Removal of contaminants of emerging concern (CEC) from urban wastewater by membrane bioreactors (MBRs)

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Outline

- Background & Challenges
  - Contaminants of emerging concern (CEC)
  - Membrane bioreactors (MBRs)
  - MBR vs. CAS
- Removal mechanisms
- Factors influencing CEC removal
- Removal of ARB & ARGs
- Hybrid systems
- Conclusions & Perspectives
- Acknowledgments

Background & Challenges:

Contaminants of emerging concern (CEC):

- Many definitions: EPA, NORMAN Network, reviews, etc.
- Chemicals that show some potential to pose risks to human health or the environment and which are not yet subjected to regulatory criteria or norms for the protection of human health or the environment

(Sauvé and Desrosiers, 2014)

Sauvé and Desrosiers *Chemistry Central Journal* 2014, **8**:15
http://journal.chemistrycentral.com/content/8/1/15

Chemistry Central Journal

REVIEW Open Access

A review of what is an emerging contaminant

Sébastien Sauvé[1*] and Mélanie Desrosiers[2]

Abstract

A review is presented of how one defines emerging contaminants and what can be included in that group of contaminants which is preferably termed "contaminants of emerging concern". An historical perspective is given on the evolution of the issues surrounding emerging contaminants and how environmental scientists have tackled this issue. This begins with global lead contamination from the Romans two millennia ago, moves on to arsenic-based and DDT issues and more recently to pharmaceuticals, cyanotoxins, personal care products, nanoparticles, flame retardants, etc. Contaminants of emerging concern will remain a moving target as new chemical compounds are continuously being produced and science continuously improves its understanding of current and past contaminants.

Review

Emerging contaminants have now become a fashionable and trendy research venue. The large number of emerging contaminants poses a challenge for regulatory agencies. How to prioritize research about emerging contaminants? How to prioritize the definition of quality criteria or norms for all of these new substances for which we generally have only sparse knowledge on their behaviour in the environment or on their toxic effects on human health or the environment? The vogue for emerging contaminants certainly partly arises from the need of data and uncover the truth and risks involved with DDT – which again was first synthesized about a hundred years before Carson's book and began to be spread generously during the second World War. We owe her for the eye-opening message that pesticides and chemicals in general can be problematic.

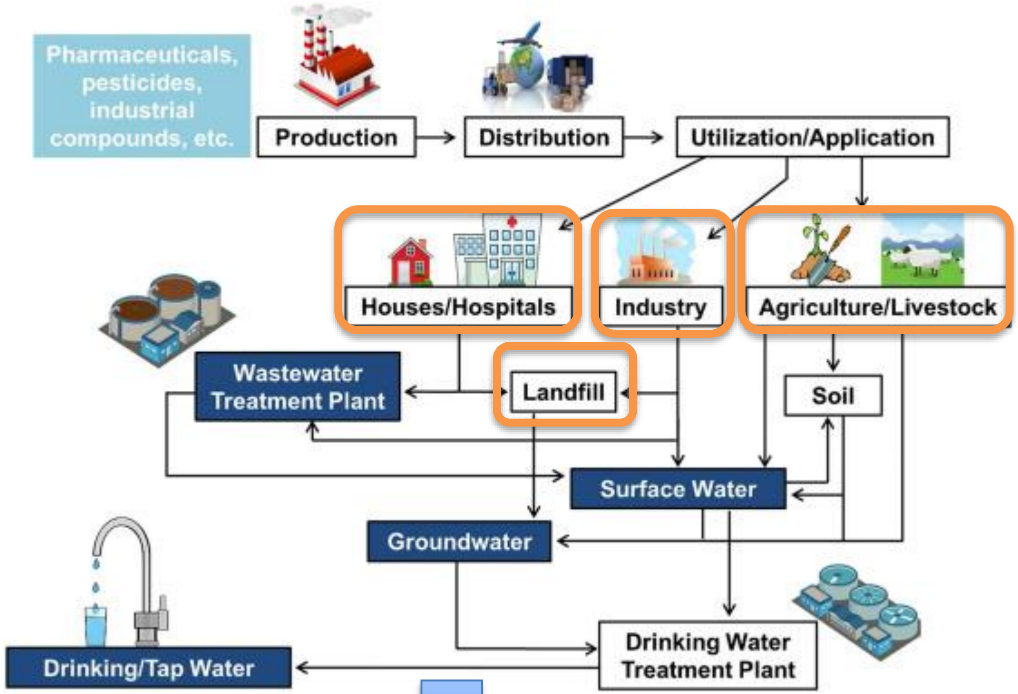
Once we focus on "emerging contaminants", we need to better define what is being targeted. Given that qualification of what is "emerging" is relative, what was emerging as an important environmental contamination issue a decade or two ago, might no longer be qualified as an emerging

Substances of actual or potential threat to human health, animals or environment.

- CEC groups: pharmaceuticals, personal care products, plasticizers, flame retardants, industrial compounds, pesticides, hormones, ARB, ARGs, …
- Yet, no standardized categorization of CEC

Background & Challenges:

- Human activities contaminate water resources
- Sources of CEC:



Barbosa et al. (2016)

CEC end up in water bodies
with negative impact on water quality

Background & Challenges:

WWTPs can reduce CEC emission, but removal of many CEC is difficult + WWTPs not designed for CEC removal

↓

only partially effective in CEC removal or degradation

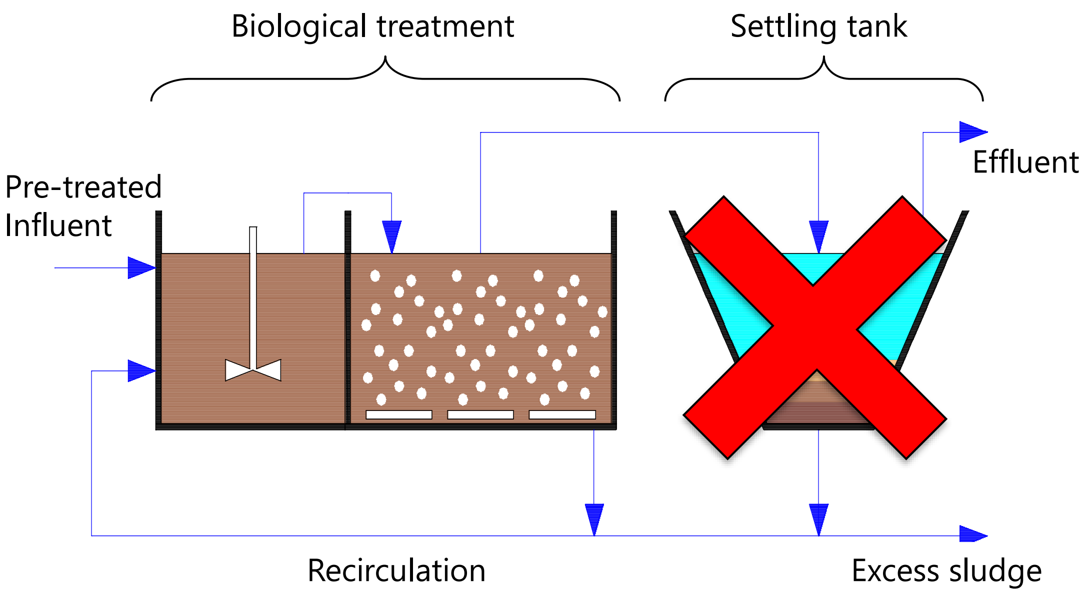
↓

CEC discharged into the environment
& WWTPs are important emission source of CEC

One potential solution? → Membrane bioreactors (MBRs)

Membrane bioreactor (MBR):

- integrates biodegradation by activated sludge, with solid-liquid separation by membrane filtration (MF/UF)



Lousada-Ferreira et al. (2015)

Membranes role – complete rejection of suspended particles;

Bioreactor role – biodegradation, adsorption, precipitation and nitrification/denitrification processes;

Membrane bioreactor (MBR):

Advantages:

- ✓ Stable and high quality effluent
  - – Particle free and largely disinfected
- ✓ Small footprint
- ✓ High biodegradation efficiency of biodegradable contaminants
- ✓ Limited excess sludge production

→ Potential for water reuse

(Judd, 2015; Krzeminski et al. 2017)

Disadvantages:

- – Capital costs (membranes, pre-treatment)
- – Operational costs (energy demand)
- – Membrane fouling control
- – Accumulation of some CEC

Membrane bioreactor (MBR):

Status:

- ✓ well-established, mature, many full-scale plants:
  - Largest municipal MBR: Henriksdal (SE) 864 000 m^3/d (2018)
- ✓ accepted process alternative for wastewater treatment and reuse;
- ✓ particularly: stringent suspended solids, nutrient, space, microbiological limits or water reuse cases
- ✓ with disinfection meets WHO standards for unrestricted irrigation

Challenges:

- membrane fouling & energy demand
- not designed to remove organic & inorganic CEC

(Krzeminski et al. 2017)

MBR vs. CAS:

- **No consensus** on MBR and CAS potential to remove CEC

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Comparison of removal of pharmaceuticals in MBR and activated sludge systems ☆

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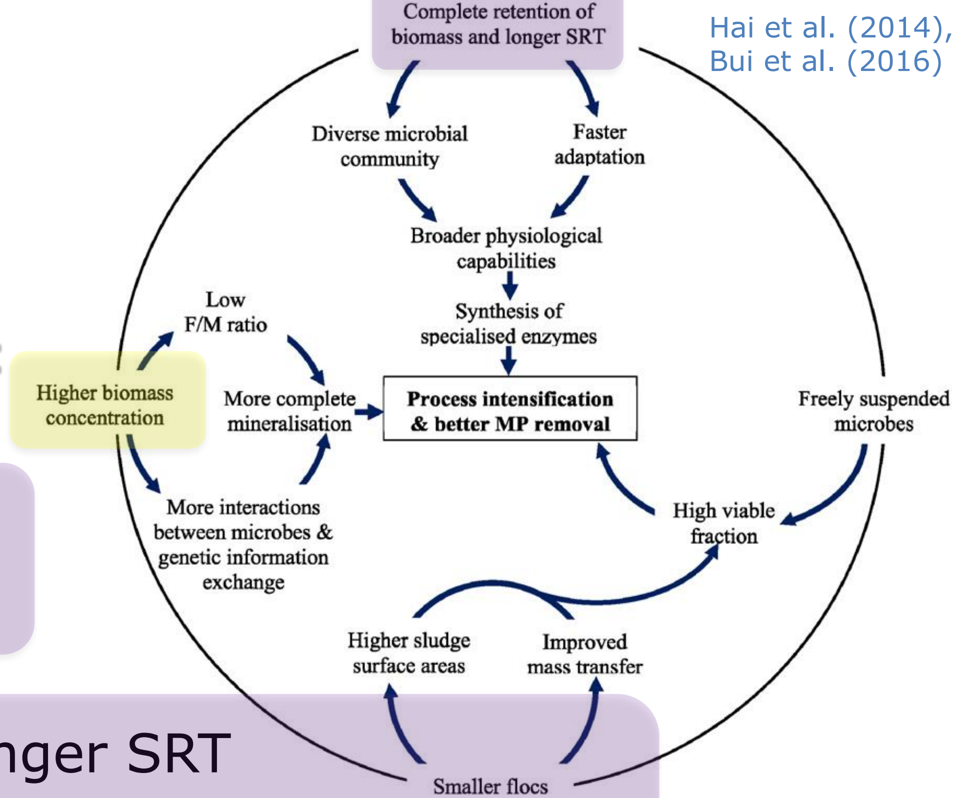
- **No distinct differences** in CEC removal, under similar operating conditions (Joss et al., 2006; Bouju et al. 2008; Abegglen et al., 2009)
- **No advantages** for well degradable & recalcitrant compounds (Weiss and Reemtsma, 2008)

+ **Superior** for compounds of intermediate removal in CAS (Sipma et al. 2010)
+ **Removes** number of CEC **not eliminated** in CAS (Radjenović et al., 2009; Luo et al., 2014)

⇓ mainly, associated with sludge

MBR vs. CAS:

Factors which may provide improved CEC removal vs. CAS:



Hai et al. (2014), Bui et al. (2016)

- complete retention of particles

⇒ sorption/cake layer entrapment

- enhanced biodegradation via longer SRT

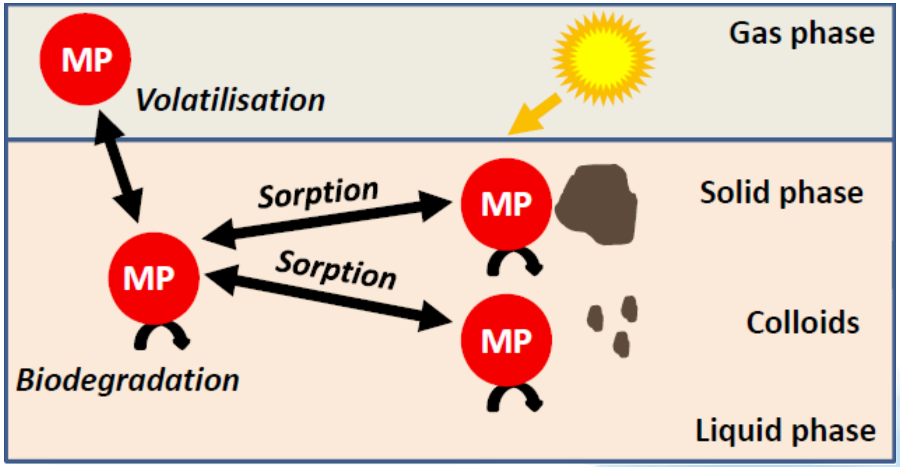
⇒ extra biological transformation & microbial community diversification (Holbrook et al., 2002; Stephenson et al., 2007)

  – however, high SRT operation = higher operating costs (higher oxygen requirements of biomass) (Krzeminski et al. 2017)

- enhanced biodegradation via higher MLSS ⇒ high biological activity per unit volume ⇒ generation of slow-growing bacteria ⇒ ability to degrade certain biologically-recalcitrant pollutants (Bernhard et al., 2006; Sipma et al., 2010; Clouzot et al., 2011; Tran et al., 2013)

CEC removal mechanisms:

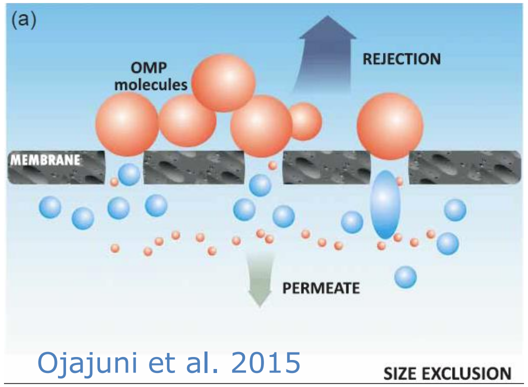
- Membrane rejection
- Air stripping (or volatilization)
- Photo-degradation
- Sorption onto sludge
- Biodegradation



M.N. Pons (2015)

CEC removal mechanisms:

- **Membrane rejection** by size exclusion



Ojajuni et al. 2015

most CECs << MF/UF membrane

<1 kDa << ca. 10-500 kDa

– Physical retention on MF/UF membrane ⇒ not relevant

– Molecular length and width/shape may play a role (Yangali-Quintanilla et al. 2009, 2010)

- **Membrane rejection** by electrostatic repulsion

– repulsive force between charged CEC and membrane surfaces

⇒ not relevant for MF/UF

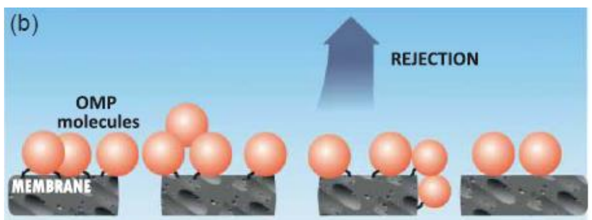
CEC removal mechanisms:

- **Membrane rejection** by adsorption

– Hydrophobic/adsorptive mechanism

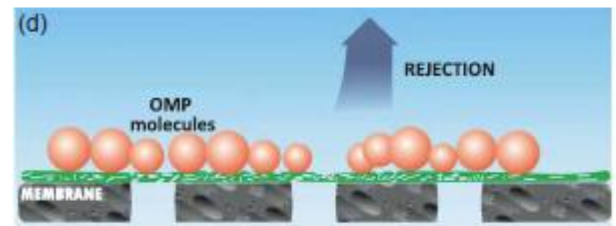
  – Not a long-term ⇒ after saturation, diffusion across the membrane Ganiyu et al. (2015)

  – Adsorption onto the membrane ⇒ not relevant



Hydrophobic intereaction

Ojajuni et al. 2015



Fouling layer intereaction

– Fouling layer interaction

  – Sludge deposits on membrane surface (fouling) ⇒ potential extra barrier increasing CECs removal (Li et al., 2015)

⇒ MF/UF membranes have no direct impact on CECs removal

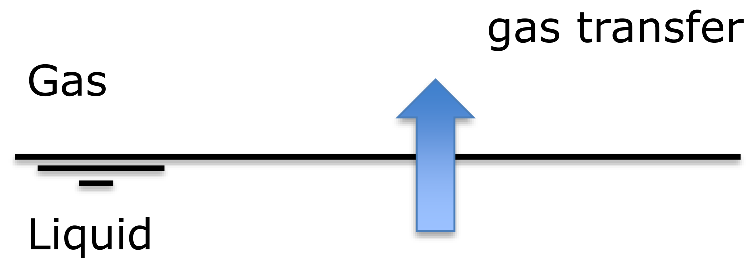
(Snyder et al., 2007)

CEC removal mechanisms:

- **Stripping or volatilization**:

Mechanical; driven by gas flowrate

Natural; surface interfacial area is a key



- compound's Henry coefficients low ⇒ not relevant
- if Henry coefficient >0.005 (musk fragrances) ⇒ potentially relevant
- Henry coefficient of most of pharmaceuticals and estrogens < 0.00001

- **Photo-degradation**:
  - little exposure to sunlight (due to turbidity + high biomass concentration) ⇒ negligible

CEC removal mechanisms:

- **Sorption onto sludge**

– Two mechanisms relevant for sorption onto particulate matter:

  – Absorption: hydrophobic interactions between CEC and sludge/microorganisms

  – Adsorption: eletrostatic interactions between CEC(+) and microorganisms(-)

– Driven primarily by hydrophobic interaction:

  – Hydrophobic (logD>3.2): adsorbed on sludge ⇒ retained by membrane & biodegraded in the reactor

    (EE2, E2, EHMC, ciprofloxacin, azithromycin, triallate, oxadiazon)

  – Hydrophilic (logD<3.2): sorption limited ⇒ biodegradation

    (most pharmaceuticals, e.g. carbamazepine)

(Phan et al., 2014; Hai et al., 2016)

logD – logarithm of distribution coefficient

CEC removal mechanisms:

- **Biodegradation**:

– Microorganisms use CEC as energy/growth substrates ⇒ CEC are transformed or degraded

– Provides true compound degradation ⇒ desired mechanism

– Metabolites produced may be more toxic

– Biodegradability classification based on biodegradation rate constant k_{biol}:

– very highly	: k_{biol}>5	L/g_{SS}.d
– highly	: k_{biol}=1-5	
– moderately	: k_{biol}=0.5-1	
– hardly	: k_{biol}<0.5	

(Suarez et al. 2008)

– Relays on microbial community structure

– Heterotrophic microbes ⇒ important for fast biodegradable CEC

– Autotrophic ammonia oxidizers and nitrification ⇒ important for slowly biodegradable CEC

– Favoring conditions at high ammonia loading rates

(Tran et al. 2013)

CEC removal mechanisms:

- **<u>Biodegradation</u>**:

– Biodegradation determined by: CEC physicochemical properties

Chemical structure

– Complex structures (alkyl chain branching)
– Toxic groups (halogens and nitro group)

⇒ resistance to biodegradation

– Chlorine presence (diclofenac) ⇒ poor biodegradability

Hydrophobicity

– Polar and non-volatile compounds ⇒ poor biodegradability

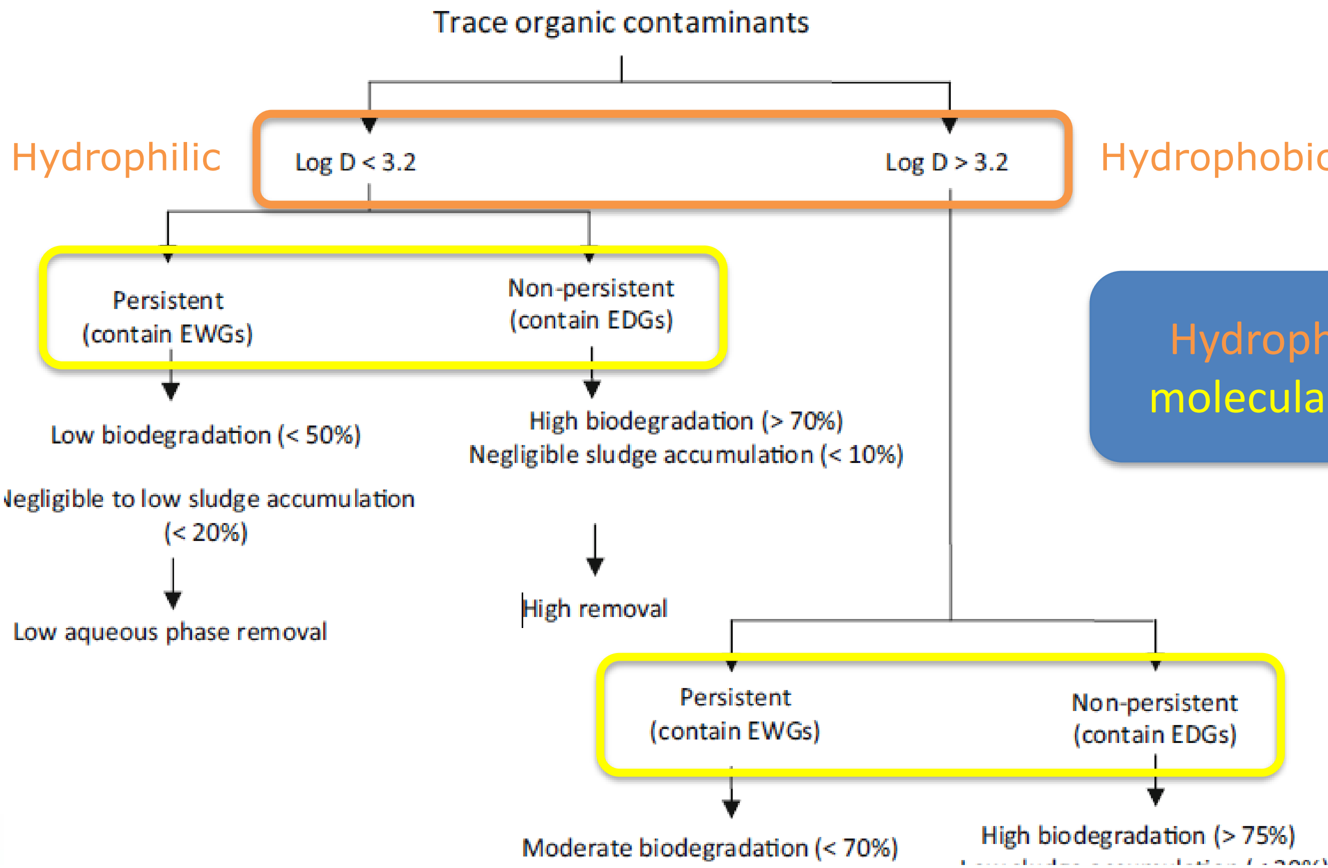
– Hydrophobic/neutral compounds ⇒ adsorption to solids & biodegradation at high SRT

– Strong electron donating functional groups (–OH, amine, methyl) ⇒ biodegradability may increase

– Strong electron withdrawing functional groups (halogen, carboxyl, amide, –Cl) ⇒ degradation difficult

(Cirja et al. 2007; Luo et al. 2014; Schröder et al. 2016)

CEC removal mechanisms:



Hydrophobicity & molecular structure

(Wijekoon et al. 2013)

(Taheran et al. 2016)

- Still, prediction of compounds removal is difficult
- Depends on compound physicochemical properties, membrane properties, membrane-compound interactions and water matrix

Fig. 4. TrOC removal mechanisms during MBR treatment. Percentages of biodegradation and accumulation in sludge are with respect to the influent loading. EWGs and EDGs represent the electron withdrawing functional groups and electron donating functional groups, respectively.

Factors influencing CEC removal:

- <u>Compound physicochemical properties:</u>
  - hydrophobicity and hydrophilicity
  - chemical structure
  - molecular weight (MW)
  - molecular diameter
  - Henry’s coefficient (H)
  - acid dissociation constant (pK_a)
  - octanol-water partition coefficient ($\log K_{ow}$)
  - sorption coefficient (K_d)
  - biological degradation rate constant (k_{biol})

(Cirja et al., 2008; Li et al. 2015; Besha et al. 2017)

Factors influencing CEC removal:

- Membrane characteristics:
  - pore size / molecular weight cut off
  - zeta potential
  - contact angle
  - roughness
- Operational parameters:
  - SRT, HRT
  - pH
  - MLSS
  - Temperature
  - Redox conditions (dissolved oxygen)
  - Conductivity
  - Composition of wastewater (OM, ionic strenght)

Factors influencing CEC removal:

- Improved removal of some CEC observed at:
  - higher SRT ⇒ increases growth of nitrifying bacteria
    - ⇒ more diverse bacteria population (slow-growing nitrifiers)
    - ⇒ mainly for moderately removed CEC
    - ⇒ different SRT for each CEC (>15d recommended)
  - lower pH ⇒ enhanced hydrophobicity/sorption of acidic PPCPs
    - ⇒ not in sludge phase, easier to degrade
  - anoxic conditions ⇒ microbial diversity, broad enzymatic range and microorganisms activity
    - ⇒ variable redox conditions ?
  - higher nitrogen loading rate

(Li et al., 2015; Tiwari et al., 2017)

Factors influencing CEC removal:

biodeg|sorption	Removal	Influencing factors	Example (Omil et al., 2009; Li et al., 2015)
$k_{biol}\downarrow$ $K_d\downarrow$	–	None, as not degraded	Carbamazepine, diazepam
$k_{biol}\downarrow\uparrow$ $K_d\downarrow$	++	HRT	Ibuprofen
$k_{biol}\uparrow$ $K_d\downarrow\uparrow$	++	None, as quickly degraded	17β-estradiol
$k_{biol}\downarrow$ $K_d\uparrow$	++	SRT	Galaxolide
$k_{biol}\downarrow\uparrow$ $K_d\downarrow\uparrow$	+	SRT	17α-ethinylestradiol
$k_{biol}\downarrow\uparrow$	+	T, VSS	Fluoxetine, citalopram, naproxen
$k_{bio}\downarrow$	+	Sludge type	Diclofenac
Ionisable	+	Coagulants, pH	Diclofenac
$K_{ow}\uparrow$	++	Fat content	Galaxolide

Removal efficiency <20% (–); 40–70% (+); >80% (++) k_{biol} biodegradability, K_d solid-liquid partition coefficient

- low k_{biol} & low K_d ⇒ **not removed** regardless of operational conditions
- high k_{biol} ⇒ well **transformed** independently of operational conditions
- moderate k_{biol} & low K_d ⇒ transformation degree depends on **HRT**
- low k_{biol} & high K_d ⇒ retained by sorption; degraded if **SRT** high enough
- moderate k_{biol} & K_d ⇒ moderately transformed, higher **SRT** improves removal
- low k_{biol} ⇒ recalcitrant ⇐ microbial diversity help degraded

CEC removal:

- <u>Antibiotic resistant bacteria & genes</u>:

– MBRs retain bacteria ⇒ reduce spreading of AR strains (Verlicchi et al. 2015)

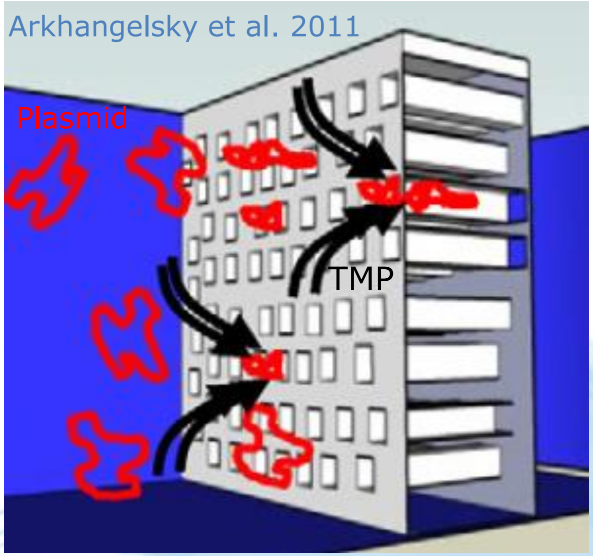
– But, complete removal not achieved:
  - 2 up to 7 log removal of different ARGs (Munir et al. 2011; Wang et al. 2015)
  - 1-100 kDa UF ⇒ 0.9-4.2 log removal of *van*A and *bla*TEM ARGs

– Improved ARG removal with colloids presence in water

– DNA removal due to: size exclusion (DNA and DNA-colloid complexes) and membrane material interactions

– but DNA can penetrate through UF (1kDa) despite size difference

long, thin and flexible molecule
⇒ DNA smaller than MW



(Arkhangelsky et al. 2018; Riquelme Breazeal et al. 2013; Rizzo et al. 2017)

Other MBR-based processes:

- **Integrated hybrid systems:**

Adsorption

- MBR-AC (PAC/GAC) (Li et al. 2011; Nguyen et al., 2012, 2013; Skouteris et al., 2015; Kaya et al., 2016)

Membrane

- MBR-NF/RO (Dolar et al., 2012; Cartagena et al., 2013; Nguyen et al., 2013)
- Osmotic MBR (OMBR) (Alturki et al., 2012; Lay et al., 2012)
- Membrane Distillation (MDBR) (Phattaranawik et al. 2008; Goh et al. 2013; Wijekoon et al. 2014)

AOPs

- MBR-ozonation (Mascolo et al. 2010; Nguyen et al., 2013)
- MBR-UV oxidation (e.g. TiO_2) (Laera et al., 2011; Choi et al., 2012)
- MBR-solar Fenton oxidation (Karaolia et al., 2016)

Bio

- Anaerobic–anoxic–oxic (A^2O-MBR) (Sun et al., 2015)
- Fungi MBR (Yang et al., 2013)

Conclusions:

- ✓ Biodegradation (hydrophilic) & sorption (hydrophobic) main removal mechanisms
- ✓ MBR may effectively remove wide range of CEC
  - ✓ Reduce AR spreading but no complete removal
- ✓ Variable CEC removal in MBRs
  - ✓ Associated with sludge removed well
  - ✓ Biologically persistent and hydrophilic removed inefficiently
- ✓ MBR alone is not sufficient for complete CEC removal
  - ⇒ coupled to post-treatment / if reuse ⇒ + disinfection
  - ⇒ integrated systems
- ✓ MBR brings other benefits: stable performance, plant flexibility, removal of many pollutants/particles, pre-treatment for other processes,

Perspectives:

- ✓ CEC removal should not justify MBR use
  - \+ water reuse, space limitations, nutrient removal, etc.
- ✓ Regardless of technology, CEC removal depends on treatment conditions and CEC physicochemical properties
- ✓ Sludge is of value (energy, nutrients, solids) but contains CEC (including ARB&Gs)
- ✓ Research is needed for MBR:
  - ✓ complete understanding of causes of CEC removal (mechanisms),
  - ✓ effective bacterial species,
  - ✓ optimal operating conditions,
  - ✓ impact of CEC on MBR process,

  and integrated systems:
  - ✓ full-scale validation, scaling up, system optimization.

(Reif et al., 2013; Li et al., 2015; Besha et al., 2017)

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