SHORT TERM AND LONG TERM RISKS OF ORGANIC POLLUTANTS IN THE AGRICULTURAL SOIL SYSTEM;
PAHs AS A CASE STUDY

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Fate and Impact of Persistant Pollutants in Agroecosystems
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PAHs

- PAHs accumulate in sediment (anaerobic system)
- Large amounts of sediments
- Dredging and reuse of dredged sediments
- 50% reuse in agriculture and nature
Landfarm experiment with dredged heavily polluted sediment

Risks

Spreading of slightly polluted sediment on agricultural land
Experiment Kreekraksluizen

- 14 years of measurement
- Intensive landfarming (cultivation)
- Passive landfarming (vegetation)
Biological degradation

Three degradable fractions

- fast
- slow
- very slow

36 rings

\[
\frac{C_t}{C_0} = F_{\text{fast}} \cdot e^{-k_{\text{fast}} \cdot t} + F_{\text{slow}} \cdot e^{-k_{\text{slow}} \cdot t} + F_{\text{very slow}} \cdot e^{-k_{\text{very slow}} \cdot t}
\]
## Results landfarm

<table>
<thead>
<tr>
<th>Sediment</th>
<th>PAHs (mg/kg d.m.)</th>
<th>Mineral oil (mg/kg d.m.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>start</td>
<td>2004</td>
</tr>
<tr>
<td>Petroleum Harbour (1994)</td>
<td>550</td>
<td>22</td>
</tr>
<tr>
<td>Wemeldinge (1994)</td>
<td>45</td>
<td>25</td>
</tr>
<tr>
<td>Geul Harbour (1990)</td>
<td>52</td>
<td>2</td>
</tr>
<tr>
<td>Zierikzee (1990)</td>
<td>65</td>
<td>15</td>
</tr>
</tbody>
</table>
## PAHs distribution

<table>
<thead>
<tr>
<th>Sediment</th>
<th>large fast available fraction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soil</td>
<td>small fast available fraction</td>
</tr>
</tbody>
</table>

### New PAHs

- Fast
- Slow
- Very slow

### Degradation

- Fast
- Slow
- Very slow
Measured availability for predicting degradation

- Prediction of fast degradation = fast available fraction
  - Solid phase (Tenax)
  - Mild extract (Hac)
  - Mild oxidation (Cuypers)
  - XAD (Northcot Jones, Tabak)
  - SFE (Hawthorne, Loibner)
  - Dextrine (Reid, Doick)
  - Mild extract (Thiele and Brunner)
Risks on a landfarm

- Retention function
- Habitat function
Retention Function

- Water dwelling organisms
  - *Vibrio Fisher* (Microtox)
  - *Daphnia Magna*

- Leaching tests

- Large effects in original sediment
- No effects after degradation of the fast available fraction

No measurable leaching

High fast available fraction = risk for retention function
Habitat Function

- **Sediment assays**
  - *Crassostrea gigas*
  - *Columphium volator*
  - *Chronomus riparius*

- **Soil assays**
  - *Lumbricus rubellus*
  - *Folsomia candidal*

- **Bioaccumulation**
  - *Oligochates*

- **Biodegradation**

- **Biological development**
  - biomass
  - incorporation of $^3$H Thymidine and $^{14}$C Leucine
  - Genetic diversity
  - Population of nematodes
Habitat function (sediment assay)

Fast available <-> effect

![Graph showing the relationship between PAHs-TENAX available and PAHs-degraded with data points for Crassotrea gigas and Corophium volutator.]
## Habitat function (soil assay)

### Lumbricus rubellus (earth worm)

<table>
<thead>
<tr>
<th>Sediment</th>
<th>Survival (%)</th>
<th>Increase in weight (mg/worm)</th>
<th>Reproduction (number of cocons)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>'95</td>
<td>'99</td>
<td>'01</td>
</tr>
<tr>
<td>KOBG = reference</td>
<td>95</td>
<td>95</td>
<td>100</td>
</tr>
<tr>
<td>Petroleum Harbour (start 1994)</td>
<td>-</td>
<td>90</td>
<td>100</td>
</tr>
<tr>
<td>Wemeldinge Harbour (start 1994)</td>
<td>-</td>
<td>90</td>
<td>100</td>
</tr>
<tr>
<td>Geul Harbour (start 1990)</td>
<td>95</td>
<td>95</td>
<td>95</td>
</tr>
</tbody>
</table>

Lumbricus rubellus (earth worm)
Habitat (genetic diversity)

1 = fresh sediment (highly polluted)
2 = partly cleaned
3 = cleaned
Habitat function

- Slower decrease of risks
- Risks are related with fast degradable fraction
- Fast degradable fraction is degraded, but the slow degradable fraction gives a new fast degradable fraction

- After >5 years risks are low
## Risks on a landfarm

<table>
<thead>
<tr>
<th>Retention function</th>
<th>Habitat function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Only in first year</td>
<td>During 5 years</td>
</tr>
<tr>
<td>Available PAHs are degraded</td>
<td>Available PAHs &gt; 12 mg/kg</td>
</tr>
</tbody>
</table>
Sediment spread on agricultural land

- **Soil**
  - Fast available fraction  5   15%
  - Very slow available fraction 60   80%

- **Sediment**
  - Fast available fraction 10   70%
  - Very slow available fraction 10   70%
Agricultural systems (spreading of sediment)

Allowed if PAHs < 10 mg/kg d.m.
Prediction of accumulation

\[
\frac{C_t}{C_0} = F_{\text{fast}} \cdot e^{k_{\text{fast}} \cdot t} + F_{\text{slow}} \cdot e^{-k_{\text{slow}} \cdot t} + F_{\text{very slow}} \cdot e^{-k_{\text{very slow}} \cdot t}
\]

<table>
<thead>
<tr>
<th>PAHs concentration (mg/kg d.m.)</th>
<th>Fast degradable fraction (%)</th>
<th>Slow degradable fraction (%)</th>
<th>Very slow degradable fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sediment-1</td>
<td>2</td>
<td>15</td>
<td>25</td>
</tr>
<tr>
<td>Sediment-2</td>
<td>5</td>
<td>15</td>
<td>25</td>
</tr>
<tr>
<td>Original soil</td>
<td>1</td>
<td>5</td>
<td>15</td>
</tr>
</tbody>
</table>

- \( k_{\text{fast}} = 9.2 \text{ year}^{-1} \)
- \( k_{\text{slow}} = 0.33 \text{ year}^{-1} \)
- \( k_{\text{very slow}} = 0.04 \text{ year}^{-1} \)
Risks for retention function

- Dredging in autumn
- Degradation starts in spring

![Graph showing the decrease of PAHs over time](image-url)
Conclusions

- PAHs are a temporary problem
- Added PAHs give a new equilibrium concentration
- Risks for retention function only in first year after addition
- Risks for habitat function during 5 years if available concentration is high enough
Landfarming of polycyclic aromatic hydrocarbons and mineral oil contaminated sediments

Joop Harmsen