also been shown to imitate natural estrogens that affect the endocrine system. These chemicals are called endocrine disruptor chemicals (EDCs).
- Organochlorine pesticides (endosulfan, lindane, methoxychlor, atrazine, DDT) and polychlorinated biphenyls (PCBs) are examples of compounds identified as endocrine disruptors.

EDC	Molecular weight (g/mol)	Water solubility at 20C (mg/L)	Log K_{ow}
Estrone (E1)	270.4	13	3.43
17β-Estradiol (E2)	272.4	13	3.94
Estriol (E3)	288.4	13	2.81
Ethinyl Estradiol (EE2)	296.4	4.8	4.15
Bisphenol A	228.0	300	3.40
Octylphenol (OP)	206.3	12.6	4.12
Nonylphenol (NP)	220.0	5.43	4.48
Nonylphenol polyethoxylates (n≥3-5)	352.0-440.0	5.88-9.48	4.2-4.3
Nonylphenoxy ethoxy acetic acid	322	soluble	1.34

Teske and Arnold 2008, 107-124

Treatability of Emerging Contaminants – Literature Review

Treatability Studies on Organic Contaminants

Stream Conc. (μg/L)	Test Water	Unit processes used	Reduction rate (%)	Influent conc. (μg/L)	Effluent conc. (μg/L)	Reference
CARBAMAZEPINE (seizure medication) **Log Kow = 2.45**, pKa = n/a, Log S = 1.25 (mg/L), Base ionization						
	River	Fe coag+ sed+ rapid sand filt	7			Vieno et al. 2007
	Sewage	Conv Activ Sludge	**0**	**0.24** (median)	0.25 (median)	Radjenovic et al. 2006
	Sewage	Prim+ Activ sludge	Up to **78**	15-**350**	15-160	Nakada et al. 2006
CAFFEINE Log Kow = -0.07, pKa = 0.6, **Log S = 4.33** (mg/L), Base ionization						
0.081	Sewage	Prim+ Activ Sludge+ (Alum+ Filt+ **Disinf)**	**17, 99.9**			Thomas et al. 2005
0.081	Distilled water	Floc/Sed+ Dual Media Filt+**GAC +Disinf**	**>94**			Bundy et al. 2007

Treatability Studies on Organic Contaminants (cont.)

Stream Conc. (μg/L)	Type of water	Unit processes used	Reduction rate (%)	Influent conc. (μg/L)	Effluent conc. (μg/L)	Reference
IBUPROFEN **Log Kow = 3.97**, pKa = 4.91, Log S = 1.32, Acid Ionization						
0.2	Sewage	**Activ Sludge**	**95**	8.45 (mean)	0.384 (mean)	Lishman et al. 2006
0.2	Sewage	Prim+ bioreactor	63			Carballa et al. 2004
0.2	River	Fe coag+ sed+ rapid sand filt	**12**			Vieno et al. 2007
0.2	River	**ozone** aft Fe coag+ sed+ rapid sand filt)	**92**			Vieno et al. 2007
0.2	Sewage	Prim+ Activ sludge	38[d],93[e]			Castiglioni et al. 2006
0.2	Sewage	Prim+ Activ Sludge+ (Alum+ Filt+ Disinf)	5[a],99.8[b]			Thomas et al. 2005
0.2	Sewage	Conventional Activated Sludge	82.5±15.8	17 (median)	2 (median)	Radjenovic et al. 2006
0.2	Sewage	Primary+ Activated Sludge	83-99	300-1200	1-110	Nakada et al. 2006

Treatability Studies on Organic Contaminants (cont.)

Stream Conc. (μg/L)	Type of water	Unit processes used	Reduction rate (%)	Influent conc. (μg/L)	Effluent conc. (μg/L)	Reference
DICLOFENAC (arthritis treatment) **Log Kow = 4.4**, pKa = 4.5, Log S = 0.37, Acid ionization						
	River	Fe coag+sed+ rapid sand filtration	8			Vieno et al. 2007
	River	**ozone** after Fe coag+sed+ sand filt	**>94**			Vieno et al. 2007
	Sewage	Prim+ Activ Sludge+ (Alum+ Filt+ Disinf)	14[a],89[b],100[c]			Thomas et al. 2005
	Sewage	Conv Activ Sludge	50.1±20.1	2.8(median)	1.2(median)	Radjenovic et al. 2006
ESTRONE (estradiol metabolite) 17α-ethynylestradiol → Kow = 3.67, pKa = n/a, Neutral ionization						
0.027	Sewage	**Lagoon**	86	**0.0295** (mean)	0.0076 (mean)	Lishman et al. 2006
0.027	Sewage	Prim+ Activ sludge	0			Castiglioni et al. 2006
0.027	Sewage	Prim+ Activ sludge	83-90	25-200	3-110	Nakada et al. 2006

Treatability Studies on Organic Contaminants (cont.)

Stream Conc. (µg/L)	Type of water	Unit processes used	Reduction rate (%)	Influent conc. (µg/L)	Effluent conc. (µg/L)	Reference
ATENOLOL (anti-anginal and anti-hypertensive) Log Kow = 0.16, pKa = 9.6, **Log S = 4.11**, Base ionization						
	River	Ferric coag+sed+ rapid sand filtration	12			Vieno et al. 2007
	River	**ozone** after Fe coag+sed+ rapid sand filt	**>73**			Vieno et al. 2007
	Sewage	Primary+ Activated sludge	10[d],55[e]			Castiglioni et al. 2006
	Sewage	Conventional Activated Sludge	<10	1.5 (median)	0.9 (median)	Radjenovic et al. 2006

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Treatability Studies on Organic Contaminants (cont.)

Stream Conc. (µg/L)	Type of water	Unit processes used	Reduction rate (%)	Influent conc. (µg/L)	Effluent conc. (µg/L)	Reference
CIPROFLOXACIN Log Kow = -0.3 – 0.3, pKa = 6.09, **Log S = 2**						
0.02	River	Fe coag+sed+ sand filt	35			Vieno et al. 2007
0.02	River	Ozone after Fe coag+sed+sand filtr	16			Vieno et al. 2007
0.02	Sewage	**Prim+ Activ sludge**	60[d],**63**[e]			Castiglioni et al. 2006
ERYTHROMYCIN (antibiotic) **Log Kow = 3.06**, pKa = 8.9, **Log S = 3**						
0.1 (metabolite)	Sewage	Prim+ Activ sludge	0			Castiglioni et al. 2006
0.1 (metabolite)	Sewage	Conventional Activated Sludge	23.8±29.2	0.15 (median)	0.08 (median)	Radjenovic et al. 2006

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Treatability Studies on Organic Contaminants (cont.)

Stream Conc. (µg/L)	Type of water	Unit processes used	Reduction rate (%)	Influent conc. (µg/L)	Effluent conc. (µg/L)	Reference
TRICLOSAN (antimicrobial) **Log Kow = 4.76**, pKa = 7.8, Log S = 1.04 (mg/L)						
0.14	Sewage	**Activated Sludge**	**93**	1.93 (mean)	0.108 (mean)	Lishman et al. 2006
0.14	Sewage	Activated sludge + filtration	**95**			Lishman et al. 2006
0.14	Sewage	Primary+ Activated Sludge+ (Alum+ Gravity Filtration+ Disinfection)	26[a],98.4[b]			Thomas et al. 2005
0.14	Sewage	Primary+ Activated Sludge	46-92	200-1000	20-200	Nakada et al. 2006

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Summary of Treatment Technology Literature Review

- Compounds with high solubility (Log S) have variable removals by activated sludge.
- Compounds with high Log K_{ow} (preferentially partition to organic phase) are typically better removed by activated sludge or ozone (limited studies with GAC). Limited removal by sand filters.
  - Sorption to organic particles in solution and subsequent settling.
  - Microbial degradation.
- Ozone effective for large organic molecules, especially recalcitrant/persistent compounds (resistant to microbial degradation).

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Treatability of Emerging Contaminants Research at the University of Alabama (Goodson 2013) and Penn State - Harrisburg

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Some of the Compounds of Interest in EPA-Funded Research during UA Research

- Ibuprofen
- Diltiazem hydrochloride
- Gemfibrozil
- 5,5-Diphenylhydantoin
- Divalproate sodium
- Dichlofenac
- Caffeine
- Trimethoprim
- Triclosan

Pathogens were not specifically addressed in this research. However, this presentation will address some of the PSH research in this area because of the interaction of ECs and pathogens and UA research on the survivability of pathogens and indicator organisms in the urban environment.

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Current Research Focus: Wet Weather Flow Samples

- Samples were collected for organic analyses during five wet weather events and three dry periods at Tuscaloosa for PAHs, other ECs, and pesticides.
- Samples were also collected during five events from ten separate stormwater sheetflow locations for these analyses, plus metals, bacteria, and conventional analyses.

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Organic Analyses at Earl Hilliard Wastewater Treatment Plant, Tuscaloosa, AL

- Six liters of wastewater were collected from four locations at the Earl Hilliard wastewater treatment plant, Tuscaloosa, AL :
  - inflow of wastewater before pre-treatment,
  - the primary clarifier,
  - the secondary clarifier, and
  - after UV disinfection.

• Four liters from each site were extracted and analyzed at the Miles College chemistry department for acidic and basic pharmaceuticals. One liter from each plant site was extracted using methylene chloride for PAH analysis. Two liters were sent to Penn State -Harrisburg for pesticide analysis.

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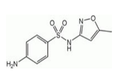
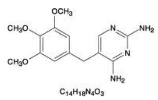
Target Pharmaceutical Emerging Contaminants

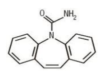
Sulfamethoxazole



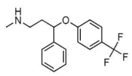
Trimethoprim



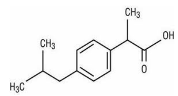
Carbamazepine



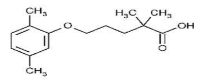
Fluoxetine



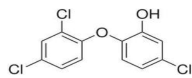
Ibuprofen



Gemfibrozil



Triclosan



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Analytical Methods

- PAHs (method 8270 SIM targeted ions)
  - Extraction by separation funnel and concentrated by KD (Kuderna-Danish) instrumentation
  - GC/MS
- Pesticides (method 508)
  - Extraction by separation funnel and concentrated by KD (Kuderna-Danish) instrumentation
  - GC/ECD
- Pharmaceuticals (method 1694 with modifications; a screening method that indicated behavior of these compounds, but not necessarily actual concentrations)
  - SPE
  - LC/UV (instead of LC/MS/MS)

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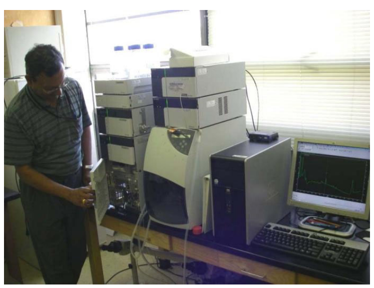

LC/UV instrumentation and SPE Extraction Manifold

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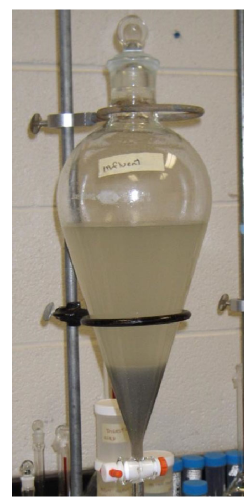
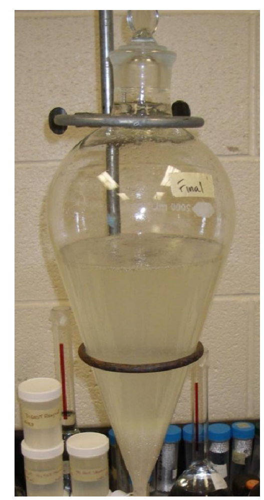
Pesticide Extraction at PSH





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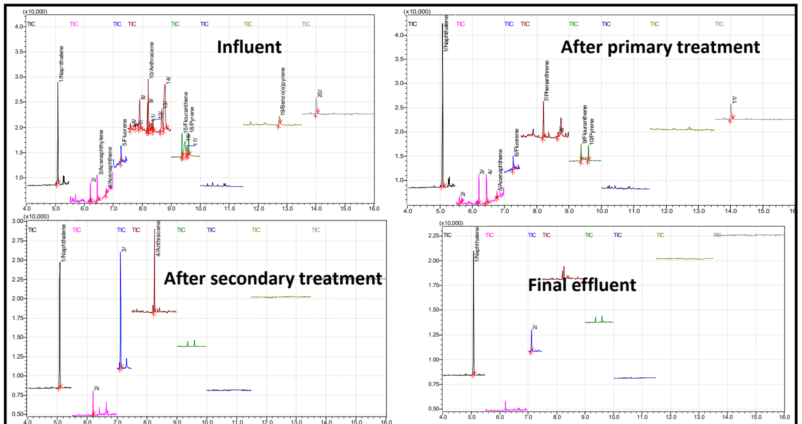
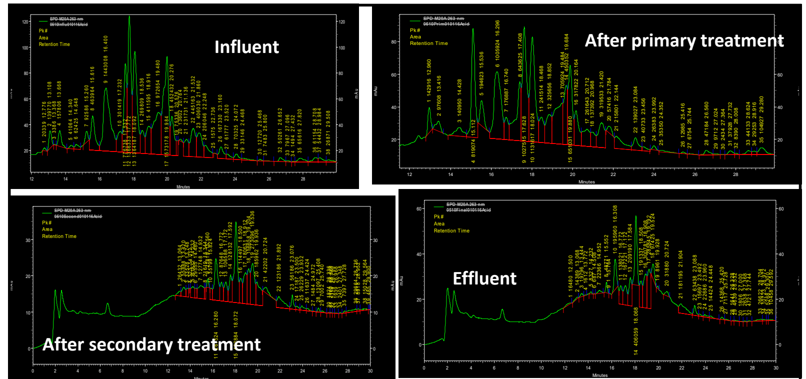


Tuscaloosa Wastewater Treatment Plant PAHs during rain event

approx ug/L	Influent	after primary	after secondary	final effluent
Acenaphthylene	57	nd	nd	nd
Acenaphthene	57	21	nd	nd
Phenanthrene	41	20	nd	nd
Fluorene	57	27	nd	nd
Anthracene	54	8	69	nd
Flouranthene	53	23	nd	nd
Pyrene	54	20	nd	nd
Benzo(a)pyrene	50	57	nd	nd

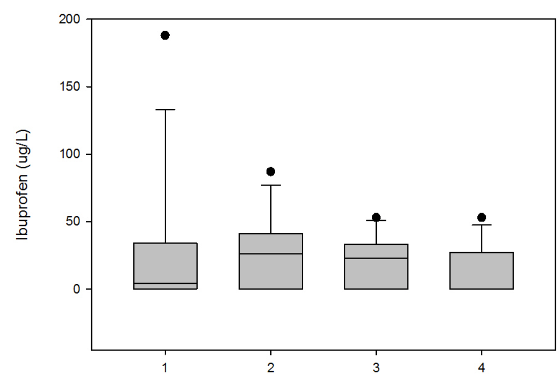


HPLC analyses for other organic ECs during rain event. Plots include acidic pharmaceuticals sulfamethoxole, trimethoprim, carbamezapine, and fluoxetine.

Calculated Influent Mass of ECs

Pollutant (Influent)	Mass per day (kg/day) Dry Weather	Mass per day (kg/day) Wet Weather
Ibuprofen	7.9 to 17	2.8 to 14
Triclosan	negligible	0.15 to 3.6
Gemfibrozil	11 to 12	nd to 1.9
Sulfamethoxazole	tbd	nd to 4.1
Trimethoprim	tbd	nd to 13
Fluoxetine	tbd	0.18 to 7.9
Carbamazepine	tbd	0.093 to 1.4
Acenaphthylene	0.0031 to 0.014	0.15 to 0.29
Anthracene	nd to 0.095	0.15 to 0.24
Pyrene	0.051 to 0.18	0.14 to 0.18

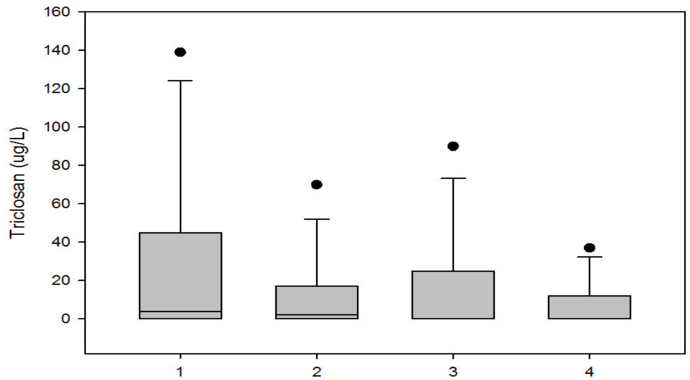
Ibuprofen Concentrations after Different Treatment Stages (Hilliard WWTP)



1: infuluent; 2: after primary; 3: after secondary; 4: effluent

Only removed the highest concentrations during early primary treatment.

Triclosan Concentrations after Different Treatment Stages (Hilliard WWTP)



1: Influent; 2: after primary; 3: after secondary; 4: final effluent

Progressive removal of highest concentrations along with moderate removal of lower concentrations with primary treatment; no further removals with secondary treatment

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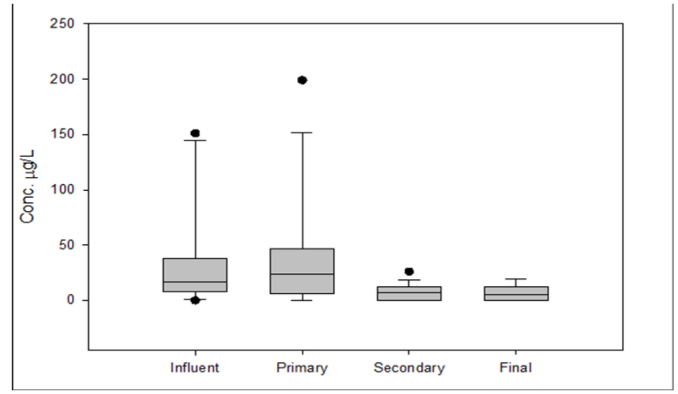
Fluoxetine Concentrations after Different Treatment Stages (Hilliard WWTP)



High concentrations removed along with moderate removal of lower concentrations during primary treatment; no further treatment during secondary treatment.

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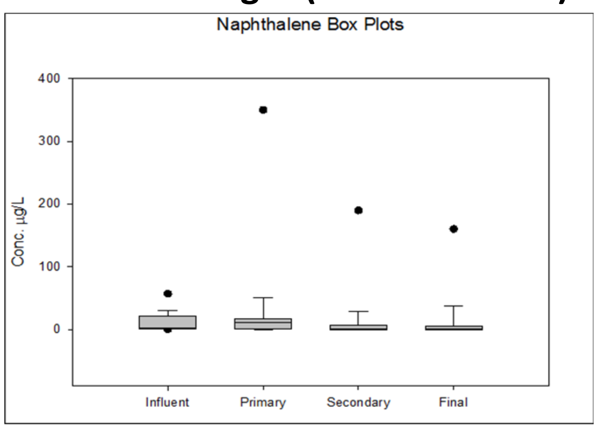
Naphthalene Concentrations after Different Treatment Stages (Hilliard WWTP)



Apparent reduction of highest concentrations; further removal of lower concentrations with secondary treatment

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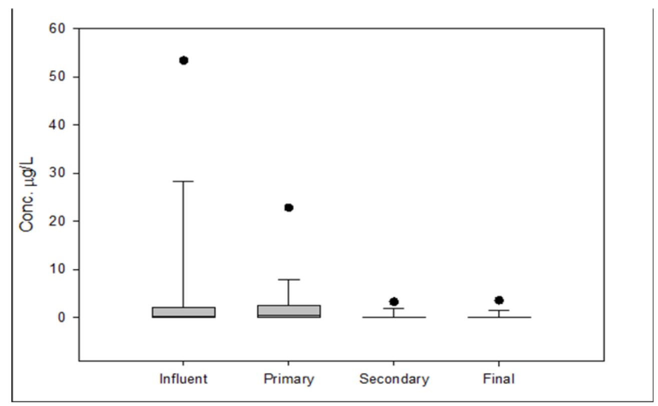
Fluoranthene Concentrations after Different Treatment Stages (Hilliard WWTP)



Treatment with primary sedimentation; no further treatment noted during secondary processes.

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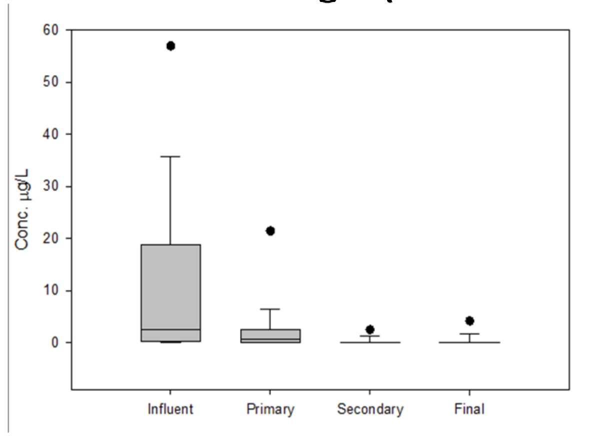
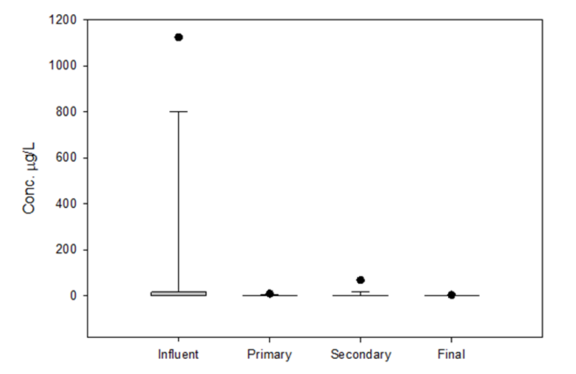
Acenaphthene Concentrations after Different Treatment Stages (Hilliard WWTP)



Large removals during primary sedimentation with additional removal during secondary treatment.

Anthracene Concentrations after Different Treatment Stages (Hilliard WWTP)



All observed treatment occurred during primary sedimentation.

Pharmaceutical Removals at Earl Hilliard WWTP during Wet and Dry Weather

Pharmaceuticals (screening analyses, indicative of relative changes, but absolute concentrations may not be accurate)	Avg Influent concentration (µg/L)	Avg Primary effluent concentration (µg/L)	Avg Secondary effluent concentration (µg/L)	Avg concentration after UV (final effluent) (µg/L)	Avg Overall Percentage Removal at ENH wastewater treatment facility	Apparent most Important treatment unit process
Gemfibrozil (w)	32.4	31.7	18.1	17.1	44.8	Secondary
Gemfibrozil (d)	80.29	23.38	22.30	18.63	70.9	Primary
Ibuprofen (w)	21.63	21.00	17.57	9.57	57.8	UV
Ibuprofen (d)	44.71	35.25	20.75	15.25	67	Secondary
Triclosan (w)	33.9	16.9	15.0	12.3	62.8	Primary
Triclosan (d)	16.72	3.29	12.86	0.43	98	UV
Carbamazepine (w)	2.38	5.00	5.00	2.57	-8	UV
Carbamazepine (d)	15.9	10.5	2.50	1.38	94	Primary
Fluoxetine (w)	14.1	41.7	3.29	1.86	86	Secondary
Fluoxetine (d)	61.7	36.8	11.6	9.63	84	Secondary
Sulfamethoxazole (w)	10.4	18.4	14.1	13.1	-33	None
Sulfamethoxazole (d)	68.7	42.6	31.1	24.4	65	Secondary
Trimethoprim (w)	3.13	3.14	3.86	2.00	33	UV
Trimethoprim (d)	16.3	28.3	21.1	21.0	-31	None

PAH Removals at Earl Hilliard WWTP during Wet and Dry Weather

Polycyclic Aromatic Hydrocarbons	Avg Influent concentration (µg/L)	Avg Primary effluent concentration (µg/L)	Avg Secondary effluent concentration (µg/L)	Avg concentration after UV (final effluent) (µg/L)	Avg Overall Percentage Removal at ENH wastewater treatment facility	Apparent most Important treatment unit process
Naphthalene (w)	15.3	4.74	25	22.7	-47	None
Naphthalene (d)	7.1	11.1	3.8	1.3	82	Secondary
Acenaphthene (w)	16.9	5.07	0.39	0.64	96	Primary
Acenaphthene (d)	7.70	0.82	0.10	0.02	99	Primary
Fluorene (w)	10.3	1.03	0.56	0.57	91	Primary
Fluorene (d)	0.67	1.19	0.04	0.05	93	Secondary
Fluoranthene (w)	10.3	4.23	0.54	0.53	95	Primary
Fluoranthene (d)	0.31	0.53	0.02	0.04	87	Secondary
Acenaphthylene (w)	10.5	0.60	0.61	0.67	92	Primary
Acenaphthylene (d)	0.08	0.58	0.01	0.02	75	Secondary
Phenanthrene (w)	6.14	4.36	0.05	0.15	98	Secondary
Phenanthrene (d)	1.56	0.77	0.16	0.12	90	Primary and secondary
Anthracene (w)	198	2.27	9.70	0.81	100	Primary
Anthracene (d)	60.07	0.18	0.24	0.15	100	Primary
Pyrene (w)	10.24	4.04	0.72	0.51	95	Primary and secondary
Pyrene (d)	0.66	0.95	0.13	0.13	80	Secondary

Summary of Hilliard WWTP Treatment Plant Results for PCPPs

- Primary treatment effective for approximately half of the compounds.
- Activated sludge.
  - Sorption to organic particles in solution and subsequent settling.
  - Microbial degradation.
- Most of the PAHs were removed after secondary treatment during wet weather
- During dry weather, most of the PAHs showed a slight increase in the primary effluent before decreasing in the secondary effluent
- Stormwater infiltration into the sewer system does not appear to reduce wastewater treatability for biological treatment but may affect primary sedimentation

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Applicability of Dry and Wet Weather Treatment Observations to Stormwater Treatment

(from comments prepared by Dr. Shirley Clark, Penn State – Harrisburg)

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Urban Wet-Weather Flows and Green Infrastructure for EC Treatment

- Stormwater pollutant sources are dispersed in the landscape.
- In many CSO areas, "green" infrastructure, primarily infiltration, is being implemented to reduce and/or delay flows to the sewer system to minimize the number of overflow events.

Therefore, how do these results translate to green infrastructure?

- Sedimentation will treat some compounds, especially those that are particulate-associated (caveat: association with colloidal-sized particulates may reduce effectiveness unless use coagulant)
- Chemical filtration/sorption in (bio)(in)filtration devices also likely to be needed for some constituents.
- Widespread installations of UV and ozone not practical for these concentrations and dispersed locations. UV may work in shallow ponds just using sunlight or if runoff is channeled to a central location.

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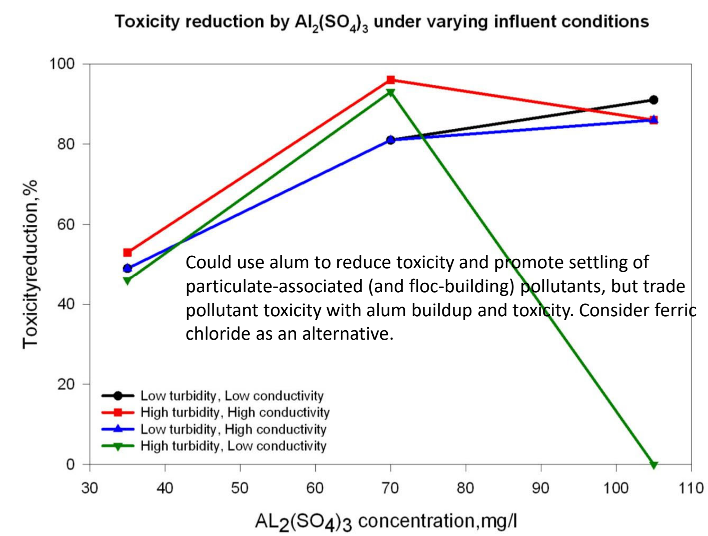

Pitt, *et al.* (1998). Treatability of urban runoff contaminants.

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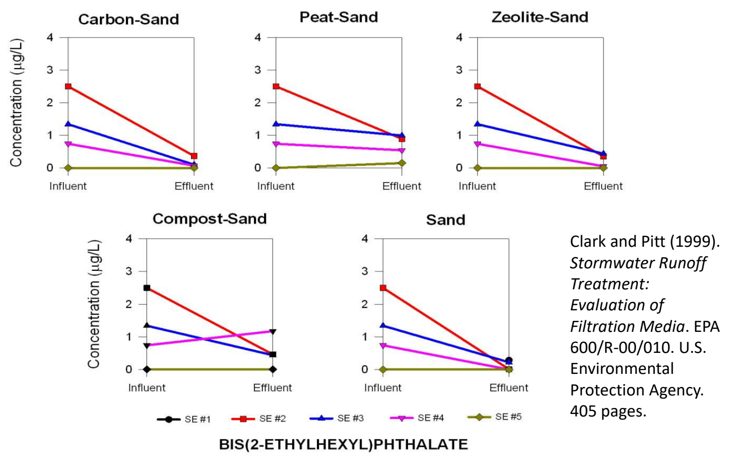
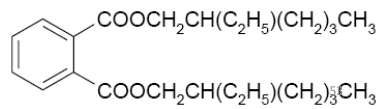


Clark and Pitt (1999). *Stormwater Runoff Treatment: Evaluation of Filtration Media*. EPA 600/R-00/010. U.S. Environmental Protection Agency. 405 pages.

Log K_{ow} = 7.5; Log S = -1.97
Associates easily with organic media and organic solids in water



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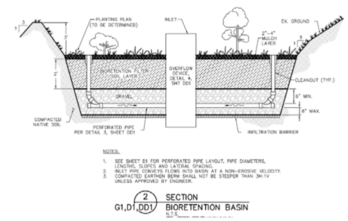
Media Filtration (Bioretention) Treatment of PPCPs



Earlier treatability studies show that treatment train concept works best.

- First stage: sedimentation (reduce clogging)
- Second stage: (bio)filtration (use more of chemical capacity if clogging delayed.

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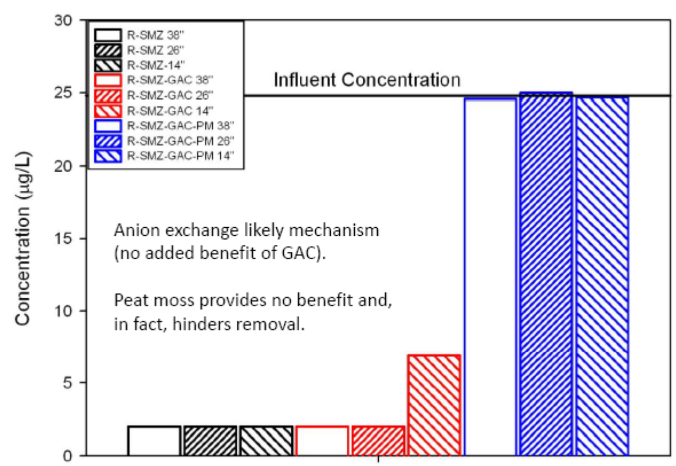
Perchlorate @ 20 m volumetric loading



Clark and Pitt. (2010). Integration of site and media characteristics to design (bio)(in)filtration Systems." *2010 World Environmental and Water Resources Congress*. ASCE, Reston, VA. CD-ROM.

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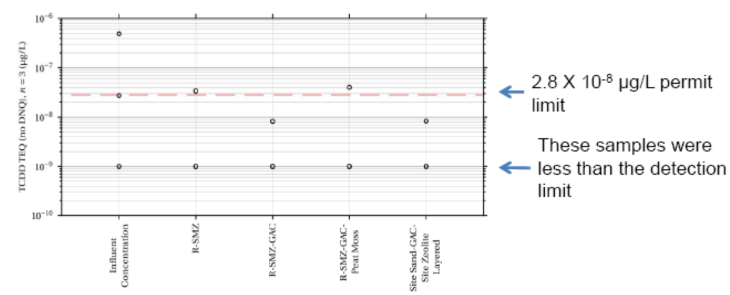
Dioxin Control Observations



- The dioxin results indicate good control, based on these few analyses.
- GAC without peat moss (mixed and layered) appeared to have best removals.
- The detected effluent concentrations were at least an order of magnitude less than the observed influent concentrations for these two media mixtures, showing good removals to close to, or below, the extremely low permit limit.

Pitt, Clark, Steets. (2010). "Laboratory evaluations to support the design of bioretention systems in the southwestern U.S." *2010 World Environmental and Water Resources Congress*. ASCE. CD-ROM.

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Reported Removal Mechanisms for Some Emerging Contaminants

- The pharmaceuticals gemfibrozil, ibuprofen, triclosan and fluoxetine were reduced by biodegradation.
- Carbamazepine had the lowest reported reduction rates of zero to 30 percent. Carbamazepine is difficult to treat, as it is resistant to biodegradation. Because carbamazepine is soluble in water, it is also not treatable by sedimentation in the primary unit processes.
- Sulfamethoxazole is highly soluble in water and therefore difficult to remove. Photodegradation removes sulfamethoxazole at some treatment facilities.
- Volatization and oxidation were the primary means of reported treatment for PAHs having lower molecular weights.
- Adsorption (and associated sedimentation of particulates) is a primary removal factor for the HMW PAH compounds.

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Summary for Media Treatment of ECs

- Most biofilter devices prematurely fail (before chemical capacity is exceeded) because of silt clogging so solids pretreatment highly recommended. This pretreatment may remove ECs that preferentially bind to sediment.
  - Design for clogging first (assume with vegetation, solids loading for most media mixes approximately 25 kg/m^2).
  - Maintenance has limited effectiveness. Vegetation likely will extend lifespan because of biological disturbance of soil and deep penetration of silt.
- GAC is the conventional media of choice to remove large organic molecules.
  - GAC-containing media removed dioxin and perchlorate.
  - Perchlorate removal showed minimal further benefits from GAC additions if a surface-modified zeolite was used in the mixture.
  - GAC may provide a host for microorganisms that will degrade these EC compounds.

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Summary for Media Treatment of ECs and Conventional Pollutants

- Evaluation of potential chemical removal.
  - Physical removal primary mechanism, even in media with “good” sorption/ion-exchange potential.
  - “Best” contact time at least 10 and 40 minutes (1 to 15 gpm/ft^2), potentially obtained using outlet flow control.
  - Removal based on influent quality (including “speciation” or “association” of pollutants with particulates of all sizes).
  - Evaluate media choices (either individually or as part of a mix) based on both adequate targeted-pollutant removal and exchanged ions.
    - CEC, AEC, OM, P-content, SAR, soil pH predict, but may not be able to quantify, removal efficiency or effluent quality. Also not precise measurements of lifespan.
    - Increasing OM and P content can have a negative effect. The media can release nutrients, color compounds, and colloids.

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