Establishing the importance of pollutant attenuation at the aquifer-river interface

Jonathan Smith
Overview of presentation

- Background and context
- Objectives of the Agency’s Hyporheic Zone project
- National scale HZ attenuation classification scheme
- Reach scale NA process research
- Knowledge transfer and dissemination
- Conclusions
Objectives of the HZ project

- to determine the importance of pollutant attenuation processes in fluvial sediments where there is GW-SW exchange;
- to identify the important attenuation processes for key pollutants at the GW-SW interface;
- to understand the controls on, and variability of, those attenuation processes;
- to apply the new scientific understanding in effective environmental management tools;
- to disseminate the results widely.
Why is this a priority now?

- WFD requires integrated management of surface and groundwater
- GW quality can affect status of surface water body, and vice-versa
- GW-SW interface a biogeochemically active zone
- Existing models and guidance often ignore the interface
The GW-SW interface

- Water exchange between stream and subsurface;
- Chemical & temperature gradients; microbiologically active;
- Organic carbon rich compared to aquifer
- ‘Last Chance Saloon’ for NA processes
- Habitat - ecotone

Courtesy USGS
Hyporheic attenuation classification

- **Aim:** To derive a classification scheme for HZ attenuation capacity(ies) for British rivers
- **ID processes expected to influence NA capacity**
  - Sediment thickness
    - stream power
    - sediment supply
  - Sediment permeability
  - Sediment geochemistry
    - $f_{OC}$, CEC, TIC
  - Each derived from contributing factors using national datasets
- **Ranking approach** (H/M/L score for each)
Example conceptual model: Fine sediment supply

[Diagram showing the model with nodes for Land Use Type, Land use Erodibility, Rainfall (SAAR), Mean Slope, Drainage Density, Potential Fine Sediment Supply, Area of Erodible Land, Area of WB catchment, Potential Supply Transportability, Sediment Transport Potential Matrix, Total Supply of Fine Sediments, Decision Matrix, and Sediment Supply.]

- Land Use Type
  - Land use Erodibility
  - Rainfall (SAAR)
  - Mean Slope
  - Drainage Density

- Area of Erodible Land
- Area of WB catchment

- Potential Fine Sediment Supply

- Potential Supply Transportability

- Sediment Transport
  - Potential Matrix
  - Transportability

- Sediment Supply

- WB catch vs corridor supply
  - Decision Matrix

- Total Supply of Fine Sediments
Each variable is assigned a H, M, L score

**Table 1 Rainfall class data table.**

<table>
<thead>
<tr>
<th>Rainfall class</th>
<th>SAAR (mma⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>&lt; 800</td>
</tr>
<tr>
<td>Moderate</td>
<td>800 - 1500</td>
</tr>
<tr>
<td>High</td>
<td>&gt; 1500</td>
</tr>
</tbody>
</table>

**Table 2 Slope class data table.**

<table>
<thead>
<tr>
<th>Slope class</th>
<th>angle (deg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low</td>
<td>&lt;3</td>
</tr>
<tr>
<td>Moderate</td>
<td>3 - 7</td>
</tr>
<tr>
<td>High</td>
<td>&gt;7</td>
</tr>
</tbody>
</table>

**Table 3 Erosivity weighting as defined by slope and rainfall (SAAR).**

<table>
<thead>
<tr>
<th>Slope</th>
<th>SAAR</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Low (1)</td>
</tr>
<tr>
<td>Low (1)</td>
<td>1</td>
</tr>
<tr>
<td>Moderate (2)</td>
<td>2</td>
</tr>
<tr>
<td>High (3)</td>
<td>2</td>
</tr>
</tbody>
</table>
HZ classification data

Sediment erosivity classes (slope; SAAR)

Fine sediment supply

Stream power

High

Low
Aquifer geochemistry

\[ R_f = 1 + \frac{K_D \cdot \rho}{n} = 1 + \frac{K_{OC} \cdot f_{OC} \cdot \rho}{n} \]

R_f = 5, 50, 500

<table>
<thead>
<tr>
<th>Pollutant attenuation class</th>
<th>( f_{OC} ) (fraction)</th>
<th>CEC (meq/100g)</th>
<th>TIC (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low attenuation potential</td>
<td>( f_{OC} &lt; 0.002 )</td>
<td>CEC &lt; 5</td>
<td>TIC &lt; 0.2</td>
</tr>
<tr>
<td>Moderate attenuation potential</td>
<td>( 0.002 \leq f_{OC} &lt; 0.02 )</td>
<td>( 5 \leq CEC &lt; 20 )</td>
<td>( 0.2 \leq TIC &lt; 2 )</td>
</tr>
<tr>
<td>High attenuation potential</td>
<td>( 0.02 \leq f_{OC} &lt; 0.2 )</td>
<td>( \geq 20 )</td>
<td>TIC ( \geq 2 )</td>
</tr>
<tr>
<td>Extremely high attenuation potential</td>
<td>( f_{OC} \geq 0.2 )</td>
<td>No class defined</td>
<td>No class defined</td>
</tr>
</tbody>
</table>

\( f_{OC} \), CEC, TIC maps show the spatial distribution of organic carbon, cation exchange capacity, and total inorganic carbon.
HZ classification

Increasing HZ NA potential
Classification testing

- National nitrate database (GW & SW TON data used for NVZ designation) re-run for baseflow (Q10) conditions
- Multiple regression analysis used to test whether the HZ classification criteria are good explanatory variables
- Correlation to sediment thickness, sediment permeability, $f_{OC}$ and overall HZ factor all statistically significant at $P<0.001$
- Combined, the HZ factors describe up to $\sim 4\%$ of the variance ($R^2$) in observed baseflow TON concentrations ($R^2\sim 0.56$). This improves existing predictions by $\sim 7\%$
### Results: analysis of variance

Accumulated analysis of variance for Sqrt(P10Ave) model

<table>
<thead>
<tr>
<th>Change</th>
<th>d.f.</th>
<th>s.s.</th>
<th>m.s.</th>
<th>v.r.</th>
<th>F pr.</th>
<th>Max % change in predicted river TON due to change in explanatory variable</th>
</tr>
</thead>
<tbody>
<tr>
<td>+ Crops</td>
<td>1</td>
<td>529.90</td>
<td>529.90</td>
<td>2101.9</td>
<td>&lt;.001</td>
<td>82</td>
</tr>
<tr>
<td>+ Grass</td>
<td>1</td>
<td>160.63</td>
<td>160.63</td>
<td>637.2</td>
<td>&lt;.001</td>
<td>62</td>
</tr>
<tr>
<td>+ Urban</td>
<td>1</td>
<td>78.18</td>
<td>78.18</td>
<td>310.1</td>
<td>&lt;.001</td>
<td>38</td>
</tr>
<tr>
<td>+ Ground</td>
<td>1</td>
<td>13.67</td>
<td>13.67</td>
<td>54.2</td>
<td>&lt;.001</td>
<td>18</td>
</tr>
<tr>
<td>+ Sediment thickness</td>
<td>2</td>
<td>24.01</td>
<td>12.00</td>
<td>47.6</td>
<td>&lt;.001</td>
<td>30</td>
</tr>
<tr>
<td>+ Aquif</td>
<td>3</td>
<td>32.67</td>
<td>10.89</td>
<td>43.2</td>
<td>&lt;.001</td>
<td>22</td>
</tr>
<tr>
<td>+ BFI</td>
<td>1</td>
<td>10.47</td>
<td>10.47</td>
<td>41.5</td>
<td>&lt;.001</td>
<td>25</td>
</tr>
<tr>
<td>+ Atmos</td>
<td>1</td>
<td>4.01</td>
<td>4.01</td>
<td>15.9</td>
<td>&lt;.001</td>
<td>11</td>
</tr>
<tr>
<td>+ SedPerm</td>
<td>2</td>
<td>7.68</td>
<td>3.84</td>
<td>15.2</td>
<td>&lt;.001</td>
<td>20</td>
</tr>
<tr>
<td>+ DischF</td>
<td>3</td>
<td>10.62</td>
<td>3.54</td>
<td>14.0</td>
<td>&lt;.001</td>
<td>14</td>
</tr>
<tr>
<td>+ Geo1 (Foc)</td>
<td>2</td>
<td>6.70</td>
<td>3.35</td>
<td>13.3</td>
<td>&lt;.001</td>
<td>16</td>
</tr>
<tr>
<td>+ Flow</td>
<td>1</td>
<td>1.38</td>
<td>1.38</td>
<td>5.5</td>
<td>0.020</td>
<td>1</td>
</tr>
<tr>
<td>+ Subsurface perm</td>
<td>2</td>
<td>0.52</td>
<td>0.26</td>
<td>1.0</td>
<td>n.s.</td>
<td></td>
</tr>
<tr>
<td>Residual</td>
<td>2702</td>
<td>681.20</td>
<td>0.25</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>2723</td>
<td>1561.63</td>
<td>0.57</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
HZ classification: results

Regression coefficient for combined HZ classification factors. X-axis varies from: Index = 1 (low NA potential) to Index = 10 (high NA potential)
Hyporheic zone attenuation

- Effort focussed on WFD-directed priority pollutants
  - nitrate;
    - Pollutant causing largest number of ‘WB at risk’ designations
    - Potential for denitrification in organic carbon-rich and lower permeability sediments
  - minewaters;
    - Co-precipitation of Mn with Fe minerals
  - industrial pollutants, e.g. chlorinated ethenes
- GW-SW exchange
  - How variable is the flux across interface?
Flow variability at reach scale

- Natural temperature time series used as a tracer of GW-SW flux
- Tested in River Tern - lowland, sand-bed river. ca. 75% sand-bed run at study reach
- High BFI: 0.72. Regional GW contours suggest gaining stream throughout catchment
- Diurnal T signal used to determine water flux locally
Tern streambed temp: time series
Temperature Time Series

Amplitude and Phase of Diurnal Component

Vertical Water Velocity

Upwards Vertical Water Flux (x 10^6 m s^-1)

-8
-6
-4
-2
0
2
4
6
8
10
12

June
July
August
September

2005

Location T1
Location T2
Location T3
Location T4
Location T5
Winter roaming survey

Dominant feature:
- Run: sand-bed
- Riffle: gravel

\[ \psi = \left( \frac{T_{12} - T_0}{0.12} + \frac{T_{36} - T_{24}}{0.12} \right) / 2 \]
Geochemical variability in sediments

- Determine how geochemical properties of sediments vary with
  - fluvial geomorphology
  - dominant sediment type
- NA-relevant properties
  - $f_{OC}$, CEC, Fe/Mn (total/bio), grain size
• ANOVA analysis: sediment chemistry varies with geomorphology and dominant grain size different (P<0.001)
## Fraction of organic carbon

<table>
<thead>
<tr>
<th></th>
<th>alluvium</th>
<th>aquifer</th>
<th>lowland reach</th>
<th>pool</th>
<th>riffle</th>
<th>run</th>
<th>till</th>
</tr>
</thead>
<tbody>
<tr>
<td>alluvium</td>
<td>0</td>
<td>0.322</td>
<td>0</td>
<td>0.363</td>
<td>0.0047</td>
<td>0.2577</td>
<td></td>
</tr>
<tr>
<td>aquifer</td>
<td>0</td>
<td>0</td>
<td>0.004</td>
<td>0.999</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>lowland reach</td>
<td>0.004</td>
<td>0.999</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0001</td>
<td></td>
</tr>
<tr>
<td>pool</td>
<td></td>
<td>0.33</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>riffle</td>
<td></td>
<td></td>
<td>0</td>
<td></td>
<td></td>
<td>0</td>
<td>0.0009</td>
</tr>
<tr>
<td>run</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.998</td>
</tr>
<tr>
<td>till</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean foc (fraction)</td>
<td>0.015</td>
<td>0.0003</td>
<td>0.012</td>
<td>0.0495</td>
<td>0.0315</td>
<td>0.0054</td>
<td>0.0027</td>
</tr>
<tr>
<td>SD</td>
<td>0.019</td>
<td>0.0001</td>
<td>0.0094</td>
<td>0.0637</td>
<td>0.0548</td>
<td>0.0141</td>
<td>0.0031</td>
</tr>
</tbody>
</table>

## Cation exchange capacity

<table>
<thead>
<tr>
<th></th>
<th>alluvium</th>
<th>aquifer</th>
<th>lowland reach</th>
<th>pool</th>
<th>riffle</th>
<th>run</th>
<th>till</th>
</tr>
</thead>
<tbody>
<tr>
<td>alluvium</td>
<td>0.999</td>
<td>0.266</td>
<td>0</td>
<td>0.876</td>
<td>0.238</td>
<td>0.968</td>
<td></td>
</tr>
<tr>
<td>aquifer</td>
<td>0.019</td>
<td>0</td>
<td>0</td>
<td>0.566</td>
<td>0.0669</td>
<td>0.991</td>
<td></td>
</tr>
<tr>
<td>lowland reach</td>
<td>0.0098</td>
<td>0.995</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0217</td>
<td></td>
</tr>
<tr>
<td>pool</td>
<td></td>
<td>0.0099</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>riffle</td>
<td></td>
<td></td>
<td>0.0108</td>
<td></td>
<td></td>
<td>0.377</td>
<td></td>
</tr>
<tr>
<td>run</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>till</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean CEC (meq/100g)</td>
<td>8.55</td>
<td>4.96</td>
<td>9.78</td>
<td>27.8</td>
<td>12.3</td>
<td>5.1</td>
<td>6.6</td>
</tr>
<tr>
<td>SD</td>
<td>11</td>
<td>1.41</td>
<td>5.94</td>
<td>29.9</td>
<td>19.1</td>
<td>6.37</td>
<td>6.06</td>
</tr>
</tbody>
</table>
Grain size control at catchment scale

\[ R^2 = 0.6348 \]

\[ R^2 = 0.5466 \]

\[ R^2 = 0.6769 \]

Mean grain size (Phi units)

Clay fraction (%)

CEC (meq/100g)

foc (%)

Linear (foc (%))

Linear (CEC (meq/100g))

Linear (Clay fraction (%))
Redox-driven N cycling in the hyporheic zone

Temporal Effects: Denitrification highest in summer and autumn and lowest in spring and winter due to temperature and OM effects.

Denitrification zone dependent on microscale conditions and redox boundary which is determined by DO, DOC and sediment properties.

Nitrification decreases, denitrification variable.

NO$_3^-$, dO$_2$, DOC decrease with depth, NH$_4^+$ increases.

High hydrologic exchange and shifting sediments lead to high colonisation beneath central river bed.

Ecological Impact: Greater hydrological exchange and biogeochemical rates means greater significance of HZ.

Bacterial abundance, pH decreases, anaerobic processes increase.

See: Riess et al. (poster).
Hyporheic ecology

- International literature also suggests HZ has a distinct ecology and habitat value, including
  - contribution to biodiversity - distinct hyporheos (permanent hyporheos)
  - larval stage of many benthic invertebrates (temporary hyporheos)
  - refuge in periods of stress?
  - fish spawning

- New GW Directive encourages future assessment of GW ecosystem quality and protection
- Review of the hypogean ecology of the UK

Syncarida: 92 species in European GW
None in SW

Courtesy: J Gibert

Parabathynella cf. stygia
The Hyporheic Network

- A NERC Knowledge Transfer Network on groundwater - surface water interactions and hyporheic zone processes;
- Runs 2007 - 2010, to disseminate science to science end-user groups and to highlight their priorities to the research community
- Prepare a Handbook on GW-SW interactions for catchment managers
- Workshops to generate new multidisciplinary research proposals and teams
- Please visit: www.hyporheic.net
Conclusions

- Growing literature suggests GW-SW interface is an important zone for pollutant cycling and retardation
- New classification scheme for the HZ NA capacity improves existing predictions of SW nitrate concentrations
- GW-SW fluxes can be highly variable, even in ‘simple’ river corridors
- HZ sediments have a greater NA potential (per unit volume) than adjacent aquifer or drift, but are spatially and temporally heterogeneous
- Decreased nitrate (R Tern) and R-Cl (R Tame) concentrations observed in most organic rich-sediments
- Sediment geochemistry (CEC, Foc) varies with both geomorphology and grain size
- Pollutant attenuation potential varies with river corridor characteristics
- But, is the interface a pollutant attenuation zone or emerging habitat?
Establishing the importance of pollutant attenuation at the aquifer-river interface
HZ project publications

**Journal papers**
- Smith & Lerner, submitted. A framework for assessing retardation capacity… *QJEGH*

**Environment Agency Reports**
- SC030155/1, 2005. *Groundwater - surface water interactions in the hyporheic zone*
- SC030155/2, 2005. *In situ monitoring of hyporheic zone biogeochemistry*
- SC030155/3, 2005. *In situ monitoring of flow at the GW-SW interface*
- SC030155/4, 2005. *A review of GW-SW interactions fieldsite infrastructure in the UK*
- SC030155/5, 2005. *A review of nitrate attenuation in the subsurface environment*
- SC030155/6, 2006. *Attenuation of mine pollution in the hyporheic zone*
- SC030155/7, 2007 (in press). *A classification scheme for HZ attenuation capacity*
- SC030155/8, 2007 (in press). *Tracer tests for determining hyporheic zone processes*
- SC030155/9, 2007 (draft). *Temp. measurements for determining aquifer-river fluxes*

Please visit: [www.publications.environment-agency.gov.uk/](http://www.publications.environment-agency.gov.uk/)