The influence of diffuse pollution on groundwater content patterns for the groundwater bodies of Germany

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Background

1. EU water framework directive (article 17)  
- Prevent and control groundwater pollution  
- Measures to achieve or restore a „good groundwater chemical status“  
  - Criteria for assessing good groundwater chemical status  
  - Criteria for the identification of significant and sustained upward trends and for the definition of starting points for trend reversals  
- A complementary Groundwater Directive has just been accepted by the parliament

2. Research Contract commissioned by the Working Group of the Federal States of Germany on Water problems (LAWA)  
- Development of a method to identify the natural background values for groundwater  
- Application to hydrogeological units in Germany

According to the EU - Water Framework Directive, Natural Background Levels (NBLs) and Threshold Values (TVs) for the groundwater should be established taking into account natural influences as well as human impacts
Solution contents of groundwater depend on...

Natural influences
- Groundwater covering layers
- Petrographical aquifer properties
- Hydrodynamical aquifer properties

Human impact
- Landcover (changes)
- Water regulations
- Mining
- Point source pollution
- Diffuse intakes from agriculture and atmosphere

A strictly “natural” groundwater may be found at best in regionally restricted areas, with mostly minor importance for water supply.

Methodological aspects for the derivation of natural background levels

1. Hydrochemical simulation of solution processes in aquifers
   - Only for well monitored small areas and time-consuming

2. Evaluation of groundwater samples free from human impact
   - Only samples from deeper aquifers or from natural reservates

3. Evaluation of groundwater samples by separation methods
   - Preselection methods: Exclusion of samples with
     - purely anthropogenic substances (e.g. PAC, pesticides)
     - concentrations of indicator substances above a certain value (e.g. NO₃ > 10 mg/l)
   - Separation of natural / anthropogenic components from concentration distributions
     - all available groundwater samples and parameters can be used
Hydrogeological differentiation

17 hydrogeological units differentiated according to petrography, stratigraphy, hydrodynamics, hydrology

- Pleistocene gravels and sands
- Sand and gravel Lower Rhine Bay
- Sand and gravel Upper Rhine Valley
- Moraine deposits of the Alps foreland
- Tertiary sediments
- Jurassic limestones
- Mixed-layered silicatic rocks
- Mixed-layered carbonatic rocks
- Triassic limestones
- Triassic sandstones
- Limestones of the Alps
- Paleozoic sediments
- Paleozoic limestones
- Basic volcanites
- Magmatites and metamorphic rocks

Allocation to hydrogeological units from monitoring station master data (depth, stratigraphy, etc.) and maps (isolated cases)

Aquifer typologies: a geographical reference for assessing Natural Background Levels (NBLs) on a European scale

- EU-STREPS project BRIDGE (Background criteria for the identification of Groundwater Thresholds)
- 27 partners from 19 countries involved
Evaluated groundwater monitoring data

1. Groundwater data from monitoring networks of 15 Federal States
   - 160000 samples from 40000 stations
   - Different monitoring networks
   - Heterogeneous data structure
   - Differences in analyzed parameters

2. Database creation
   - Removing of samples with incorrect ion balance
   - Attachment of monitoring data to investigated hydrogeological units
   - Elimination of time series by median averaging

3. 25971 monitoring stations with one representative groundwater analysis each remained

Parameter specific number of used stations

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Number of groundwater samples used</th>
</tr>
</thead>
<tbody>
<tr>
<td>BB</td>
<td></td>
</tr>
<tr>
<td>BE</td>
<td></td>
</tr>
<tr>
<td>BW</td>
<td></td>
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<tr>
<td>BY</td>
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<td>HB</td>
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<td>NI</td>
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<tr>
<td>NW</td>
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<td>RP</td>
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<td>SH</td>
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<td>SN</td>
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</tr>
<tr>
<td>ST</td>
<td></td>
</tr>
<tr>
<td>TH</td>
<td></td>
</tr>
</tbody>
</table>
Components in concentration profiles

Procedure of component separation

Step 1: Classification of data into concentration ranges and creation of frequency distributions of a groundwater parameter in a hydrogeological unit

Step 2: Selection of two statistical distribution functions representing the natural component and the influenced component

Step 3: Finding those distribution parameters which get an optimal representation of the observed distribution by the sum of both components

Step 4: Identification of natural groundwater concentration by the 80% confidence interval of natural component
Derived background values

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Pleistocene sands and gravel</th>
<th>Jurassic limestones</th>
<th>Triassic limestones</th>
<th>Triassic sandstones</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductivity µS/cm</td>
<td>186 - 521</td>
<td>387 - 704</td>
<td>637 - 939</td>
<td>50 - 296</td>
</tr>
<tr>
<td>O₂ mg/l</td>
<td>0.2 - 4.6</td>
<td>6 - 11</td>
<td>3 - 10</td>
<td>8 - 11</td>
</tr>
<tr>
<td>pH</td>
<td>6.0 - 7.8</td>
<td>7.1 - 7.7</td>
<td>7.0 - 7.5</td>
<td>6.8 - 7.7</td>
</tr>
<tr>
<td>DOC mg/l</td>
<td>0.8 - 5.0</td>
<td>0.3 - 1.3</td>
<td>0.4 - 1.2</td>
<td>0.3 - 1.6</td>
</tr>
<tr>
<td>Ca mg/l</td>
<td>29 - 143</td>
<td>69 - 126</td>
<td>99 - 154</td>
<td>7 - 29</td>
</tr>
<tr>
<td>Mg mg/l</td>
<td>3 - 30</td>
<td>4 - 37</td>
<td>17 - 50</td>
<td>2 - 23</td>
</tr>
<tr>
<td>Na mg/l</td>
<td>6 - 24</td>
<td>1.3 - 8.3</td>
<td>3.0 - 9.2</td>
<td>2 - 16</td>
</tr>
<tr>
<td>K mg/l</td>
<td>0.8 - 4.0</td>
<td>0.3 - 1.9</td>
<td>0.6 - 2.1</td>
<td>1.3 - 3.6</td>
</tr>
<tr>
<td>NH₄ mg/l</td>
<td>&lt;0.01 - 0.5</td>
<td>&lt;0.01 - 0.01</td>
<td>&lt;0.01 - 0.01</td>
<td>&lt;0.01 - 0.01</td>
</tr>
<tr>
<td>Fe mg/l</td>
<td>0.1 - 5.0</td>
<td>&lt;0.01 - 0.15</td>
<td>&lt;0.01 - 0.1</td>
<td>&lt;0.01 - 0.1</td>
</tr>
<tr>
<td>Mn mg/l</td>
<td>0.04 - 0.64</td>
<td>&lt;0.01 - 0.01</td>
<td>&lt;0.01 - 0.01</td>
<td>&lt;0.01 - 0.01</td>
</tr>
<tr>
<td>HCO₃ mg/l</td>
<td>150 - 426</td>
<td>278 - 380</td>
<td>287 - 446</td>
<td>6 - 96</td>
</tr>
<tr>
<td>Cl mg/l</td>
<td>9 - 43</td>
<td>5 - 37</td>
<td>9 - 49</td>
<td>4 - 17</td>
</tr>
<tr>
<td>SO₄ mg/l</td>
<td>4 - 68</td>
<td>13 - 32</td>
<td>30 - 147</td>
<td>9 - 58</td>
</tr>
<tr>
<td>NO₃ mg/l</td>
<td>&lt;0.01 - 0.1</td>
<td>*</td>
<td>*</td>
<td>*</td>
</tr>
</tbody>
</table>

Significant different concentration ranges of natural groundwater concentrations between the groundwater units

Potassium in Jurassic Limestones

(dominant) natural component
- at low concentrations
- indicates K-poor minerals in groundwater covering layers and aquifers of the jurassic limestones
- Natural concentration < 1.9 mg/l

influenced component
- in broad, high concentration range
- indicates the impact of potassium containing fertilizers

„Prototype“ distribution type for most parameters
**Protons (pH) in Triassic Sandstones**

**Natural Component**
- pH: 6.7 - 7.6
  - (High H⁺-concentration = low pH)

**Dominant Influenced Component**
- pH < 6.7
  - Indicates degree of acidification (vulnerability) of (buffer-poor) sandstone aquifers and their covering layers.

**Magnesium**

**Dominant Natural Component**
- < 22 mg Mg/l
  - Lack of Mg-containing minerals

**Influenced Component**
- Impact of measures against soil acidification
  - Mg-containing fertilizers

**Two Natural Components**
- < 40 mg Mg/l
  - Rising degree of dolomitisation from SW to NE

**No Influenced Component**
Iron (II): redox-sensitive parameter

Two natural components
- < 5 mg Fe/l
- Indicates redox-stratification
- Oxidized groundwater zone (below ca. 5 m)
- Reduced groundwater zone (above ca. 5 m)

No influenced component

No natural components

Iron (II): redox-sensitive parameter

One natural component
- < 0.15 mg Fe(II)/l
- Typical distribution of redox-sensitive parameters in oxidized groundwaters

No influenced component

Nitrate: redox-sensitive parameter

No natural components

Two influenced components
- Indicated redox-stratification
- Small concentrations (< 1 mg NO3/l) result from denitrification processes in reduced groundwater rather than small or missing nitrate inputs

No natural components

Two influenced components
- Indicates diffuse nitrate pollution
- Indicates absence of significant "natural" nitrate sources in soils and aquifer
Conclusions

<table>
<thead>
<tr>
<th>Components</th>
<th>Concentration distributions</th>
<th>Hydrogeologic unit examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na, K, Cl, SO₄, LF</td>
<td>Usually two components</td>
<td>Usually indicating anthropogenic influences</td>
</tr>
<tr>
<td>Ca, Mg, HCO₃</td>
<td>One or two components</td>
<td>dominated by source rock and/or facies differences</td>
</tr>
<tr>
<td>pH</td>
<td>Usually two components</td>
<td>Acidification influence in buffer-poor soils and rocks</td>
</tr>
<tr>
<td>O₂, Fe, Mn, NO₂, NH₄, DOC</td>
<td>One or two components</td>
<td>Mainly influenced by redox status and depth</td>
</tr>
<tr>
<td>Heavy metals, Al</td>
<td>Usually one component</td>
<td>Influenced by acidification and detection limits</td>
</tr>
<tr>
<td>PO₄, NO₃</td>
<td>One component</td>
<td></td>
</tr>
</tbody>
</table>

Summary

1. Component separation method was applied
   ➢ to 17 hydrogeological units of Germany
   ➢ using samples from 26000 monitoring stations
   ➢ for a total of 31 inorganic parameters

2. Evaluation of separated components with respect to
   ➢ Anthropogenic influences
   ➢ Facies influence
   ➢ Impact of Redox conditions

3. Derivation of natural background values
   ➢ Consistent for each parameter and unit
   ➢ Large differences between units due to the different petrographic and hydrodynamical / hydrological conditions
   ➢ Not all parameters show significant anthropogenic influences