ESR1 project: Reactive barriers for enhanced attenuation of micropollutants.

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11.12.2019 EU Water Innovation Conference 2019. Zaragoza, España.

MARSoluT Managed Aquifer Recharge ITN

Introduction

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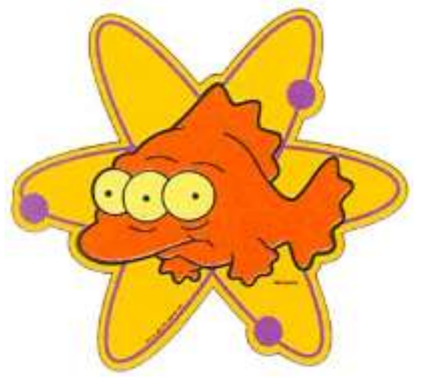
- Over the last two decades there has been a growing interest in the occurrence and fate of **unregulated** organic contaminants in the aqueous environment, including groundwater [1].

- **Emerging organic contaminants (EOCs):** pharmaceuticals (human and animal), personal care products, industrial chemicals, among others.

- Even if most of these compounds are present at low concentrations ranging from ng/L to µg/L, many of them show considerable environmental concerns due to its **persistency**, **bioaccumulation** and **toxicity** [1].

- Groundwater contamination with EOCs may result from: agriculture, cattle raising, waste water leakage and **managed aquifer recharge techniques** [2].



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Remediation of EOCs

Attenuation mechanisms for EOCs

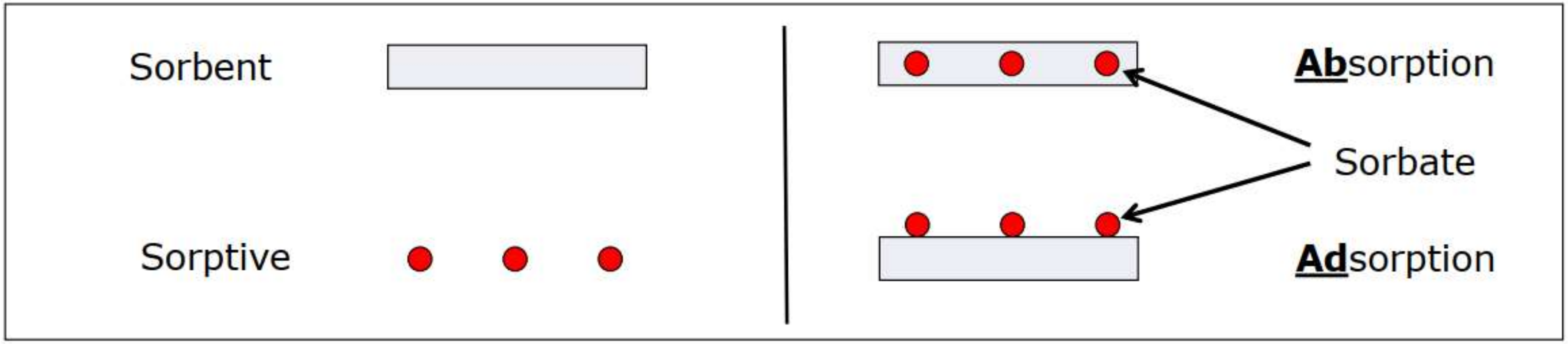
Sorptive processes

Biodegradation

Both processes depend on the soil, composition of water, physicochemical properties of EOCs and environmental conditions

Sorptive processes of EOCs

- **Sorption:** Physical and chemical process by which one substance becomes attached to another.



- In natural systems, absorption and adsorption may occur at the same time and usually can not be distinguished easily. Therefore, both processes are summarized as sorption.

Sorptive processes of EOCs

- Only **retard** transport until all sorption sites are occupied. Desorption is possible.
- Influence of the **organic carbon content of the soil**: High organic carbon content ($\mathbf{f_{OC}}$ > 0.3% wt) promotes more sorption [2] [3] [4] [5].
- **Hydrophobic** (non-polar) compounds have affinity to sorb (poor solubility) [6] [7].
- Depends on the **charge** of the compounds. Commonly stronger sorption is observed in organic **cations**, then **neutral** and finally organic **anions** [8] [9] [10].
- Environmental conditions: **pH** controls speciation of EOCs [8] [11]. **Temperature** can change solubilities [18]. Influence of redox conditions are less understood [12].

Sorptive processes of EOCs

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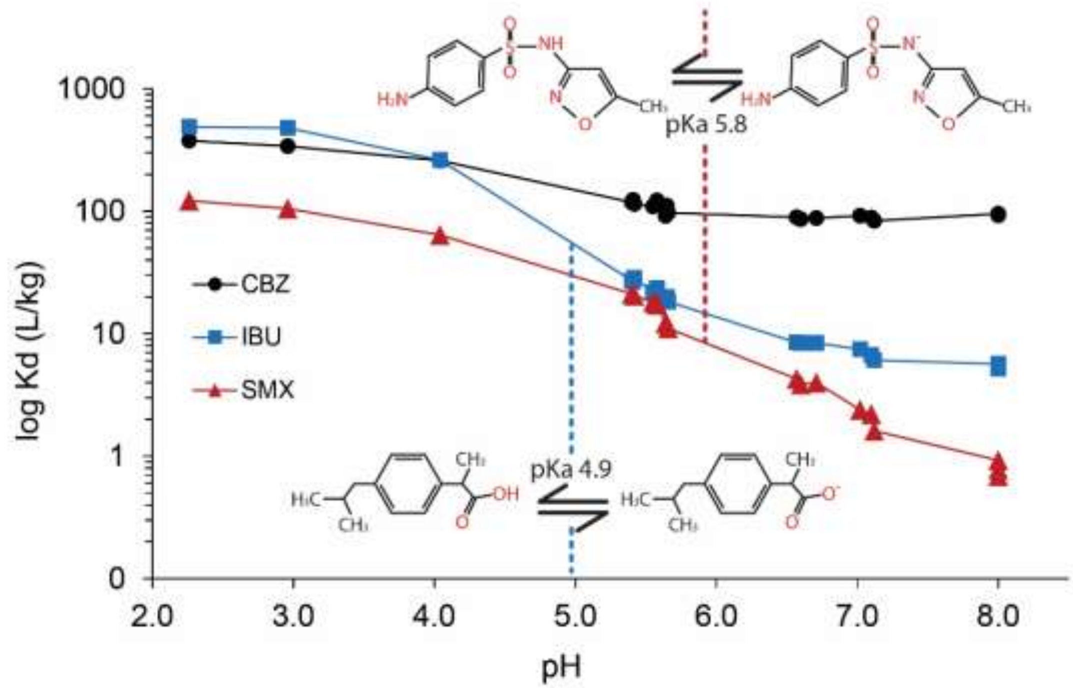
Effect of pH on sorption

- For Ibuprofen and Sulfomethoxazole the distribution coefficient K_d might be 100 times lower for the charged species, compared to the neutral one.
- The pKa for these compunds is in the pH range (or close to that) of natural waters.

$$K_d = \frac{C_S}{C_w}$$

Cs = Concentration in the soil (mg/kg).

Cw = Concentration in the water (mg/l).



Raza *et al*. (in preparation)

Biodegradation of EOCs

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- Degradation by **microorganisms**. Probably EOCs are biotransformed by co-metabolism [9] [13].

- Microorganisms require a primary substrate to grow, i.e. **BDOC**. Bioavailability of **BDOC** affects the microbial community structure. Components of BDOC are also important [5] [8] [9] [13] [14] [15].

- High BDOC availability can produce greater biomass, but commonly less diverse. **Oligotrophic** conditions can result in an increase in **diversity** of the microbial activity, and in consequence improve degradation [13] [14] [16] [17].

- Biotransformation involves **redox** reactions, then electron acceptors are needed (e.g., O_2, NO_3^-, SO_4^{2-}).

- **Oxic** conditions enhance degradation for the majority of EOCs [2] [16] [18] [19] [20]. Some studies found better degradation of some EOCs under **anoxic** conditions [3] [12] [13].

Biodegradation of EOCs

- Increase in **retention** or **travel time** results in enhanced degradation [5] [15] [18] [21] [22].

- Higher **temperatures** are expected to intensify biological processes. Some EOCs in experimental studies present changes in attenuation as function of °T, with no clear trends. [2] [18] [20] [23].

- As **pH** controls the speciation of EOCs, it affects biodegradation. Different behaviors have been observed [7] [11] [24].

- **Adaptation time** is necessary in order to allow the microbial community to get used to EOCs [5] [19] [25].

- Higher **initial EOCs concentrations** lead to shorter lag phases and higher degradation rates [19].

- Some studies have shown differences in the influence of the **functional groups** of EOCs in degradation [6] [18] [22].

Biodegradation of EOCs

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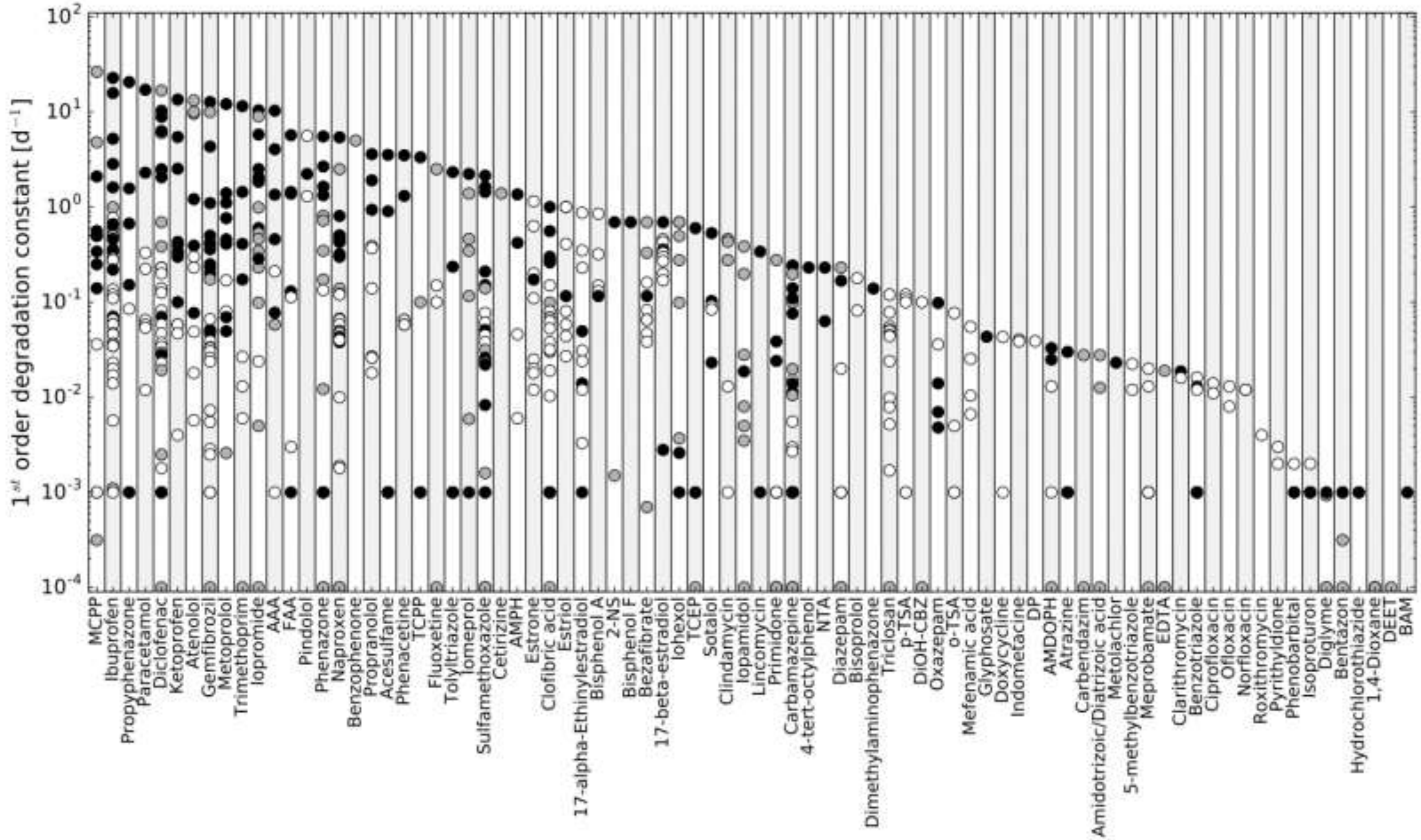

○ Batch ● Column ● Field

Source: [2] Greskowiak *et al*., 2017.

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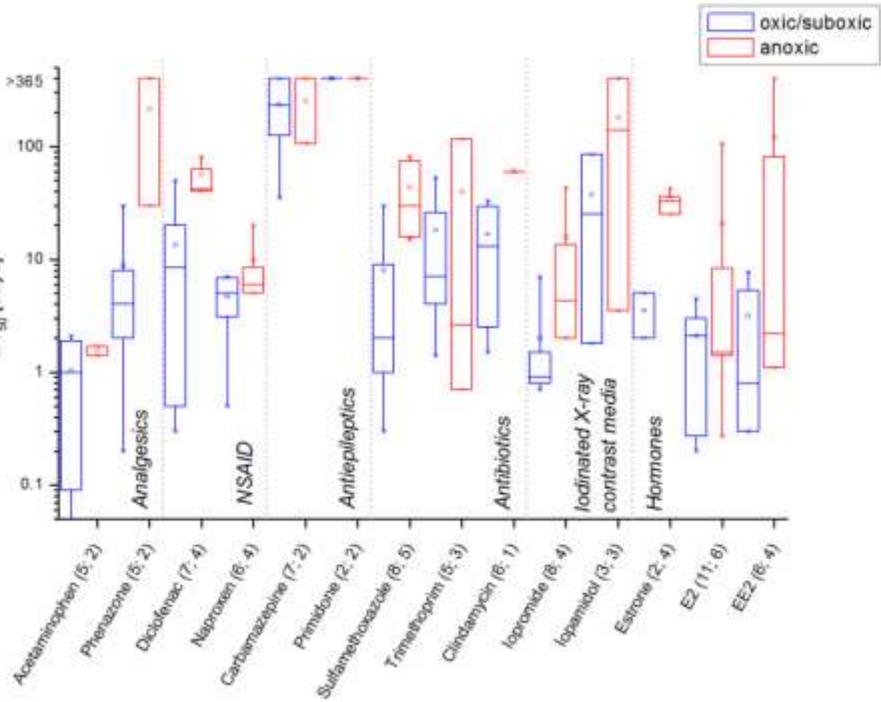
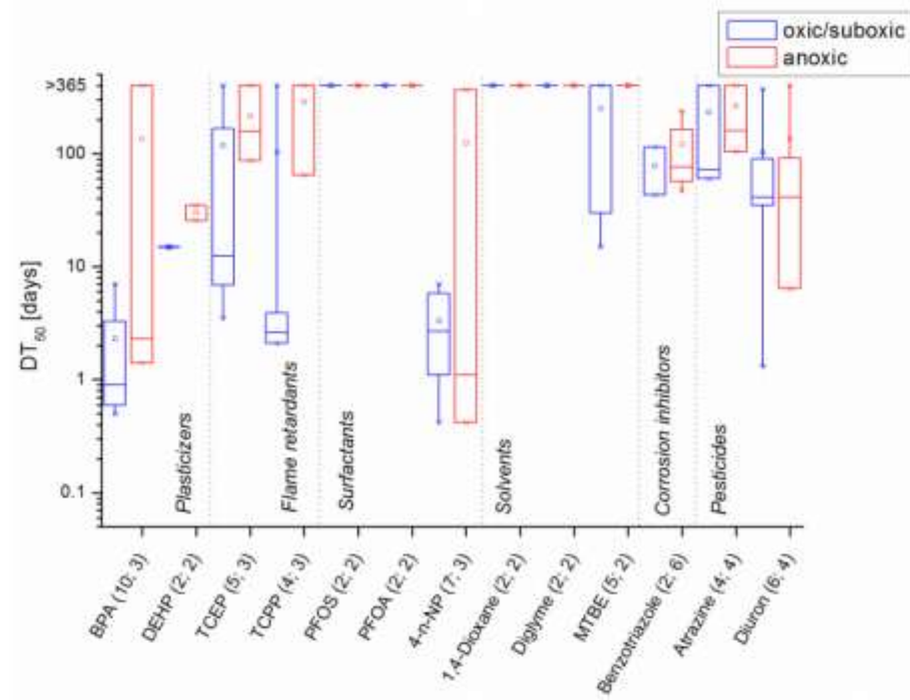
Biodegradation of EOCs



Pharmaceuticals



Industrial chemicals

Source: [18] Regnery *et al*., 2017.

Important parameters and considerations for column experiments

- Organic carbon and clay content of the soil.
- Components of the influent water: DOC, DO, ions.
- Physicochemical properties of EOCs: pKa, log D, charge, functional groups, solubility.
- Influent concentrations of EOCs in the same order that are detected in nature (i.e., ng/L to µg/L).
- Control of environmental conditions: pH and °T.
- Analysis of redox conditions and oxygen concentration inside the column. Biodegradation rates change between oxic, suboxic and anoxic states.
- Give a proper adaptation time to the microbial community.
- Retention time (hopefully similar to field sites).

Reactive barriers or methods to enhance attenuation of EOCs

- **Compost:** Release DOC into infiltrated water. Strong sorption for cations. Faster degradation of certain compounds [8] [9].
- **Activated carbon:** Increase the surface area available for adsorption. Good results in attenuation of certain compounds [26] [27].
- **Biochars (oak hard wood):** Good effects in attenuation of pharmaceuticals (included carbamazepine), but not in industrial chemicals [28].
- **ZVI:** Good effects in attenuation of pharmaceuticals (included carbamazepine), but not in industrial chemicals [28].
- **Biofilm coated adsorbent barrier:** Modified clay composite in the form of pellets coated with biofilm. Good results in degradation, but they used 1 mg/L of pharmaceuticals [22].

Reactive barriers or methods to enhance attenuation of EOCs

- **Advanced oxidation processes:** Oxidation using Ozone (O_3) have shown improved degradation, including persistent compounds [16] [26].
- **Catalytic wet peroxide oxidation:** Oxidation using H_2O_2 and magnetite as catalytic. Good results in batch experiments [29].
- **Manganese oxides:** MnO_2 was utilized in batch experiments to attenuate diclofenac with good results [30].
- Other innovative techniques include nanofiltration, reverse osmosis [27], sonolysis [31] and electrochemical oxidation [32].

Innovative technologies for remediation

- **Regenesis®:** American company that provides scientifically proven products and services for groundwater and soil remediation at contaminated sites since 1994.

- They have dealt with compounds such as petroleum hydrocarbons, chlorinated solvents, PAHs, BTEX, pesticides and heavy metals, among others.

- Their techniques include sorption using activated carbon, in situ chemical oxidation, in situ chemical reduction, aerobic and anaerobic enhanced biodegradation.

Innovative technologies for remediation

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- **Liquid activated carbon (LAC):** PlumeStop®. Very fine particles of AC (1-2 µm) suspended in water that increase sorption. Tested on the field with PFAS.

- **In situ chemical oxidation (ISCO):** RegenOx®. Due to its chemical composition, it produces perhydroxyl, hydroxyl and superoxide radicals that oxidizes recalcitrant compounds.

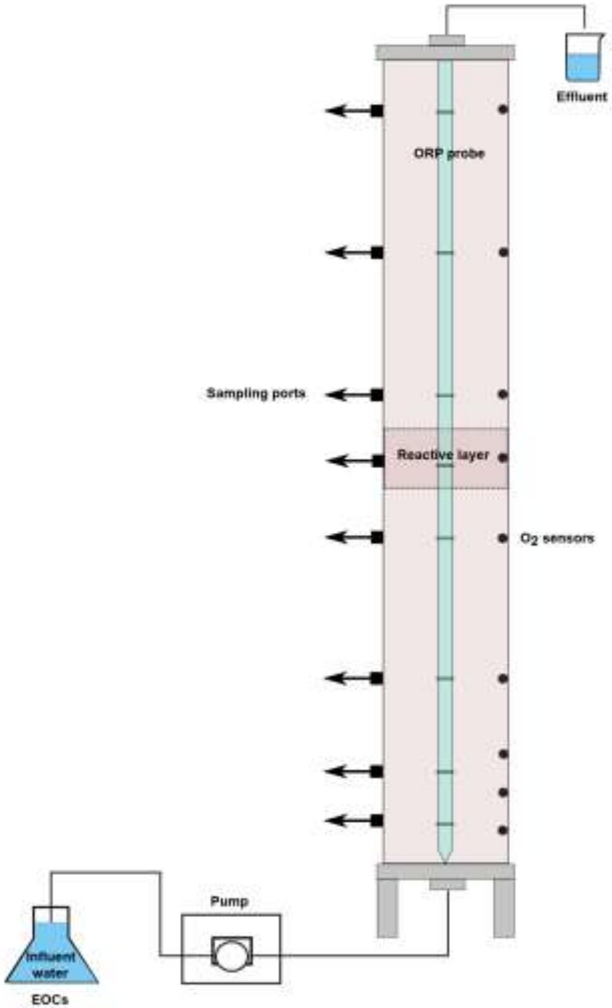
- **In situ chemical reduction (ISCR):** CRS® and MicroZVI®. Sources of Fe^{2+} and Fe^{0}, respectively, that create a reducing environment.

- **Enhanced in situ aerobic bioremediation:** ORC Advanced®. Produce a controlled release of molecular oxygen.

- **Enhanced in situ anaerobic bioremediation:** HRC®. Produce a controlled release of hydrogen. Some microbes use hydrogen for methanogenesis.

Final summary

- Design of column experiments that include a complete measurement system of the parameters of interest.
- Characterization of the soil and the influent and effluent water is an important step of the experiments.
- Analyze the effect of diverse reactive layers/compounds in the fate of EOCs.
- Take samples inside the column will let us to define a concentration field **C(x,t)** that we could model using a **kinetical** reactive transport approach.



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