

CECs—Where are we now?

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Thursday August 27, 2020

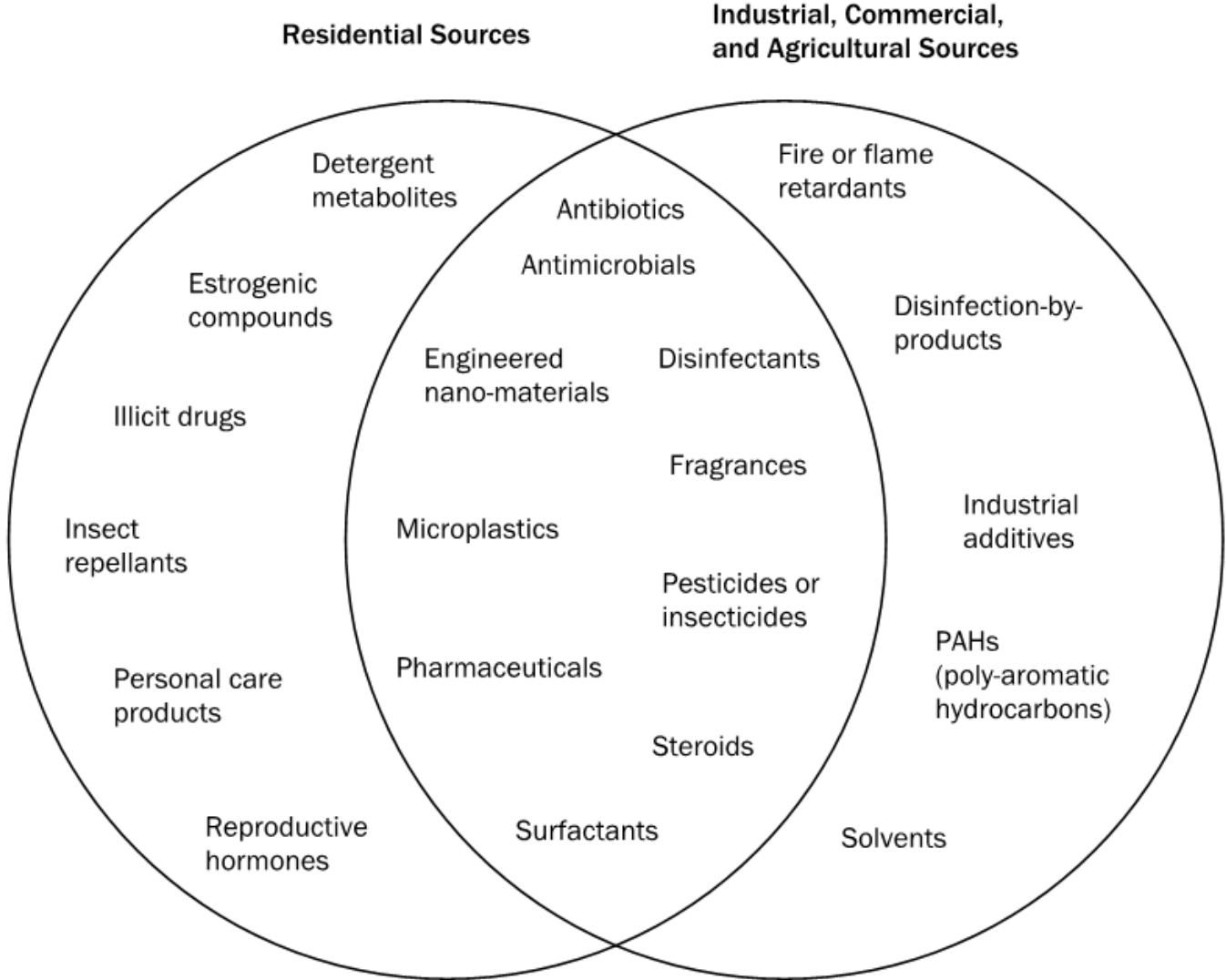


Agenda

- Recap on Webinar 1: CEC 101- What are they?
- Mechanisms for removal– fate and transport
- Potential for removal in engineered systems (WRRFs)
 - Biological process removal
 - Advanced treatment removal
- What can we do as wastewater professionals?



Common Classes of CECs



With permission from John Ross

Common Classes of CECs

Associated Effects	CEC Categories
Antibiotic resistance	Antibiotics, Antimicrobials, Personal care products
Carcinogenicity or increased risk of cancer	Fire retardants (PFAS), Prescription drugs
Endocrine disruption	Personal care products, pesticides, plasticizers, reproductive hormones, solvents, steroids
General toxicity (incl. geno-, cytotoxicity)	Disinfectants, Industrial additives
Negative effect on animal reproductive activity	Life-style products (Caffeine, Nicotine)
Organ damage	Prescription drugs

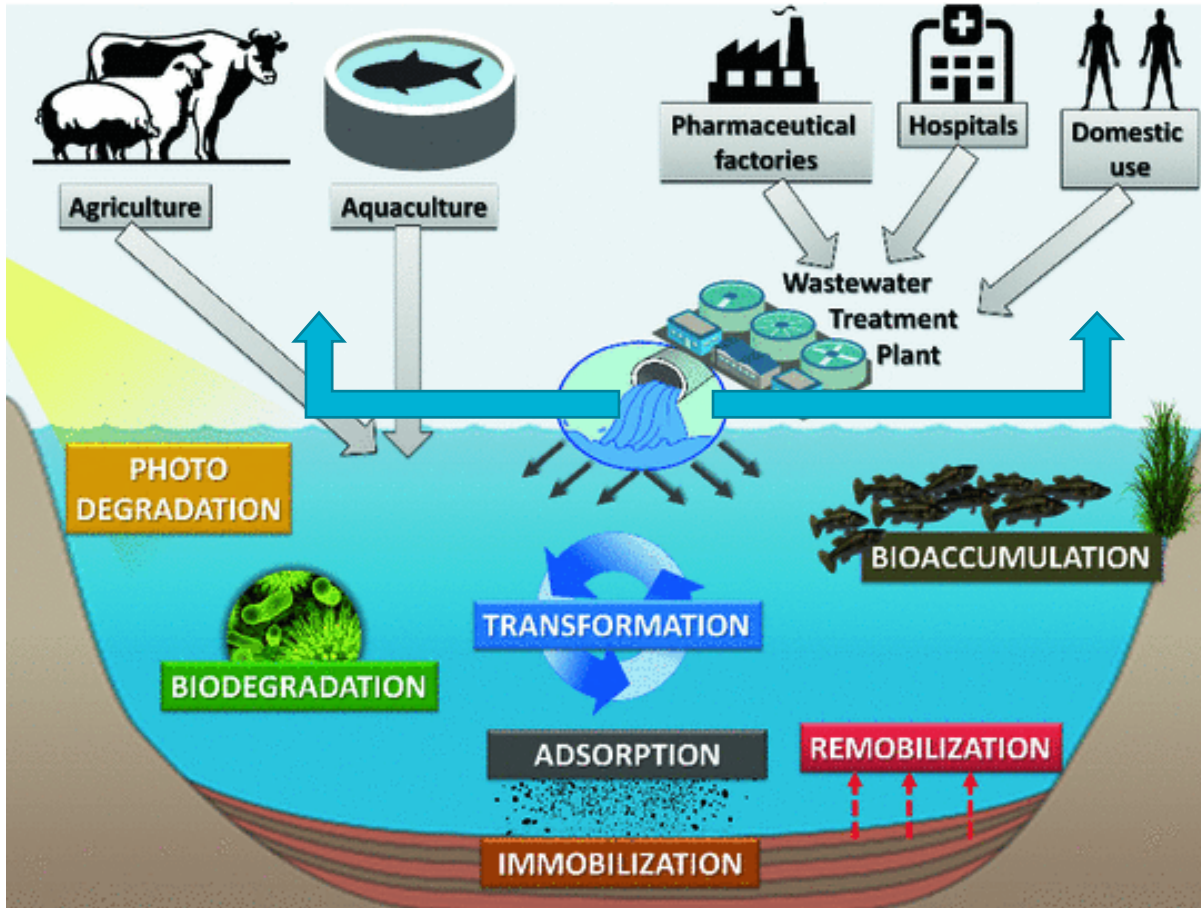


Concern for CECs

- Receptors in aqueous phase (to land, stream, ocean, groundwater, reuse) and solid phase (incineration to atmosphere) / biosolids (land application)
- Commonly present in waters at trace concentrations, ng/L to $\mu\text{g/L}$ (ppt to ppb)
- Can pass through water resource recovery facilities (WRRFs) by virtue of their characteristics and persistency and/or the continuous introduction
- Short-term and long-term toxicity, endocrine disrupting effects and antibiotic resistance of microorganisms
- Need for research on synergistic, additive, and antagonistic effects



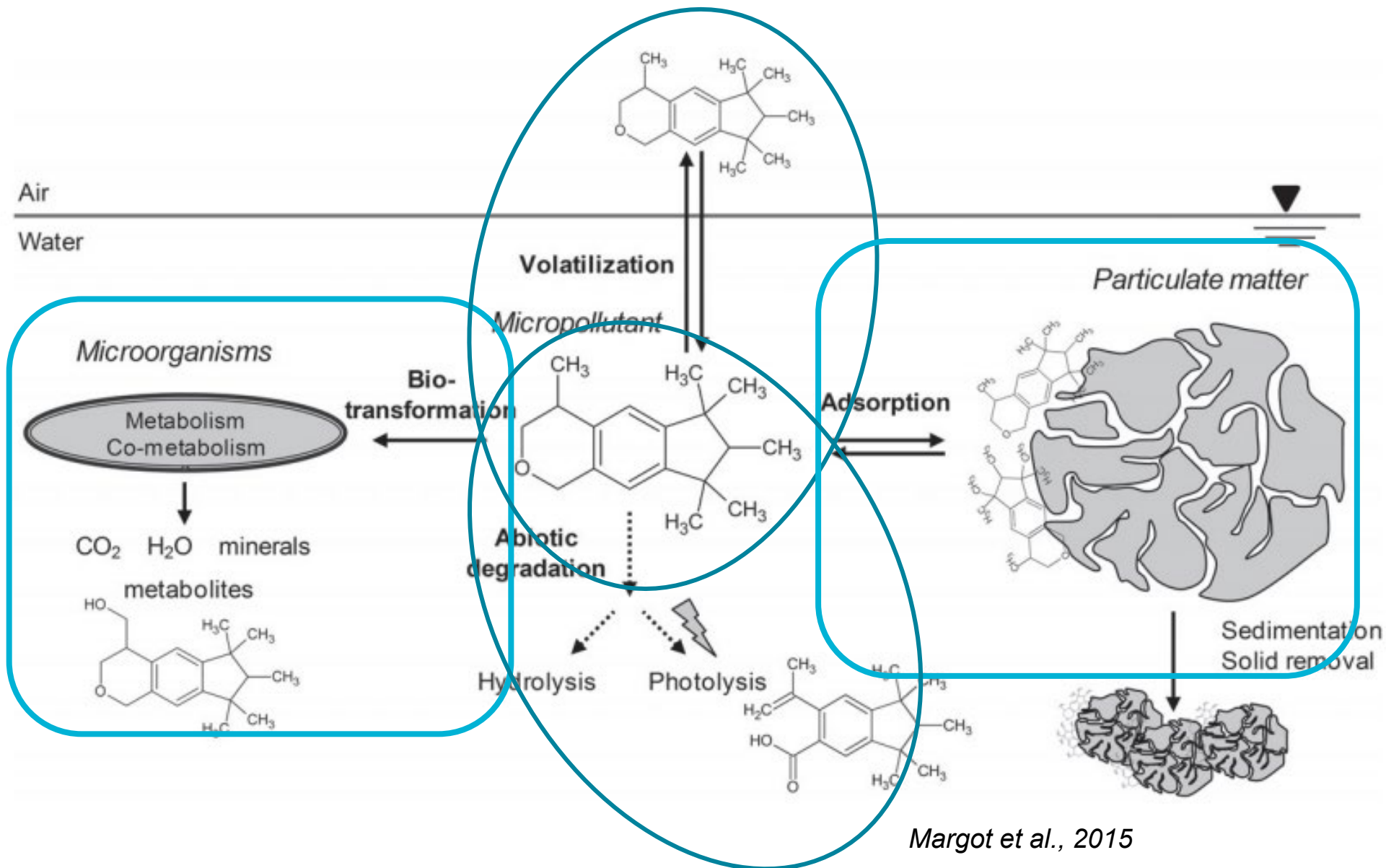
Fate and Transport



Klimaszyk and Rzymiski (2018)

- CECs introduced in waste streams by:
 - Consumer use/Excretion
 - Hospital/industrial wastewater discharges
 - Household water usage (washing/bathing)
 - Disposal by toilet flushing/ landfills
- Currently no regulations of CEC for non-potable discharges by WRRFs
 - not specifically designed to eliminate CECs
- WRRFs are receivers of CECs and point sources into the environment
- The fate of these compounds can be influenced by natural treatment mechanisms

Mechanisms defined



Margot et al., 2015

Variability of removal efficiency

Dependent on physio-chemical properties of each specific chemical compound, concentration, and treatment conditions



Treatment Condition	Effects on CEC Removal
pH	Sorption (acid dissociation constant pKa), effect on biodegradation (low pH inhibits nitrification)
Temperature	Biodegradation; volatilization, solubility
ORP	Biodegradation, aerobic conditions more efficient, anoxic/anaerobic less efficient
HRT	Contact time (hours) is typically enough for biodegradation and sorption equilibrium for flocculant sludge
SRT	Diversity in activated sludge; slow growing nitrifying bacteria

Removal in engineered systems

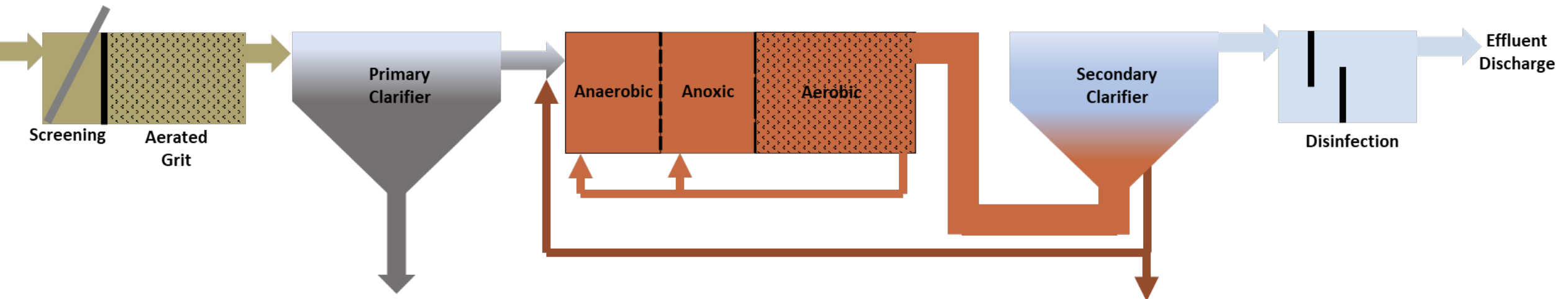
Water Resource Recovery Facilities:

CECs are frequently detected in both raw influent and treated effluents of WRRFs at concentrations, ranging from ng/L to mg/L

Not primarily designed to remove CECs, however fortuitous removal occurs

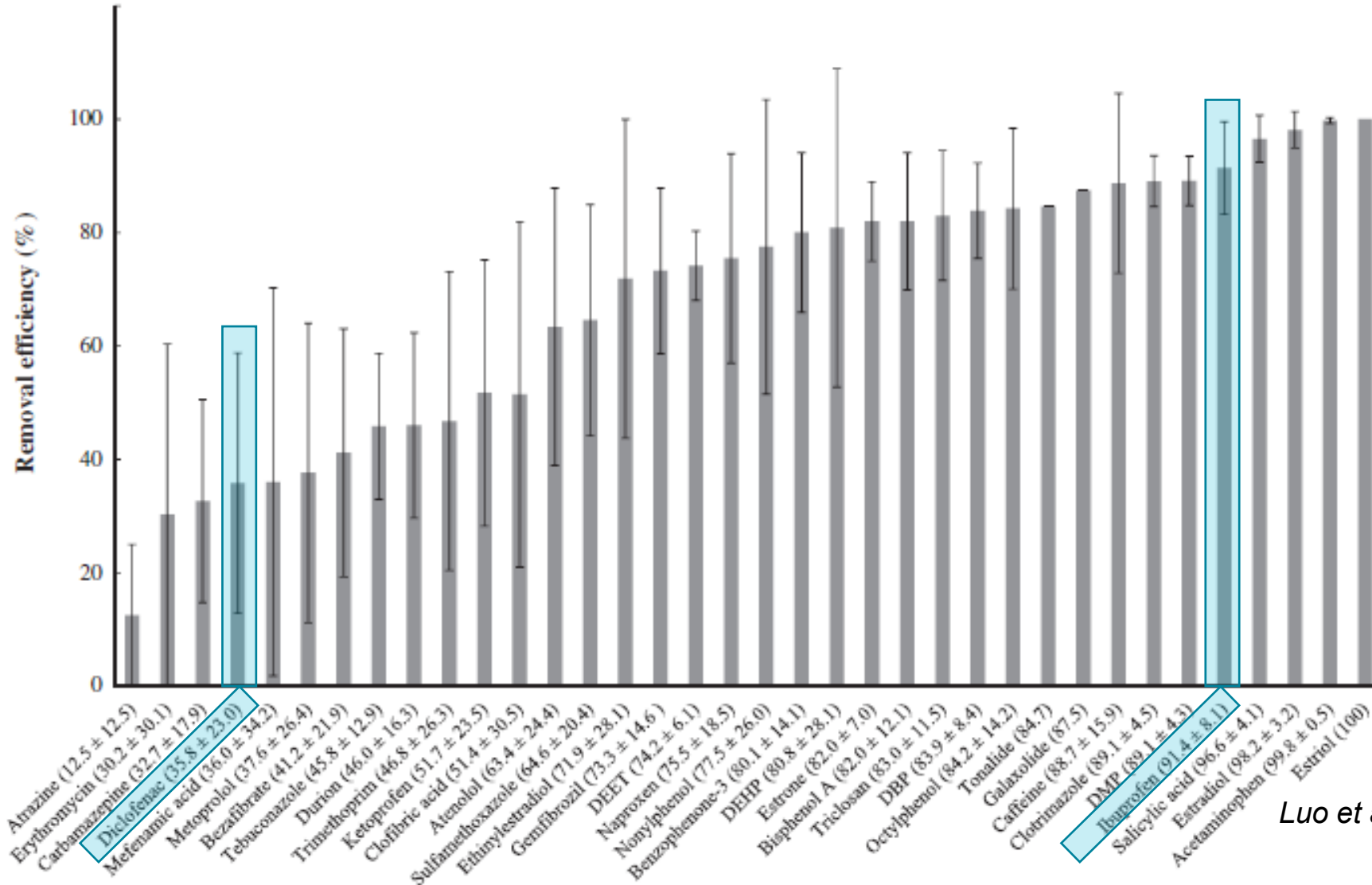
Luo et al., 2014 reviewed WRRF “overall” removal efficiencies from 14 countries/regions (removal from aqueous phase)

- Caffeine: >80% (most abundant compound)
- Fragrances: >85%
- Lipid regulators & Beta blockers: 38-73%
- Antibiotics: 30-65%
- Steroid hormones: 70-100%
- NSAIDs: 35-90%



Removal in engineered systems

Water Resource Recovery Facilities:



Luo et al., 2014

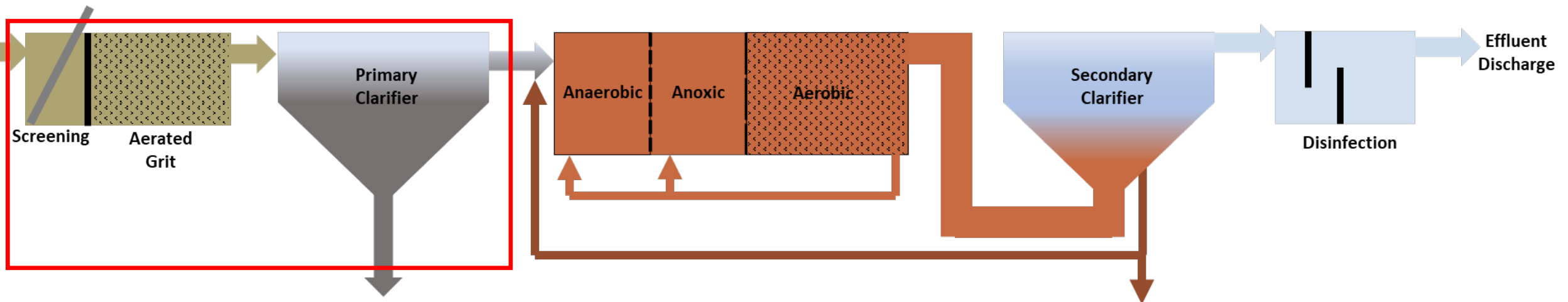
Removal in engineered systems

Primary treatment process:

Aims to reduce the suspended solids (i.e. oils and fats, grease, sand, grit, and settable solids), but usually not as effective in eliminating most CECs, particularly for hydrophilic contaminants ($\log D_{ow} < 1.0$)

Sorption onto biomass hydrophobic CECs ($\log D_{ow} > 3.0$), tend to sorb onto primary sludge and are partially removed from dissolved phase

Fragrances: up to 40%
PhACs/hormones: up to 28%



Removal in engineered systems

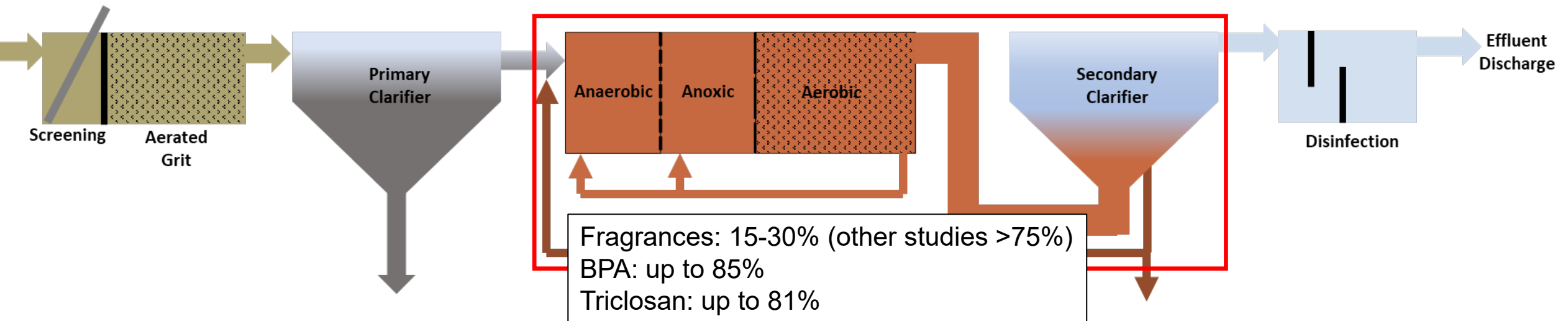
Secondary treatment process:

CECs can be biologically degraded to varying degrees: mineralization or incomplete degradation into transformation products.

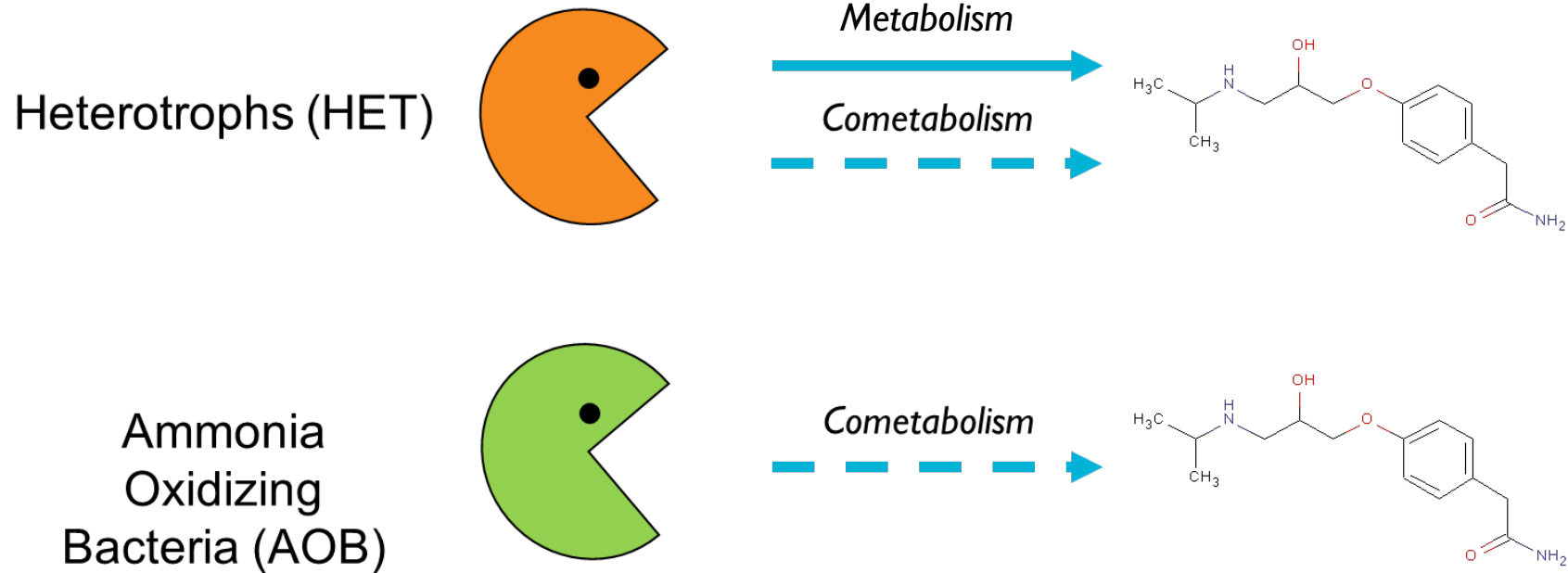
Two main **biotransformation** mechanisms:

- **Metabolism:** microorganisms use CECs as the sole energy and/or carbon source to maintain their biomass and produce the relevant enzymes and cofactors for their oxidation/reduction- CECs need to be non-toxic to microbial growth, and at a high enough concentration to support biomass
- **Cometabolism:** microorganisms are able to degrade CECs (i.e. non-growth substrate) in the obligatory presence of growth substrate

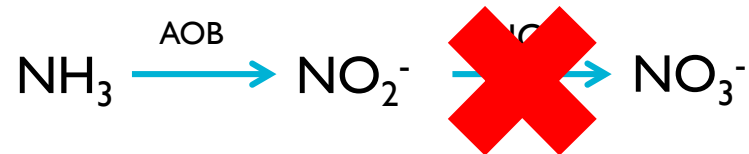
Sorption onto biomass



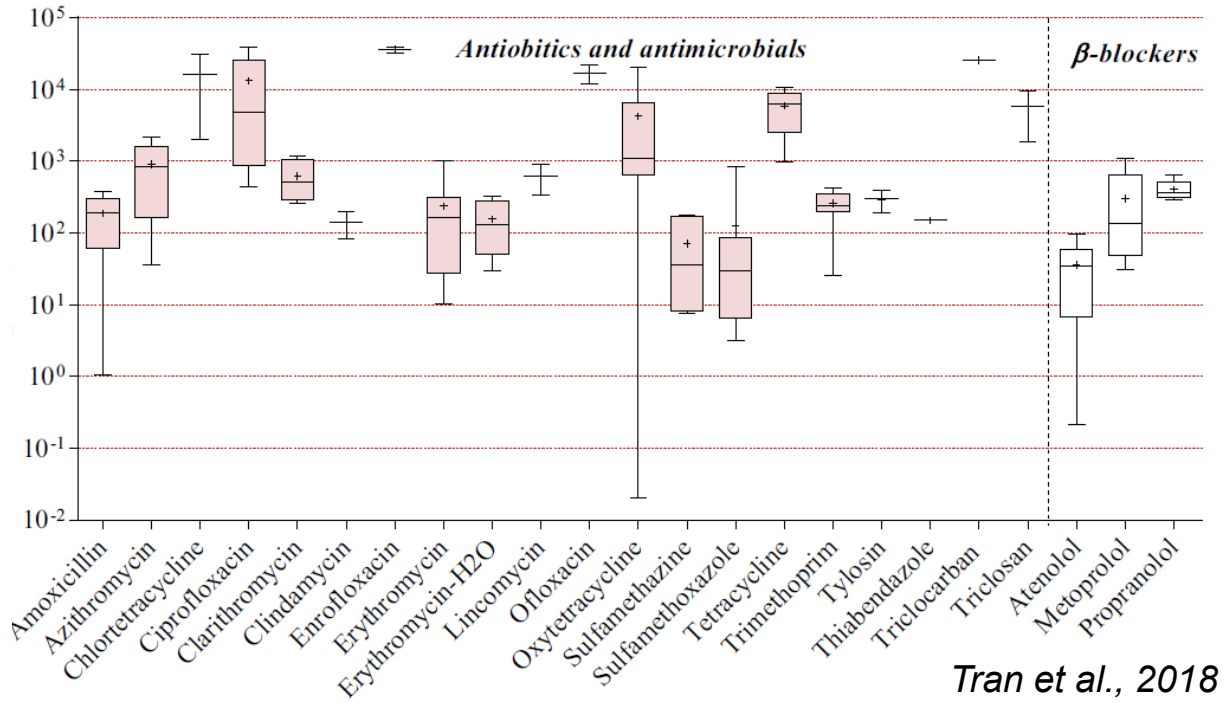
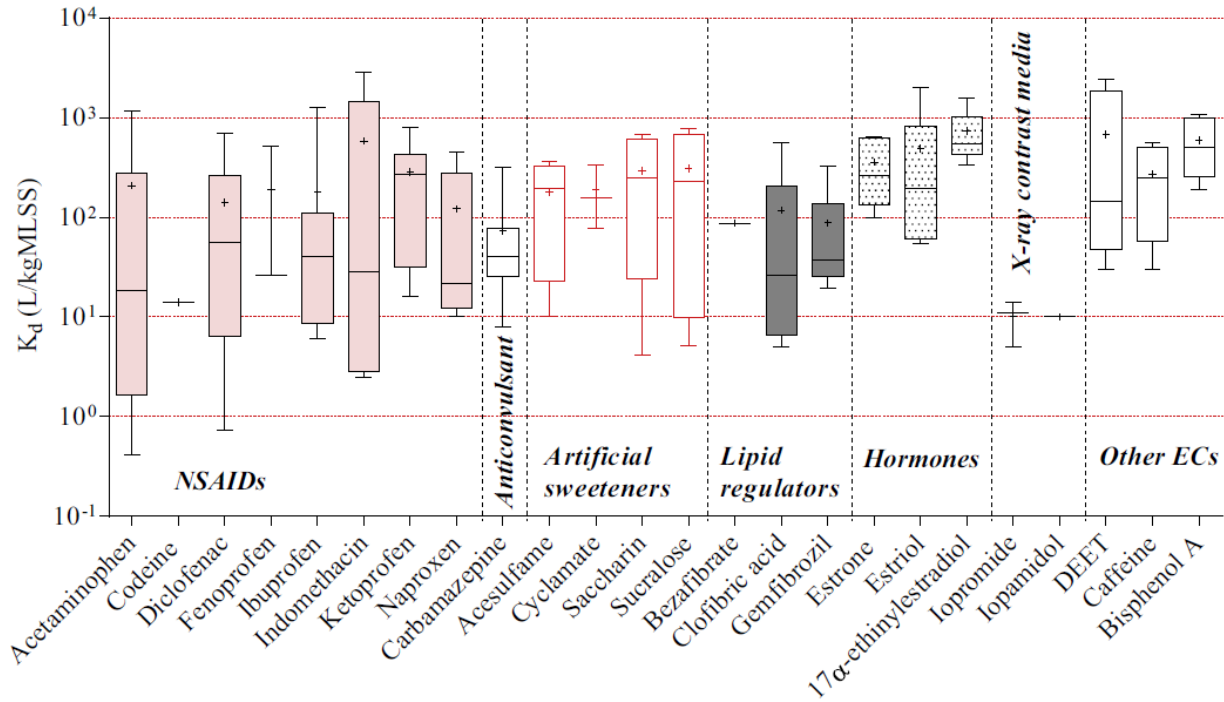
Metabolism and Cometabolism



- Nitrification usually enhances biotransformation- CEC biotransformation correlates to nitrification rates



Sorption



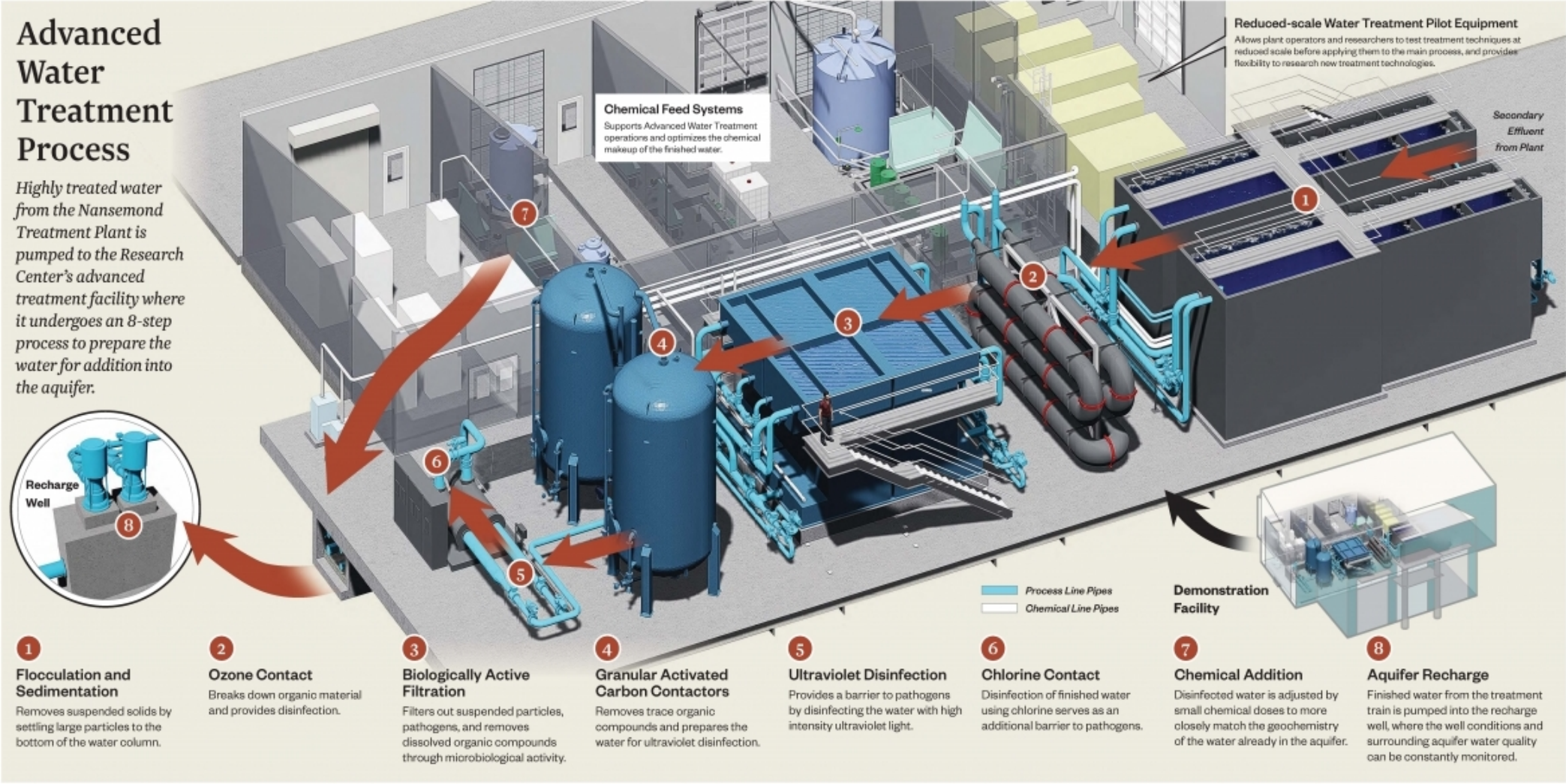
Tran et al., 2018

Sorption on activated sludge is negligible when $K_d < 300$ L/kg ($\log K_d < 2.48$)

Sorption potential: low: $\log K_{OW} < 2.5$, medium: $2.5 < \log K_{OW} < 4$, high: $\log \log K_{OW} > 4$

Wastewater – Indirect Potable Reuse

Hampton Roads Sanitation District SWIFT Facility – Wastewater Reuse Via Aquifer Recharge



Advanced Treatment Processes

PFAS Removal Across Tertiary and Advanced Treatment

Type	Process	PFAS Removal Efficacy
Physical – filtration	Granular media	Low
	MF/UF	Low
	Reverse Osmosis (RO)	High
Physical – adsorption	Granular Activated Carbon (GAC)	High
Chemical	Chlorine	Low
	Chloramine	Low
	Ozone & ozone-peroxide	Low
Irradiation	UV disinfection	Low
	UV-AOP	Low
Hybrid	Biologically Active Carbon (BAC)	Moderate
	Soil-Aquifer Treatment (SAT)	TBD - Site-Specific
Ion exchange	Ion Exchange (IX)	High

With permission from Vijay Sundaram

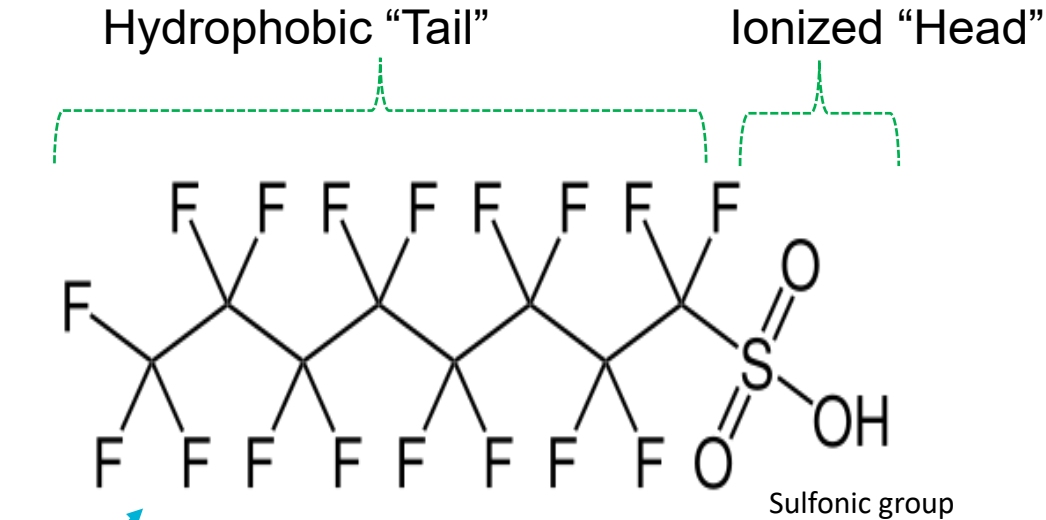
Advanced Treatment Processes: Activated Carbon



- Granular (GAC), powdered (PAC), pellet, etc.
- CECs may have low affinity for retention onto sludge but, high affinity to interact with other sorbent agents such as activated carbons
- Sorption efficiency is dependent on CEC characteristics
 - Electrical charge
 - Distribution coefficient ($\log D$)– high value readily sorbes e.g. carbamazepine
 - Octanol-water distribution coefficient (K_{ow})
 - Acid dissociation constant (pKa)
- Applications:
 - PAC dosage to activated sludge or post treatment has been shown to improve CEC removal
 - Tertiary treatment with GAC vessel/column

Ion Exchange (IX) Resin vs. Carbon

PFOS – Perfluoroalkyl Sulfonic Acid



GAC

removes by adsorption
using hydrophobic "Tail"

Selective IX Resins

removes by both ion exchange and
adsorption using both "Head" & "Tail"



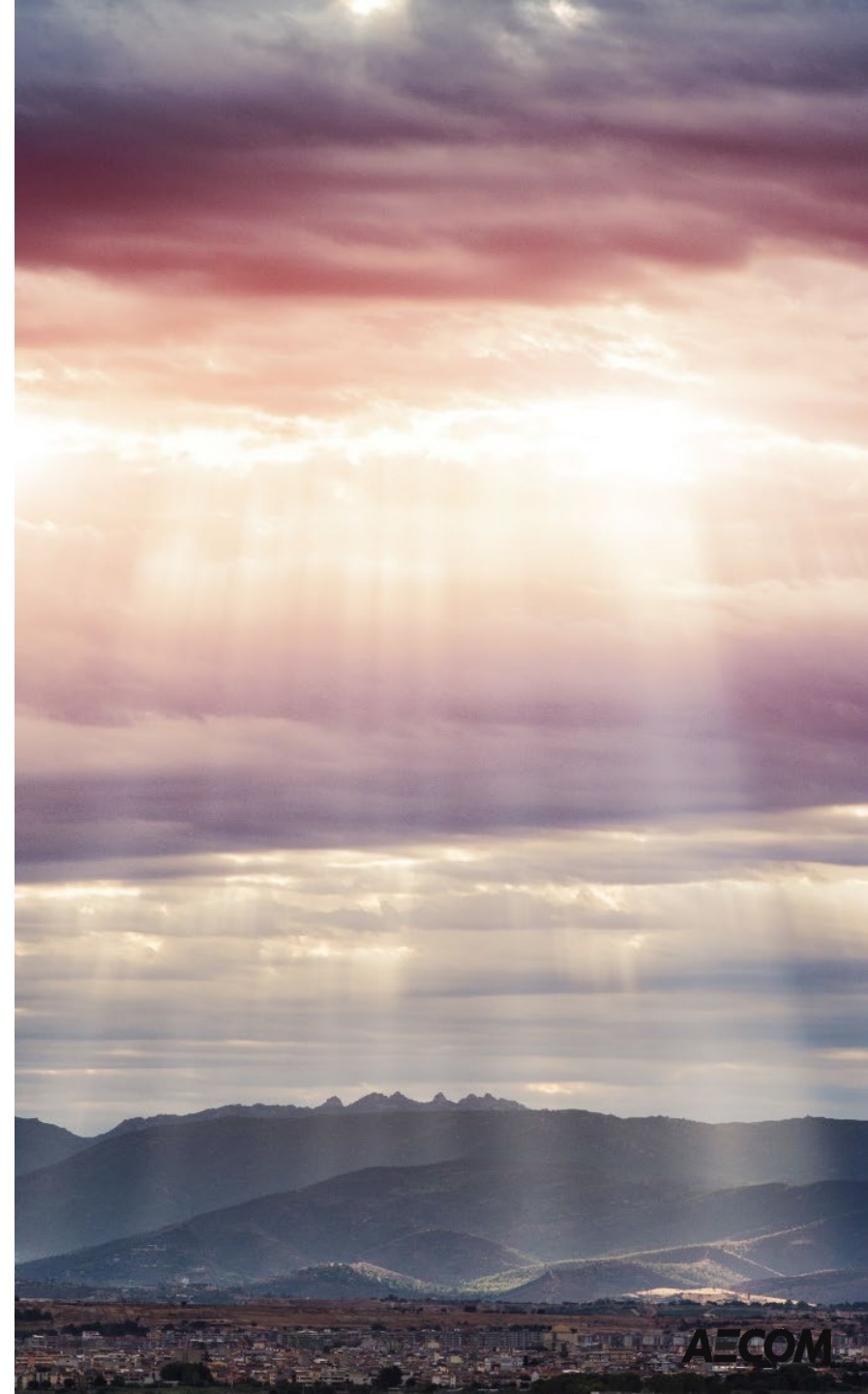
- ✓ Shorter EBCT
- ✓ Smaller footprint
- ✓ Better short-chain removal
- ✓ Regeneration available

Advanced Treatment Processes: UV

- UV/photolysis– compounds absorb photons and the energy released drives oxidation processes induced by light
- In the UV/Hydrogen Peroxide (UV/H₂O₂) process, the photolysis of hydrogen peroxide generates hydroxyl radicals, which oxidize target compounds.

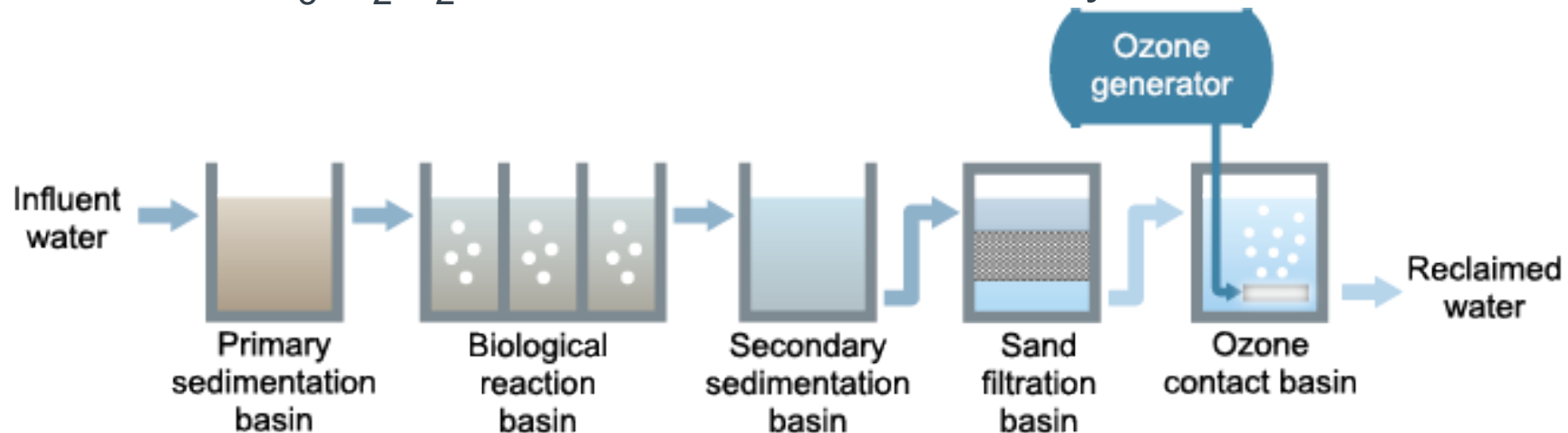
Study by De la Cruz et al., 2012:

- UV alone could remove 45% of 32 CECs after 10 min CT
- UV/H₂O₂ improved to 81% after 10 min CT
- UV/H₂O₂ improved to 97% after 30 min CT



Advanced Treatment Processes: Ozone

- O_3 can degrade contaminants directly and indirectly – via formation of stronger and less selective oxidizing agent, hydroxyl radicals ($\bullet OH$)
- Efficient redox technologies
 - High degradation rates
 - Non-selectivity
 - Disinfecting effects
 - Applicable for reuse
- Gerrity et al., 2011: O_3/H_2O_2 showed removal efficiency of $>90\%$ for 30 CECs



Advanced Treatment Processes: Membrane Bioreactor

- Membrane bioreactor (MBR) process combine activated sludge biological treatment and membrane filtration
 - High effluent quality
 - Control of high SRT- higher biomass concentrations
 - Effectively remove wide spectrum of CECs
 - Retain sludge which CECs sorb to
 - Membrane surface intercepts compounds
 - Longer SRT promotes higher microbial diversity with enhanced biotransformation (nitrifiers)
- Trinh et al., 2012: studied 48 CECs, most >90% removal; select few (carbamazepine, diazepam, diclofenac) 24-68 % removal



Biosolids

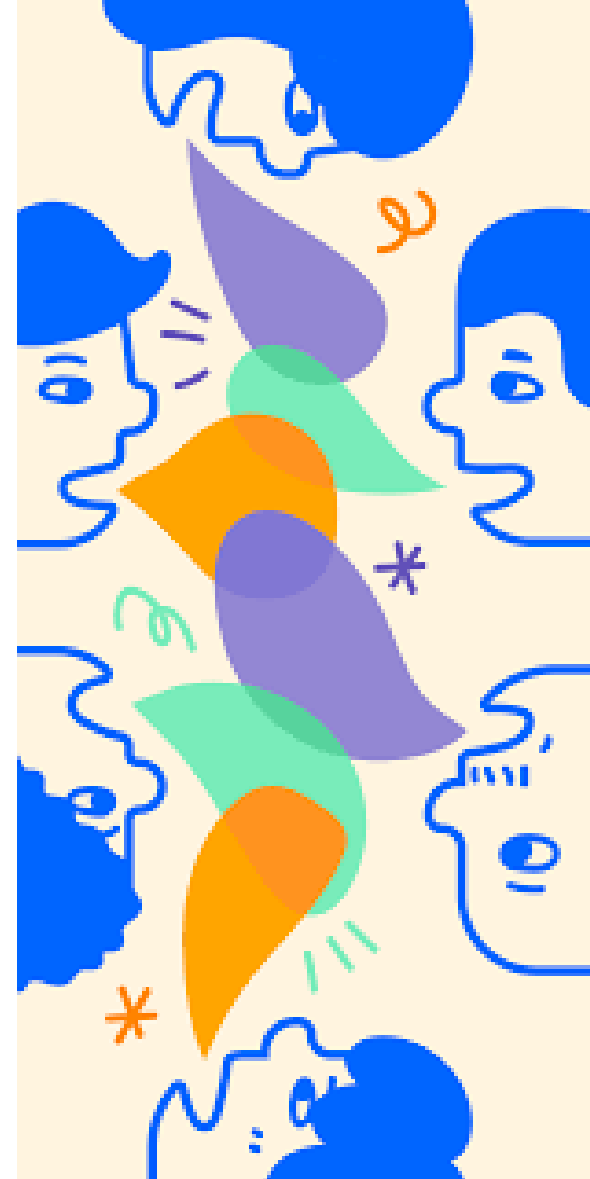
Alternative Options to Land Application or Landfill

- What do you do if you cannot land apply or landfill due to PFAS concerns?
- Several technologies are being considered or in development
 - Incineration
 - Alternative combustion (Kruger BioCon ERS)
 - Pyrolysis (Bioforcetech)
 - Gasification (Aries Clean Energy or Ecoremedy)
 - Supercritical water oxidation (374 Water)
 - Hydrothermal liquefaction (Genifuel)
- Data is still limited



What can we do now?

- Develop needed communication tools about CECs for wastewater professionals and for the general public.
- Reduce source through a combination of preventive measures
 - PFOA Stewardship Program
 - Microplastics discontinued use in PCPs
 - enhanced communication to the public on rational drug use
 - disposal of pharmaceuticals (e.g. avoid flushing unused drugs down the toilet)
 - education for prescribers
 - systematic drug take-back programs



What can we do now?

- Support and advocate for research of CECs in water and WRRF processes
- Advocate for timely health and environmental assessments for CECs
- Support increase in funding for research and technology development that can help address CECs in our large and small communities
- Advocacy at the local, state, regional and national level by leveraging the collective knowledge and expertise to educate policy makers and legislators on the criticality of creating good water policy, regulations and laws based on sound science



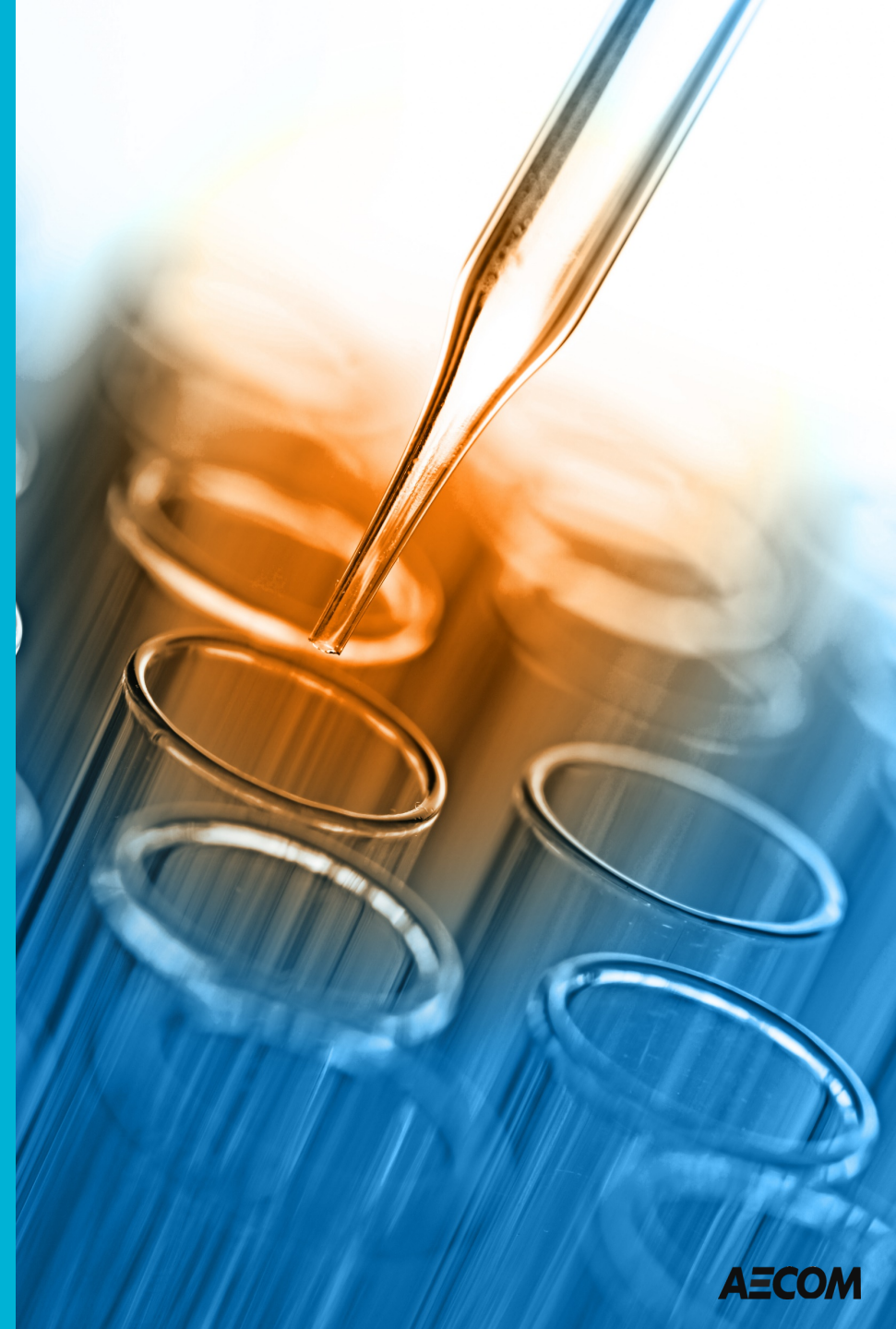
Thank you

Next Webinar:

Addressing CECs with Innovation

Thursday, Sept 24

**Presenter: Julie Bliss Mullen,
Aclarity Water**



Mechanisms defined

Mechanism	Definition
Biodegradation	Microbial process converting large molecular weight compounds to those with lower complexity e.g. organic compounds → simple inorganic molecules (i.e. H ₂ O and CO ₂) (also: Mineralization)
Transformation	Any alteration or change to the molecular structure of a compound. Biotransformation is any biologically mediated change to a molecule; Can be degradation and formation
Sorption	Comprises two mechanisms: Absorption from the aqueous phase onto lipid fraction of the sludge due to CEC hydrophobicity Adsorption onto solids surface due to electrostatic interactions between positively charged CECs and negatively charged surface of biomass cells
Photodegradation	Process by which the absorption of photons—particularly those with wavelengths in the UV–visible spectrum—causes a molecule to degrade
Bioaccumulation	Increase in CEC concentration via uptake by organisms due to environmental exposure
Volatilization	Transfer of chemical across liquid-gas interface or solid-gas interface as vapor. Dependent on physiochemical properties (Henry's law constant) and WRRF operation conditions e.g. aeration, temperature, atmospheric pressure