Management of micropollutants in the urban water cycle: The Swiss approach

Wastewater 4.0

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Micropollutant problem in urban water management

- > 100’000 synthetic compounds are registered in the EU
- About 30’000 synthetic compounds are in daily use
- Several hundred pesticides
- > 8000 chemicals as food supplements
- > 3000 chemicals are used as human pharmaceuticals
- Numerous natural compounds (taste and odor, cyanotoxins)
- Improvements in analytical chemistry

Micropollutants can be found in wastewater, water resources and drinking water
Men fight against boldness with the contraceptive pill

To fight hair loss, desperate men mix contraceptive pills with shampoo. This works, but may have serious side effects…
Urban water systems: Micropollutant cycle and mitigation processes
Adressing micropollutants in urban water management in Switzerland

- Risk-based: Environmental health as an important driver, drinking water quality as a decisive argument
- Public perception is important (fish decline)
- International obligations/responsibility
- Avoidance where possible: Measures in agriculture, source control
- Elimination of point sources
- Cost-benefit: Yes, but…Environmental issues high on agenda, tourism as selling point
- Willingness to pay is high (ca. 100 USD/p/y)
Assessment and mitigation of micropollutants: Activities in various countries

- Good overview of developments in Europe: Competence Centre Micropollutants, http://www.masterplan-wasser.nrw.de/
- Germany
  - Federal project: Risk management of emerging compounds and pathogens in the water cycle (30 Mio €, 12 projects, 90 research groups)
  - North Rhine Westfalia: Safe Ruhr River (5 Mio people): drinking and bathing water quality; assessment of micropollutants
- Netherlands
  - STOWA/KWR: new report on behavior and mitigation of pharmaceuticals in wastewater and drinking water
- International commission for the protection of the Rhine River
  - 58 Mio people live in Rhine catchment, 96% connected to municipal WWTP, up to 20% wastewater contribution in Rhine
- Australia: Guidelines for Water Recycling
- USA: Water Recycling, Contaminant Candidate List 3 (CCL3)
Swiss projects related to micropollutants in the aquatic environment (1998 – 2011) - I


   - Wastewater treatment plants are the major point source
   - Problems in waters with insufficient dilution of wastewater effluents
Swiss projects related to micropollutants in the aquatic environment (1998 – 2011) - II


Situation analysis

- Modelliertes Diclofenac-Risikopotential in Fließgewässern bei Minimalabfluss Q_{min} in Mikrogramm pro Liter ohne Metabolite

- Situation analysis
- Assessment concept
- Measures

Diclofenac: Receiving waters of 125 WWTPs > quality criteria (15% of P.E.)

Substance selection
- Development of quality criteria
- Selection of technologies
Swiss Strategy Micropoll

- Swiss EPA recommends upgrading of wastewater treatment plants to remove micropollutants (reduction of 50% of the load)
- Swiss parliament decided to go forward with it (March, 2014)
- Change of water protection law was accepted
- Upgrade of ca. 100 WWTPs (out of 700) over the next 20 years
  - Large WWTPs (>100,000 inhabitants) to reduce the load (economics and international responsibility - Rhine river)
  - WWTPs discharging into rivers with high percentage of wastewater (ecosystems protection)
  - WWTPs discharging into rivers with important bankfiltration (protection of drinking water resources)
Swiss Strategy Micropoll
Treatment, cost and energy

- Treatment options: Ozonation or Powdered Activated Carbon
- Investment costs: 1.3 billion $, additional yearly costs 130 Mio $
- Ca. 13 $/person/year
- Increase of costs at WWTPs: 2-25%
- Overall increase in electricity consumption (0.1%), mostly compensated by additional biogas production and photovoltaics
Factors for the decision between ozonation and PAC

- PAC removes of micropollutants
- Ozone transforms micropollutants
- Ozonation leads to partial disinfection
- Toxicity assessment
- Energy requirements
- Handling of ozone vs PAC
- Local circumstances: Space
- Type of wastewater (industrial contribution)
Comparison of micropollutant removal:
Biological treatment, PAC and ozonation

Data: Pilot experiments  Eawag, Kloten/Opfikon, Lausanne, Regensdorf
## Full-scale ozonation—ecotoxicity (*in vitro* / enriched wastewater)

<table>
<thead>
<tr>
<th>Organism</th>
<th>Endpoint</th>
<th>Effect of Ozonation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bioluminescence inhibition test</td>
<td>Effect on energy transfer / ATP synthesis</td>
<td><img src="#" alt="Green" /></td>
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<tr>
<td>Green algae</td>
<td>Specific effect on photosynthesis (herbicides)</td>
<td><img src="#" alt="Green" /></td>
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<tr>
<td>Green algae</td>
<td>Non-specific narcotic effect</td>
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<tr>
<td>YES test</td>
<td>Estrogenic effect</td>
<td><img src="#" alt="Green" /></td>
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<tr>
<td>Acetylcholinesterase inhibition test</td>
<td>Effect of organophosphates (insecticides)</td>
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<tr>
<td>Umu test</td>
<td>Genotoxicity</td>
<td><img src="#" alt="Green" /></td>
</tr>
</tbody>
</table>

- **Yellow**: No effect of ozonation
- **Green**: Significant positive effect of ozonation
- **Red**: Significant negative effect of ozonation

*Escher et al., 2008, J. Env. Monitor. 10, 612-621*
## Full-scale ozonation– ecotoxicity (*in vivo/* whole effluent toxicity)

<table>
<thead>
<tr>
<th>Organism</th>
<th>Endpoints</th>
<th>after:</th>
<th>OZ</th>
<th>SF</th>
<th>AC</th>
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<tbody>
<tr>
<td><em>Chironomus riparius</em></td>
<td>Mortality</td>
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<td><em>Lumbriculus variegatus</em></td>
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<td><em>Potamopyrgus antipodarum</em></td>
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<td><em>Dreissena polymorpha</em></td>
<td>DNA damage</td>
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<td><em>Oncorhynchus mykiss</em> (FELST)</td>
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</table>

Significant effects compared to sec. effluent:  
- **red** negative;  
- **green** positive;  
- **yellow** no effect
Micropollutant abatement during ozonation

Kinetics

Transformation products

Oxidation by-products

Biological effects
Efficiency of oxidation: Kinetics of ozone reactions

- Typically second order processes

\[ \frac{d[P]}{dt} = k \times [ox] \times [P] \]
\[ \ln \frac{[P]}{[P]_0} = k \times [ox] \times t \]

- Ozone stability in the water

- Second-order rate constants \( k \) available in literature and web-based data bases (\( \sim 500 \) \( k \)-value for ozone)
  - Measurement of second-order rate constants \( k \) by direct or indirect methods (competition kinetics)
  - Quantitative Structure Activity Relationships (QSARs)
  - Quantum chemical calculations
Product formation: Transformation of 17α-ethinylestradiol (EE2) by ozone

Postulated primary products

attack on ethinyl

attack on phenol

17α-ethinylestradiol (EE2)

Huber et al., ES&T, 2004
Oxidation of 17\(\alpha\)-ethinylestradiol (EE2) by \(O_3\): Kinetics and biological effect

Huber et al., 2004
Conclusions

- PAC and ozone can be applied for enhanced wastewater treatment for micropollutant removal at reasonable costs
- The efficiency of ozone depends on various parameters:
  - Ozone stability
  - Kinetics of the ozone-micropollutant reaction
  - No full mineralization of target compounds
  - Toxicity assessment after ozonation
  - Assessment of feasibility: Novel test system for wastewater treatment plants
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Age-factor

1995

2014