Applied Tracer Techniques in Contaminant Hydrogeology

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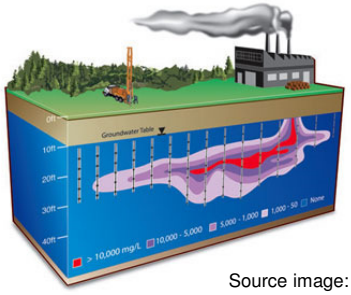
In most groundwater pollution studies, a sound characterization relies on a good understanding of the fate of dissolved pollutants in groundwater….

- Groundwater fluxes?
- Occurrence and magnitude of transport processes?
- Degradation – transformation mechanisms?



Source image:
http://www.solinst.com/Prod/660/660d2.html

Tracer technologies can be efficient tools to answer to these questions

The transport of contaminants in the subsurface is governed by complex, overlapping physicochemical processes

effective porosity

Koc, foc
Kd
kinetics

diffusion coefficient
longitudinal /
transverse dispersivity

Source strength
and behaviour

mobile water

sorption

diffusion
dispersion

source

$$\frac{\partial(\theta_m C)}{\partial t} + \frac{\partial(\theta_{im} C_{im})}{\partial t} + \rho_b \frac{\partial(C_s)}{\partial t} = -\underline{\nabla} \cdot (\underline{v}_D C) + \underline{\nabla} \cdot (\theta_m \underline{\underline{D}}_h \cdot \underline{\nabla} C) - \lambda(\theta_m C + \theta_{im} C_{im}) + qC'$$

physical retardation

advection

degradation

Darcy fluxes

chemical reaction constants
biodegration potential

diffusion
dual porosity
first order constant
…

If we want to solve the groundwater pollution issue, we need first to solve this equation…

… And in this context, different questions may arise

Are we able to identify the processes affecting the fate of contaminants in the subsurface and to differentiate them from other producing similar effects?

Can we quantify the parameters associated to these ongoing processes?

In some cases, can we evaluate their dynamics /evolution with time or space?

Lab experiments are nice, but what about the issues of heterogeneity and scale?

…

We can "trace" the information from the subsurface by …

Monitoring the contaminants by themselves
Concentration evolution in time and space, co-reactive compounds, …

Investigating other compounds present in the subsurface
Natural or environmental tracers: stable isotopes …

Most often, little control on the source of pollution (when, where, strength, composition…)

→ The "do it yourself" option
Apply tracers with known characteristics, in controlled conditions, with specific objectives in mind

Scope of this presentation : Applied Tracer Techniques in contaminant hydrogeology

1. General aspects on applied tracer techniques
2. Measuring and monitoring groundwater fluxes
3. Identification and quantification of solute transport mechanisms
4. Hydrogeological assessment: recharge processes in fractured chalk
5. Reactive transport with a focus on biodegradation processes
6. Conclusions & Perspectives

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Applied tracers: definition

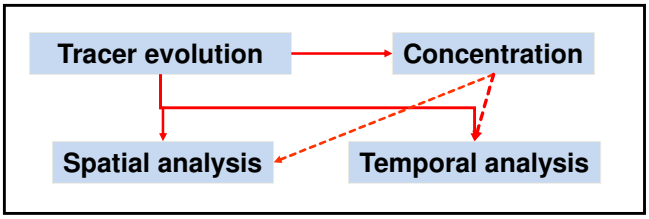
Any chemical compound / any product

- Of **known** chemical composition or physical properties
- **Volontarily introduced** in groundwater : generally a known quantity on a short duration at a selected location
- With the idea in mind of **identifying** and/or **quantifying properties / characteristics of groundwater or the subsurface medium in general**, such as groundwater flow direction, hydrodispersive properties, subsurface reactivity …

Applied tracers: basic concept

Tracer injection at one location (e.g. piezometer, sinkhole …)

Monitoring tracer at one or more locations (e.g. sampling at recovery well, spring, downgradient piezometer)



How do we proceed?

In theory, very easy, just dissolve the tracer in water and inject it into the subsurface / aquifer

In practice, experimental protocols can be sophisticated and experimental conditions can have a significant influence on the results and interpretation

From an operational perspective, classifying applied tracer techniques is not just a matter of fact …

		Groundwater flow conditions	
		Natural	**Forced-gradient**
Number of piezometers / well required	**1**	**Point dilution**	**Push-Pull / Dipole flow**
	2 or more	**Natural gradient**	**Many! In particular radially-converging flow**

Potentially, we have an infinite number of tracers at our disposal

Practically, a limited number of products are commonly used
Detection limit, background concentration, costs, health and environmental risks, non-conservative behaviour, interactions / interferences …

Inorganic compounds (salt)
Most common : chloride, bromide, iodide, nitrate, lithium…

Fluorescent organic compounds
Uranine (fluoresceine), rhodamines, tinopal, naphtionate, eosin Y…

Non-fluorescent organic compounds
labelled contaminants, lactate, acetate, …

"Others"
microspheres, nanotracers …

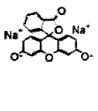
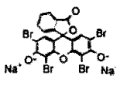
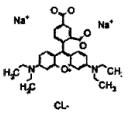
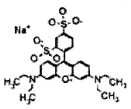
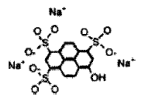
Saline tracers

- As soluble as possible (most often Na or K salts)
- Low backgrounds in groundwater
- Anions usually more conservative than cations
- Quantities usually on the order of kgs to tens of kgs
- Most commonly used:
  - iodide I^- → 3-10 ppb
  - bromure Br^- → ~100 ppb?
  - lithium Li^+ → 3-10 ppb
  - chlorure Cl^-
  - nitrate NO_3^-
  - Potassium K^+
  - Sodium Na^+
  - Strontium Sr^{2+}

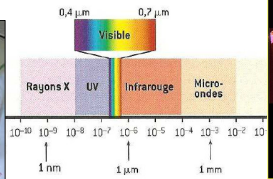
Strongly background dependent (usually applied on short distances or in specific cases)

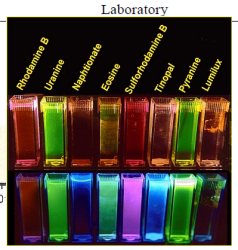
Fluorescent organic compounds

Table 1. Physical and Chemical Characteristics of Fluorescein, Eosine, Rhodamine WT, Sulforhodamine B, and Pyranine

Dye	Fluorescein[a] (Acid Yellow 73)	Eosine (Acid Red 87)	Rhodamine WT (Acid Red 388)	Sulforhodamine B (Acid Red 52)	Pyranine (Solvent Green 7)
Group	Xantenes	Xantenes	Rhodamines	Rhodamines	Aromatic hydrocarbons
Structure[b]					
Formula[c]	$C_{20}H_{10}O_5Na_2$	$C_{20}H_6Br_4O_5Na_2$	$C_{29}H_{29}N_2O_5Na_2Cl$	$C_{27}H_{30}N_2O_7S_2Na_2$	$C_{16}H_7O_{10}S_3Na_3$
Molecular weight (g/mol)	376	692	566	604	524
Detection limit[c] (ppb)	0.002	0.01	0.006	0.007	0.008
Excitation/emission wavelength (nm)[c]	492/513	515/535	558/583	560/584	460/512
Log K_{ow}[b]	−0.39	−1.33	−1.33	−2.02	−0.68
Provider	Kingscote Chemicals	Ozark Underground Laboratory	Formulabs	Ozark Underground Laboratory	Ozark Underground Laboratory

[a]Known as Uranine in Europe.
[b]Field et al. (1995).
[c]Behrens (1986).





We can also classify our tracers according to the way they generally behave in the underground …

The referential for that is most often (ground)water
(water is a very sorptive compound!)

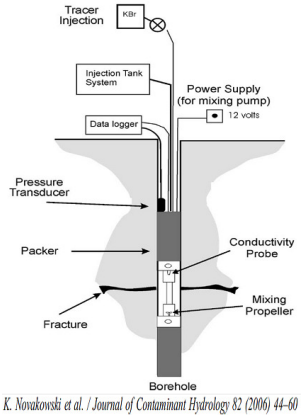
Ideal tracers
Tracers that are supposed to behave just like water in the underground

Conservative tracers
Tracer that do not sorb or react in the subsurface
In practice, mostly a myth!

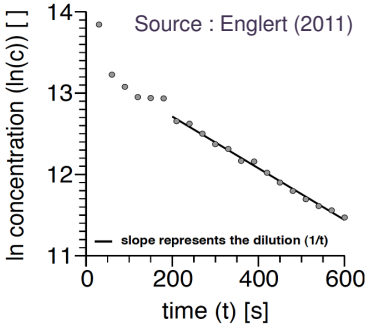
Reactive tracers
Probably 99% of the applied tracers react somehow!

Measuring groundwater fluxes is essential because this is the main driver of pollutants

Most common tracer technique : the **Point Dilution Method**
Monitoring concentration exponential decline in the column of water located in a piezometer due to groundwater flow across the screens



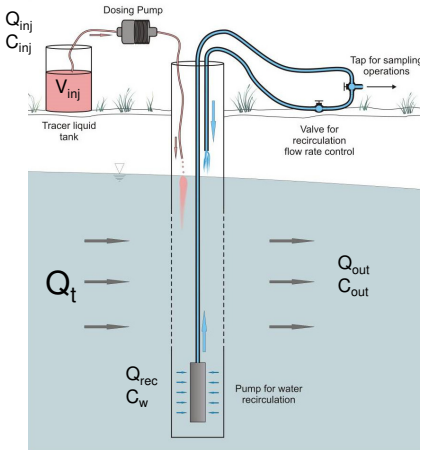
K. Novakowski et al. / Journal of Contaminant Hydrology 82 (2006) 44–60

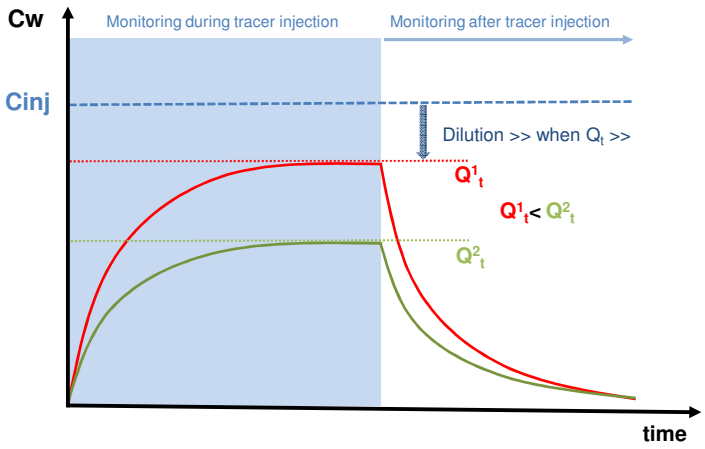


An alternative to PDM : the FVPDM

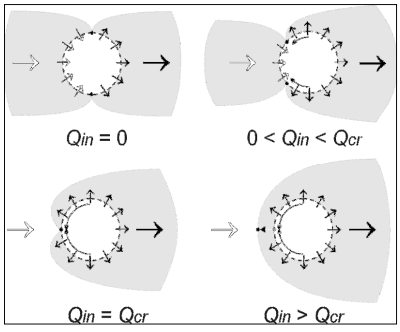
(developed by our research group)

FVPDM stands for **F**inite **V**olume **P**oint **D**ilution **M**ethod
The tracer is injected at a low, continuous injection rate





The success of the experiment relies on a controlled, low injection rate



If $Q_{inj} > Q_{cr}$

$Q_t = 0$

If $Q_{inj} \le Q_{cr}$

$$Q_t = 2r_w e V_w \sin\left(\arccos Q^*\right) - \frac{Q_{inj}}{2\pi}\left(2\arccos Q^*\right)$$

$Q^* = Q_{inj}/Q_{cr}$ and $Q_{out} = Q_{inj} + Q_t$

It can be shown that the injection rate (Qinj) should be less than 3 times the transit flow rate (Qt) that we try to quantify

Brouyère (2003), based on Bideaux & Tsang (1991) potential theory

$$Q_{cr} = 2\pi e_{scr} r_w v_{ap} = 2\pi e_{scr} \alpha_w |v_D| \approx \pi \times Q_t^0$$

The concentration evolution is obtained using a tracer mass-balance in the injection well

Water conservation

Further details in Brouyère (2001) and Brouyère et al. (2008)

$$\frac{\partial V_w(t)}{\partial tt} = \pi r_w^2 \frac{\partial h_w}{\partial t} = Q_{inj}(t) + Q_t(t) - Q_{out}(t)$$

Tracer conservation

$$\frac{\partial M_t}{\partial t} = \frac{\partial}{\partial t}(V_w C_w) = r_w^2 \left(C_w \frac{\partial h_w}{\partial t} + h_w \frac{\partial C_w}{\partial t} \right) = Q_{inj} C_{inj} + Q_t C_t - Q_{out} C_{out}$$

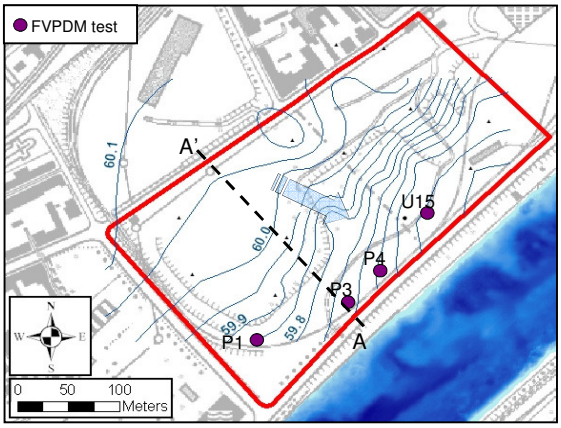
Concentration evolution in the injection well

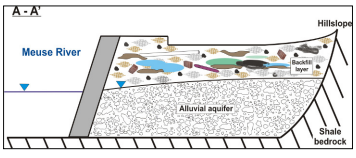
$$C_w(t) = \frac{Q_{inj} C_{inj} - (Q_{inj} C_{inj} - Q_{out} C_{w,0}) \exp\left(-\frac{Q_{out}}{V_w}(t - t_0) \right)}{Q_{out}}$$

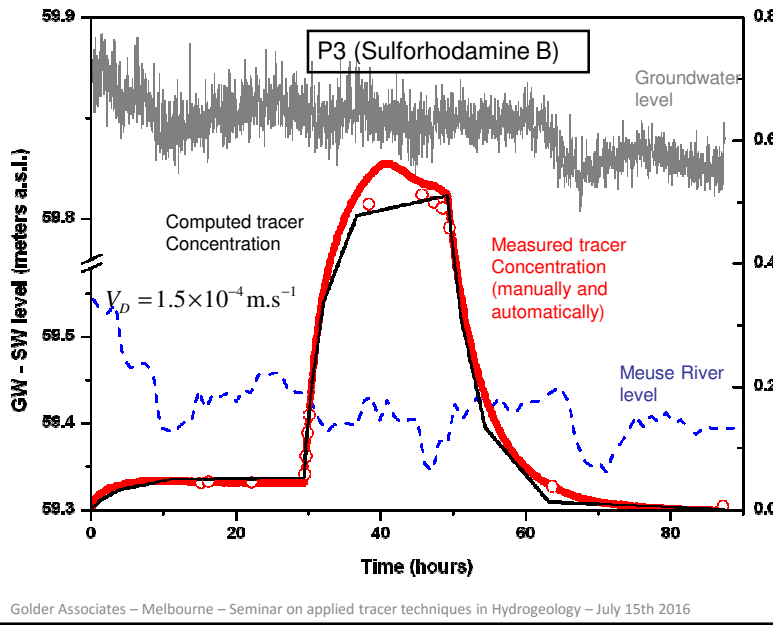
$$Q_t = Q_{out} - Q_{inj}$$

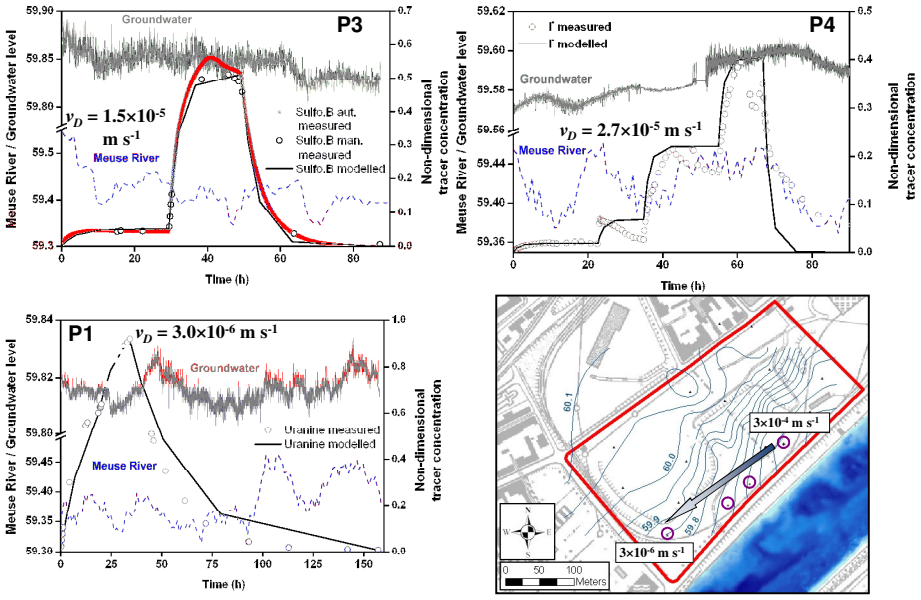
The FVPDM was successfully applied in piezometers located at the border of a contaminated brownfield

The objective was to measure groundwater discharge rates from a contaminated alluvial aquifer to the Meuse river (Liège, Belgium)






P3 (Sulforhodamine B)
Groundwater level
Computed tracer Concentration
$V_D = 1.5\times10^{-4}$ m.s^{-1}
Measured tracer Concentration (manually and automatically)
Meuse River level
GW - SW level (meters a.s.l.)
Non-dimensional tracer concentration (-)
Time (hours)
59.9
59.8
59.5
59.4
59.3
0.8
0.6
0.4
0.2
0.0
0
20
40
60
80



FVPDM recent applications and ongoing developments

Application in fractured cristalline bedrock with a double packer system to confirm fracture connectivity and to quantify fracture fluxes

Monitoring changes in groundwater fluxes in dynamic groundwater systems (e.g. connected groundwater – river, groundwater discharge to the sea…)

Development of a « Fast-FVPDM » that allows reducing significantly the duration of the experience

Coupled passive sampling – FVPDM for quantifying pollutant mass flux in groundwater

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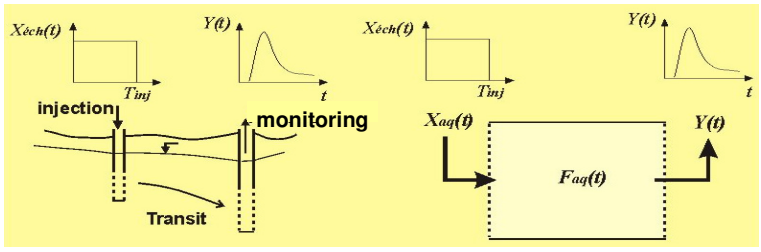
We can also use applied tracers as surrogates of contaminants …

Tracers are injected in controlled conditions (quantity, duration, injection rate, groundwater flow conditions…) at selected locations

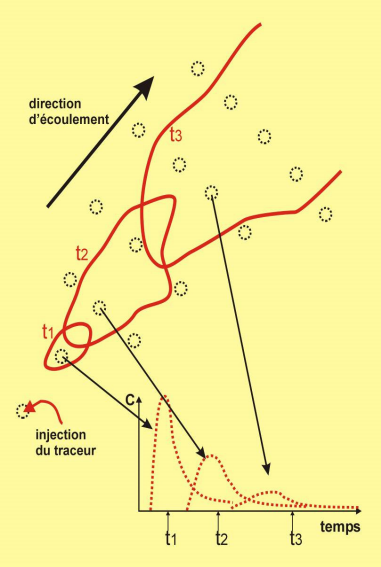
Concentration evolutions monitored down gradient from the injection is used to determine and quantify transport processes



Two main categories

Natural flow and radially converging flow tracer experiments

Natural flow experiments are more representative of groundwater pollution problems

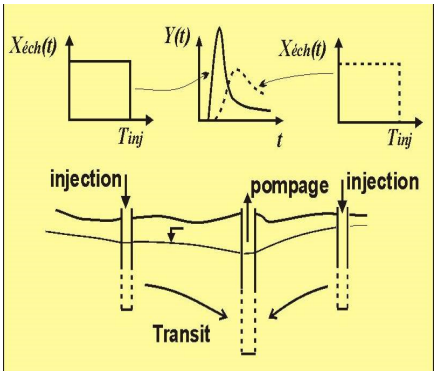


Advantages and drawbacks

- Natural groundwater flow conditions
- Groundwater not pumped, just sampled
- Monitoring system potentially costly
- Interpretation not straightforward (moment analysis)

Cape Cod, MA, USA (USGS)

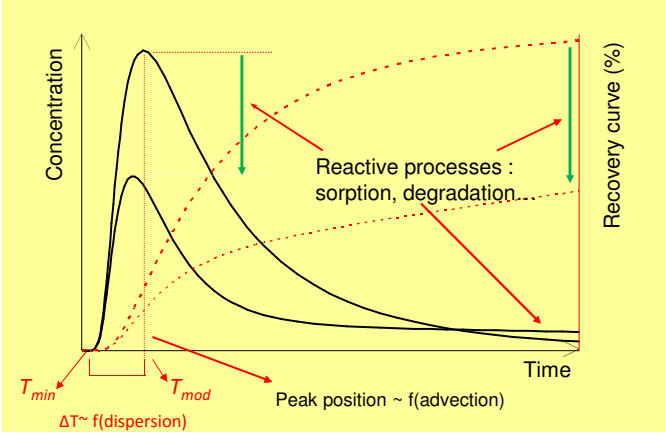
Radially converging flow tracer experiments provide more quantitative results



Advantages and drawbacks

- Quantitative interpretation based on concentration evolution and tracer mass recovery
- Faster because of forced gradient
- Abstracted groundwater = further costs + restrictions on where to perform on contaminated sites
- Modified groundwater flow conditions

The breakthrough curve is the recorder of underground transport processes



Again, a detailed control of injection conditions might save your experience …

Tracer mixing and capturing in the injection well

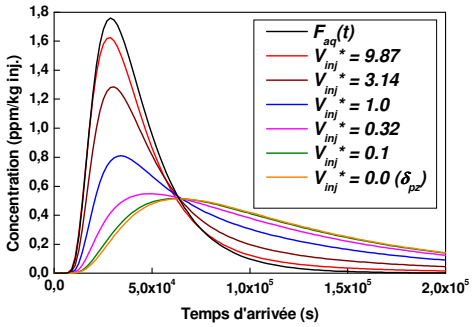
Vin : volume of injected traced water

Vw : volume of water initally present in the well

Mixing factor : $Vin^* = Vin / Vw$

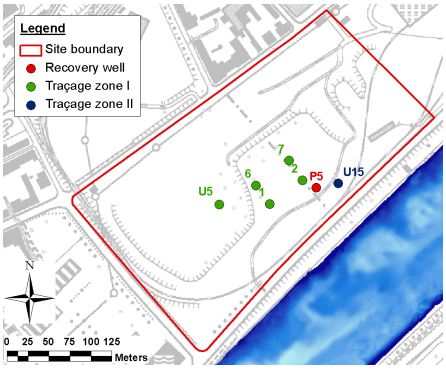
+ capturing in the well

Brouyère et al., Ground Water (2005)



Solution : monitor the concentration evolution in the injection well and model it explicitely afterwards (same theory as FVPDM)

Lessons from a tracer experiment in a brownfield

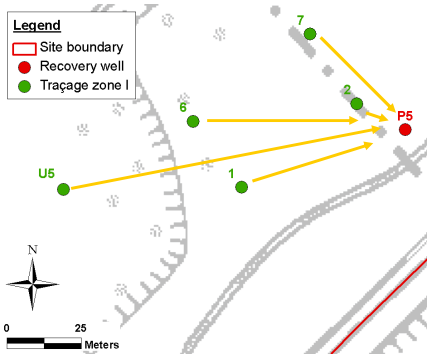


Tracer experiments performed in radially converging flow conditions around P5 (located in a uncontaminated groundwater sector)

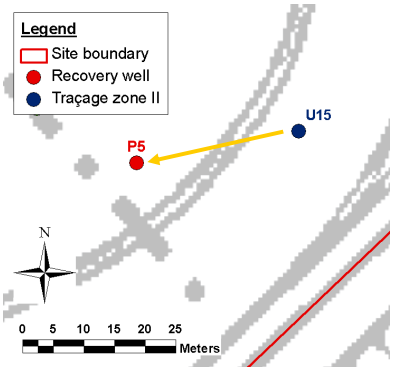
Objectives: to obtain information on solute transport processes and parameters for the site

Batlle-Aguilar et al., J.Hydrol (2008)
Batlle-Aguilar, PhD thesis, ULg (2008)

2 injection phases performed



Pz 1: Li^+ (1.39 kg)
Pz 2: NO_3^- (12.16 kg) + sulpho B (0.10 kg)
Pz 6: I^- (3.28 kg)
Pz 7: Naphtionate (1 kg)
Pz U5: Fluorescein (0.2 kg)



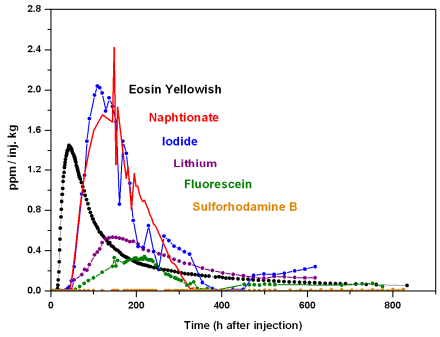
Pz U15

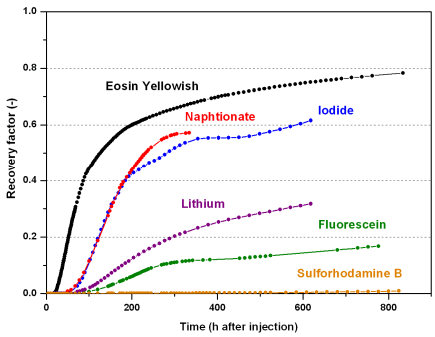
Eosin Yellowish (1 kg)
Naphtionate (0.01 kg)
Sulpho B (0.01 kg)
Fluorescein (0.01 kg)
Li^+ (0.6 kg)
I^- (0.76 kg)

Very contrasted results …!

- Phase 1: No arrival of the tracers injected upgradient in the site ...
- Phase 2: Different breakthrough curves (concentration and mass recovery) for the different salt and dye tracers, injected in the same piezometer (U15)

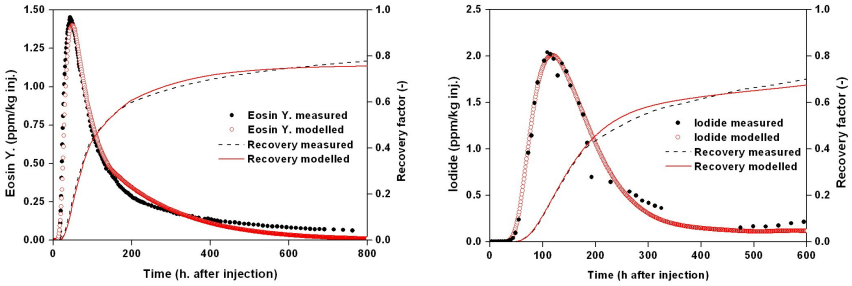
⇒ ≠ physico-chemical properties



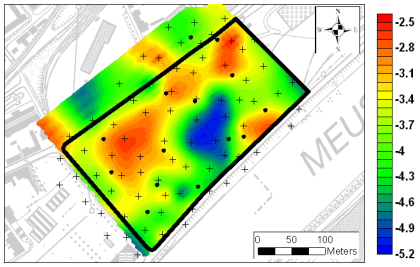


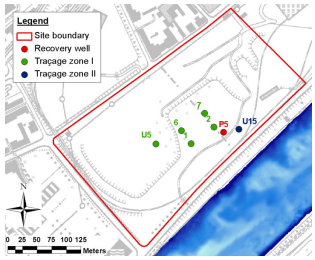
MT3DMS (Zheng and Wang, 1999)

Paramètres hydrodispersifs	
Effective porosity (θ_m) (-)	0.03 – 0.045
Long. dispersivity (α_L) (m)	1.5 – 2.5
Trans. dispersivity (α_T) (m)	0.3 – 0.5
Effets de retard	
Immobile water porosity (θ_{im}) (-)	0.05 – 0.1
1st order coefficient (α) (s^{-1})	2×10^{-7} - 8×10^{-8}



Tracer experiments are better explained considering the heterogeneity of the alluvial deposits





K-field heterogeneity highlighted through modelling of variations in groundwater levels with changes in river stage, using a pilot point approach

Pz1 Pz2 Pz6 Pz7 U5 not recovered because of a low pervious zone on the way to P5

U15 : recovery at P5 which drained most probably water from the Meuse River

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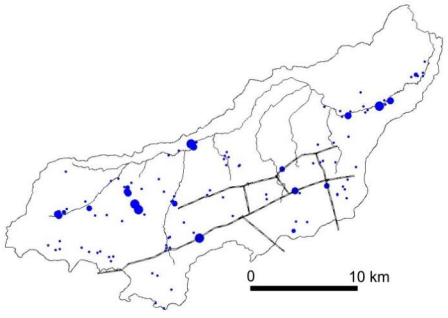
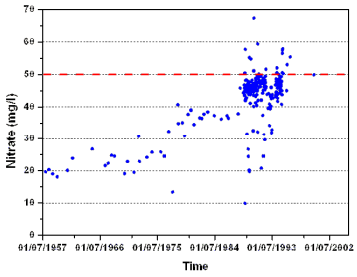
Context : nitrate in excess in a chalk aquifer intensively used for groundwater abstraction (area of Liège, Belgium)

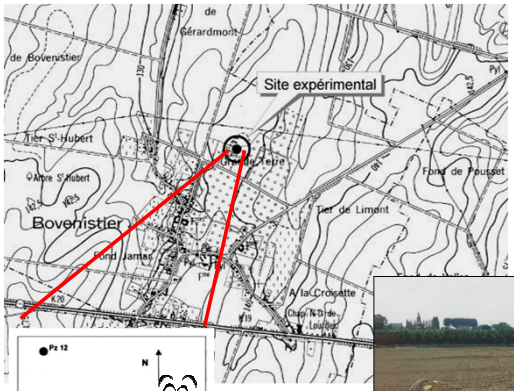


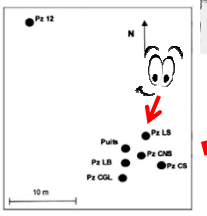


→ What are the pollutant **recharge mechanisms** across the thick unsaturated zone above the chalk aquifer?

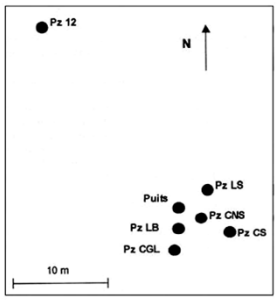
→ **How fast do the pollutant migrate** vertically across this unsatured zone?

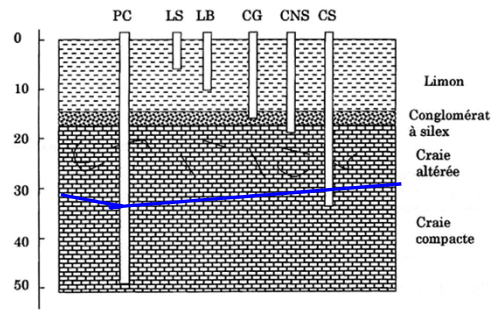
Tracer experiments in the unsaturated chalk





Experimental site
1 recovery (pumping) well
5 piezometers screened at different depths in the unsaturated and saturated zone





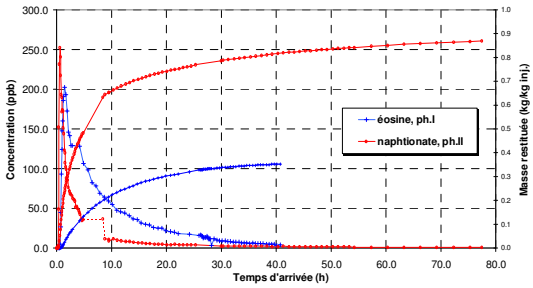
Various experiments performed in this site

- Borehole drillling + collection of undisturbed samples
- Samples → laboratory experiments and measurement
- Infiltration tests in the unsaturated zone (Lefranc)
- Pumping tests in the saturated zone
- Tracer experiments in the saturated zone
- Tracer experiments across the unsaturated zone

Tracer experiments in the saturated chalk aquifer

Pz CS → PC, distance : 6m

	Phase 1	Phase 2
Tracer	Eosin Y	Naphtionate
Q rate PC (m^3/h)	1.2	6.0
Injected quantity (g)	5,3	5,1
Vinj (m^3)	0.010	0.010
Tinj (h)	1min53s	2min11s
Vch (L)	127	132
Tch	17min 20s	12min 56s
Tmin(h)	0.58 (35min)	0.25 (15min)
Vmax (m/h)	10.2	24
Tmod (h)	1.42 (85min)	0.5 (30min)
Vmod (m/h)	4.2	1.2
Taux de restitution (%)	35 (after 40 h)	87 (after 77 h)

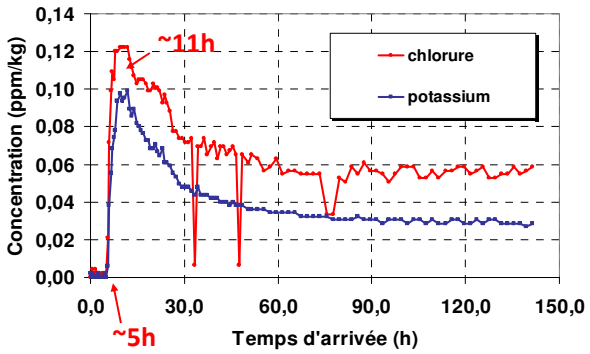


Very short traver times
Very high transfer velocities

Tracer experiments across the unsaturated chalk (1/2)

Pz CNS → PC, horizontal distance : 6m
Vertical distance (thickness of unsat. chalk) : 10m
Tracer injection in Pz CNS **under artificial recharge conditions**

Tracer: KCl
Q rate at PC : 6,5 m³/h
M_{inj}: 100 kg
V_{inj}: 300 L
T_{inj}: ~1 h
Q_{ch}: ~300 L/h

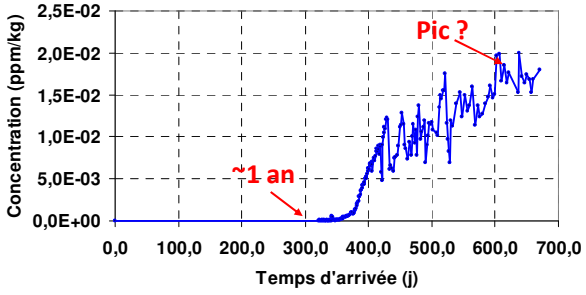


A nouveau, temps de transfert relativement courts
Effets de retard assez prononcés (queues de restitution prolongées)

Tracer experiments across the unsaturated chalk(2/2)

Pz CNS → PC, horizontal distance : 6m
Vertical distance (thickness of unsat. chalk) : 10m (at beginning of exp.)
Tracer injection in Pz CNS **under natural recharge conditions** (no water added after tracer injection)

Tracer: iodide (in KI)
Qrate at PC : 3 to 6m³/h
M_{inj}: 10 kg
V_{inj}: 30 litres
T_{inj}: 6 min
Q_{ch}: 0 m³/h



Very long traver time!
Knowing that a rise in groundwater level observed during that period facilitated the recovery of the tracer!

In terms of travel time, a 1000 factor is observed between the two experiments performed in the unsaturated chalk
→ from a few hours to almost one year!

Explanation : **Dual porosity – dual permeability of chalk**

Chalk matrix

Associated porosity very high : n_M ~ 30 - 40%

Microporosity (≈ 1µm) → very high capillary tensions

Low hydraulic conductivity: $K_{s,M}$ << ~10^{-9} à 10^{-8} m/s

Chalk fissures

Associatd porosity very low: $n_F \leq 1\%$

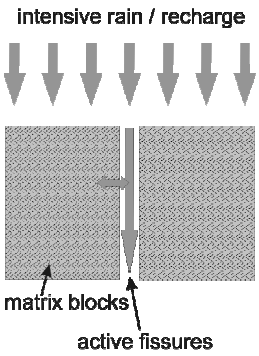
Larger openings → low capillary tensions

High hydraulic conductivity: $K_{s,F}$ >> 10^{-3} m/s, even more

In the saturated zone and in the unsat. zone under intense recharge conditions:

$K_{s,M}$ << $K_{s,F}$: progressive drainage of water stored in the chalk matrix and fast transfer through fissures

Fast migration of dissolved comppounds through the fissures ($K_{s,F}$ >> and n_F <<) + retardation in the chalk matrix (dual-porosity effects)

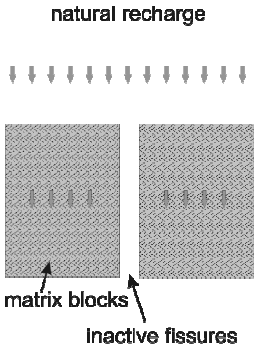


In the unsaturated zone under natural recharge conditions

(the chalk is overlain by loess deposits that attenuate recharge processes) :

Fast desaturation of fissures et water flow restricted to the matrix compound

Slow migration migration of solutes through the matrix ($K_{s,M}$ << and n_M >>)



1. General aspects on applied tracer techniques
2. Measuring and monitoring groundwater fluxes
3. Identification and quantification of solute transport mechanisms
4. Hydrogeological assessment: recharge processes in fractured chalk
5. Reactive transport with a focus on biodegradation processes
6. Conclusions & Perspectives

Motivations

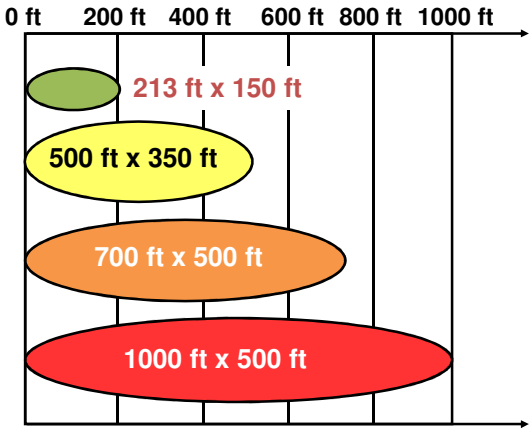
Organic compounds are common pollutants, developing more (i.e. VOCls) or less (i.e. BTEX) important dissolved plumes in groundwater

BTEX plumes at 42 retail LUST sites

Chlorinated solvent plumes such as TCA, DCA) at 29 sites

Chloride, salt water plumes at 25 sites

Chlorinated ethene (PCE, TCE, DCE, or VC) plumes at 88 sites



Source: adapted from US statistics (API, Newell & Connor, 1998)

Motivations

Whatever the option is to go to active or passive (MNA) remediation, it is always useful and important to obtain lines of evidence of any organic pollutant degradation or transformation, biologically mediated or not

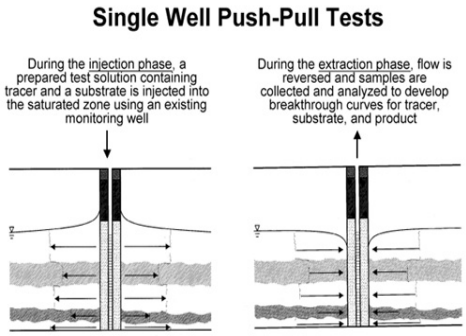
Different options for that (among others)

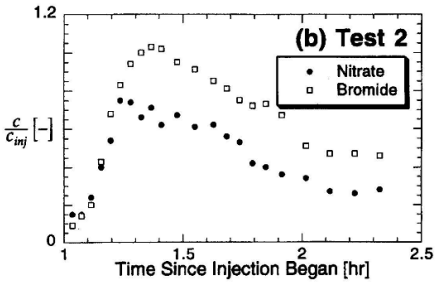
- Use reactive (applied) tracers that demonstrate the occurrence of microorganisms active in bioremediation
- Directly trace (bio)degradation in the reactive compounds using isotopic fractionation in the reacting molecules

Reactive products used to assess the degradation potential of organic products in the underground

Experimental setup

Source : http://www.niehs.nih.gov





Nitrate is depleted as compared to bromide injected at the same time in a petroleum product contaminated aquifer (Haggerty et al. 1998)

- Isotopes
  - Atom = nucleus made of neutrons (n^0) and protons (p^+) + peripherical electrons (e^-)
  - Chemical element: different types of atoms differing from each other by their number of neutrons = **isotopes**
    Ex.: Hydrogene
    - Hydrogen atom ^1H : 1 p^+ + 0 n^0
    - Deuterium atom ^2H: 1 p^+ + 1 n^0
    - Tritium atom ^3H: 1 p^+ + 2 n^0
  - Categories of isotopes
    - Instable (radioactive) isotopes (^3H, ^{14}C, ^{36}Cl …)
      ➔ Datation of water (^3H)
    - **Stables isotopes** ($^{18}O/^{16}O$, $^2H/^1H$, $^{13}C/^{12}C$, $^{34}S/^{32}S$, $^{15}N/^{14}N$ …)
      ➔Meteoric origin of water ($^{18}O/^{16}O$, $^2H/^1H$)
      ➔Pollution sources, chemical transformations of organic / inorganic reactions (biotic or abiotic)

- Stable isotopes and isotopic fractionation
  - The isotopic ratio is defined as:

$$R = \frac{\text{abondance heavier isotope}}{\text{abondance de lighter isotope}}$$

  - The isotope enrichement factor is defined as

$$\delta = \left(\frac{R_E}{R_S} - 1 \right) . 1000$$ (in ppm ou ‰)

R_S = Etalon de référence pour les isotopes stables, from the National Bureau of Standards (USA)
(e.g. for water : SMOW : Standard Mean Ocean Water)

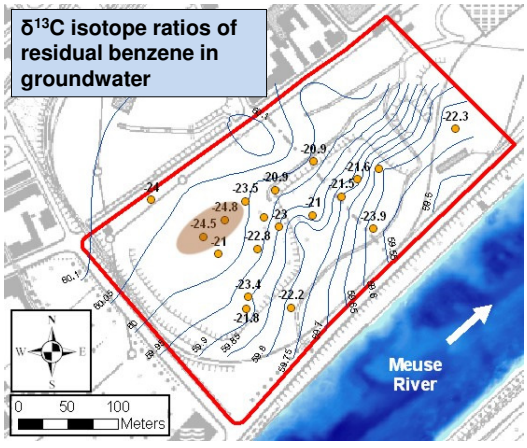
- Isotopic fractionation
  - The **natural abondance** of a chemical element is the percentage of each of its isotopes as observed in nature
    E.g. : Oxygen : 99,762% ^{16}O, 0,038% ^{17}O and 0,2% ^{18}O
  - These isotopes have similar chemical properties but not exactly the same weight
    → under spectific circomstances, enrichment of a particular isotope can be observed **= Isotopic fractionation**
  - Isotopic fractionation can be related to physical or biological processes
    e.g: evaporation and biodegradation tend to increase the abondance of heavier isotopes in the remaining molecules

Many applications in groundwater quality and pollution studies

- Evidence of natural attenuation of organic pollutants
  - E.g.: $\delta^{13}C$ in benzene and PAHs,
    $\delta^{13}C$ and $\delta^{37}Cl$ in chlorinated solvents
- Identification of pollution sources and chemical reactions involving inorganic compounds
  - E.g. : $\delta^{15}N$ and $\delta^{18}O$ in NO_3 (origin of NO_3 and denitrification)
    $\delta^{34}S$ and $\delta^{18}O$ in SO_4 (origin of SO_4 and sulfatoreduction,
    $\delta^{11}B$ in boron (natural or anthropogenic origin)

Benzene biodegradation in a brownfield in Liège (Meuse alluvial aquifer)

- Isotopic fractionation C^{13}/C^{12} ($\delta^{13}C$)
- Preferential degradation of lighter isotopes ➔ enrichement of C^{13} in remaining benzene molecules



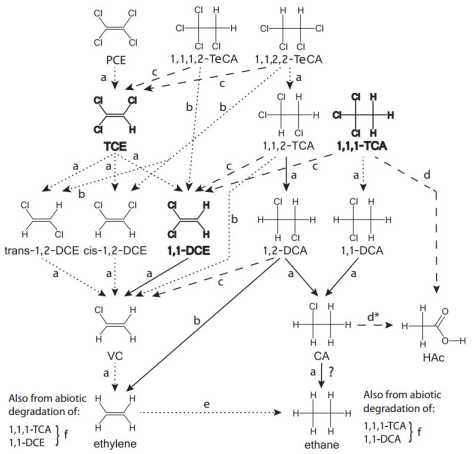
$k = -\Delta\delta^{13}C/(\varepsilon \times t)$

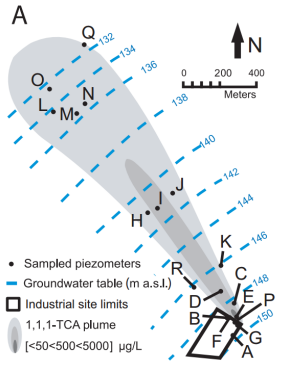
- $\Delta\delta^{13}C$=3 ‰
- v = 1.04×10^{-5} m s^{-1}
- ε = -2.4 ‰

➔ ***k*** **= 0.017/d**
➔ **t ½ =41 d**

CSIA dual coumpound

The different 1,1,1-TCA degradation processes do not produce the same patterns of isotopic fractionation in the d37Cl vs d13C diagramme…
Example : contamination with 1,1,1-TCA in the chalk aquifer near Liège in Belgium



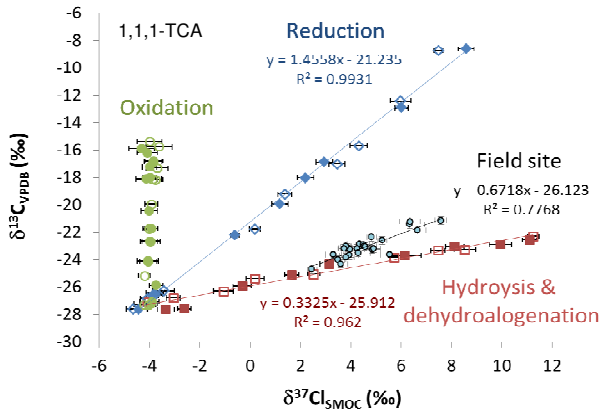


Use of carbon - chlorine dual isotope analysis to assess the degradation pathways of 1,1,1-trichloroethane in groundwater, Jordi Palau, Pierre Jamin, Alice Badin, Nicolas Vanhecke, Bruno Haerens, Serge Brouyère and Daniel Hunkeler. Under review

Mise en évidence du processus de dégradation

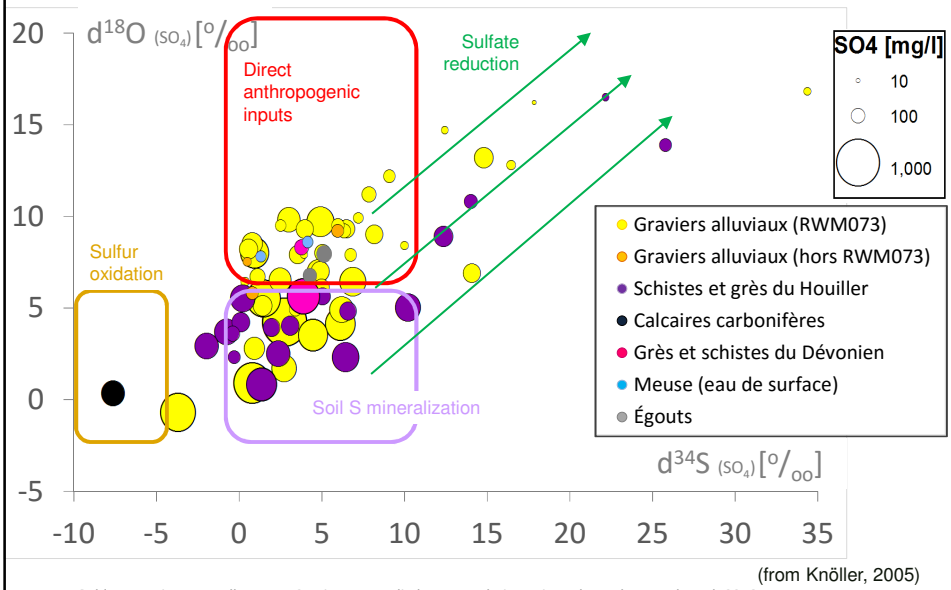
Carbon versus chlorine isotope ratios of 1,1,1-TCA

Dual isotope approach



Palau and Hunkeler (2015)

Meuse river alluvial plain in the area of Liège (Belgium):
Origin of elevated SO_4 concentrations based on isotopic signatures



(from Knöller, 2005)

Conclusions & Perspectives

Applied tracer techniques cover a range of applications in the field, in particular contaminated sites

However, the contamination of groundwater might be a limiting factor to the use of tracer techniques (groundwater abstraction…)

When planning an applied tracer experiment

- Clearly define your objectives from the beginning and select the appropriate operational mode and tracers according to
- Never neglect the possible influence of the experimental setup on the results
- Measure and monitor as much as possible your experience from injection to recovery

Do not believe too much in the "myth" of "ideal" or "conservative" tracers

Rather use several tracers, with contrasted properties, in order to see, to explain and to take advantage of their differences

Conclusions & Perspectives

Deeper understanding of the reactivity of tracers as more efficient surrogates of contaminants

A better distinction has to be made between subsurface medium properties and tracer properties in the explanation of their interactions → more reliable extrapolation to other compounds

Residence times and kinetics

Applied tracer techniques usually investigate the short term of the processes (hours to days). For some reactions to develop, longer residence times are required (e.g. biodegradation). How could we increase the tracer residence time in the underground without mass loss? Flow interruption methods? Recirculation?

Thank you for your attention!

Acknowledgement:

-P.Meus for providing a ppt on tracer techniques (D14)
-J.Palau & D.Hunkeler (U.Neuchâtel) for fruiteful collaborations on isotopic fractionation
- Colleagues for collaborations, support and field work (J.Batlle-Aguilar, P.Orban, P.Jamin…)