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

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OUTLINE

INTRODUCTION

INTRODUCTION

DIFFERENCES BETWEEN APPLIED AND ENVIRONMENTAL TRACERS

Applied Tracers

- Voluntarily introduced in groundwater
- Known quantity
- More controlled

Examples: Bromide, fluorescein

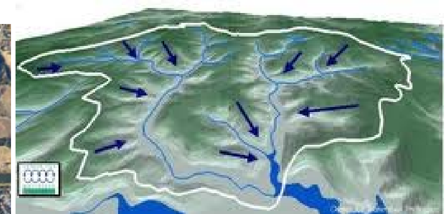
Environmental Tracers

- Already present in groundwater
- Unknown quantity
- Less controlled

Examples: Temperature, major ions, contaminants, isotopes

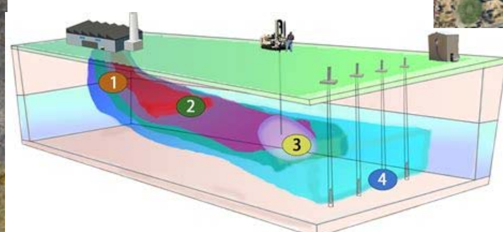
INTRODUCTION

AT WHAT SCALE DO YOU NEED TO WORK?



Catchment

Site



Plume

Localised Zone

10^{-1} m   1 m   10 m 10^{2} m 10^{3} m

INTRODUCTION

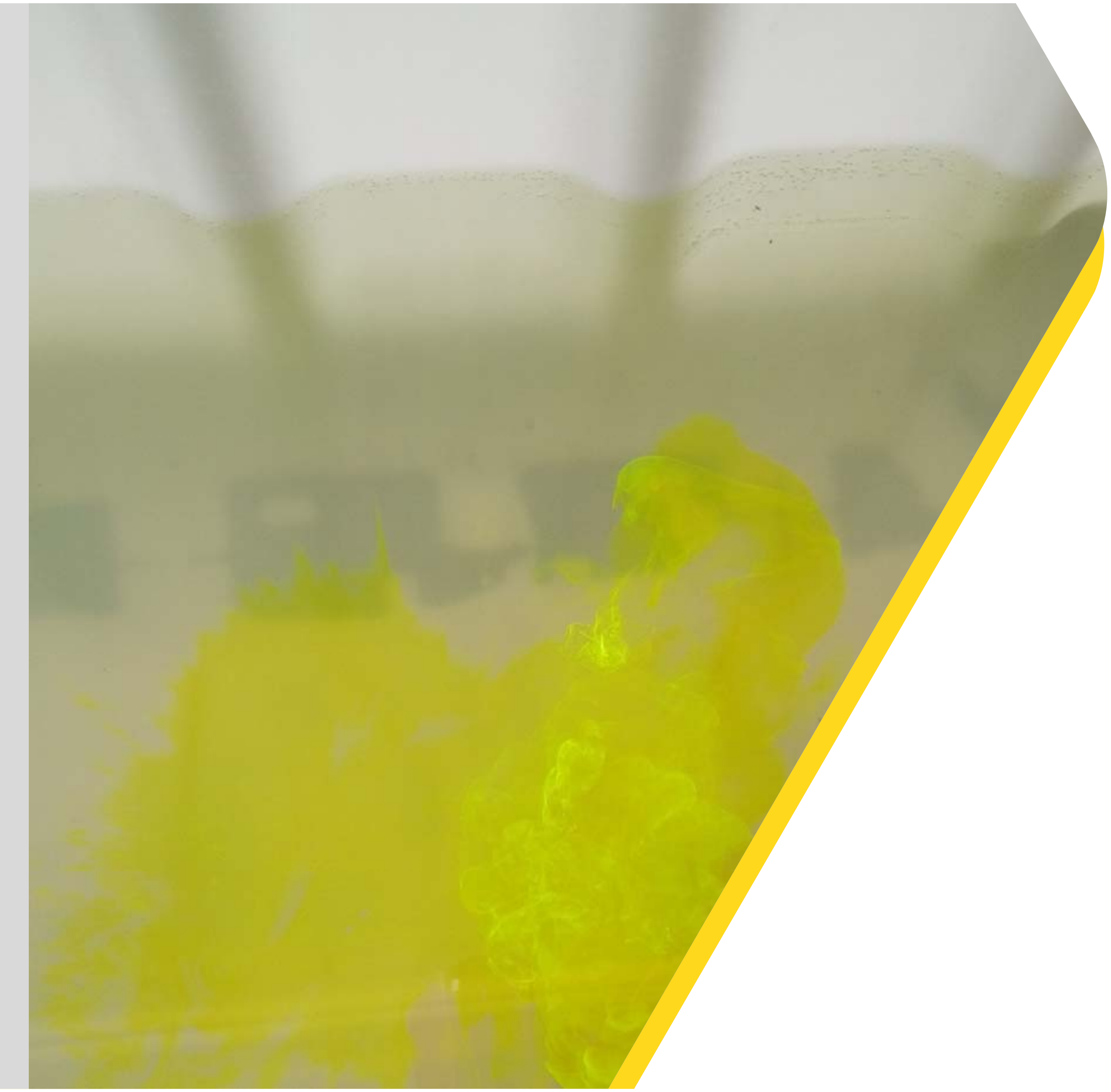
OTHER KEY CONSIDERATIONS

- 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

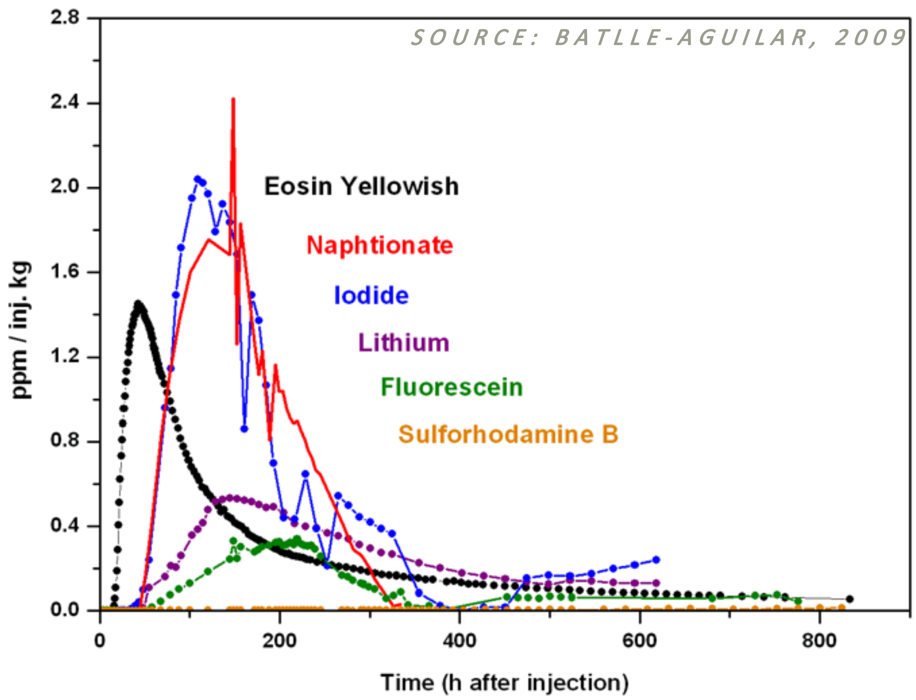
GOLDER



GOLDER

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

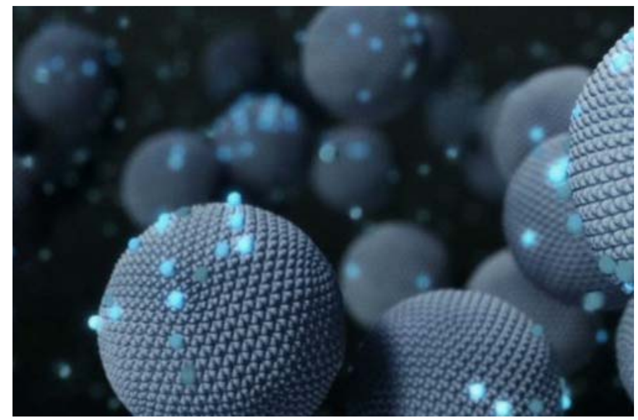
- Analysis is conventional
- Higher detection limit (10 – 100 µg/L)
- Background can be high
- Toxicity

FLUORESCENT DYES

- Very low detection limit (0.001 µg/L)
- Background, interferences
- Innocuous (USEPA, German EPA)

(Amino-G acid excited by UV)

NANO TRACERS



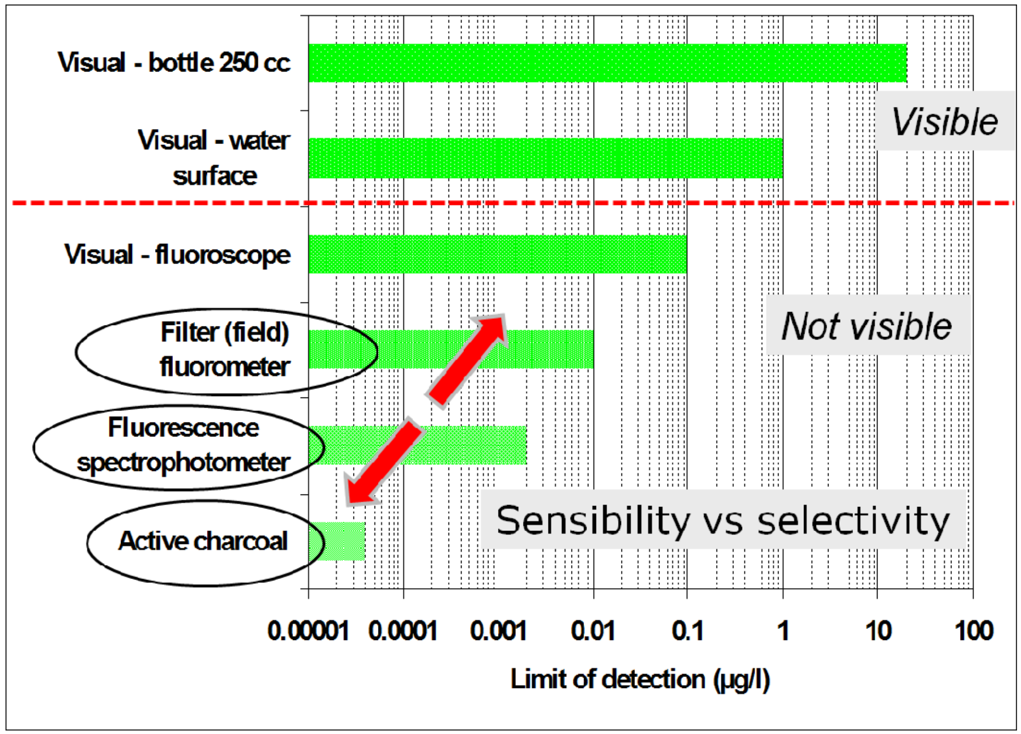
- Analysis is unconventional
- Specificity
- Requires specific risk assessment

INSTRUMENTATION LIMITS FOR FLUORESCENT DYES

TYPICAL DETECTION LIMITS

Fluorescent tracer	Limit of detection (µg/L)
Fluorescein	0.002
Sulforhodamine B	0.006
Eosine	0.01
Tinopal	0.01
Amino G acid	0.02
Pyranine	0.02
Naphthionate	0.05
Photine	1

ANALYSIS TYPE - FLUORESCEIN



GOLDER

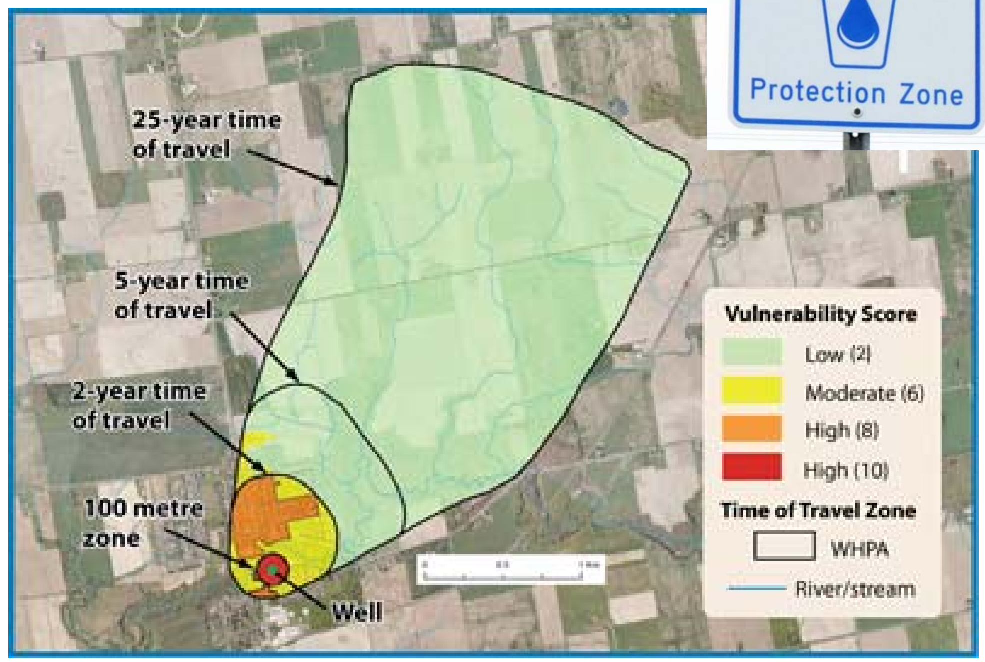
PROTECTION ZONES

OPPOSITE TO GQRUZ

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

$$v = \frac{K\,i}{n_e}$$

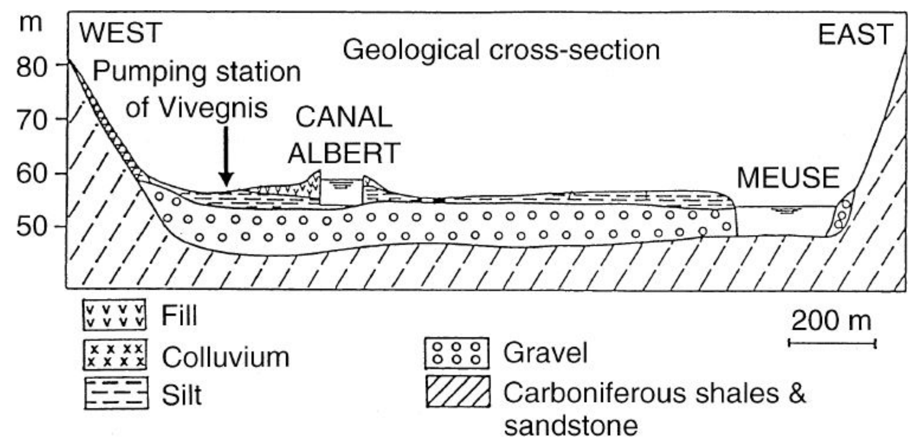


PROTECTION ZONES

APPLICATION

SOURCE: DEROUANE AND DASSARGUES, 1998

- 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

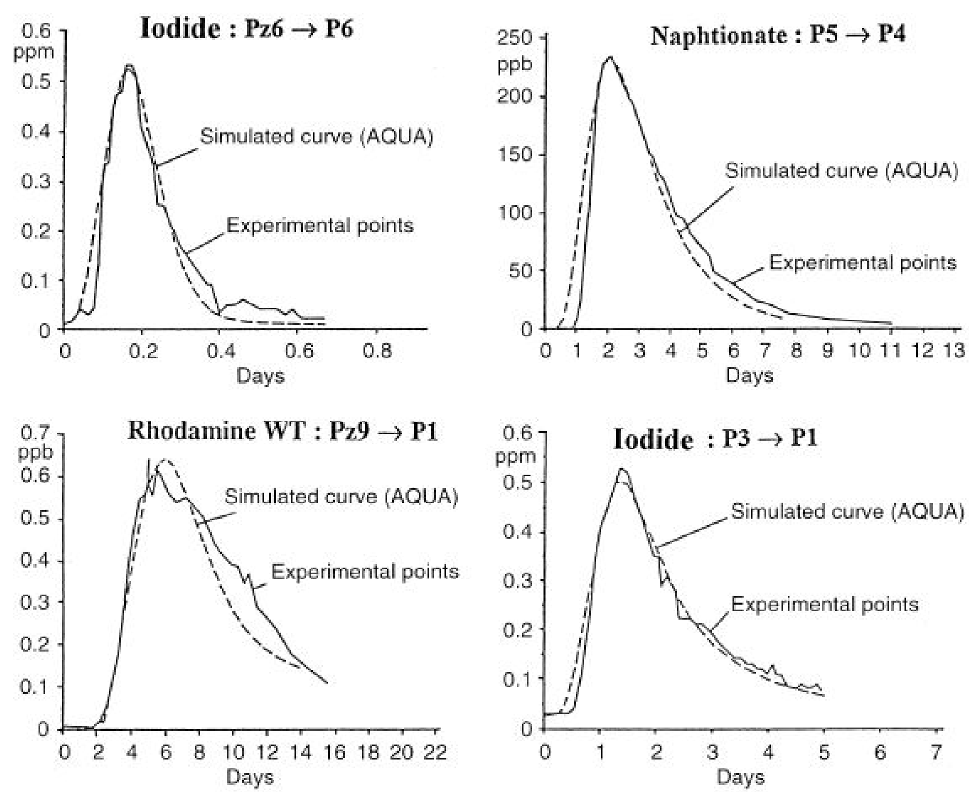


PROTECTION ZONES

APPLICATION - RADIALLY CONVERGING FLOW

SOURCE: DEROUANE AND DASSARGUES, 1998

Distance (m)	Tracer	Effective Porosity n_e (%)
27	KI	4.8
49	KI	7.2
78	Naphthionate	5.6
88	LiCl	8.2
91	Fluorescein	5.8
115	Rhodamine WT	4.7

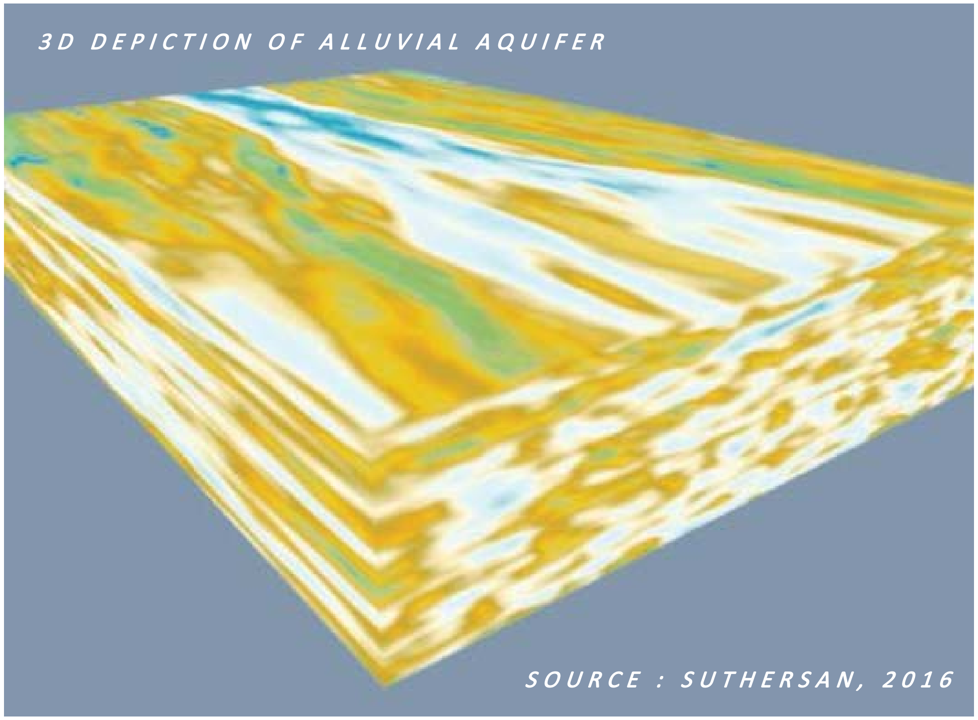


GOLDER

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 Sy 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.



UNSATURATED ZONE

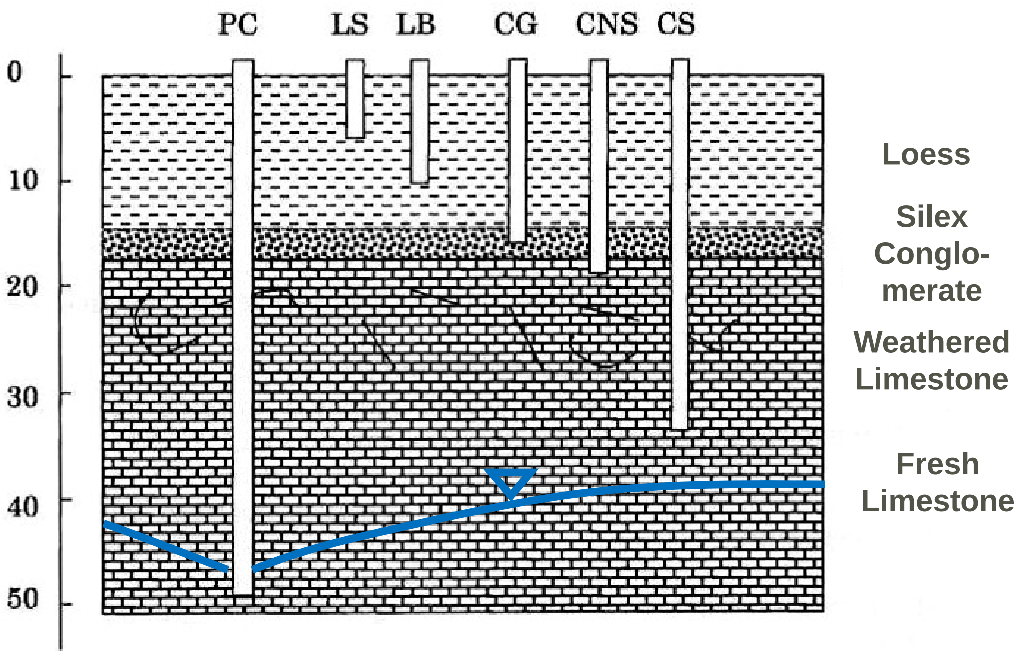
CONTEXT

- 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

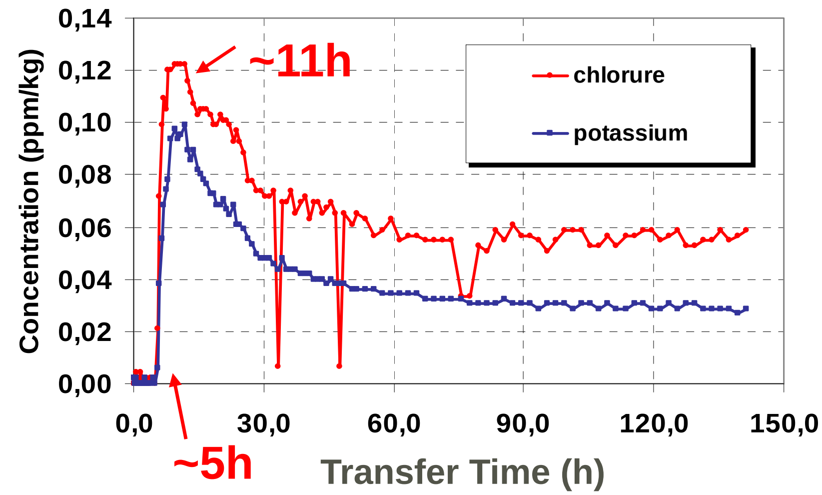


UNSATURATED ZONE

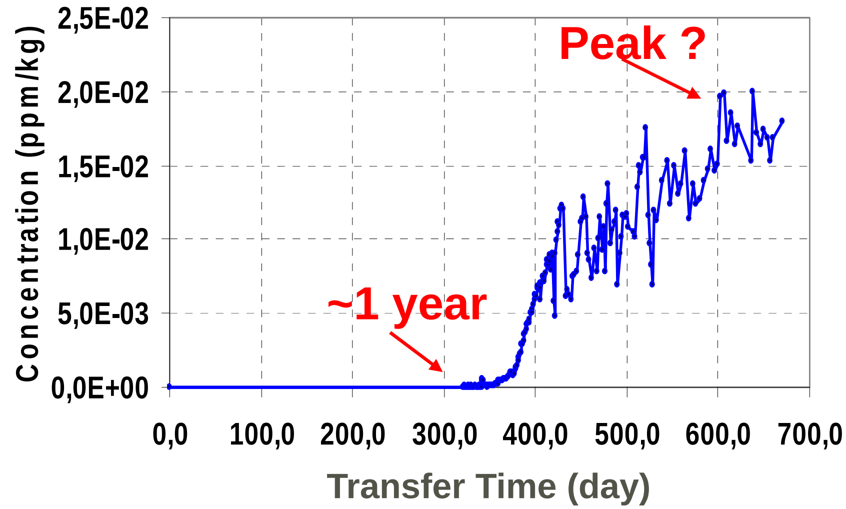
APPLICATION *SOURCE: BROUYERE, 2004*

Key Parameters	First Test	Second Test
Vertical Distance	10 m	10 m
Tracer	KCl	KI
Mass injected	100 kg	10 kg
Volume injected	~ 300 L	30 L
Chaser	300 L/h	0 L/h

FIRST TEST



SECOND TEST

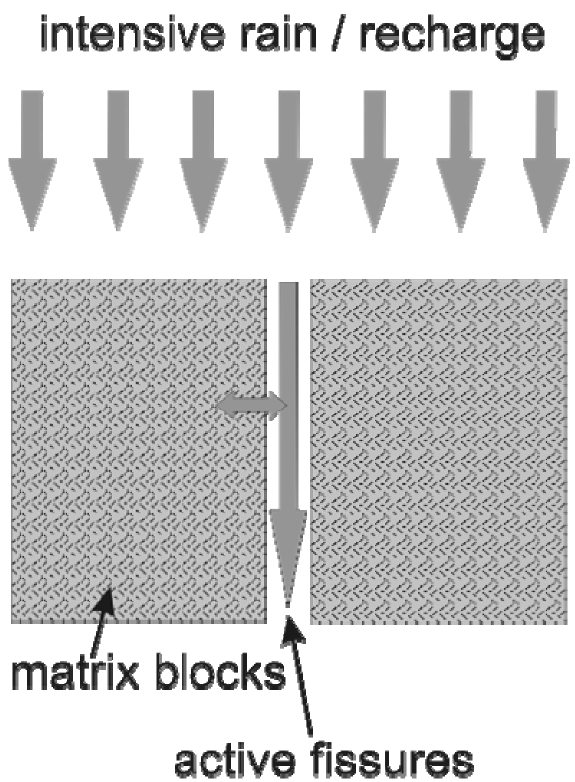


GOLDER

UNSATURATED ZONE

OUTCOMES

SOURCE: BROUYERE, 2004



LIMESTONE MATRIX

- High porosity: n_m ~ 30 – 40 %
- Microporosity (~ 1 μm) $\Rightarrow$ very high capillary tension
- Low hydr. conductivity: $K_{s,M} << 10^{-9}$ to 10^{-8} m/s

LIMESTONE FRACTURES

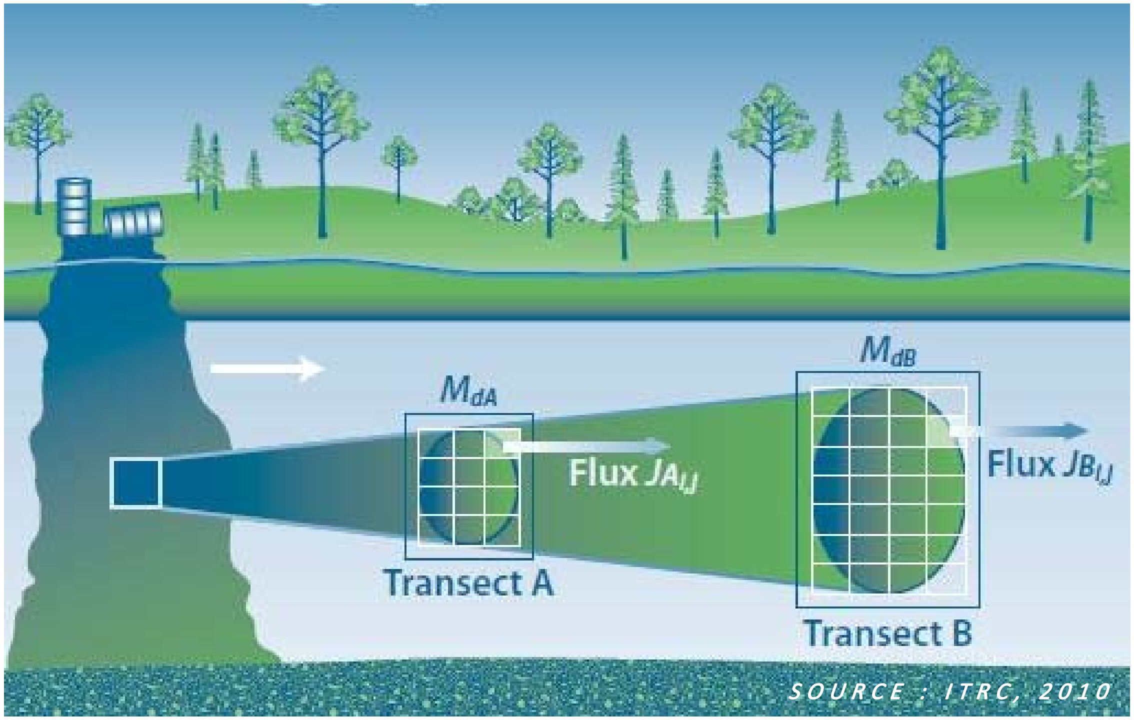
- Low porosity: $n_f < 1\%$
- Larger openings $\Rightarrow$ lower capillary tension
- High hydr. conductivity: $K_{s,F} >> 10^{-3}$ m/s

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

GROUNDWATER FLUX

CONTEXT

SOURCE: ITRC, 2010



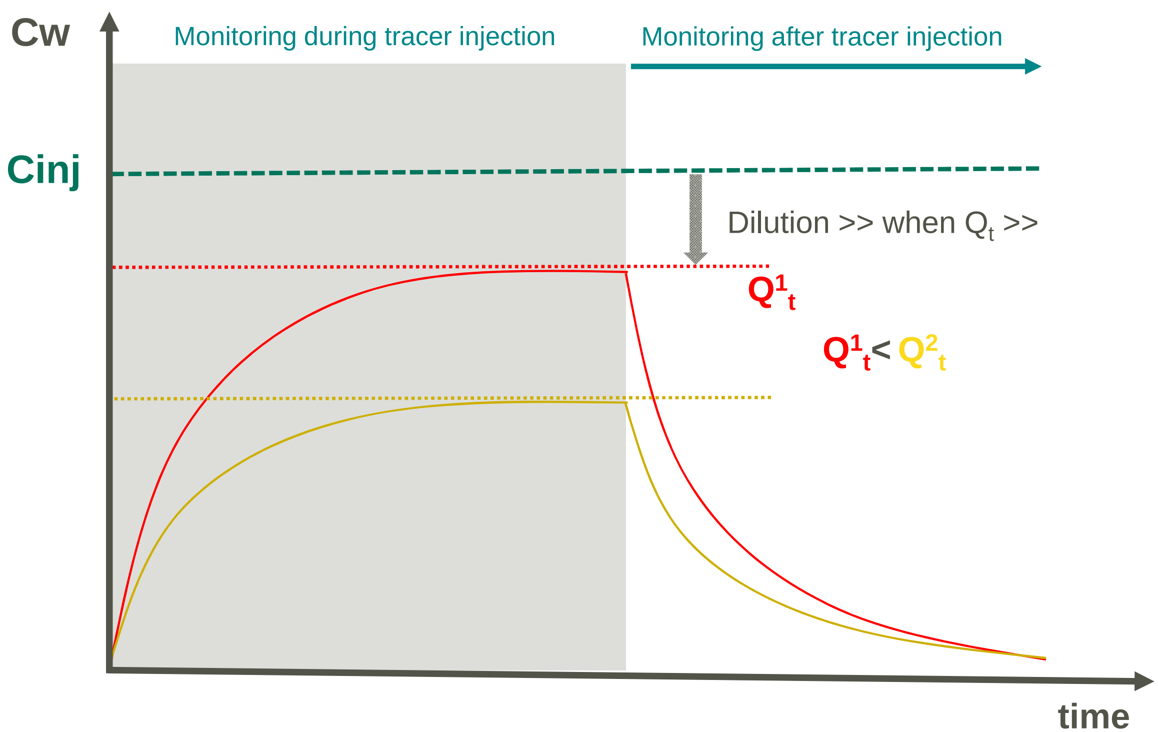
- Most decisions regarding contaminated groundwater are driven by contaminant concentrations.
- However, exceeding concentration criteria does not necessarily mean that the groundwater contamination poses an unacceptable risk
- Making decisions regarding contaminated groundwater can be improved by also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

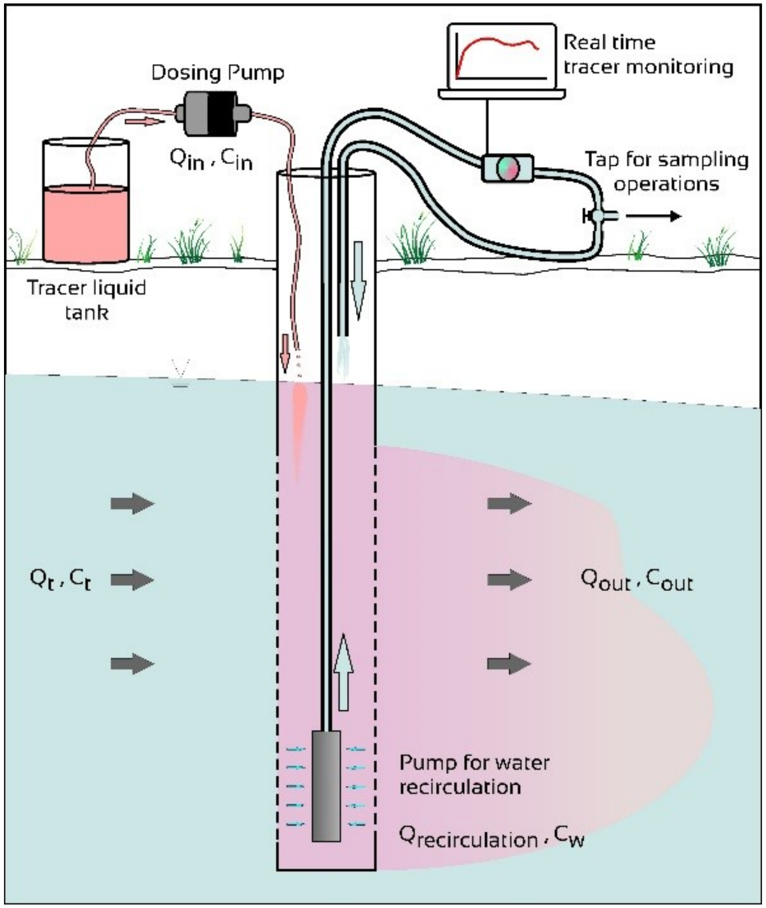
$$J = K\ i\ C$$
$$Q = K\ i$$

GROUNDWATER FLUX

FINITE VOLUME POINT DILUTION METHOD

SOURCE: BROUYERE, 2008





GROUNDWATER FLUX

APPLICATION – FINITE VOLUME POINT DILUTION METHOD

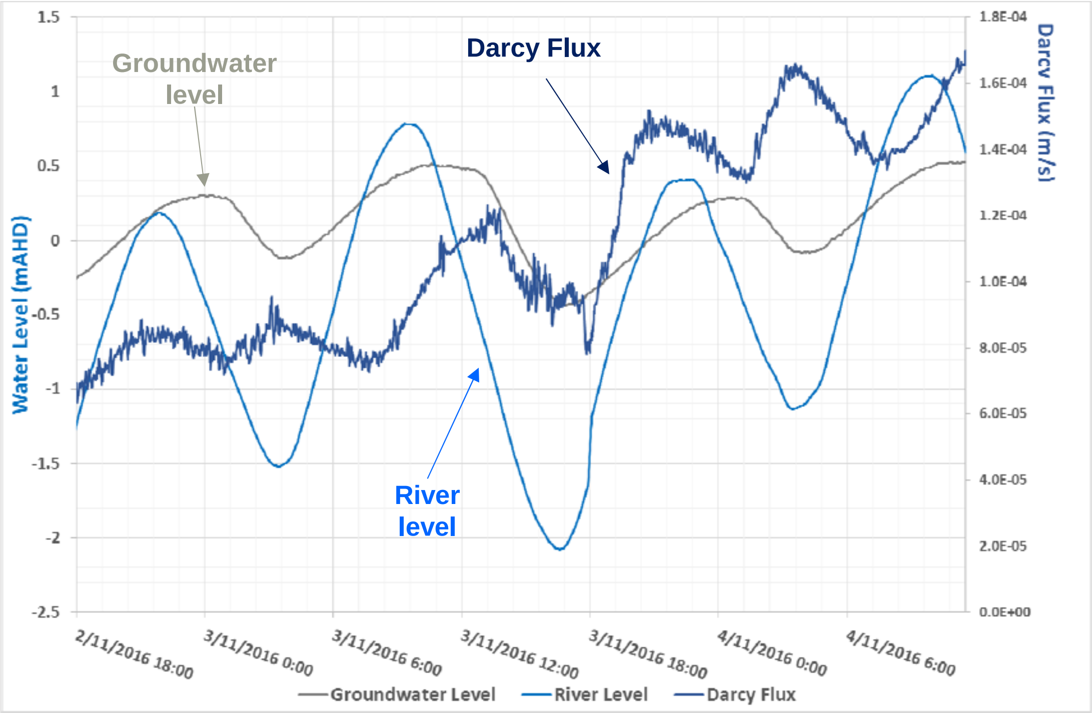
SOURCE: THIELE, 2017

- 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)



CONCLUSION

APPLIED TRACERS

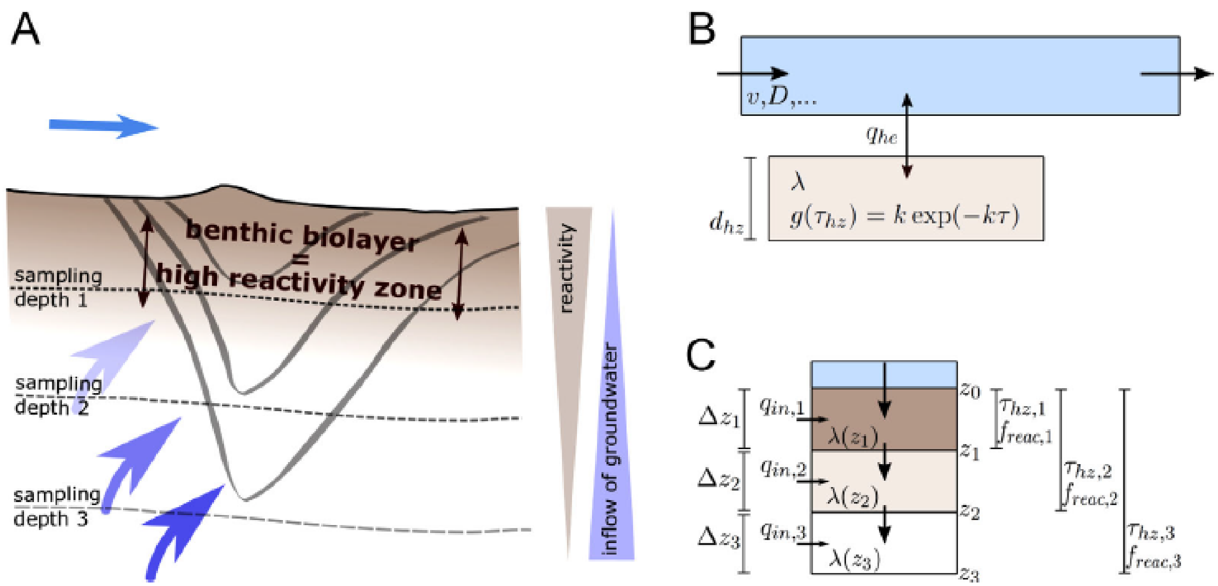
- Another “toolbox” to test aquifers
- Versatile - Nearly infinite number of approaches
- Importance of developing a hypothesis to be tested
- Design applied tracer test to verify this hypothesis
- Key design considerations include – Injection approach, tracer choice, tracer monitoring, QA/QC

FUTURE DEVELOPMENT

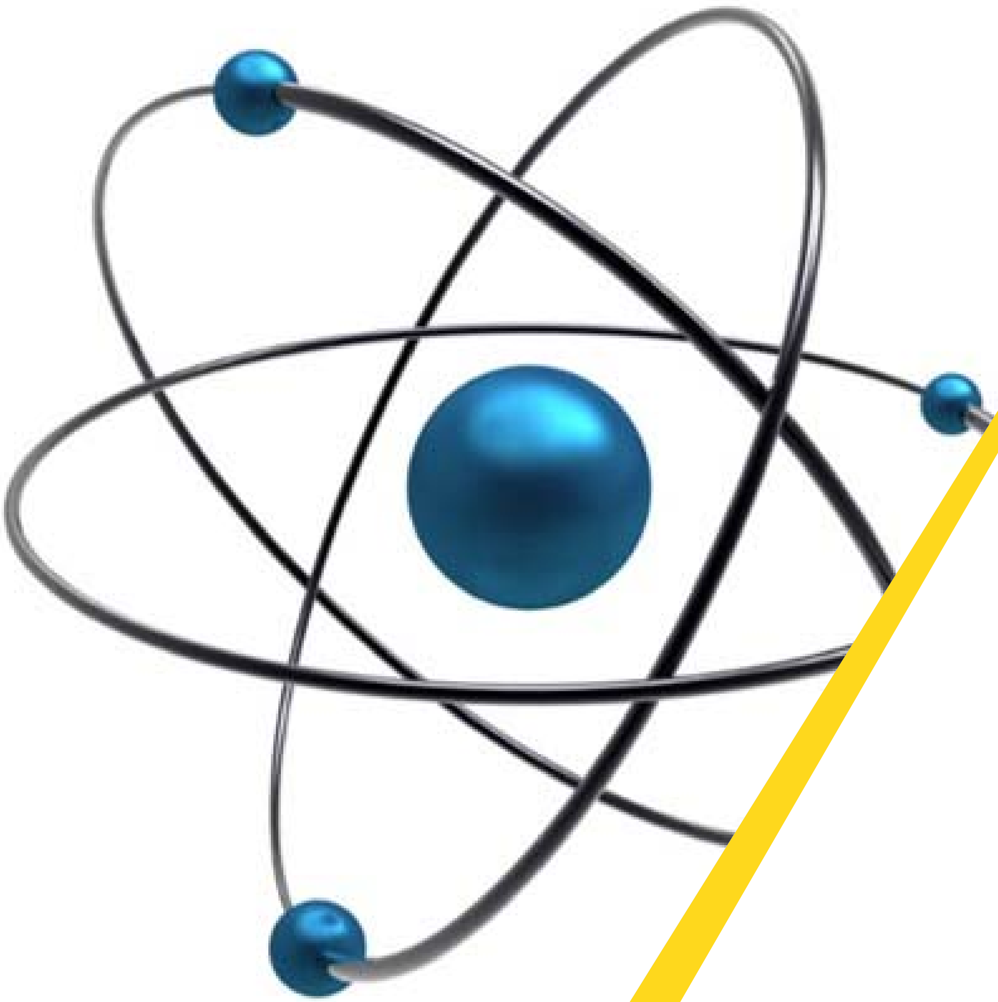
SOURCE: KNAPP, 2017

"SMART" APPLIED TRACERS

Resazurin + e⁻ -> Resorufin



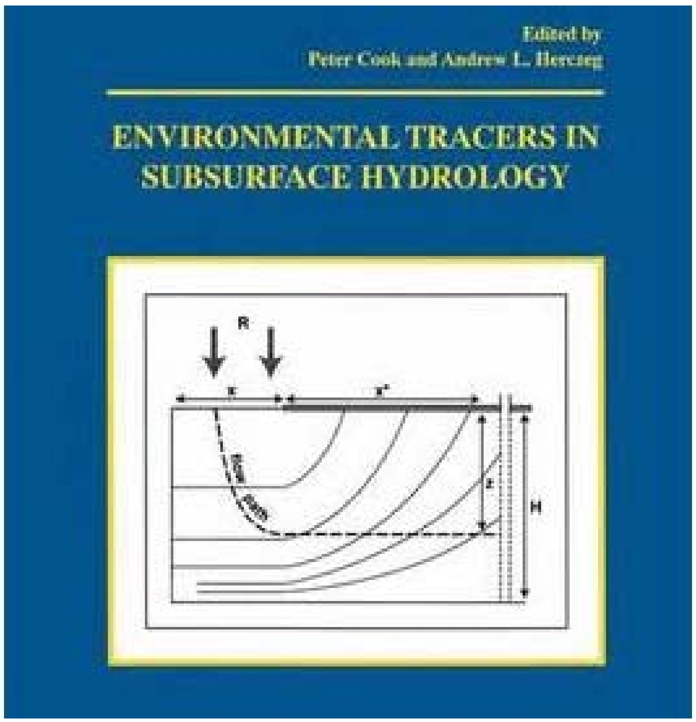
ENVIRONMENTAL TRACERS



GOLDER

ENVIRONMENTAL TRACERS

KEY PRINCIPLES



BASIC IDEA

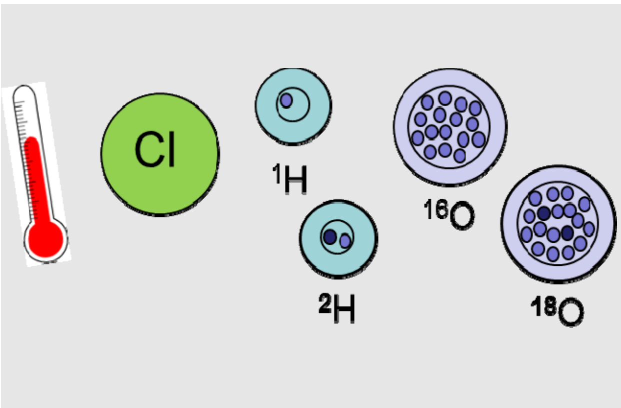
- Use parameters that are “freely” available in the environment
- Monitor spatial or temporal distribution of parameters

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!

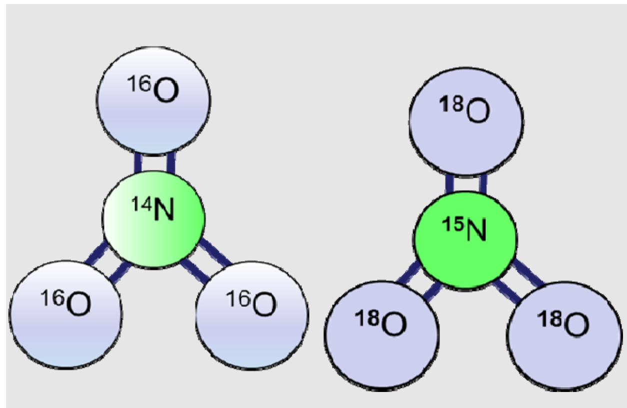
ENVIRONMENTAL TRACERS

FIELD PARAMETERS, MAJOR IONS, ISOTOPES



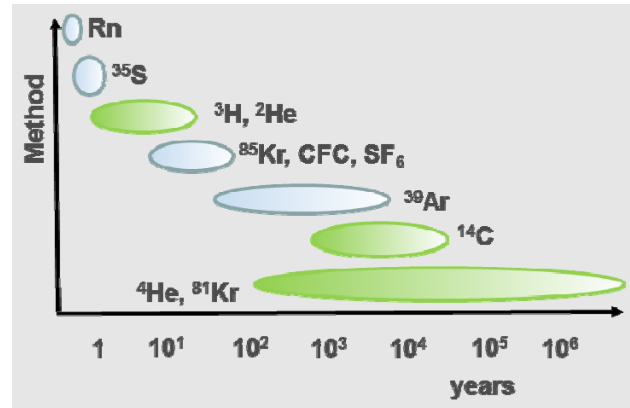
- Relatively low to moderate cost
- Typically used to assess mixing processes

COMPOUND SPECIFIC ISOPOTOPE ANALYSIS



- Moderate cost
- Typically used to assess degradation processes

AGE DATING AND RADIOACTIVE TRACER



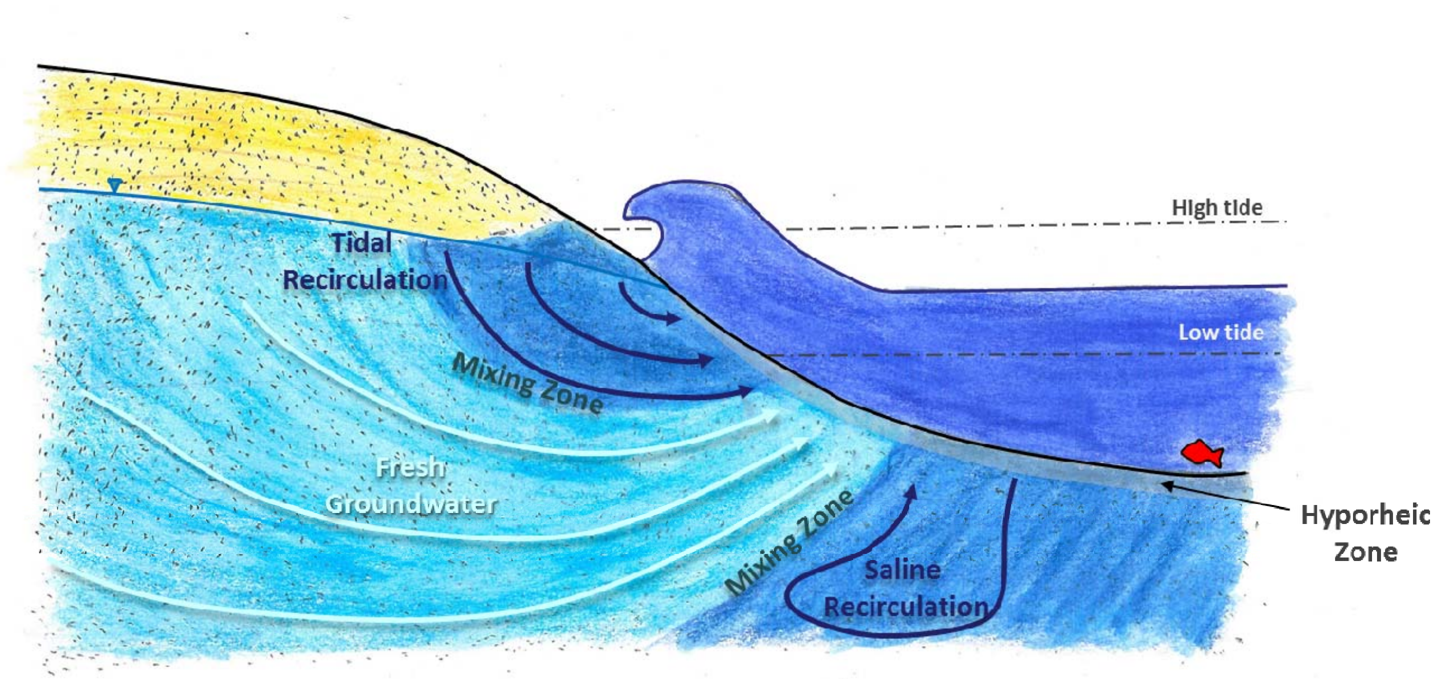
- Moderate to high cost
- Connectivity and flowpaths

Background and QA/QC!!!

GROUNDWATER DISCHARGE

CONTEXT

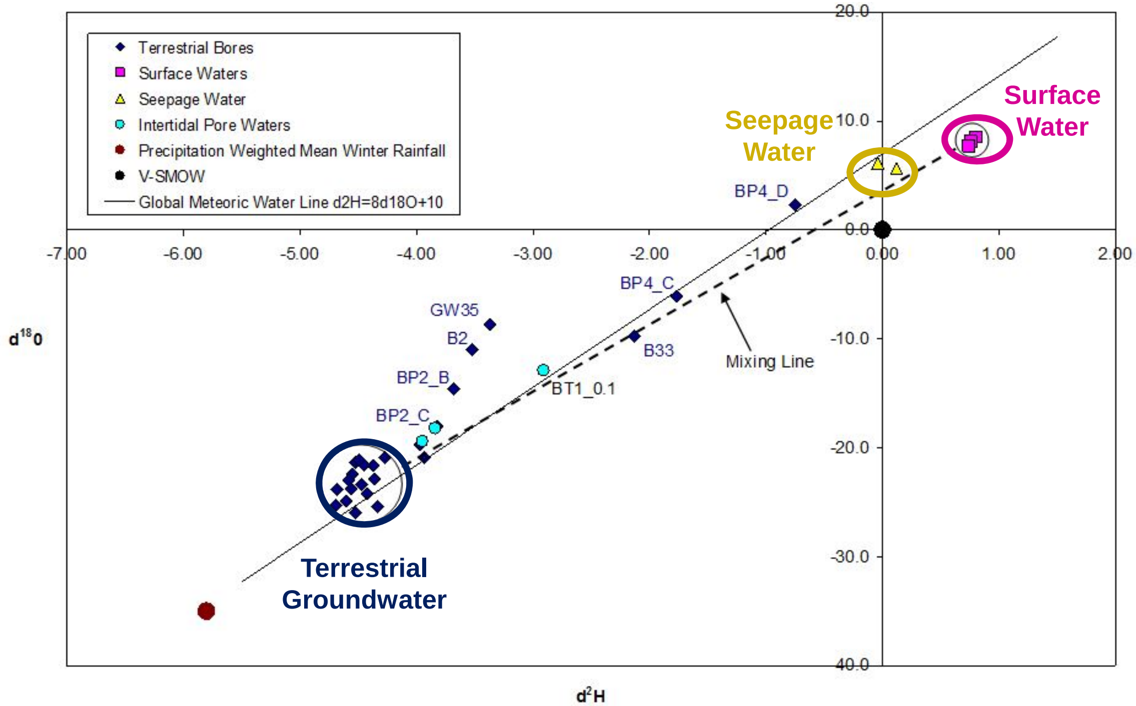
- Measuring the rate of groundwater discharge is key to aquatic ecology studies
- The groundwater – surface water interface is a dynamic zone with a number of mixing processes involved
- This interface is also subject to strong redox gradients, resulting in biological activity



GROUNDWATER DISCHARGE

HEAVY ISOTOPE DATA IN WATER

SOURCE: DURAN, 2012



- Surface water is enriched in δ^2H and δ^{18}O due to evaporation
- Terrestrial groundwater is depleted in δ^2H and δ^{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

GOLDER

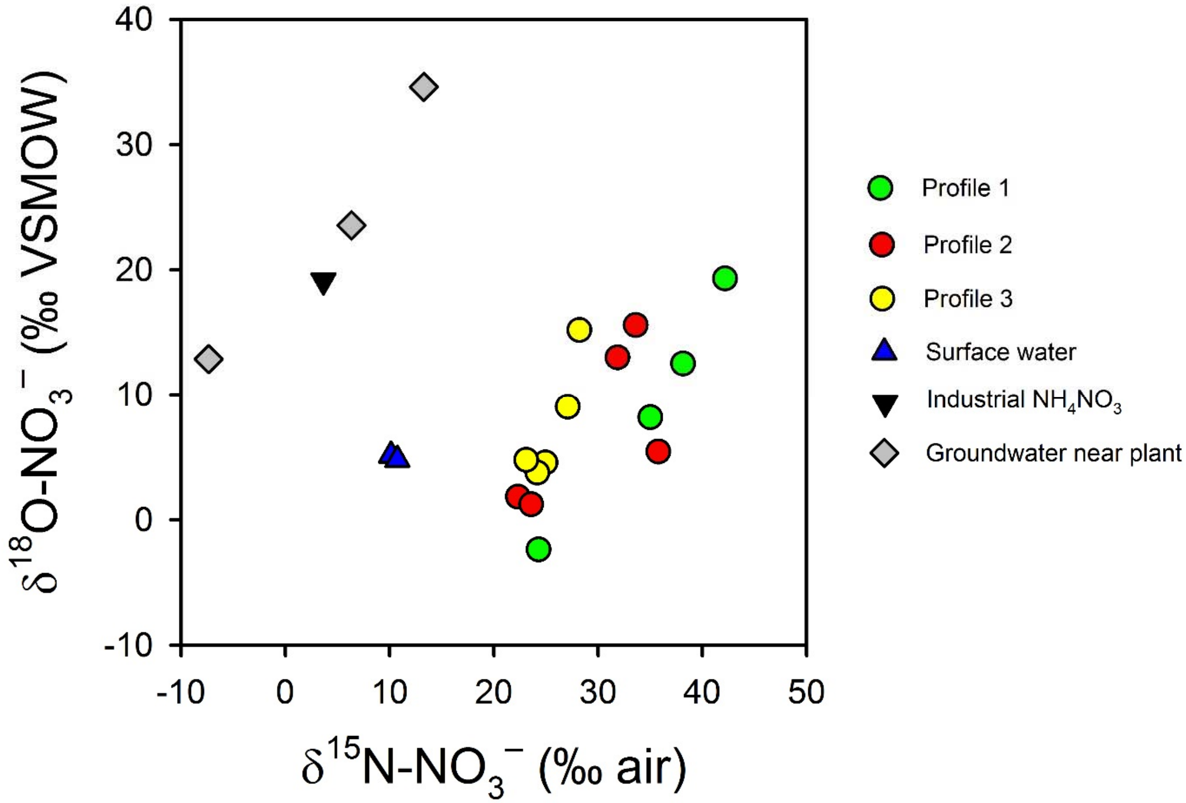
GROUNDWATER DISCHARGE

COMPOUND SPECIFIC ISOTOPE ANALYSIS

SOURCE: LAMONTAGNE, 2018

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

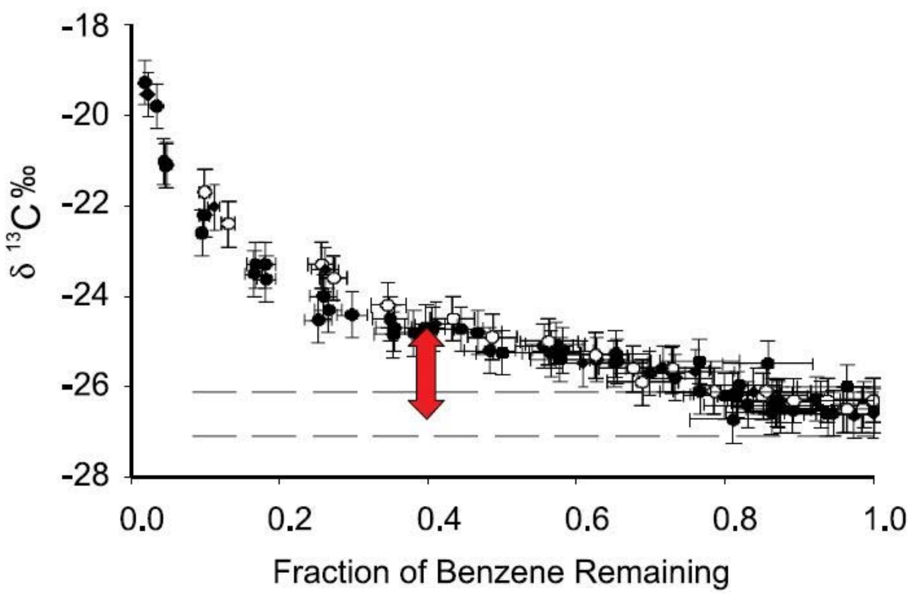
- Enrichment in heavy isotope from the deep part to the shallow part of the hyporheic zone
  - ➢ Indicates significant nitrogen removal rate (up to 80% removal)



CONTAMINANT DEGRADATION

CONTEXT – ISOTOPIC FRACTIONATION

SOURCE: USEPA, 2009

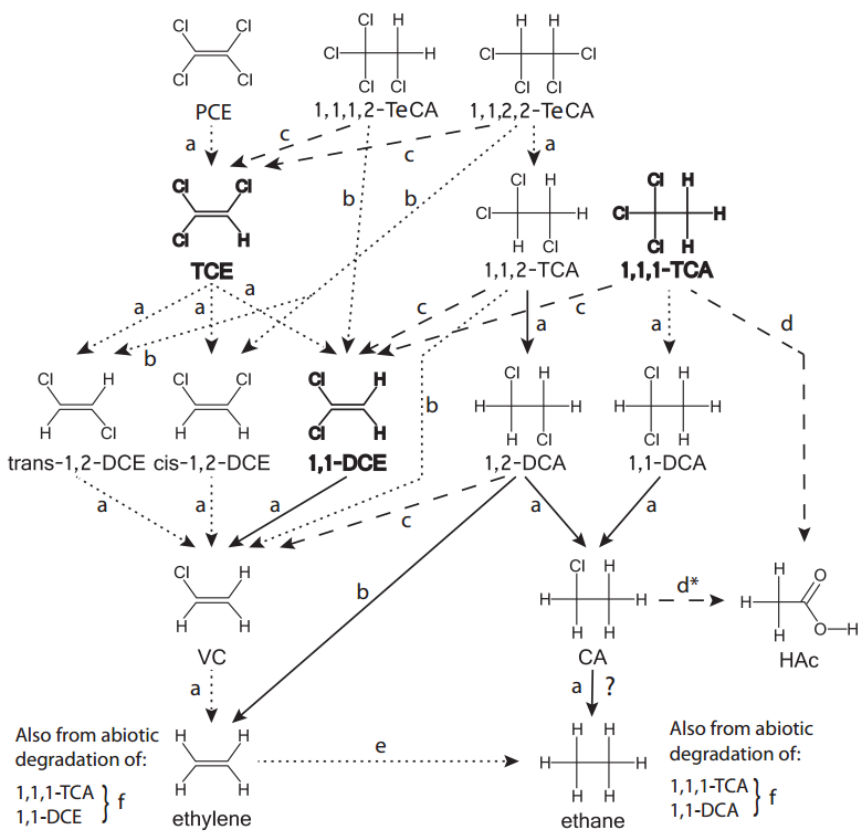


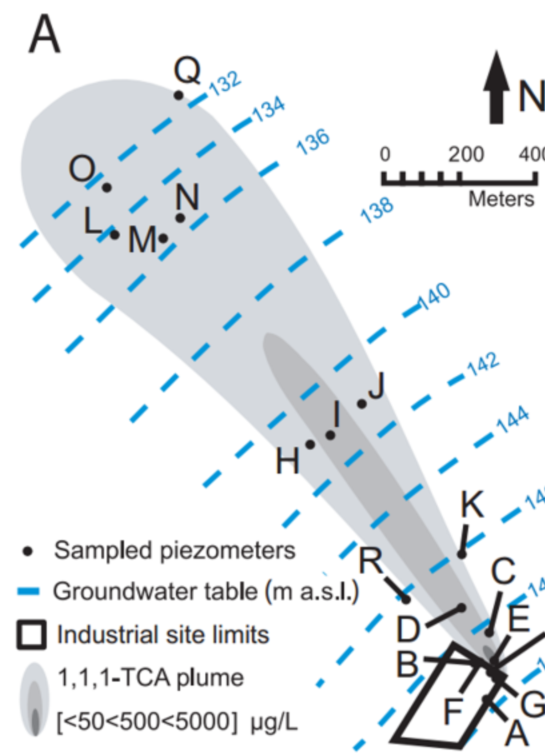
- Assessing contaminant degradation is key to risk assessment or remedial design
- Enhanced bioremediation is one of the most cost-effective remediation techniques over other in-situ techniques (ISCO, thermal, surfactant)
- Sometimes monitored natural attenuation can be the most practical remediation 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

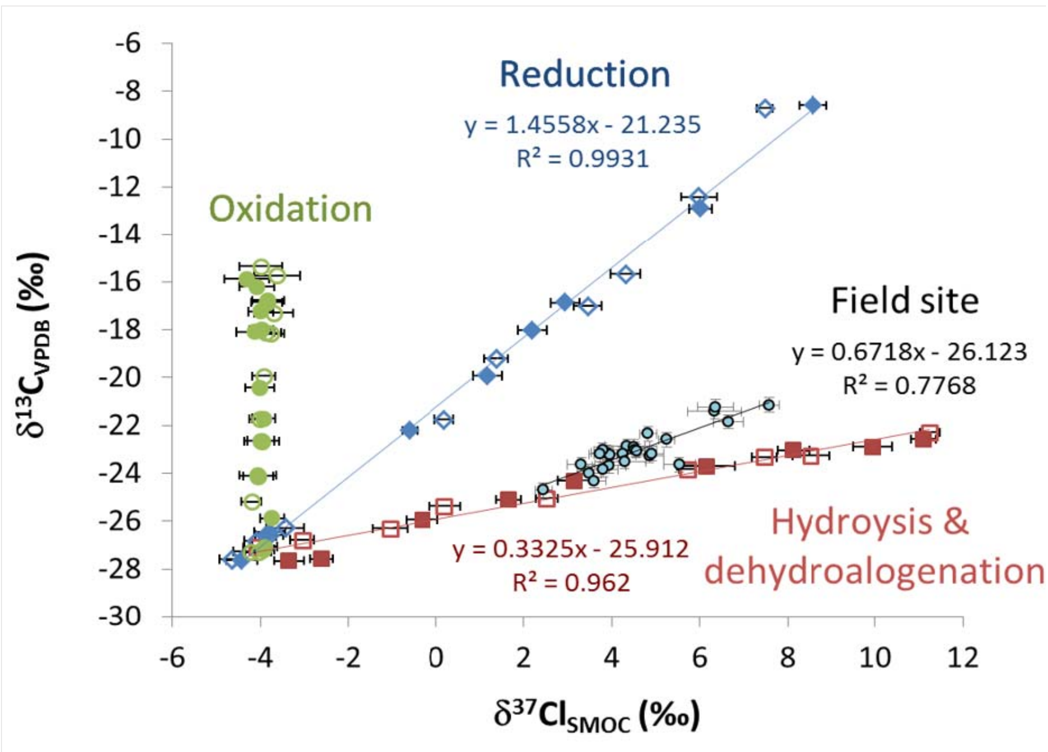




CONTAMINANT DEGRADATION

RESULTS AND OUTCOME

SOURCE: PALAU, 2015



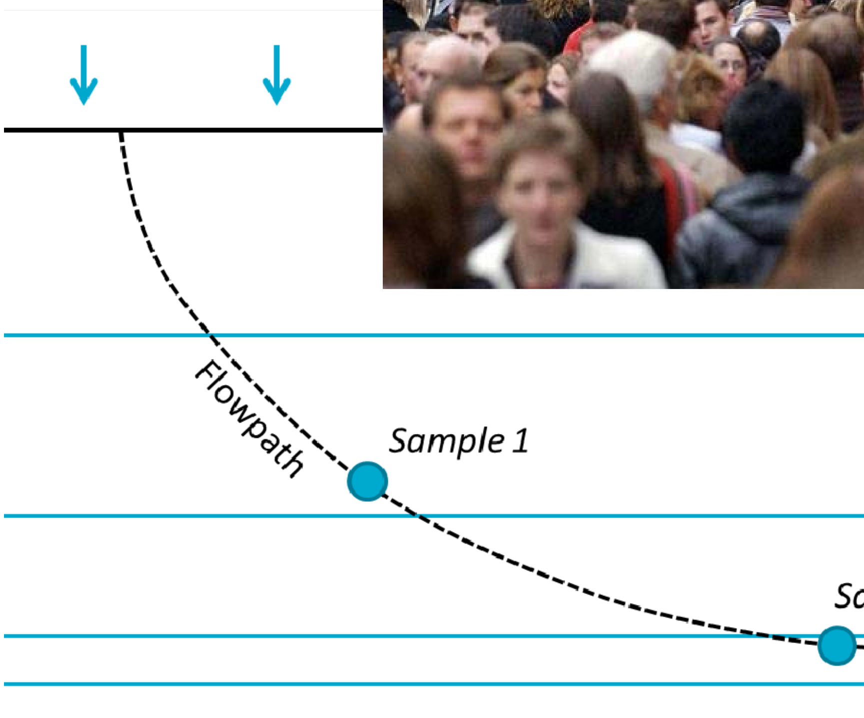
- Fractionation results for reduction and oxidation obtained via batch testing (laboratory)
- Field data indicate that 1,1,1-TCA tends to degrade following abiotic reaction
- Abiotic degradation is slow and difficult to monitor using more conventional analysis
- Provides possible perspective on remedial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

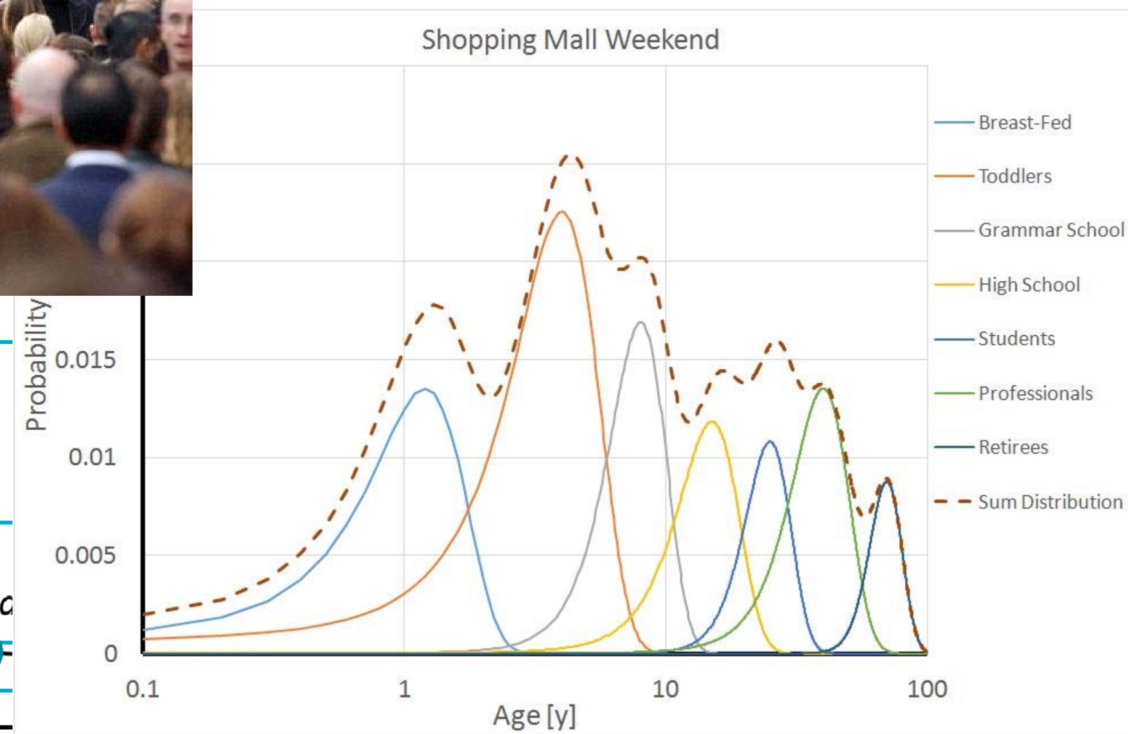
GROUNDWATER RECHARGE

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

CONTEXT

SOURCE: SUCKOW, 2014





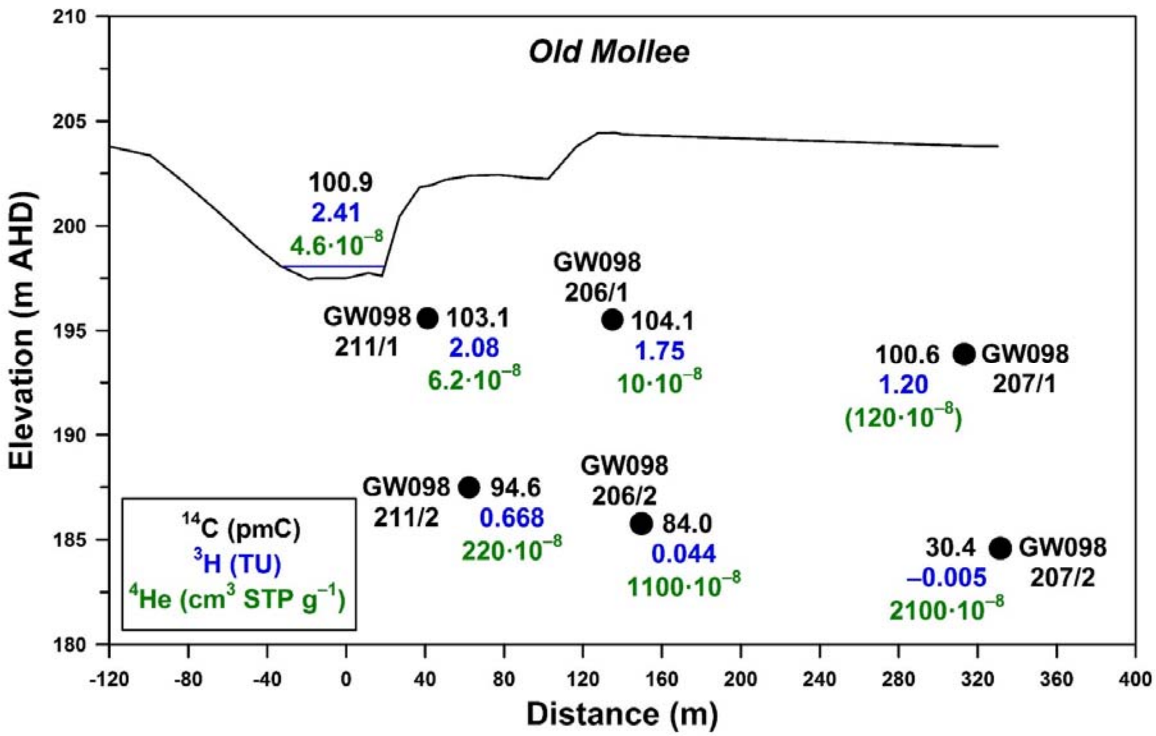
GROUNDWATER RECHARGE

GROUNDWATER – SURFACE WATER INTERACTION

SOURCE: LAMONTAGNE, 2015

- ^{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



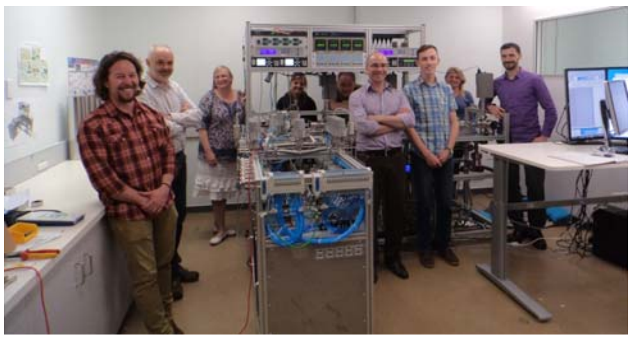
CONCLUSION

ENVIRONMENTAL TRACERS

- 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}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

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