Applied Tracer Techniques in Contaminant Hydrogeology

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Université de Liège

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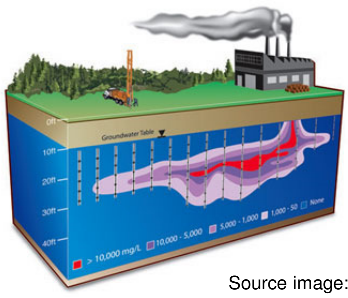
In most groundwater pollution studies, a sound characterization relies on a good understanding of the fate of dissolved pollutants in groundwater….

- 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

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. Case study: lessons learned from tracer experiments in a brownfield in Belgium
5. Some conclusions …

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 …

Saline tracers

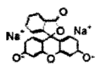
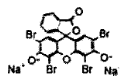
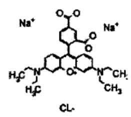
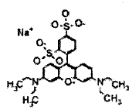
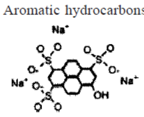
- As soluble as possible (most often Na or K salts)
- Low backgrounds in groundwater
- Anions usually more conservative than cations
- Quantities usually on the order of kgs to tens of kgs
- Most commonly used:
  - Iodide I^- → 3-10 ppb
  - bromide Br^- → ~100 ppb?
  - lithium Li^+ → 3-10 ppb
  - chloride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

Strongly background dependent (usually applied on short distances or in specific cases) [applies to chloride, nitrate, potassium, sodium and strontium]

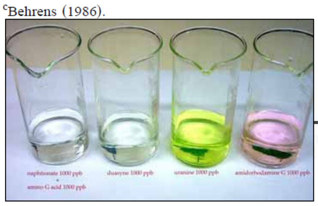
Source: P.Meus (EWTS)

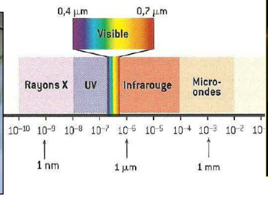
Fluorescent organic compounds

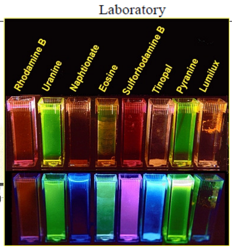
Table 1. Physical and Chemical Characteristics of Fluorescein, Eosine, Rhodamine WT, Sulforhodamine B, and Pyranine

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

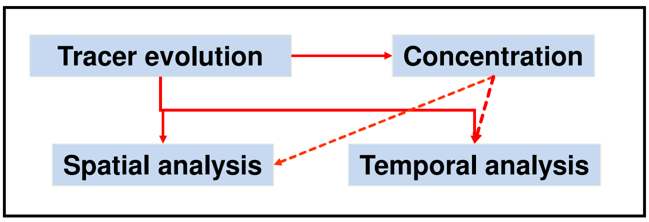
Conservative tracers
Tracer that do not sorb or react in the subsurface
In practice, mostly a myth!

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

Applied tracers techniques: 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**

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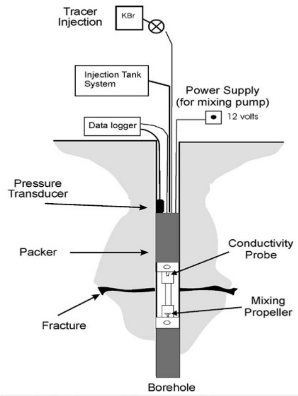
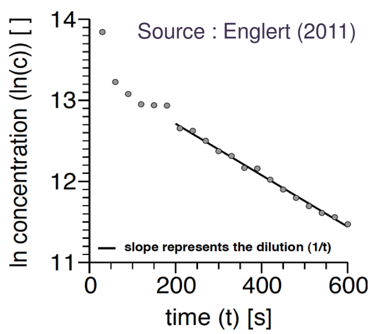
Measuring groundwater fluxes is essential because this is the main driver of pollutants

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

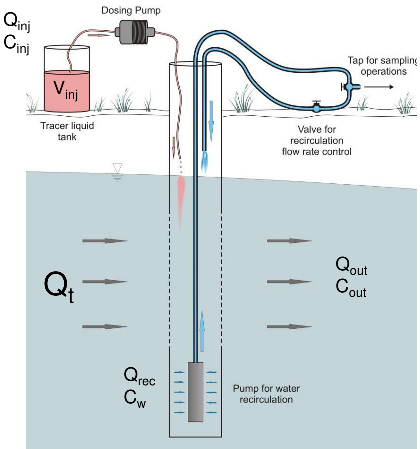


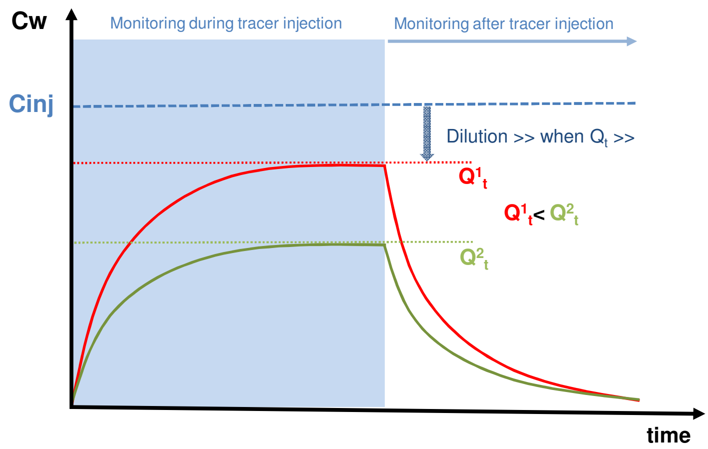
An alternative to PDM : the FVPDM

(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 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

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

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

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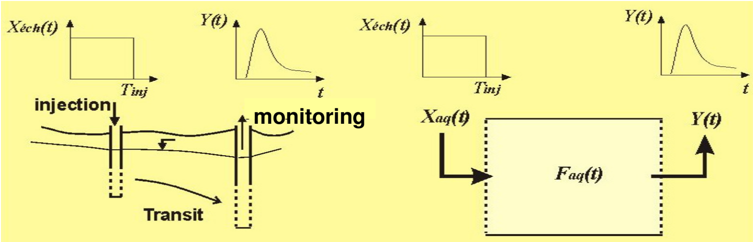
We can also use tracers as “controlled” pollutants …

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

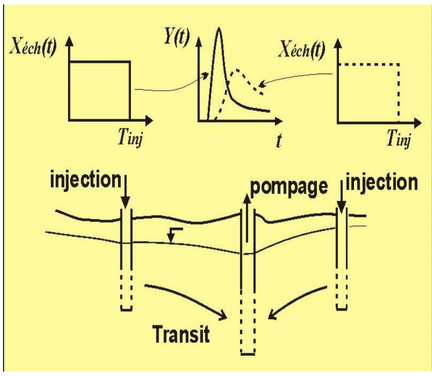
Concentration evolutions monitored down gradient from the injection is used to determine and quantify transport processes



Two main categories

Natural flow and **<u>radially converging flow tracer experiments</u>**

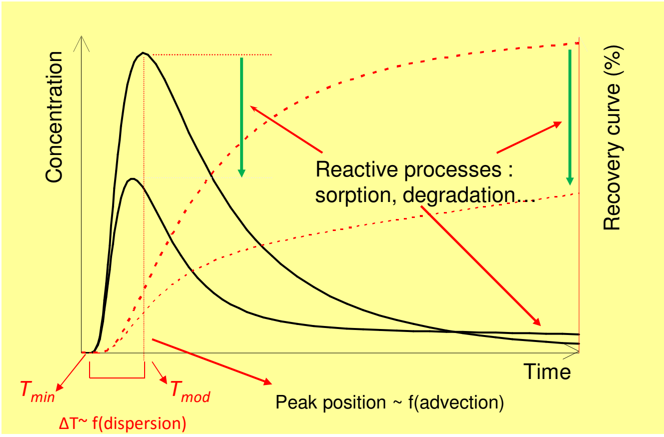
Radially converging flow tracer experiments provide useful quantitative results based on mass recovery



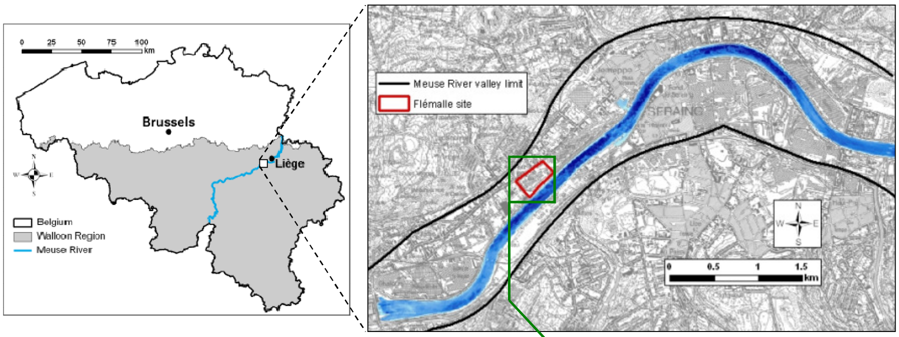
Advantages and drawbacks

- 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

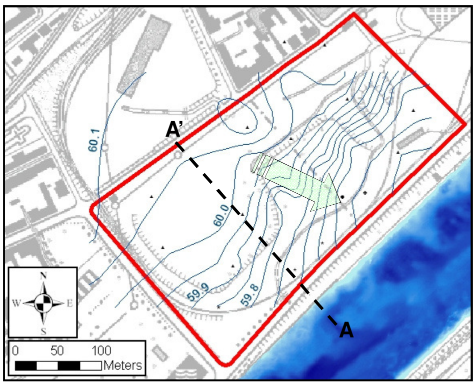


General context of the investigation

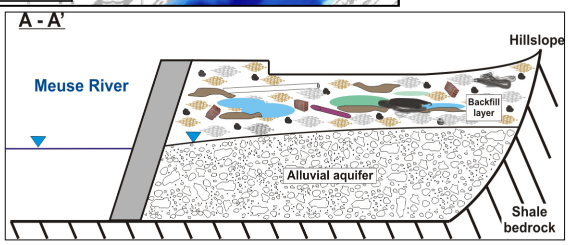


- Former coke factory with activities from 1922-1984
- Proximity to the Meuse River (25 m);
- Alluvial aquifer;
- Soil and groundwater highly polluted by organic (BTEX and PAHs) and inorganic (metals, Fe and sulphate) components.

Geology and Hydrogeology



Hydraulic gradient towards the river (0.15% to 0.45%)



- backfill (+/- 5 m)
- Alluvial deposits(+/-8 m)
- Shale bedrock (prof: +/-14 m)

Environmental status

Soil contamination

• **Heavy metals**. Mainly Cd, As, Zn and Pb. Mainly present in the backfill layer, although its horizontal delimitation is not perfectly known,

• **Cyanide**. Mainly located in the soil surface and locally up to 3 m depth. Its presence in the soil surface is specially important in the North-West part of the brownfield,

• **Mineral oils**. Present as hotspots in the backfill layer, high concentrations in North-East and West area,

• **BTEX**. Present in the backfill layer, important concentrations in the center and West area of the brownfield.,

• **PAHs**. Generally present in the backfill layer and up to the aquifer, mainly in the center – North – East – West area of the brownfield.

Groundwater contamination

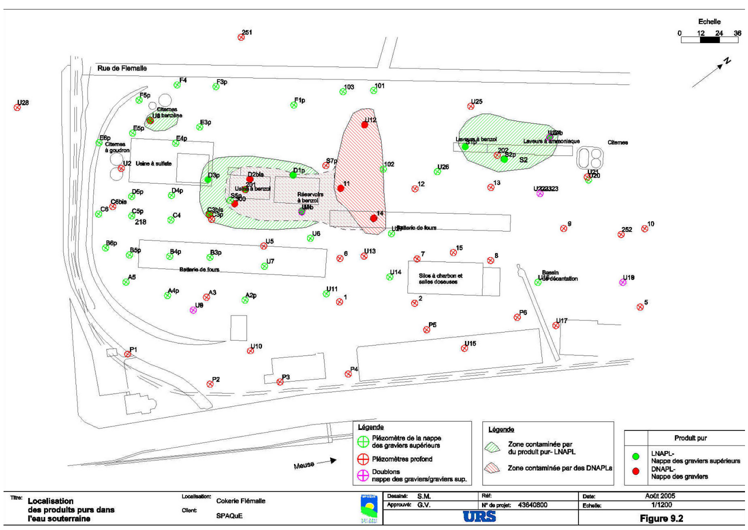
• **Mineral oils**, **BTEX** and **PAHs**. Dramatically high concentrations in the gravel aquifer,

• **Heavy metals**. Relatively low concentrations in groundwater except some hotspots of Zn and Cd,

• **Sulphates** and **ammoniacal-N**,

• No presence of organic contaminants next to the Meuse River.

In particular NAPLs (BTEX) on groundwater



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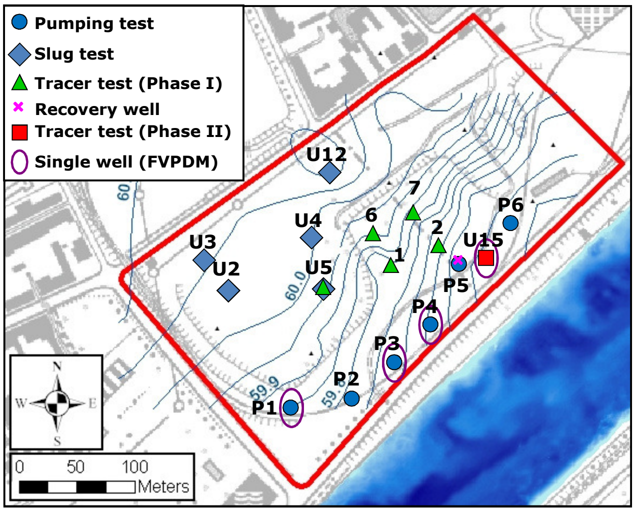
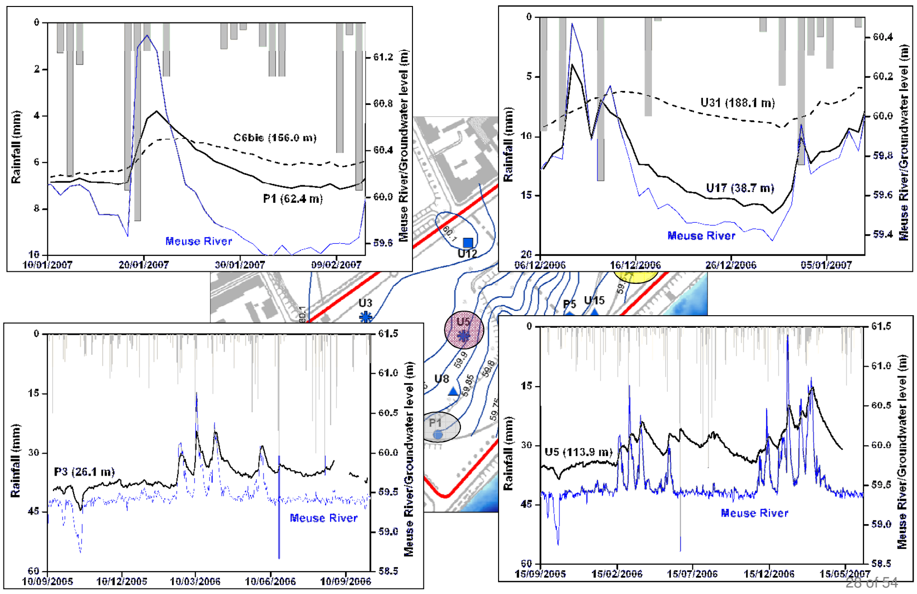
Summary of ULg field investigations



+ meteo data (dam close to site)
+ river levels in front of the site (every 15 min)
+ piezometric campaigns
+ hourly monitoring of piezometry with data loggers

Data acquisition (monitoring)

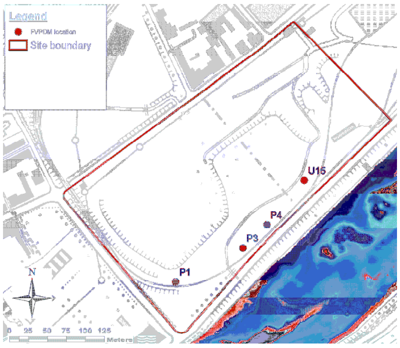


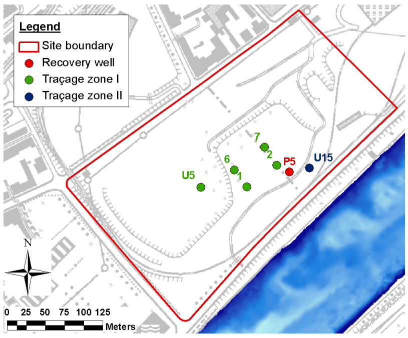
Tracer experiments performed in the brownfield

2 methods used

1. FVPDM → Quantification of groundwater flux + GW – river dynamics at the border of the site

2. Radially converging flow → Identification and quantification of transport processes in the alluvial aquifer





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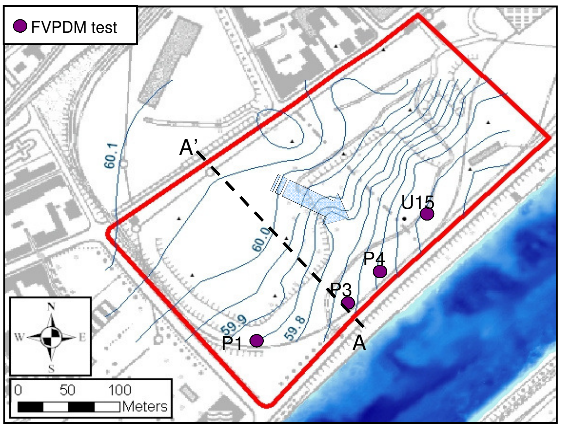
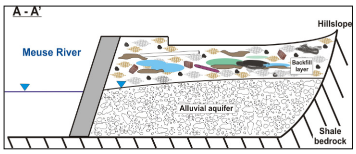
The FVPDM was successfully applied in piezometers located at the border of a contaminated brownfield

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





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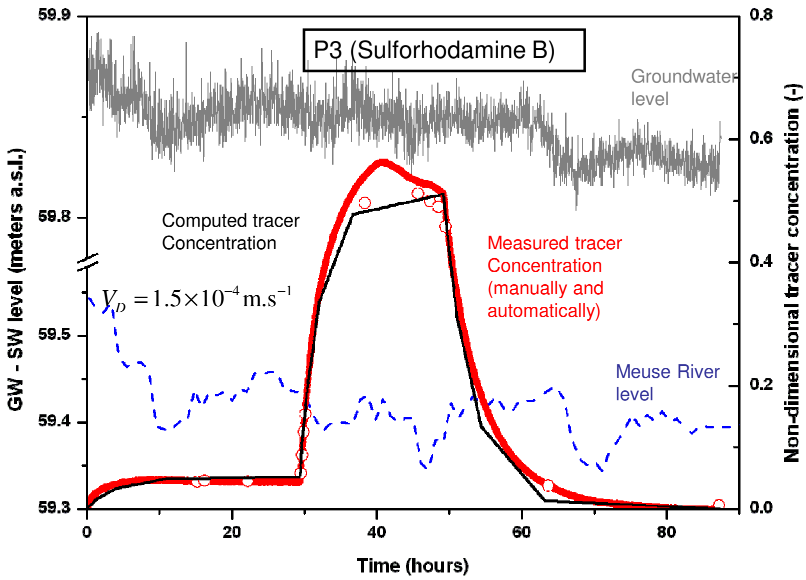
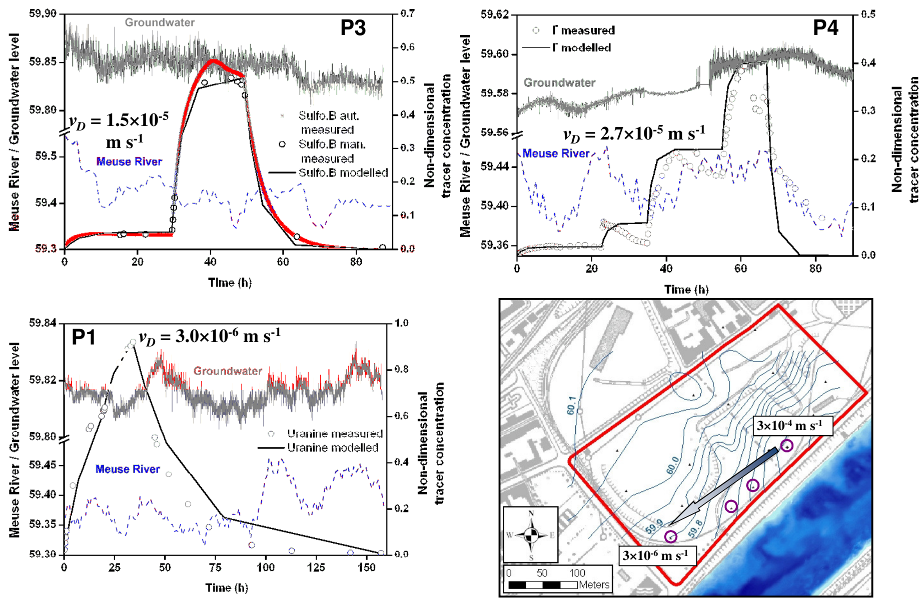
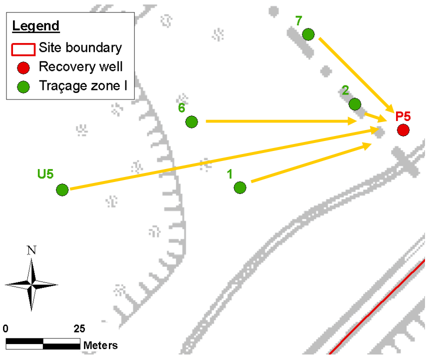


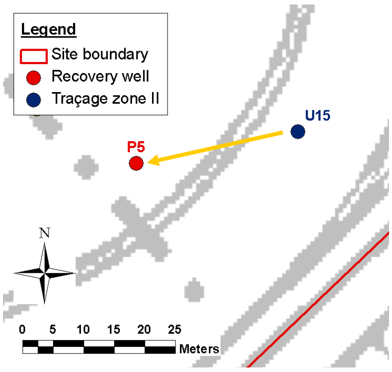
P3 (Sulforhodamine B)
Groundwater level
Computed tracer Concentration
$V_D = 1.5 \times 10^{-4}\,\mathrm{m.s^{-1}}$
Measured tracer Concentration (manually and automatically)
Meuse River level
GW - SW level (meters a.s.l.)
59.9
59.8
59.5
59.4
59.3
Non-dimensional tracer concentration (-)
0.8
0.6
0.4
0.2
0.0
0
20
40
60
80
Time (hours)



Radially converging flow: 2 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)

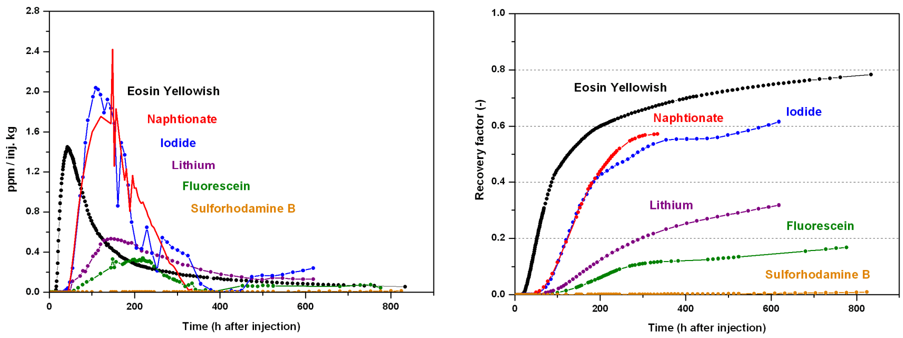


Pz U15
Eosin Yellowish (1 kg)
Naphtionate (0.01 kg)
Sulpho B (0.01 kg)
Fluorescein (0.01 kg)
Li^+ (0.6 kg)
I^- (0.76 kg)

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

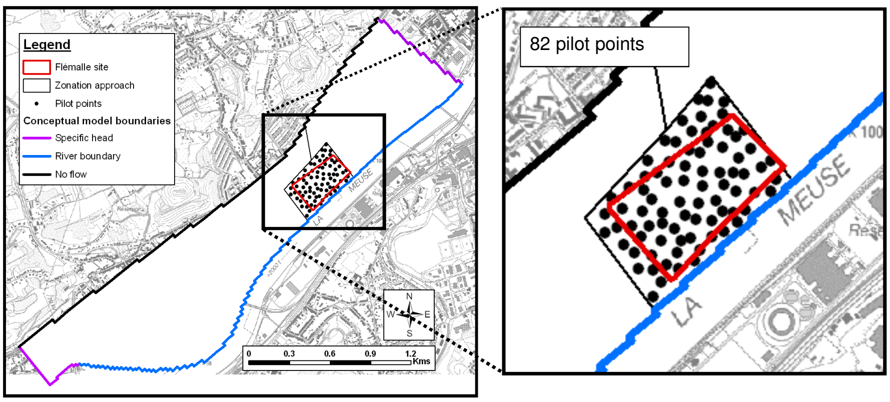


Modelling groundwater flow

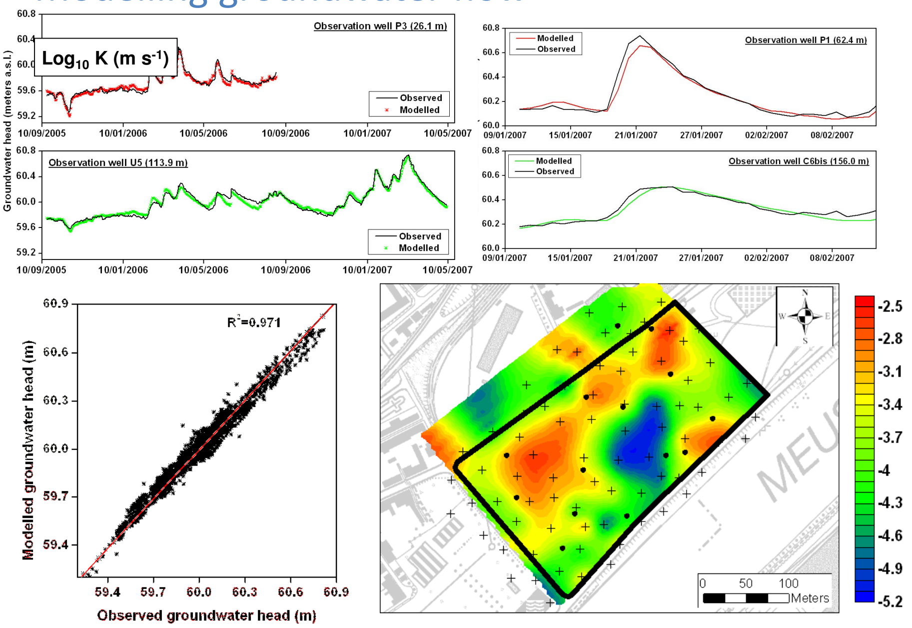
MODFLOW-2000 with inverse modelling implemented with PEST, using zonation (regional) and pilot points (local) approaches as parameterisation techniques

Pilot points (de Marsily *et al.*, 1984)

Parameterisation technique resulting in a smoothed variation of the hydraulic property over the model domain.



Modelling groundwater flow



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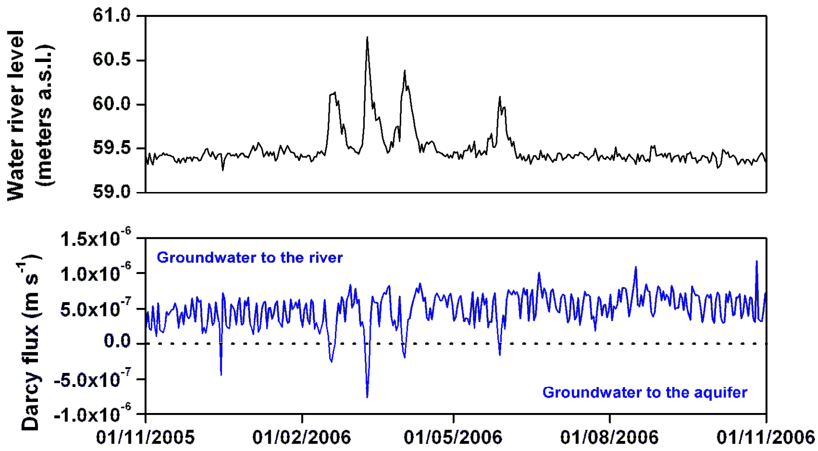
Modelling groundwater flow



- Darcy flux continuously changing in the river – aquifer interface
- Hydraulic gradient inversed when water river level over ~60 m

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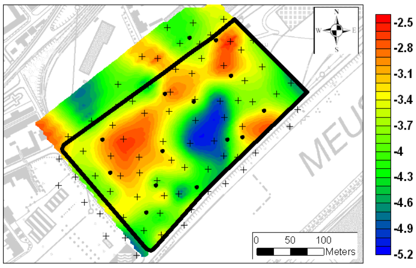
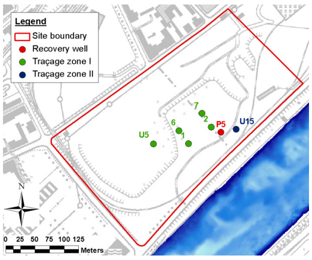
Field data are better explained considering the heterogeneity of the alluvial deposits





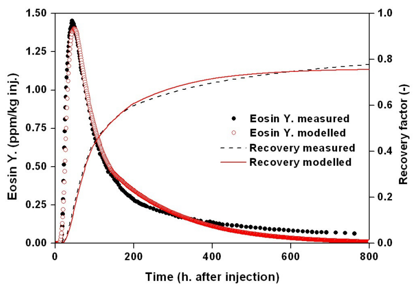
K-field heterogeneity highlighted through modelling of variations in groundwater levels with changes in river stage, using a pilot point approach

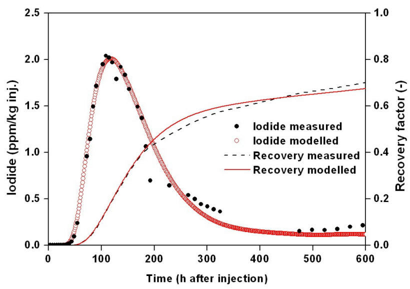
Pz1 Pz2 Pz6 Pz7 U5 not recovered because of a low pervious zone on the way to P5

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

Modelling tracer experiments

MT3DMS (Zheng and Wang, 1999)





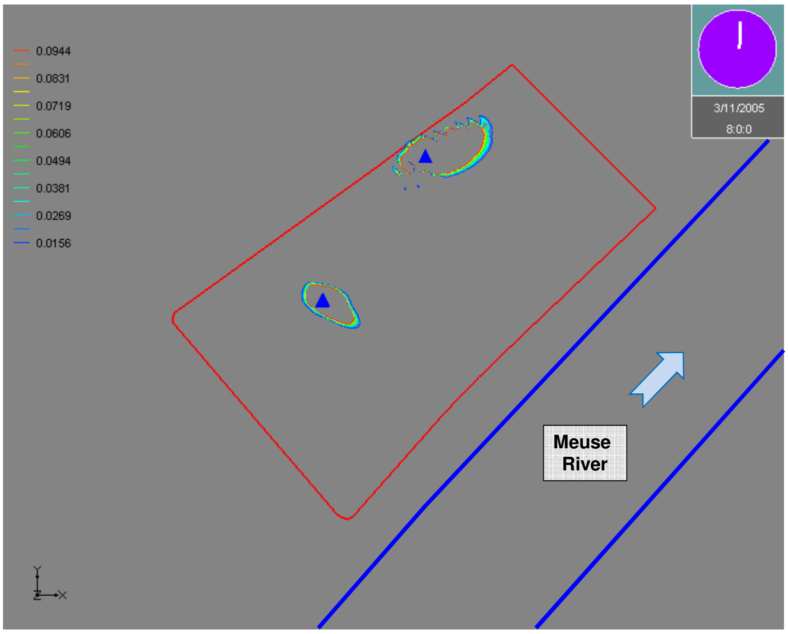
HYDRODISPERSIVE PARAMETERS	
Effective porosity (θ_m) (-)	0.03 – 0.045
Long. dispersivity (α_L) (m)	1.5 – 2.5
Trans. dispersivity (α_T) (m)	0.3 – 0.5
RETARDATION EFFECTS	
Immobile porosity (θ_{im}) (-)	0.05 – 0.1
Exchange coefficient (α) (s^{-1})	2×10^{-7} - 8×10^{-8}

Modelling reactive transport of benzene

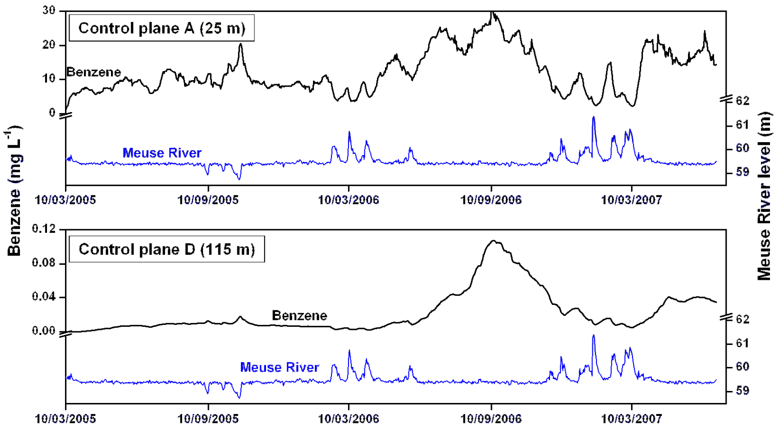
HYDRODISPERSIVE PARAMETERS	
Effective porosity (θ_m) (-)	0.04
Long. dispersivity (α_L) (m)	2.5
Trans. dispersivity (α_T) (m)	0.5
RETARDATION EFFECTS	
Immobile porosity (θ_{im}) (-)	0.1
Exchange coefficient (α) (s^{-1})	1×10^{-7}
Soil sorp. coef. for soil organic carbon (K_{oc}) ($m^3\ kg^{-1}$)	0.083
Soil organic carbon (%)	0.05
Distrib. coef. (K_d) ($m^3\ kg^{-1}$)	4.15×10^{-5}
Bulk density (ρ_b) ($kg\ m^{-3}$)	2,000
BENZENE BIODEGRADATION	
Biodegradation ct. rate* (λ) (s^{-1})	3×10^{-7}

$$R = 1 + \frac{\rho_b \times K_d}{\theta_m}$$

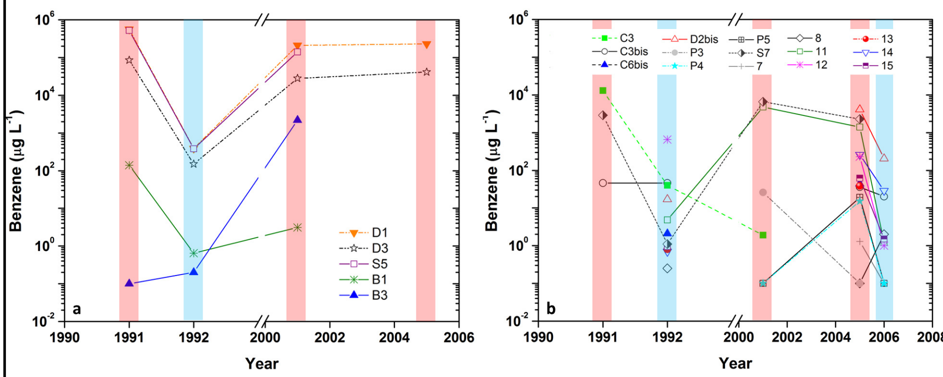
*First order rate constant calculated using $^{13}C/^{12}C$ isotope ratios of residual benzene in groundwater.



Scenario 4 (transient evolution of benzene plume)



Field data are better explained considering the dynamics of GW – river interactions



During summer, low levels in the river and benzene plume migration downgradient → increasing concentrations
During winter, higher river stages and inversion of GW – river gradient → surface water intrusion in the alluvial aquifer → benzene plume pushed back upgradient

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
- 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

Groundwater flow systems are very dynamics!

- Should be taken into account at each step of investigation
- Applied tracers may help understanding / highlighting!

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!

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