20 Years of Long-Term Atrazine Monitoring in a Shallow Aquifer in Western Germany.

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Introduction

• How do the groundwater concentrations of a substance evolve over time after the substance (atrazine) was banned?
• How can we explain this evolution over time?

• Long term monitoring of atrazine concentrations in the 'Zwischenscholle' aquifer.
Zwischenscholle aquifer: Hydrogeology

- Semi confined aquifer in quaternary sandy and gravelly Rhine and Maas sediments

- Aquifer thickness from ca. 15 meters in the southwest up to 35 meters in the northeast.

- Shallow depths to the groundwater table (0.9 m – 8 m) up to 30 m in region of the Rurrand fault zone.
Zwischenscholle Groundwater Monitoring

- Monitoring points:
  - 60 Observation wells (15 currently being sampled)
  - Filter depth below groundwater table between 0-14.2 m (mean 4.7 m)
  - Filter screen lengths between 1-10 m (mean 3.1 m)

- Parameters:
  - 36 pesticides
  - 14 pharmaceuticals
  - 6 physico-chemical parameters
# Chemical Parameters of Zwischenscholle Aquifer

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Range</th>
<th>Arithmetic mean</th>
</tr>
</thead>
<tbody>
<tr>
<td>electrical conductance [µS/cm]</td>
<td>282 – 921</td>
<td>735</td>
</tr>
<tr>
<td>pH</td>
<td>5.41 – 8.1</td>
<td>6.7</td>
</tr>
<tr>
<td>Redox-Potential [mV]</td>
<td>-70 – 319</td>
<td>184</td>
</tr>
<tr>
<td>Nitrate [mg/l]</td>
<td>n.d. – 153</td>
<td>53</td>
</tr>
<tr>
<td>Dissolved Organic Carbon (DOC) [mg/l]</td>
<td>n.d. – 77</td>
<td>4.61</td>
</tr>
</tbody>
</table>
Mean ATR concentrations in Observation wells

- High spatial variability in ATR concentration distribution

- In 6 of 34 Obs wells, the long term ATR concentration exceeds 0.1 µg/l

- Evolution of atrazine concentrations over time varies between different wells

- Overall mean of Atrazine:
  - **0.06 µg/l** (all observation wells tapping the Zwischenscholle aquifer)
  - 822951 and 872121 are excluded
Treatment of Censored Datasets

Assume LOQ = 0.02 $\mu$g l$^{-1}$

40 % of the measurements is above LOQ

“regression on order statistics” (ROS)
Evolution of Atrazine Concentration Distributions in Different Years.
Distributions of Atrazine concentrations in Different Observation Wells

Observation wells
Atrazine Concentrations in Wells

Observation well 1691 a)

Observation well 20230 d)

Observation well 873051 c)

Observation well 20233 b)
Observation well 873051

Depth to Groundwater
Atrazine
Desethylatrazine
Desisopropylatrazine
Simazine
Threshold value

DAR = 0.71

Concentration [µg/l]

2002 2003 2004 2005 2006 2007 2008 2009 2010
Time [years]

r_{ATR-Gw-Table} = 0.09

Depth [m]
Atrazine Concentrations as a Function of Filter Depth
(only wells with filter length < 3m)
Capture Zone of a Well

- $N = 0.175 \text{ m year}^{-1}$
- $K_s = 2.11E-03 \text{ m s}^{-1}$
- Hydraulic gradient = 0.2%

Dimensions:
- 10.9m
- 5m
- 3800m
Groundwater Exchange Times

\[ N = 0.175 \text{ m year}^{-1} \]

\[ \theta = 0.25 \]
\[ K_d = 0.2 \text{ l kg}^{-1} \]
\[ R = 2.3 \]

Water exchange time = 15.5 years
Leaching time of atrazine = 35.3 years
Relation With Other Groundwater Parameters

PCA – Results

PCA results showing the relationship between various groundwater parameters.

- Diffuse anthropogenic impact
- Desisopropylatrazine
- Diuron
- Simazine
- Propazine
- TOC
- EC
- Atrazine
- Deethylatrazine
- Nitrate

Agrosphere, IBG-3
Deethylatrazine (DEA) to Atrazine Ratio (DAR)

- Transformation of ATR to DEA occurs mainly in the organic-rich and biological most active topsoil

- The longer the contact time, the more transformation, increasing the DAR
  - Is the case when dispersed on fields as non point source

- For a more direct transport into the aquifer via preferential flow or via local point source contaminations (=less contact time for transformation) the DAR decreases

DAR → 1  → diffuse (nonpointsource) contamination
DAR → 0  → point source contamination
## Deethylatrazine to Atrazine Ratio (DAR)

DAR $\rightarrow$ 1 $\rightarrow$ diffuse (nonpoint-source) contamination  
DAR $\rightarrow$ 0 $\rightarrow$ point source contamination

<table>
<thead>
<tr>
<th>Range of ATR concentration (µg/l)</th>
<th>Thurman et al., 1998</th>
<th>Zwischenscholle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Median DAR</td>
<td>Samples</td>
<td>Median DAR</td>
</tr>
<tr>
<td>0.01 to 0.05</td>
<td>-</td>
<td>1.00</td>
</tr>
<tr>
<td>0.05 to 0.1</td>
<td>1.8</td>
<td>61</td>
</tr>
<tr>
<td>0.1 to 0.2</td>
<td>0.58</td>
<td>14</td>
</tr>
<tr>
<td>0.2 to 0.4</td>
<td>0.6</td>
<td>14</td>
</tr>
<tr>
<td>0.4 to 0.8</td>
<td>0.23</td>
<td>12</td>
</tr>
<tr>
<td>0.8 to 2.1</td>
<td>0.23</td>
<td>9</td>
</tr>
</tbody>
</table>

Non point source

Point source!
Evolution of DAR over Time
DAR versus Depth of Filter below GW Table

![Graph showing the relationship between DAR and depth of filter below the groundwater table.](image-url)
Conclusions

• Atrazine concentrations vary considerably in space, but the spatial pattern is rather stable over time.
• Temporal variations are related to groundwater table dynamics: due to dilution, concentrations are lower when groundwater tables are high.
• A clear overall decline of atrazine concentrations cannot be observed.
  • Atrazine hardly degrades in this aquifer (also evidenced by the constant DAR ratio)
  • Simple calculations also suggest a long time before atrazine is leached out the aquifer (35 years).
• Atrazine pollution could be classified as diffuse pollution
  • DAR ratios
  • Correlation with Nitrate and EC