Endocrine Disruptors in Water and Wastewater Treatment

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What is an Endocrine Disruptor?

- An endocrine disruptor (ED) is an exogenous substance that causes adverse health effects in an intact organism, or its progeny, secondary to changes in endocrine function
- The focus to date has been on disruption of the hormones central to the control of reproduction and development
- More recently looked at disruption of thyroid function, mainly as it relates to the development process
- Recent evidence that EDs affect the immune system, and have neurotoxic effects

The Main Suspects:

Chemicals with hormonal activity that are potentially Endocrine Disruptors:

- Natural hormones – human or animal
- Natural chemicals – such as substances produced by plants – e.g. phyto-estrogens
- Synthetic pharmaceuticals intended to be hormonally active – such as the contraceptive pill
- Other man-made chemicals. A very wide range including cosmetics, medical compounds, pesticides, industrial chemicals such as:
  - Alkylphenols; polycyclic aromatic hydrocarbons; organohalogens; triorganotins

Current Understanding and Recent Findings

- Many species of aquatic organisms are impacted by EDs at the levels now commonly observed in some natural waters
- Low levels of exposure to EDs have been observed in regions remote from major civilization, including the Arctic. Due to atmospheric and oceanic movement of persistent, bioaccumulative compounds.
- Individual EDs, even though at individually harmless concentarions, can have an additive effect when present as a mixture.
- Wastewater treatment – particularly higher SRTs (nitrification and BNR) can provide significant removals.

Sources of EDCs

Sources	Category	Substances
• Incineration, landfill	Polychlorinated compounds (from industrial production or by-products of mostly banned substances)	Polychlorinated dioxins, polychlorinated biphenyls
• Agricultural runoff / atmospheric transport	Organochlorine pesticides (found in insecticides, many now phased out)	DDT, dieldrin, lindane
• Agricultural runoff	Pesticides currently in use	Atrazine, trifluralin, permethrin
• Harbours	Organotins (found in antifoulants used to paint the hulls of ships)	Tributyltin
• Industrial and municipal effluents	Alkylphenols (Surfactants—certain kinds of detergents used for removing oil—and their metabolites)	Nonylphenol
• Industrial effluent	Phthalates (found in placticizers)	Dibutyl phthalate, butylbenzyl phthalate
• Municipal effluent / agricultural runoff	Natural hormones (produced naturally by animals); synthetic steroids (found in contraceptives)	Estradiol, estrone, and testosterone; ethynyl estradiol
• Pulp mill effluents	Phytoestrogens (found in plant material)	Isoflavones, lignans, coumestans

Source: Environment Canada "Endocrine Disrupting Substances in the Environment," 1999.

Regulated Chemicals Known to Cause Endocrine Disfunction

Organic	MCLG1 (mg/L)2	MCL or TT1 (mg/L)2	Potential Health Effects from Ingestion of Water	Sources of Contaminant in Drinking Water
Atrazine	0.003	0.003	Cardiovascular system or reproductive problems	Runoff from herbicide used on row crops
Benzo(a)pyrene (PAHs)	0.0	0.0002	Reproductive difficulties; increased risk of cancer	Leaching from linings of water storage tanks and distribution lines
Carbofuran	0.04	0.04	Problems with blood, nervous system,or reproductive system	Leaching of soil fumigant used on rice and alfalfa
2,4-D	0.07	0.07	Kidney, liver, or adrenal gland problems	Runoff from herbicide used on row crops
1,2-Dibromo-3-chloropropane (DBCP)	0.0	0.0002	Reproductive difficulties; increased risk of cancer	Runoff/leaching from soil fumigant used on soybeans, cotton,pineapples, and orchards
Di(2-ethylhexyl) adipate	0.4	0.4	General toxic effects or reproductive difficulties	Discharge from chemical factories
Di(2-ethylhexyl) phthalate	0.0	0.006	Reproductive difficulties; liver problems; increased risk of cancer	Discharge from rubber and chemical factories
Dinoseb	0.007	0.007	Reproductive difficulties	Runoff from herbicide used on soybeans and vegetables
Dioxin (2,3,7,8-TCDD)	0.0	0.00000003	Reproductive difficulties; increased risk of cancer	Emissions from waste incineration and other combustion;discharge from chemical factories
Ethylene dibromide	0.0	0.00005	Problems with liver, stomach,	Discharge from

Regulated Chemicals Known to Cause Endocrine Disfunction

Ethylene dibromide	0.0	0.00005	Problems with liver, stomach, reproductive system,or kidneys; increased risk of cancer	Discharge from petroleum refineries
Glyphosate	0.7	0.7	Kidney problems; reproductive difficulties	Runoff from herbicide use
Hexachlorobenzene	0.0	0.001	Liver or kidney problems; reproductive difficulties; increased risk of cancer	Discharge from metal refineries and agricultural chemical factories
Methoxychlor	0.04	0.04	Reproductive difficulties	Runoff/leaching from insecticide used on fruits, vegetables, alfalfa,livestock
Polychlorinated biphenyls (PCBs)	0.0	0.0005	Skin changes;thymus gland problems;immune deficiencies; reproductive or nervous system difficulties;increased risk of cancer	Runoff from landfills; discharge of waste chemicals
Toxaphene	0.0	0.003	Kidney, liver, or thyroid problems; increased risk of cancer	Runoff/leaching from insecticide used on cotton and cattle
1,2,4-Trichloro-benzene	0.07	0.07	Changes in adrenal glands	Discharge from textile finishing factories
Inorganic				
Cyanide (as free cyanide)	0.2	0.2	Nerve damage or thyroid problems	Discharge from steel/ metal factories;discharge from plastic and fertilizer factories

Source:U.S.Environmental Protection Agency

Groups of EDCs

- Steroid compounds
- Surfactants
- Pesticides, herbicides, fungicides
- Polyaromatic compounds
- Organic oxygen compounds (phthalates, bisphenol A)

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Steroid Compounds

- Example: estrogens
- Steroid hormones in food (meat, fish, eggs, dairy)
- Used in the U.S. for over 50 years (hormone levels in animal tissue approximately twice that in untreated herds)
  - Ingestion by this means not thought by FDA to be significant
- Estradiol is a potent endogenous estrogen
- Ethinyl estradiol derived from oral contraceptives
- Typically present in wastewater effluents from non-detect to 50 ng/l

Potency of Steroid Compounds

EDC	Lowest observed effective concentration (LOEC) - Rainbow trout	WWTP effluent concentrations
Estradiol	1 ng/l	<0.2 - 3 ng/l
Ethinyl estradiol	0.1 ng/l	<0.2 - 3 ng/l
Nonylphenol	14,000 ng/l	<80 - 923 ng/l
Bisphenol A	25,000 ng/l	8 - 33 ng/l

(German study - Berlin-Ruhleben WWTP - Hansen et al, 1998)

Surfactants

- Alkyl Phenol Ethoxylates (APEO) widely used in industries
- Nonylphenol ethoxylate is the most common
- APEOs tend to be degraded to more potent endocrine disrupting compounds during wastewater treatment

Pesticides

- Largest group of EDCs
- DDT, dieldrin, 2,4-D, tributyltin, atrazine, metolachlor, cyanazine, alachlor
- All herbicides, fungicides, pesticides
- Atrazine the most difficult to remove

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Polyaromatic compounds

- Examples: Polyaromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), brominated flame retardants

Bisphenol-A

- Polycarbonates and epoxy resins (Lacquers to coat metal products)
- Ubiquitous in environment
- Moderate water solubility
- Low volatility
- Degrades relatively easily

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Phthalates

- Plasticizer in a range of plastics, including PVC (also in cosmetics, medical products)
- Main species: Di-(2-ethylhexyl)phthalate
- Low water solubility
- High sorption to solid phase
- Low evaporation potential

Understand Properties to Predict Physical Processes

Property	Potential	Units	Low	High
Water Solubility	Dissolving	mg/l	<1	1000
Henry's Law Constant	Evaporation	atm m^3/mole	$>10^{-2}$	$<10^{-7}$
Organic/Carbon Partition Coefficient	Sorption	log K_{oc}	<3	>3
Log octanol/water partition	Bioconcentration	log K_{ow}	<2.5	>4

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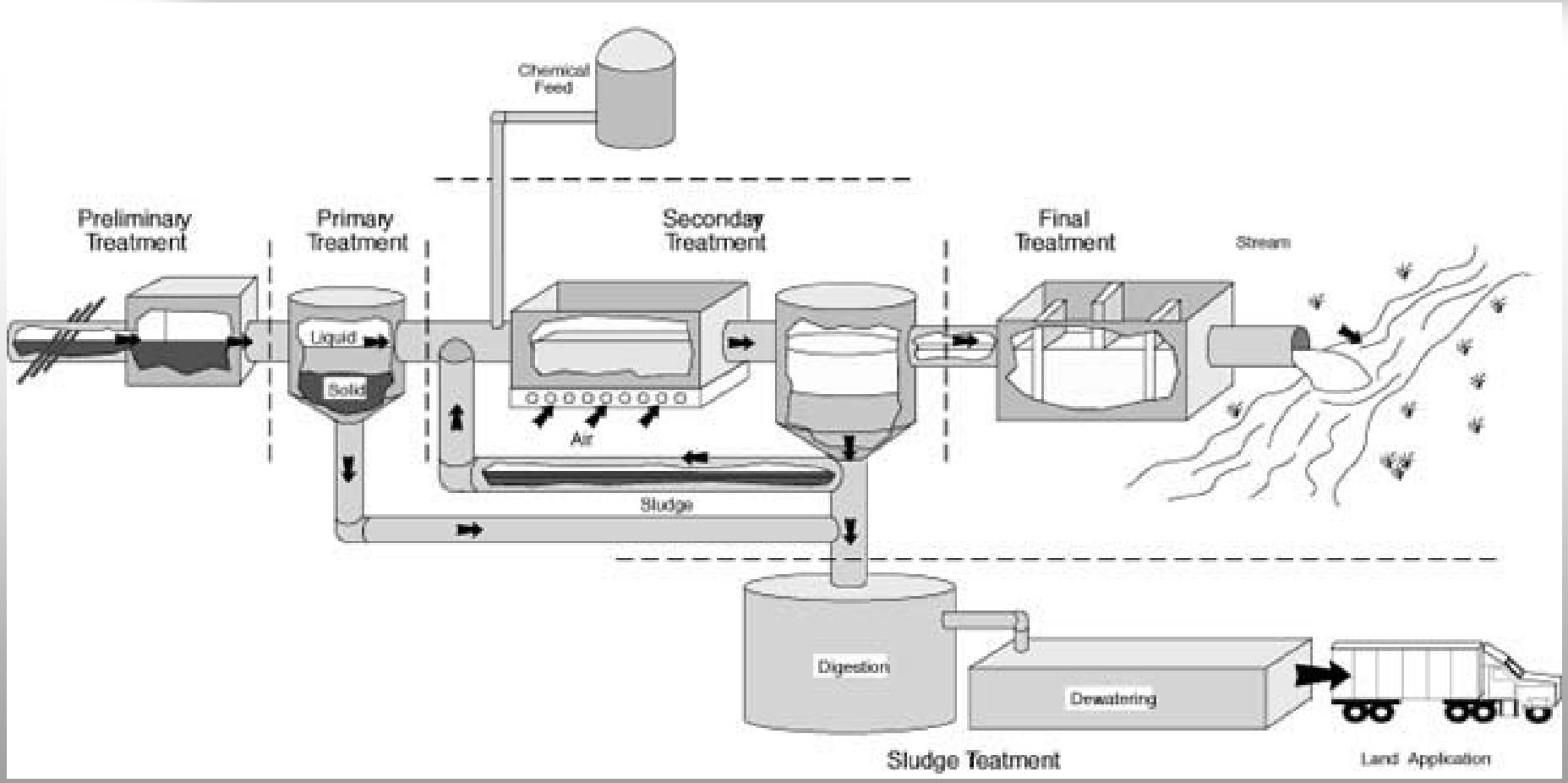
Typical Wastewater Treatment



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Removal Pathways in Wastewater Treatment

- Adsorption (TSS, fats, oils)
- Aerobic/anaerobic biodegradation
- Chemical degradation
- Volatilization

- Extent of biological/chemical degradation depends on structure of compound
- Halogen, sulfonate, methoxy or nitro group substitutions inhibit degradation
- Shorter chains, highly branched chains not as readily degraded

Removal Pathways in Wastewater Treatment

- Long SRTs required for very hydrophobic (high K_{ow}) materials for biodegradation
- Activated sludge surfaces more hydrophobic at higher SRTs
- Naturally occurring compounds more amenable to biodegradation than anthropogenic compounds. Latter requires longer acclimation periods by organisms
- Air stripping of volatile compounds generally less significant than their biodegradation during secondary treatment

Removal of SOCs and EDCs in Wastewater Treatment

Dependent on parameters such as:

- Temperature
- Sludge age, SRT
- HRT
- Influent concentrations
- Co-metabolite transformations
- Treatment type (AS, TF, MBRs)
  - Probably lower EDC concentrations from MBR systems due to retention of both particulate and colloidal material. Membrane systems appear to form colloid complexes to a greater extent than conventional systems

Removal Mechanisms in Wastewater Treatment Processes

Primary Sedimentation

- Adsorption onto settled solids, as well as onto fats, oils and grease
- Surface loading, temperature and influent solids are important parameters
- Little effect on polar dissolved organics
- Some reductions in PCB, AP, but little change in CPH (chlorophenoxy herbicides)
- CEPT (coagulant/flocculant addition) may enhance organics removal

Removal Mechanisms in Wastewater Treatment Processes

Secondary Treatment

- Adsorption onto biological flocs (activated sludge) or onto biofilm (trickling filters)
- Biological and/or chemical degradation
- Transformation and volatilization during aeration
- Little effect on polar dissolved organics
- Main removal mechanism for EDCs from WWTPs may be adsorption since biotransformation rates low at low substrate concentrations

Principal Removal Mechanisms inWWTPs

EDC	Principal Removal Mechanism	Comments
Nonylphenol polyethoxylates	Adsorption	Removals increase with SRT, temperature
Steroids	Degradation	Removals increase with SRT, temperature
Organochlorines	Adsorption	
Lindane	Degradation	Removals increase with lower SRTs
Triazines	Adsorption Degradation (probably less important)	SRT and suspended solids have little effect on removals
Polychlorinated biphenyls (PCB)	Adsorption	Removals increase with SRT and HRT
Organotins	Adsorption	
Phthalates	Biodegradation	Removals increase with temperature
Polyaromatic hydrocarbons (PAH)	Adsorption during primary treatment Volatilization/biodegradation during secondary treatment	Low MW PAH increased removal with TSS loading High MW PAH removal independent of HRT

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WWTP Removals for Select EDCs

EDC	Treatment Process	Removal Efficiency
PCB	Trickling filter (TF)	90%
	Activated sludge (AS)	96%
	TF-AS	99%
NP	AS - High load non-nitrifying	37%
	As - Low load nitrifying	77%
NP_1EO	AS - High load non-nitrifying	-3%
	AS - Low load nitrifying	31%
NP_2EO	AS - High load non-nitrifying	-5%
	AS - Low load nitrifying	91%
NP_6EO	AS - High load non-nitrifying	78%
	AS - Low load nitrifying	98%
NP_2EO	AS - High load non-nitrifying	-5%
	AS - Low load nitrifying	91%
Steroid estrogen - E1	AS - SRT 6 to 11 days, 20°C	75 to 98%
Steroid estrogen - E2	AS - SRT 6 to 11 days, 20°C	75 to 94%
17β estradiol/17α ethinylestradiol (removals from influent)	Sand filtration - Microfiltration	70%
	Reverse osmosis	95%
Organotins	Primary treatment	-5%
	Secondary treatment	91%
	Tertiary treatment	98%
Triazines	Conventional two stage	<40%

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EDC concentrations found in biosolids

EDC	Concentration in biosolids (mg/kg)
NP	100 - 2500
NPEO	10 - 200
Phthalates	0.1 - 200
PAH	0.1 - 80
Bisphenol-A	0.08 - 20
total PCB	0.01 - 10
DDT/DDE	0.01 - 0.5

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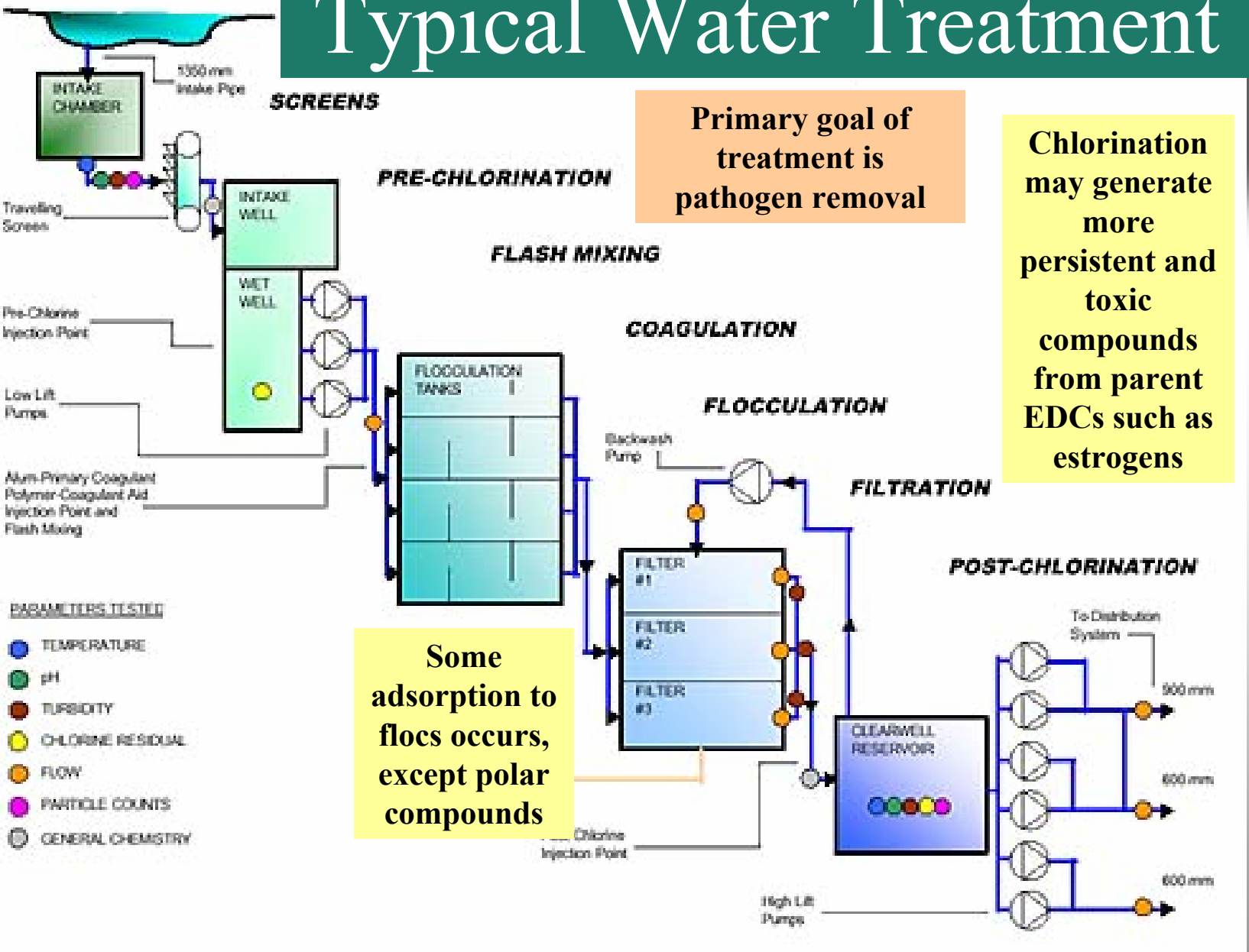
Fate of EDCs in Biosolids Treatment

Anaerobic Digestion

- Some compounds degraded, some to 90%
- Many compounds persistent and resist degradation – still present in treated biosolids
  - Dichloroprop, MCPP, Dieldrin, DDE, Aroclor 1260, Organotins, PAHs (some studies do show 50-70% reduction)
- Alkylphenol polyethoxylates: removal of ethoxylate groups to form parent alkylphenol

Typical Water Treatment



Primary goal of treatment is pathogen removal

Chlorination may generate more persistent and toxic compounds from parent EDCs such as estrogens

Some adsorption to flocs occurs, except polar compounds

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Advanced treatment processes

Granular activated carbon

Reverse osmosis

Advanced oxidation

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Concentrations of Steroid Estrogens After Treatment Processes

Treatment Process	Steroid Estrogen		
	Estrone (E1)	17β-estradiol (E2)	17α-ethinylestradiol (EE2)
Spiked amount (ng/l):	1580	810	1100
After pre-ozonation	450	580	380
After clarification	350	380	310
After sand filter	980	1050	1000
After post-ozonation	180	200	190
After GAC	4	10	10

GAC

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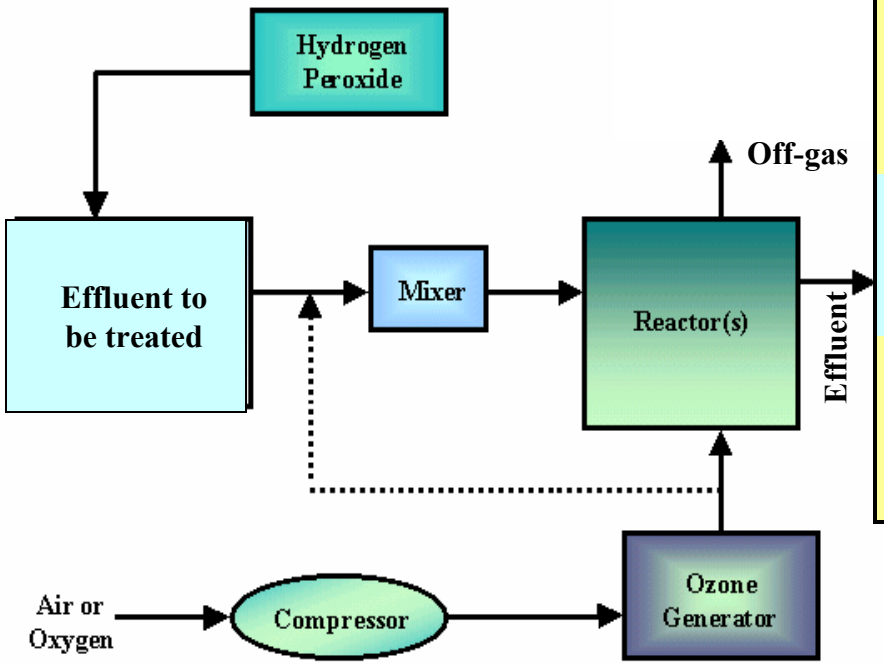
Effectiveness of Treatment Processes with Some EDCs

Treatment Process	Targeted EDCs	Comments
GAC	APs, APEOs, PCP, methoxychlor, endosulfan, diethyl phthalate, di-(2ethyl hexyl) phthalate, PCBs	EPA BAT for some contaminants
Reverse osmosis	Alkylphenol polyethoxy carboxylates (APnECs), PCP	Most EDC compounds removed by RO.
UV+catalyst	APs, bisphenol A, E2, EE2, lindane, 2,4-D,	
Ozone+H_2O_2	Atrazine	2 min. EBCT. EU regs may not be met
Coagulation, sedimentation and filtration	2,3,7,8 TCDD	Adsorbed to floc particles



General removal efficiencies of treatment processes

EDC Classification	Coagulation/ Flocculation	Softening/ metal oxides	CL2/ ClO2	UV	Ozone/ AOPs	Activated Carbon	BAC	NF	RO
Pesticides	<20%	70-90%	70->90%	>90%	20->90%	>90%	>90%	70->90%	>90%
Industrial chemicals	<20-40%	<20-40%	<20%	>90%	40-90%	>90%	>90%	>90%	>90%
Steroids	<20%	<20-40%	>90%	>90%	>90%	>90%	>90%	70->90%	>90%
Metals	40-90%	40-90%	<20%	<20%	<20%	70-90%	70-90%	70->90%	>90%
Inorganics	<20%	70-90%	<20%	<20%	<20%	<20-40%	40-70%	70->90%	>90%
Organometalics	<20-40%	<20-40%	<20-70%	40-90%	20->90%	70->90%	70->90%	70->90%	>90%

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Questions

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