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Integrated assessment of the impact of aqueous contaminant stressors on surface water ecosystems

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Impacts of chemical stressors

Part I: Which contaminated sites are problematic?
   - How can we prioritize these sites?
   - Which management strategy makes sense?

Part II: Which chemical stressors are problematic?
   - Do groundwater pollutants impact surface water?
     - Chlorinated solvents
     - Pesticides
   - Are ecosystems at risk (how do we determine “good” ecological status)?
EU Water Framework Directive

Member states must guarantee “good” ecological status of their waters

Outline

How to assess WFD goals??

Other contaminants/stressors?

Integrated Field & Modelling Studies

A case study

Ecological impacts

Identify human activities impairing water resources

Determine if pollutant loads in groundwater harm ecosystems

Evaluate if contaminants are harmful

Which methods are suitable for evaluating ecological risk?
Mapped contaminated sites

- V1 Mapped (possible) contaminated site (11,309)
- V2 Risk to groundwater (10,839)

Site density
Whole country: 0.5 contaminated sites / km²
Urban areas: 2 contaminated sites / km²

Contaminated sites are often < 25 m from surface water. There are 1,326 such contaminated sites in Region Hovedstad alone. (Jensen og Svensson, 2008)
No initiatives will be taken in the planning period with regard to groundwater chemical impact on streams, lakes, coastal waters.

There is insufficient knowledge to adequately describe the contact between surface and groundwater and insufficient methods to model that impact.
Case study – Skensved stream

TCE > water quality criteria* (EU, 2006)

10 µg/L

17 µg/L TCE

300 m

750 meter

(Christensen & Raun, 2005)
Methods to evaluate ecological risk

**DSFI**


**SPEAR**


**Aquatox**


Field-based methods

- **Danish Stream Fauna Index (DSFI)**
  - *Official method* for biological assessment of running waters
  - Primarily developed to detect impact of nutrients: taxa analyzed represent gradient in tolerance to low O2 levels
  - Kick-samples + hand-picked samples used to determine index value on basis of indicator taxa and number of diversity groups in sample

- **SPEcies At Risk Index (SPEAR)**
  - Bio-indicator system based on biological traits; focused on various types of contaminants in fresh waters
  - Spear organics: for *chronic* exposures to xenobiotics
    - Indicative of degree of sensitivity of ecosystem community (sensitive towards community shifts)
    - Not currently linked to WFD classes
  - Spear pesticides: for *pulse* exposures to pesticides
    - Linked to WFD water quality classes (>33 = good ecological status)
Field-based methods (1)

- **DSFI**: Moderate status

- **Reference site values**: 5-7
Field-based methods (2)

- **Spear organics:** Not yet linked to WFD classes

- **Overview:** more negative values $\rightarrow$ ecosystem less sensitive to xenobiotics
  - Indication for xenobiotic pollution $\rightarrow$ ecosystem has adapted to “pressure”

- **Reference site values:** $Si = -0.30; -0.18; -0.36; -0.46; -0.14; -0.24$
Field-based methods (3)

- **Spear pesticides:**
  - March data: “poor” status
  - August data: “bad” to “poor” status, upstream “moderate”
  - Un-impacted streams should NOT show seasonal differences

- **Reference site values:** SPEAR pest. = 46.5; 43.6; 34.7; 32.2; 49.7; 38.4
  - ≥33: “**good**” ecological status
No initiatives will be taken in the planning period with regard to groundwater chemical impact on streams, lakes, coastal waters. There is insufficient knowledge to adequately describe the contact between surface and groundwater and insufficient methods to model that impact.
**Integrated modelling approach**

**Modelling Steps**
- Mass release & GW transport
- Coupling of groundwater – surface water systems
- Ecosystem Dynamics

**Approach**
- System Dynamics – CARO-plus
- Analytical volatilization model
- Indices + modeling

**Dominant processes**
- Dispersion
- Advection
- Sorption
- Biodegradation
- Volatilization
- Physical (stream) characteristics
- Partition coefficients (e.g. detritus, organisms)
- Transformations
- Nonequilibrium kinetics
- Ecotoxicology

McKnight et al. (2010): *Ecological Engineering* 36, 1120-1127
Predictive modeling methods: ecosystem health

- Hazard Quotient (HQ) index
  - Screening-level risk calculation to compare levels of chemical contamination (at sites) to levels known to cause harm

\[ \text{HQi} = \frac{\text{EECi}}{\text{LC50i}} \]

- HQ\(_i\) = Hazard Quotient for compound \(_i\)
- EEC\(_i\) = Environmental concentration
- LC50\(_i\) = Conc. where 50% species dies

- AQUATOX
  - *Process-based model*, explicitly simulates biological and ecological processes in an ecosystem
  - Predicts the environmental fate and ecological effects of various environmental stressors (nutrients + toxicants)
    - Lots of unknown parameters (used literature values)
Modelling for decision support (DSS)

- **Compare modeling approaches with different levels of ecosystem complexity**
  - Evaluate necessity of using complex, “fully-functional” models

- **Determine threshold values for ecological impact**
  - Compare to (contaminated site) source mass flux ranges

- **Generalize findings**
  - Extend model for additional compounds
## Hazard Quotient Index

### HQ$_i$ (LC$_{50i}$) mortality* [mg/L]

*regression necessary to produce ecotoxicity data (Web-ICE, US EPA 2010)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chironomid</th>
<th>D. Magna</th>
<th>Stonefly</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>34.0</td>
<td>59.6</td>
<td>130.0</td>
</tr>
<tr>
<td>TCE</td>
<td>42.0</td>
<td>18.0</td>
<td>70.0</td>
</tr>
<tr>
<td>PCE</td>
<td>1.3*</td>
<td>9.1</td>
<td>3.6</td>
</tr>
<tr>
<td><strong>Naphthalene</strong></td>
<td>2.8</td>
<td>2.2</td>
<td><strong>0.011</strong>*</td>
</tr>
<tr>
<td>MCPA</td>
<td>55.0</td>
<td>3.0</td>
<td>6.2*</td>
</tr>
<tr>
<td>Metamitron</td>
<td>40.2*</td>
<td>101.7</td>
<td>1.1*</td>
</tr>
<tr>
<td><strong>Glyphosate</strong></td>
<td><strong>0.353</strong>*</td>
<td>11.0</td>
<td><strong>0.023</strong>*</td>
</tr>
<tr>
<td>4-nonylphenol</td>
<td><strong>0.013</strong>*</td>
<td>0.104</td>
<td><strong>0.004</strong>*</td>
</tr>
</tbody>
</table>

Measured TCE conc.: 0.017 [mg/L] in 2008
AQUATOX prediction of ecosystem impacts

Threshold: 150g to 1500g
Aquatox – threshold values – mass discharge [kg/yr]

Source mass flux ranges: 0.0003 to 58,400 kg/yr
(ITRC, 2010)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chironomid</th>
<th>Stonefly</th>
<th>Brown trout</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>55-550</td>
<td>55-550</td>
<td>55-550*</td>
</tr>
<tr>
<td>TCE</td>
<td>55-550</td>
<td>55-550</td>
<td>55-550*</td>
</tr>
<tr>
<td>PCE</td>
<td>5.5-55*</td>
<td>55-550</td>
<td>55-550*</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>55-550</td>
<td>0.5-5.5</td>
<td>5.5-55*</td>
</tr>
<tr>
<td>MCPA</td>
<td>&gt;55000*</td>
<td>55-550*</td>
<td>&gt;55000</td>
</tr>
<tr>
<td>Metamitron</td>
<td>550-5500*</td>
<td>55-550*</td>
<td>550-5500*</td>
</tr>
<tr>
<td>Glyphosate</td>
<td>550-5500</td>
<td>55-550*</td>
<td>0.5-5.5</td>
</tr>
<tr>
<td>4-nonylphenol</td>
<td>0.2-0.5*</td>
<td>0.02-0.2*</td>
<td>0.5-5.5*</td>
</tr>
</tbody>
</table>

*regression necessary to produce ecotoxicity data (Web-ICE, US EPA, 2010)
### Aquatox – biomass [g/m2 dry] perturbation concentration [ug/L]

<table>
<thead>
<tr>
<th>Compound</th>
<th>Chironomid</th>
<th>Stonefly</th>
<th>Brown trout</th>
<th>Concentration in surface water (Location) [ug/L]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>350</td>
<td>375</td>
<td>500*</td>
<td>11 (Japan)</td>
</tr>
<tr>
<td>TCE</td>
<td>400</td>
<td>550</td>
<td>35*</td>
<td>17 (Denmark)</td>
</tr>
<tr>
<td>PCE</td>
<td>7*</td>
<td>30</td>
<td>50*</td>
<td>23 (Canada)</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>550</td>
<td>1.5</td>
<td>20</td>
<td>1 (Spain)</td>
</tr>
<tr>
<td>MCPA</td>
<td>&gt;120,000*</td>
<td>600*</td>
<td>&gt;120,000</td>
<td>3 (Denmark)</td>
</tr>
<tr>
<td>Metamitron</td>
<td>6000*</td>
<td>180*</td>
<td>4000*</td>
<td>1 (Denmark)</td>
</tr>
<tr>
<td>Glyphosate</td>
<td>4350</td>
<td>160*</td>
<td>5</td>
<td>300** (Denmark)</td>
</tr>
<tr>
<td>4-nonylphenol</td>
<td>0.08*</td>
<td>0.14*</td>
<td>1.5*</td>
<td>0.6 (China)</td>
</tr>
</tbody>
</table>

*regression necessary to produce ecotoxicity data (Web-ICE, US EPA, 2010)
**Glyphosate: max. conc. value extracted from NOVANA database
Conclusions

- Ecological impact of TCE (contaminated site): seems to be minimal at Skensved. Caution: Spear organics result!

- Need suitable field methods to appropriately characterize ALL stressors acting on an ecosystem: need to distinguish stressor effects and capture seasonal trends. Typically have multiple stressor environments!

- Modelling to predict ecological risk: sufficient methods available! Ongoing research: finalization of DSS (point sources in gw → gw-sw interactions → ecological impacts)

- Which sites/chemical stressors are problematic?
  - 4-nonylphenol & naphthalene: potentially risky to ecosystems
  - Glyphosate, metamitron & PCE: depends on which organisms/method utilized
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