Groundwater tracing: Breathing new life into a practical approach to testing aquifers

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### INTRODUCTION

#### DIFFERENCES BETWEEN APPLIED AND ENVIRONMENTAL TRACERS

<table>
<thead>
<tr>
<th>Applied Tracers</th>
<th>Environmental Tracers</th>
</tr>
</thead>
<tbody>
<tr>
<td>• Voluntarily introduced in groundwater</td>
<td>• Already present in groundwater</td>
</tr>
<tr>
<td>• Known quantity</td>
<td>• Unknown quantity</td>
</tr>
<tr>
<td>• More controlled</td>
<td>• Less controlled</td>
</tr>
</tbody>
</table>

*Examples: Bromide, fluorescein*  
*Examples: Temperature, major ions, contaminants, isotopes*
INTRODUCTION

AT WHAT SCALE DO YOU NEED TO WORK?

- Localised Zone
- Plume
- Site
- Catchment
INTRODUCTION

OTHER KEY CONSIDERATIONS

• Costs
• Site constraints
• Aquifer conditions
• Detection limits
• Laboratory or field analysis (Sampling method)
• Background concentrations
• Quality assurance/quality control (QA/QC)
• Likely spatial and temporal distribution

➢ Begin with the end in mind!
➢ Come up with hypotheses to design your data collection
APPLIED TRACERS
APPLIED TRACERS

KEY PRINCIPLES

BASIC IDEA

- Dissolve a known quantity of tracer in water
- Introduce the solution into an aquifer via:
  - Injection well
  - Sinkhole, subsurface vault, pond, dam, etc.
- Monitor changes in tracer concentrations
  ➢ Obtain breakthrough curves

IN PRACTICE

- Seems easy but tracer test methodology can be sophisticated
- Results can be highly dependent upon adopted methodology
APPLIED TRACERS

**SALTS**
- Analysis is conventional
- Higher detection limit (10 – 100 µg/L)
- Background can be high
- Toxicity

**FLUORESCENT DYES**
- Very low detection limit (0.001 µg/L)
- Background, interferences
- Innocuous (USEPA, German EPA)
  (Amino-G acid excited by UV)

**NANO TRACERS**
- Analysis is unconventional
- Specificity
- Requires specific risk assessment
### INSTRUMENTATION LIMITS FOR FLUORESCENT DYES

#### Typical Detection Limits

<table>
<thead>
<tr>
<th>Fluorescent tracer</th>
<th>Limit of detection (µg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fluorescein</td>
<td>0.002</td>
</tr>
<tr>
<td>Sulforhodamine B</td>
<td>0.006</td>
</tr>
<tr>
<td>Eosine</td>
<td>0.01</td>
</tr>
<tr>
<td>Tinopal</td>
<td>0.01</td>
</tr>
<tr>
<td>Amino G acid</td>
<td>0.02</td>
</tr>
<tr>
<td>Pyranine</td>
<td>0.02</td>
</tr>
<tr>
<td>Naphthionate</td>
<td>0.05</td>
</tr>
<tr>
<td>Photine</td>
<td>1</td>
</tr>
</tbody>
</table>

#### Analysis Type - Fluorescein

![Graph showing detection limits for different techniques.](image-url)

- **Visible**
- **Not visible**

Sensibility vs selectivity.
PROTECTION ZONES

CONTEXT

• Many EU countries rely heavily on groundwater for their potable water supply

• Some areas are densely populated and there is a need to define protection zones inside which activities are regulated or prohibited

• When an accident occurs, there is also a need to predict contaminant migration and support logistics of intervention

• In most EU countries, protection zones are typically defined using fluorescent dye tracers due to their ability to quantify effective porosity

\[ v = \frac{K \ i}{n_e} \]
PROTECTION ZONES

APPLICATION

- Alluvial gravel layer is about 7 m thick
- T ranges from $1.10^{-4}$ m$^2$/s to $2.10^{-1}$ m$^2$/s with average being $3.10^{-2}$ m$^2$/s
- Average storage coefficient ($S_y$) is 0.10

SOURCE: DEROUANE AND DASSARGUES, 1998
PROTECTION ZONES
APPLICATION - RADially CONVERGING FLOW

<table>
<thead>
<tr>
<th>Distance (m)</th>
<th>Tracer</th>
<th>Effective Porosity (n_e) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>27</td>
<td>KI</td>
<td>4.8</td>
</tr>
<tr>
<td>49</td>
<td>KI</td>
<td>7.2</td>
</tr>
<tr>
<td>78</td>
<td>Naphthionate</td>
<td>5.6</td>
</tr>
<tr>
<td>88</td>
<td>LiCl</td>
<td>8.2</td>
</tr>
<tr>
<td>91</td>
<td>Fluorescein</td>
<td>5.8</td>
</tr>
<tr>
<td>115</td>
<td>Rhodamine WT</td>
<td>4.7</td>
</tr>
</tbody>
</table>

Source: Derouane and Dassargues, 1998
PROTECTION ZONES

OUTCOMES

• Effective porosity is lower than the Specific Yield ($S_y$) up to a factor of two
• Transfer time can be underestimated if relying on $S_y$ derived from pumping test
• The distribution in effective porosity is variable, reflecting the aquifer heterogeneities
• Lower effective porosities reflect that contamination will follow the “path of least resistance” (i.e. via advective zones) while $S_y$ is more a bulk parameter
• This is even more pronounced in fractured rock aquifers. For example, effective porosities as low as 0.03 % have been measured in limestone.

SOURCE: SUTHERSAN, 2016
Limestone is a dual porosity medium (fracture and matrix) that is used extensively as an aquifer for potable water supply in the UK and Northwest EU.

A key factor of vulnerability is migration of nitrogen and pesticides resulting from agricultural activities through the unsaturated zone.

There is a need to better predict the recharge mechanisms and integrate these into the vulnerability.
UNSATURATED ZONE

APPLICATION

SOURCE: BROUYERE, 2004
# UNSATURATED ZONE

**APPLICATION**  
*Source: Brouyere, 2004*

<table>
<thead>
<tr>
<th>Key Parameters</th>
<th>First Test</th>
<th>Second Test</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vertical Distance</td>
<td>10 m</td>
<td>10 m</td>
</tr>
<tr>
<td>Tracer</td>
<td>KCl</td>
<td>KI</td>
</tr>
<tr>
<td>Mass injected</td>
<td>100 kg</td>
<td>10 kg</td>
</tr>
<tr>
<td>Volume injected</td>
<td>~ 300 L</td>
<td>30 L</td>
</tr>
<tr>
<td>Chaser</td>
<td>300 L/h</td>
<td>0 L/h</td>
</tr>
</tbody>
</table>

![Graph showing concentration data over time](image)

- **First Test**
  - Chloride peak at ~11h
  - Potassium peak at ~5h

- **Second Test**
  - Peak not clearly indicated
  - Transfer time ~1 year

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*Source: Brouyere, 2004*
LIMESTONE MATRIX
- High porosity: $n_m \sim 30 - 40\%$
- Microporosity ($\sim 1 \, \mu m$) $\Rightarrow$ very high capillary tension
- Low hydr. conductivity: $K_{s,M} \ll 10^{-9}$ to $10^{-8} \, m/s$

LIMESTONE FRACTURES
- Low porosity: $n_f < 1\%$
- Larger openings $\Rightarrow$ lower capillary tension
- High hydr. conductivity: $K_{s,F} >> 10^{-3} \, m/s$

➢ First test shows long tail in breakthrough curve, reflective of strong back diffusion of tracer into fractures

SOURCE: BROUYERE, 2004
Most decisions regarding contaminated groundwater are driven by contaminant concentrations. However, exceeding concentration criteria does not necessarily mean that the groundwater contamination poses an unacceptable risk. Making decisions regarding contaminated groundwater can be improved by also considering the contaminant mass flux:

\[ J = K i C \]

\[ Q = K i \]
GROUNDWATER FLUX

FINITE VOLUME POINT DILUTION METHOD

SOURCE: BROUYERE, 2008

Monitoring during tracer injection
Monitoring after tracer injection

Dilution >> when \( Q_t >> \)

\[ Q_1^t < Q_2^t \]

\( C_{\text{cw}} \)
\( C_{\text{inj}} \)

\( Q_t, C_t \rightarrow Q_{\text{out}}, C_{\text{out}} \)

Tracer liquid tank

Real time tracer monitoring

Dosing Pump

Tap for sampling operations

Pump for water recirculation

\( Q_{\text{recirculation}}, C_{\text{cw}} \)
• Groundwater flux measurement depends on:
  • Detection limit of tracer (0.01 μg/L to 1 μg/L)
  • Control on tracer injection and sampling flow rates (< 0.1 L/min)

➢ Basis of accuracy

• Real-time measurement

➢ Particularly suited to dynamic environments (e.g. tidal zones, discharge to surface water, active remediation)
• Another “toolbox” to test aquifers
• Versatile - Nearly infinite number of approaches
• Importance of developing a hypothesis to be tested
• Design applied tracer test to verify this hypothesis
• Key design considerations include – Injection approach, tracer choice, tracer monitoring, QA/QC
FUTURE DEVELOPMENT

“SMART” APPLIED TRACERS

SOURCE: KNAPP, 2017

Resazurin + e⁻ → Resorufin

A

B

C

\[
g(h) = k \exp(-kT)
\]

\[
\frac{\Delta Z_1}{q_{in,1}} = \lambda(z_1) \frac{Z_1}{f_{rec,1}}
\]

\[
\frac{\Delta Z_2}{q_{in,2}} = \lambda(z_2) \frac{Z_2}{f_{rec,2}}
\]

\[
\frac{\Delta Z_3}{q_{in,3}} = \lambda(z_3) \frac{Z_3}{f_{rec,3}}
\]
ENVIRONMENTAL TRACERS
ENVIRONMENTAL TRACERS

KEY PRINCIPLES

BASIC IDEA
- Use parameters that are “freely” available in the environment
- Monitor spatial or temporal distribution of parameters

IN PRACTICE
- Can accommodate for large scale and slow groundwater movement
- Sampling and analysis can require stringent conditions (e.g. lab turnaround time for some tracer can be in the order of 3 to 6 months)
- Australia is a global leader in this!
ENVIRONMENTAL TRACERS

FIELD PARAMETERS, MAJOR IONS, ISOTOPES

- Relatively low to moderate cost
- Typically used to assess mixing processes

COMPOND SPECIFIC ISOTOPOPE ANALYSIS

- Moderate cost
- Typically used to assess degradation processes

AGE DATING AND RADIOACTIVE TRACER

- Moderate to high cost
- Connectivity and flowpaths

Background and QA/QC!!!
Measuring the rate of groundwater discharge is key to aquatic ecology studies.

The groundwater – surface water interface is a dynamic zone with a number of mixing processes involved.

This interface is also subject to strong redox gradients, resulting in biological activity.
Surface water is enriched in $\delta^2$H and $\delta^{18}$O due to evaporation.

Terrestrial groundwater is depleted in $\delta^2$H and $\delta^{18}$O.

Mixing proportion can be estimated using mixing line between the two end members.

Seepage water (i.e. water actually discharging) is dominated by river water (~90%).

Indicates significant mixing before discharge in the river.
GROUNDWATER DISCHARGE

COMPONENT SPECIFIC ISOTOPE ANALYSIS

• Contrast in isotopic signature between plant, groundwater, hyporheic zone and surface water
  ➢ Enables an understanding of different contributors in nitrogen

• Enrichment in heavy isotope from the deep part to the shallow part of the hyporheic zone
  ➢ Indicates significant nitrogen removal rate (up to 80% removal)

SOURCE: LAMONTAGNE, 2018
Assessing contaminant degradation is key to risk assessment or remedial design.

Enhanced bioremediation is one of the most cost-effective remediation techniques over other in-situ techniques (ISCO, thermal, surfactant).

Sometimes monitored natural attenuation can be the most practical remediation option.

When organic contaminants degrade, there is an enrichment of heavy isotopes in the remaining contaminant pools (Environmental forensics).

Compound specific isotope analysis can:
- Support an assessment of spatial and temporal trends in biodegradation
- Form a basis to derive degradation rates
CONTAMINANT DEGRADATION

1,1,1-TCA IN FRACTURED LIMESTONE

SOURCE: PALAU, 2015
CONTAMINANT DEGRADATION

RESULTS AND OUTCOME

- Fractionation results for reduction and oxidation obtained via batch testing (laboratory)
- Field data indicate that 1,1,1-TCA tends to degrade following abiotic reaction
- Abiotic degradation is slow and difficult to monitor using more conventional analysis
- Provides possible perspective on remedial approach:
  - Enhanced biodegradation – limestone aquifer with long plume, amendment delivery and zone of influence
  - Monitored natural attenuation – slow degradation rate

SOURCE: PALAU, 2015
GROUNDWATER RECHARGE

**CONTEXT**

Groundwater is "ageing" along the flowpath, with surface water being the youngest. The following environmental tracers can be used to "date" groundwater:

- Noble gases (e.g. He)
- Natural radionuclides (e.g. radon-222)
- Radionuclides with both natural and anthropogenic sources (e.g. $^3$H)
- Anthropogenic tracers (e.g. CFCs)

Age dating can be used to evaluate:

- Connectivity with geological formations
- Aquitard leakage
- Aquifer recharge rates
- Groundwater – surface water interaction

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A groundwater sample never has a unique “Age” but an Age Distribution

*Source: Suckow, 2014*
GROUNDWATER RECHARGE

GROUNDWATER – SURFACE WATER INTERACTION

- $^{14}$C expressed in pmC (percent modern carbon)
  - Higher value indicative of younger groundwater
- $^3$H expressed in TU (tritium units)
  - Higher values indicative of younger groundwater
- $^4$He expressed in cm$^3$ STP g$^{-1}$ (standard temperature and pressure)
  - Higher values indicative of older groundwater

- Losing stream, influenced by recent pumping activities

SOURCE: LAMONTAGNE, 2015
• Toolbox is complementary to “Applied Tracers”
• Also versatile - Nearly infinite number of approaches
• Multiple lines of evidence
• Importance of involving practitioners for scoping, sample collection, laboratory analysis and data interpretation (Don’t try to replicate ten years worth of research)
FUTURE DEVELOPMENT

INTEGRATED LABORATORY AND RESEARCH FACILITY

• Increase accessibility to $^{34}\text{S}$ analysis
  ➢ Useful in geochemical analysis
    (MAR/ASR, acid mine drainage, etc)

• Development of noble gases analysis
  ➢ Alternative to overcome anthropogenic influence in age dating assessment
QUESTIONS?
References

IN ORDER OF APPEARANCE


References (Cont’d)

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References (Cont’ed)

