Understanding the Fate and Risk of selected Pharmaceuticals in Soil-Aquifer material prior to Artificial Recharge

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Water scarcity

\textit{drought} \textit{water scarcity} \textit{human water security} (sensu Vörösmarty et al. 2010)

Irregular water supply and rising water demands

Direct impact on citizens and economic sectors that use and depend on water (agriculture, tourism, industry, energy and transport)

Enhanced impact on ecosystems: remaining water is not sufficient

\textit{Example:} 2007-2008 drought in NE Spain, with an extremely high societal, economical and environmental cost
Potential alternatives and needs with respect to existing water resources

- Culture of water-saving and valuing ecosystem services
- Improvement of wastewater treatment quantitatively and qualitatively (Advanced Technology/Natural)
- Reuse of treated effluents and sludge
- Treatment of drinking water - Desalination
- Protection of aquifers

Current research on POSSIBLE SOLUTIONS:

- **Advanced Treatments in WWTP:**
  - MBR (see examples), ozonation, advanced oxidation, nanofiltration, reverse osmosis, …
  - (EXPENSIVE, ENERGY CONSUMING, …)

- **complementary/alternative Waste Water Treatment:**
  - physical-chemical-biological processes within the subsoil
  - **ADVANTAGE:**
  - long retention times
  - **EFFECT:**
  - Natural water depuration:
    - overall quality improvement
    - a number of organic contaminants removed
  - application: Artificial Recharge of Groundwater
Fate, removal and distribution of PhACs in wastewater treatment (MBR vs. CAS)

Target compounds: β-blocker atenolol; hypoglycemic agent glibenclamide

Sewage sludge inoculums: CAS sludge (SRT~3 days); MBR sludge (SRT~3 months)

Initial concentrations: 10 mg/L; 50 μg/L

Experiment duration: 26 days

- Sampling and pH control every day
- Centrifugation of samples
- Analysis of supernatants

Fate, removal and distribution of PhACs in wastewater treatment (MBR vs. CAS): BIODEGRADATION AND SORPTION STUDY

Comparison of CAS and pilot-scale MBR performances

Comparison of CAS and pilot-scale MBR performances

CAS elimination, %
<10%
10-70%
>70%

MBR elimination, %
0
10
20
30
40
50
60
70
80
90
100

CAS elimination, %
1-naproxen
2-ketoprofen
3-ibuprofen
4-diclofenac
5-indomethacin
6-acetaminophen
7-nifenamic acid
8-propyphenazone
9-ranitidine
10- loratidine
11-carbamazepine
12- ofloxacin
13- sulfamethoxazole
14- erythromycin
15- atenolol
16- metoprolol
17- hydrochlorothiazide
18- glibenclamide
19- gemfibrozil
20- bezafibrate
21- famotidine
22- pravastatin
23-sotalol
24-propranolol
25-trimethoprim

Radjenović et al. Wat. Res. 43 (2009), 831-841

Human metabolism of atenolol

**Phase II conjugation**

- **O-Glucuronate of ATENOLOL**
  - C.8-4.4% fraction in urine
  - 0% fraction in faeces

- **Hydroxy atenolol**
  - 0.8-4.4% fraction in urine
  - 0% fraction in faeces

**Atenolol:**
- 33-40% fraction in urine
- 36-56% fraction in faeces

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**A) Fate, removal and distribution of PhACs in wastewater treatment (MBR vs. CAS): BIODEGRADATION AND SORPTION STUDY**

**Atenolol, CAS sludge experiments**

- 10 mg/L concentration

**Atenolol, MBR sludge experiments**

- 10 mg/L concentration

**A/A₀** - peak area vs. initial peak area of the parent compound


These are biodegradation curves representing the disappearance of the parent compound atenolol in batch experiment with MBR and with CA sludge. The degradation was faster in MBR sludge reactor. As far as microbial metabolite is concerned, it was formed in CA sludge reactor till the day 5 and did not degrade any further. This metabolite was identified as a product of bacterial hydrolysis of amide bond, denominated atenololic acid. Atenololic acid was identified for the first time as a biodegradation product of atenolol, and it is different from human metabolites of this b-blocker. On the contrary to the results obtained with CA sludge, in MBR sludge experiments product of microbial degradation of atenolol was degraded after around 20 days, as it can be seen from the diagram below. Thus, the ultimate biodegradability of atenolol was higher in MBR than in CA batch reactor.

CID: 17/06/2009
Esterase Pérez, S.; Barceló, D. Anal. Chem. (accepted)

- Acetaminophen: anti-inflammatory drug
- Main metabolites in the human body: diclofenac and 4'-hydroxy-diclofenac
- Since now not detected in the environment

- Diclofenac: anti-inflammatory drug
- Main metabolite: 4'-hydroxy-diclofenac
- It has been detected in wastewater, surface and drinking waters (low elimination in WWTP)

Human Metabolism of Aceclofenac

(-)-ESI-QqToF-MS of DCF and its identified metabolites
What is Artificial Recharge of Groundwater (AR of GW)?

To introduce water into the aquifer by means of properly designed facilities:

1. CHANNELS, PONDS, MEANDERING
2. WELLS (Conventional and "Aquifer Storage and Recovery")
3. DRY WELLS

CHALLENGE: REMOVAL of EMERGING ORGANIC MICROPOLLUTANTS

The case of Berlin (Germany):

- Lake Tegel sites
- Lake Wannsee site

- Mostly anoxic soil passage
- Retention time ~4.5 – 5 months
- Mostly oxic soil passage
- Retention time ~50 days

% removal: INFLUENCE of REDOX CONDITIONS

Removal of several emerging micropollutants removed from Massmann et al., 2008

Retention time ~ 3 months from Jekel et al., 2009

Redox zonation
Overall objectives:

- monitoring of water quality changes/improving during AR of GW. (Vadose & Saturated zone)
- is AR of GW an alternative treatment for emerging organic micropollutants? May we (and how) control/enhance their removal?

**LABORATORY EXPERIMENTS**

**TOOLS**

**FIELD WORK at Test Site:**
- infiltration pond
  (Llobregat river water / Tertiary effluent from WWTP)

**Numerical MODELING**

**SPECIFIC OBJECTIVE – Laboratory experiments**

To investigate on the potential **effect of redox** conditions on the **fate in aquifer material** of selected **organic micropollutants** (most of them “emerging”).

Ultimate aim: to identify the most favourable conditions for their removal from water, for their following **stimulation in AR of GW field applications** (Test Site).
Experimental METHODOLOGY

\[ \text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{HCO}_3^- + \text{H}^+ \]

\[ \text{CH}_2\text{O} + 0.8\text{NO}_3^- \rightarrow \text{HCO}_3^- + 0.4\text{N}_2 + 0.4\text{H}_2\text{O} + 0.2\text{H}^+ \]

\[ \text{CH}_2\text{O} + 2\text{MnO}_2(\text{s}) + 3\text{H}^+ \rightarrow \text{HCO}_3^- + 2\text{Mn}^{2+} + 2\text{H}_2\text{O} \]

\[ \text{CH}_2\text{O} + 4\text{Fe(OH)}_3(\text{s}) + 7\text{H}^+ \rightarrow \text{HCO}_3^- + 4\text{Fe}^{2+} + 10\text{H}_2\text{O} \]

\[ \text{CH}_2\text{O} + 0.5\text{SO}_4^{2-} \rightarrow \text{HCO}_3^- + 0.5\text{HS}^- + 0.5\text{H}^+ \]

\[ \text{CH}_2\text{O} + 0.5\text{H}_2\text{O} \rightarrow 0.5\text{HCO}_3^- + 0.5\text{CH}_4 + 0.5\text{H}^+ \]

Stimulating specific redox conditions

Sequence of overall redox reactions for full organic matter oxidation (mediated by microorganisms)

- **Aerobic respiration**
  \[ \text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{HCO}_3^- + \text{H}^+ \]

- **Nitrate reduction**
  \[ \text{CH}_2\text{O} + 0.8\text{NO}_3^- \rightarrow \text{HCO}_3^- + 0.4\text{N}_2 + 0.4\text{H}_2\text{O} + 0.2\text{H}^+ \]

- **Mn oxides reduction**
  \[ \text{CH}_2\text{O} + 2\text{MnO}_2(\text{s}) + 3\text{H}^+ \rightarrow \text{HCO}_3^- + 2\text{Mn}^{2+} + 2\text{H}_2\text{O} \]

- **Fe ox./hidrox. reduction**
  \[ \text{CH}_2\text{O} + 4\text{Fe(OH)}_3(\text{s}) + 7\text{H}^+ \rightarrow \text{HCO}_3^- + 4\text{Fe}^{2+} + 10\text{H}_2\text{O} \]

- **Sulfate reduction**
  \[ \text{CH}_2\text{O} + 0.5\text{SO}_4^{2-} \rightarrow \text{HCO}_3^- + 0.5\text{HS}^- + 0.5\text{H}^+ \]

- **Methanogenesis**
  \[ \text{CH}_2\text{O} + 0.5\text{H}_2\text{O} \rightarrow 0.5\text{HCO}_3^- + 0.5\text{CH}_4 + 0.5\text{H}^+ \]
**SEDIMENTS**
- 120g of d < 1mm
  - (natural, from Test Site)
  - (containing natural Mn(III/IV) and Fe(III))

**WATER**
- 240 mL
  - (synthetic, similar to recharge water at Test Site)
  - [0.2mM O₂, 0.2mM NO₃⁻, 2mM SO₄²⁻ etc.]

**Gas phase**
- 15 mL

**e⁻ donor**
- easily degradable organic substrate
  - (Na-acetate & Methanol)
- micropollutants

**e⁻ acceptor**
- NO₃⁻ or Mn(III/IV) or Fe(III) or SO₄²⁻

**BATCH EXPERIMENTS DESIGN**
- easily degradable organic substrate
  - (Na-acetate & Methanol)
- micropollutants

**DISASSEMBLING the experiments**
- temporal evolution of processes

- bottles sacrifice (in duplicate):
  - PARAMETER MEASUREMENTS
    - (Eh, pH, T, Alk, C.E.)
  - ANALYSIS
    - (DOC, major & minor ions, micropoll.)
  - in WATER

- TOTAL DURATION:
  - 2 weeks to ~7 months
  - (depending on the experiment)
Understanding the fate of micropollutants

Biodegradation + abiotic processes (sorption, chemical hydrolysis, …)

- BIOTIC Experiment vs ABIOTIC Experiment (sterilizing + HgCl₂)

Biodegradation + abiotic processes

Selected (emerging) organic MICROPOLLUTANTS

**Batch tests - Group 1**

**Pesticides:** Atrazine, Simazine, Terbutylazine, Prometrine, Diadiazon, Dicuron, Chlorphenazine

**Estrogens:** Estrone

**Drugs:** Atenolol, Diclofenac, Ibuprofen, Carbamazepine, Gemfibrozil, Sulfamethoxazole

1 µg/L each compound (environmental concentrations)

LC-MS-MS (QqQ) with preconc.: IDAEA-CSIC

**Batch tests - Group 2**

**Drugs:**
- Contrast media
- Antihypertensive agents
- Ulcer treatment
- Antibiotics
- Anticonvulsants, sedative
- Lipid regulators
- Anti-inflammatory
- Antihistamines
- Analgesic

**Total of 27 compounds:** 1 mg/L each compound

HPLC-MS-MS (TQS) without preconc.: GZG (Universität Göttingen)
SUMMARY of the EXPERIMENTS PERFORMED

**Batch tests - Group 1 (1μg/L)**

**BIOTIC**
- NO$_3^-$ reducing experiment [21 days]
- Mn(III/IV) reducing experiment [~200 days]
- Fe(III) reducing experiment [~200 days]
- SO$_4^{2-}$ reducing experiment [~200 days]
- “Natural conditions” experiment [~200 days]

**ABIOTIC** → 1 long term experiment as reference for ALL BIOTICS [~200 days]

**Batch tests - Group 2 (1mg/L)**

**BIOTIC**
- NO$_3^-$ reducing experiment [88 days]

**ABIOTIC** → 1 long term experiment as reference for the BIOTIC experiment [88 days]
RESULTS and Discussion

part I of RESULTS

BULK WATER CHEMISTRY
CONCLUSIONS - part I (BULK WATER CHEMISTRY)

- expected redox conditions quite succesfully created and sustained. Exception/complications related to natural sources of Mn and Fe. (e.g.: mixed Fe&SO_4^{2-} redox condit. in the Fe-red. experim.)

- to assess & understand main processes occurring: thorough monitoring of water chemistry (redox sensitive species, maj.&min. ions) + minerals precipitations (useful: SEM) and biomass production

- sampling schedule adequate, reproducibility of duplicate results

- numerical MODELING: to quantify and confirm processes

part II of RESULTS

ORGANIC MICROPOLLUTANTS
MICROPOLLUTANTS – Overall trends & fate –

1) NO REMOVAL

2) ABIOTIC REMOVAL

3) BIOTIC REMOVAL

4) drop & rebound

REVERSIBLE PROCESS
in the BIOTIC experim.

REDOX EFFECT

3) BIOTIC REMOVAL – Fate of atenolol

Batch tests Group 1 (1μg/L)

ABIOTIC REMOVAL ~ 45 %

BIOTIC REMOVAL

REDOX EFFECT

BIOTIC REMOVAL
(or, to be precise, REMOVAL related to BIO-ACTIVITY)

= mineralized or biotransformed?

3) BIOTIC REMOVAL – Fate of atenolol

Batch test Group 2 (1mg/L)

ABBIOTIC REMOVAL:
~ 14%

BIOTIC REMOVAL
under NO3-reducing conditions
~ 52%

atenolol mineralized or biotransformed?
Fate of atenolol: mineralized or biotransformed?

**Batch test Group 2 (1mg/L)**

- 0 - order reaction.
- \( V_r \approx 6 \mu g/L/d \)
- ATENOLOL
- ATEN. ACID

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4) drop&rebound: Fate of SMX and diclofenac

**Batch tests Group 1 (1μg/L)**

- BIOTIC
- REVERSIBLE PROCESS in presence of \( NO_2^- \)

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unreported
Fate of SMX and DCF: Transformation products

![Graph showing transformation products](image)

**Batch tests**
**Group 1**
(1μg/L)

4-Nitro-SMX and Nitro-DCF found in the NO3-red. BIOTIC experiment

4) drop&rebound: Fate of SMX and DCF

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>Reaction Status</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfamethoxazole (SMX)</td>
<td><img src="image" alt="SMX structure" /></td>
<td>primary amine reacted totally</td>
</tr>
<tr>
<td>Diclofenac (DCF)</td>
<td><img src="image" alt="DCF structure" /></td>
<td>secondary amine reacted partially</td>
</tr>
</tbody>
</table>


Nödler et al., "Evidence for reversible and non-reversible sulfamethoxazole transformation products during denitrification". Submitted.
CONCLUSIONS and COMMENTS

- **design & experimental methodology**: adequate to objectives

- **expected redox conditions**: quite successfully created and sustained

- **processes assessment**: importance of
  - thorough monitoring of water chemistry
  - taking into account minerals precipitation, biomass production
  - numerical modeling to confirm and quantify processes

MASS BALANCE and INTERPRETATION of BULK CHEMISTRY

INTERPRETATION of MICROPOLLUTANTS FATE
CONCLUSIONS and COMMENTS

• FATE of (EMERGING) ORGANIC (MICRO)POLLUTANTS under the studied conditions:
  ✓ recalcitrants
  ✓ removed abiotically
  ✓ removed biotically biotransformation or mineralization?
  ✓ reversible processes potential environmental implications

REDOX EFFECT
Nevertheless, exact patterns/rates could not be isolated for each specific redox state

• Some of the Removal % under SAT for the target pollutants were at least comparable with those from conventional treatments in WWTP
• Biotransformation products (Atenololic acid, NO3-Diclofenac) similar In Membrane Bioreactor(MBR) and Soil Aquifer Treatment (SAT)

THANKS FOR YOUR ATTENTION

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