ESR1 project: Reactive barriers for enhanced attenuation of micropollutants.

Edinsson Muñoz Vega

Civil Hydraulic Engineer, MSc., Universidad de Chile

PhD Student, Institute of Applied Geosciences, TU Darmstadt, Germany

Supervisor: Christoph Schüth
Introduction

- 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].
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 ($f_{oc}$ > 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

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 compounds is in the pH range (or close to that) of natural waters.

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

$C_s =$ Concentration in the soil (mg/kg).
$C_w =$ Concentration in the water (mg/l).

Raza et al. (in preparation)
Biodegradation of EOCs

• 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

Biodegradation of EOCs

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

- **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 Fe²⁺ and Fe⁰, 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.
References


References


