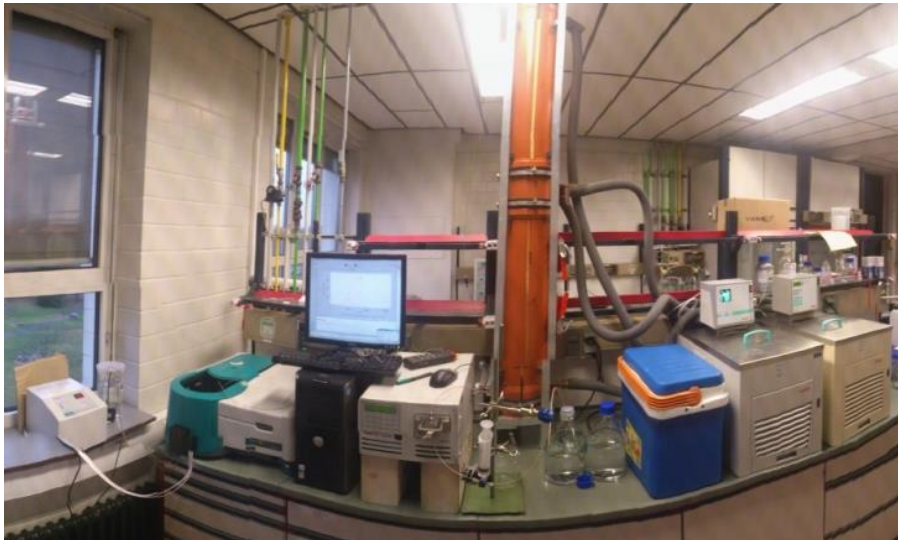
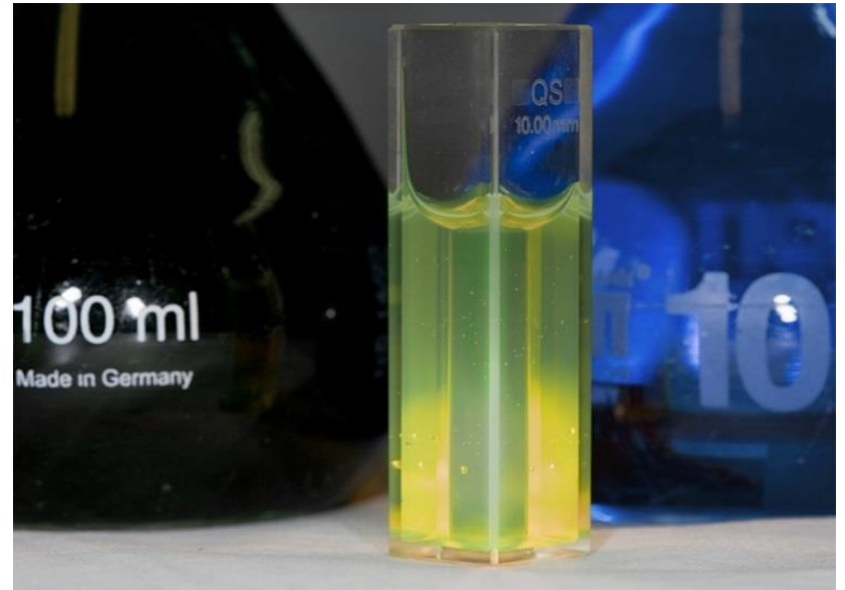




Hydrogeochemie



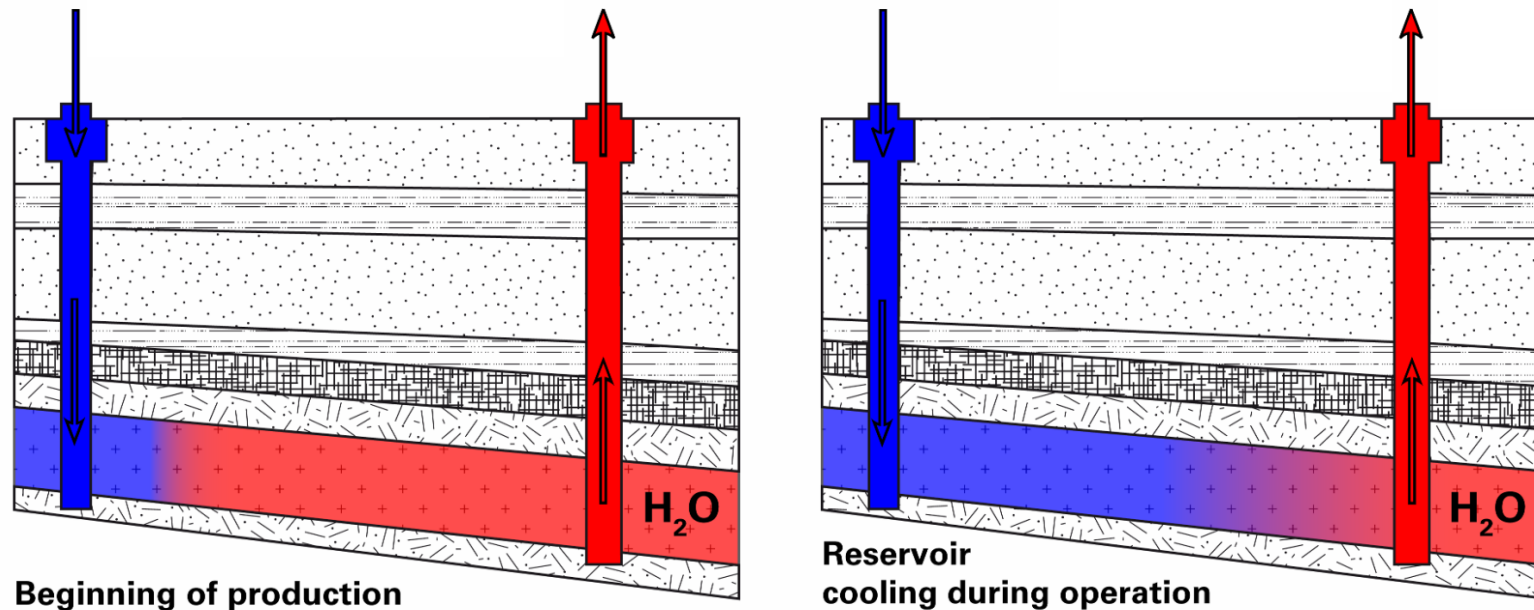
New tracer classes for improved reservoir management

Licha, Tobias¹; Mario, Schaffer²

¹Ruhr-Universität Bochum, Deutschland;

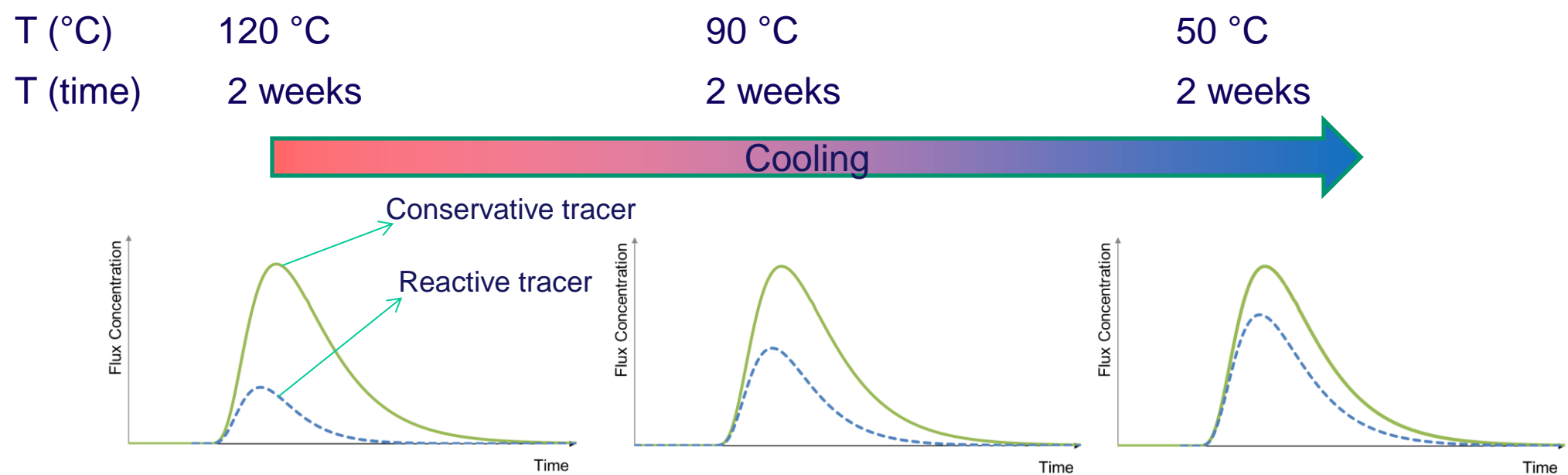
²Nds. Landesbetrieb für Wasserwirtschaft, Küsten- und Naturschutz, Hildesheim, Deutschland

- **Main process:**
 - ✓ Temperature driven chemical reaction (**Hydrolysis**) with the reservoir brine.
- **Target parameter:**
 - ✓ Temperature and its distribution (cooling fraction).



How fast?

Tracer test in reservoir to quantify thermal drawdown



Recovery of Conservative tracer – Recovery of Reactive tracer = Temperature in the Reservoir

Development of thermo-sensitive tracers (Esters)

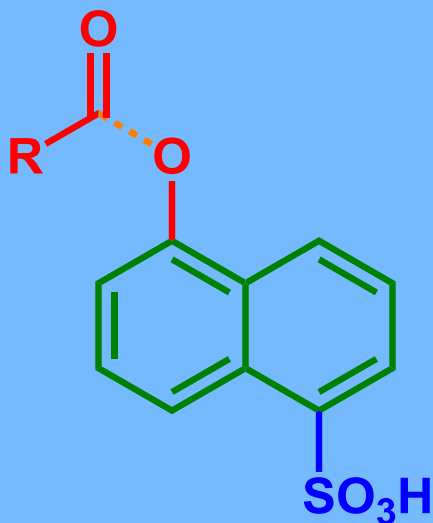
4

Established tracer for georeservoirs



Naphthalene sulfonates

Introducing a group enabling the use of hydrolysis as temperature sensitive reaction



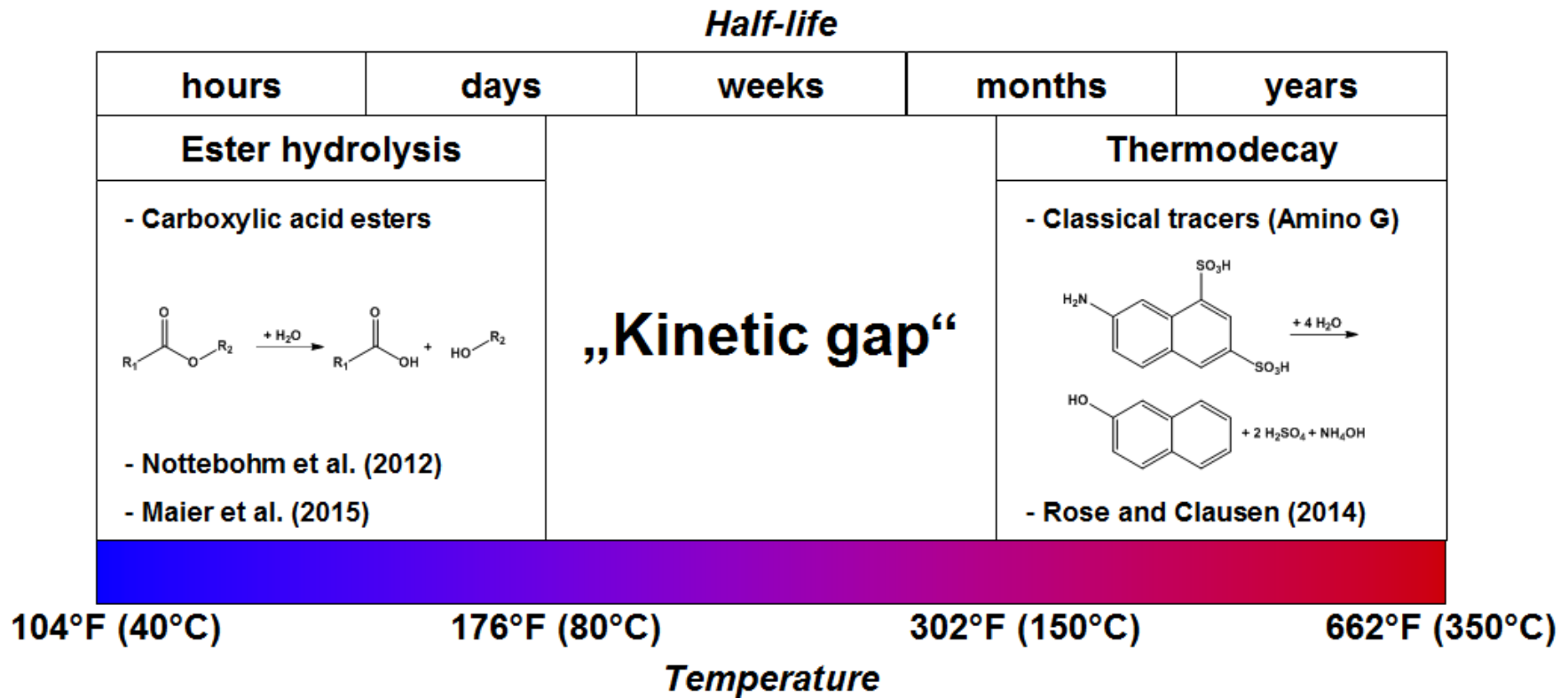
thermo-sensitive properties by hydrolysis reaction

thermally stable, highly fluorescent (ester is not fluorescent, reaction product is)

high aqueous solubility

Nottebohm M, Licha T, Sauter M (2012): Tracer design for tracking thermal fronts in geothermal reservoirs. Geothermics 43: 37–44.

- „Kinetic gap“ between hydrolyzable esters and thermodecay of classical tracers



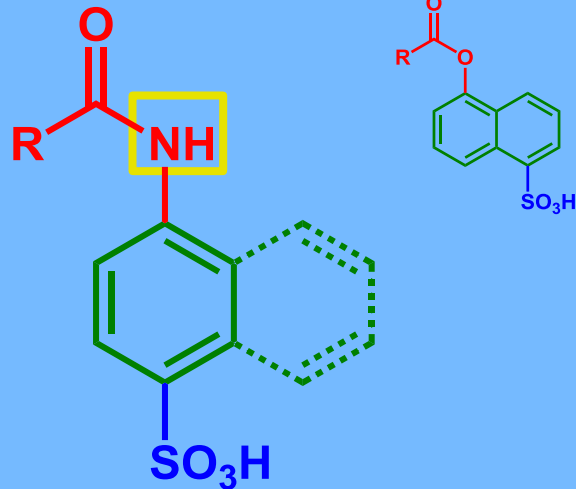
Approach to fill the „Kinetic Gap“: Amides

Established tracer for georeservoirs



Naphthalene sulfonates

Introducing a group enabling the use of hydrolysis as temperature sensitive reaction



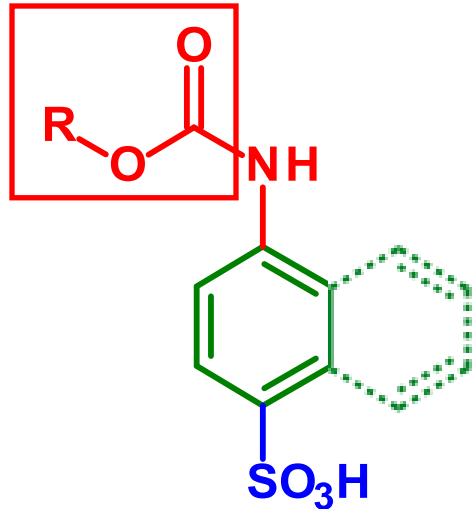
Thermo-sensitive properties by hydrolysis reaction

Thermally stable, highly fluorescent (amide is not fluorescent, reaction product is)

High aqueous solubility

Schaffer M, Idzik K R, Wilke M, Licha T (2016): Amides as thermo-sensitive tracers for investigating the thermal state of geothermal reservoirs. Geothermics 64: 180–186.

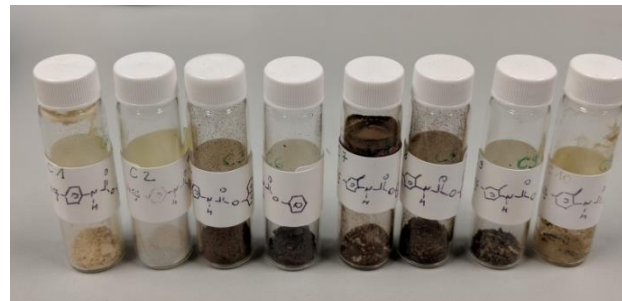
Varying acid part



Thermosensitive properties
by hydrolysis

Carbamate is not fluorescent,
reaction product is

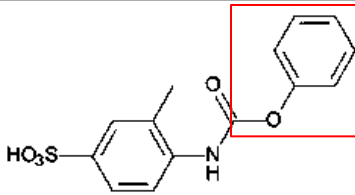
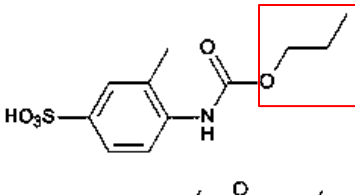
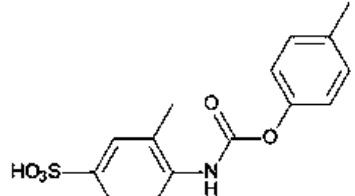
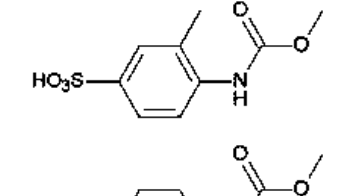
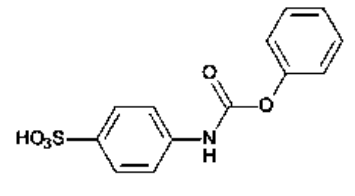
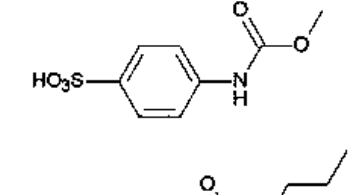
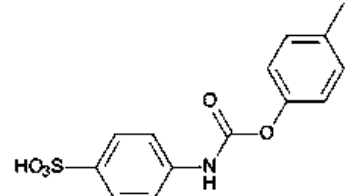
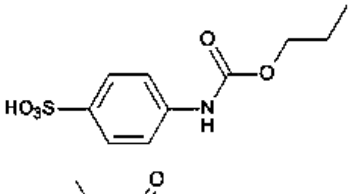
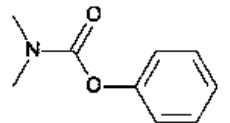
High aqueous solubility



Source: Idzik et al. (2015)

Source: Cao, V., Schaffer, M., Licha, T., 2018. The feasibility of using carbamates to track the thermal state in geothermal reservoirs. Geothermics 72. doi:10.1016/j.geothermics.2017.12.006

Overview on carbamate hydrolysis ($T = 95\text{ }^{\circ}\text{C}$, $\text{pOH} = 7$)

Carbamate structure	$k_h/k_{h,max}$	Carbamate structure	$k_h/k_{h,max}$
C5 	1.00000	C8 	0.00007
C6 	0.77002	C7 	0.00005
C1 	0.46723	C3 	0.00002
C2 	0.18599	C4 	0.00002
		C9 	0.000001

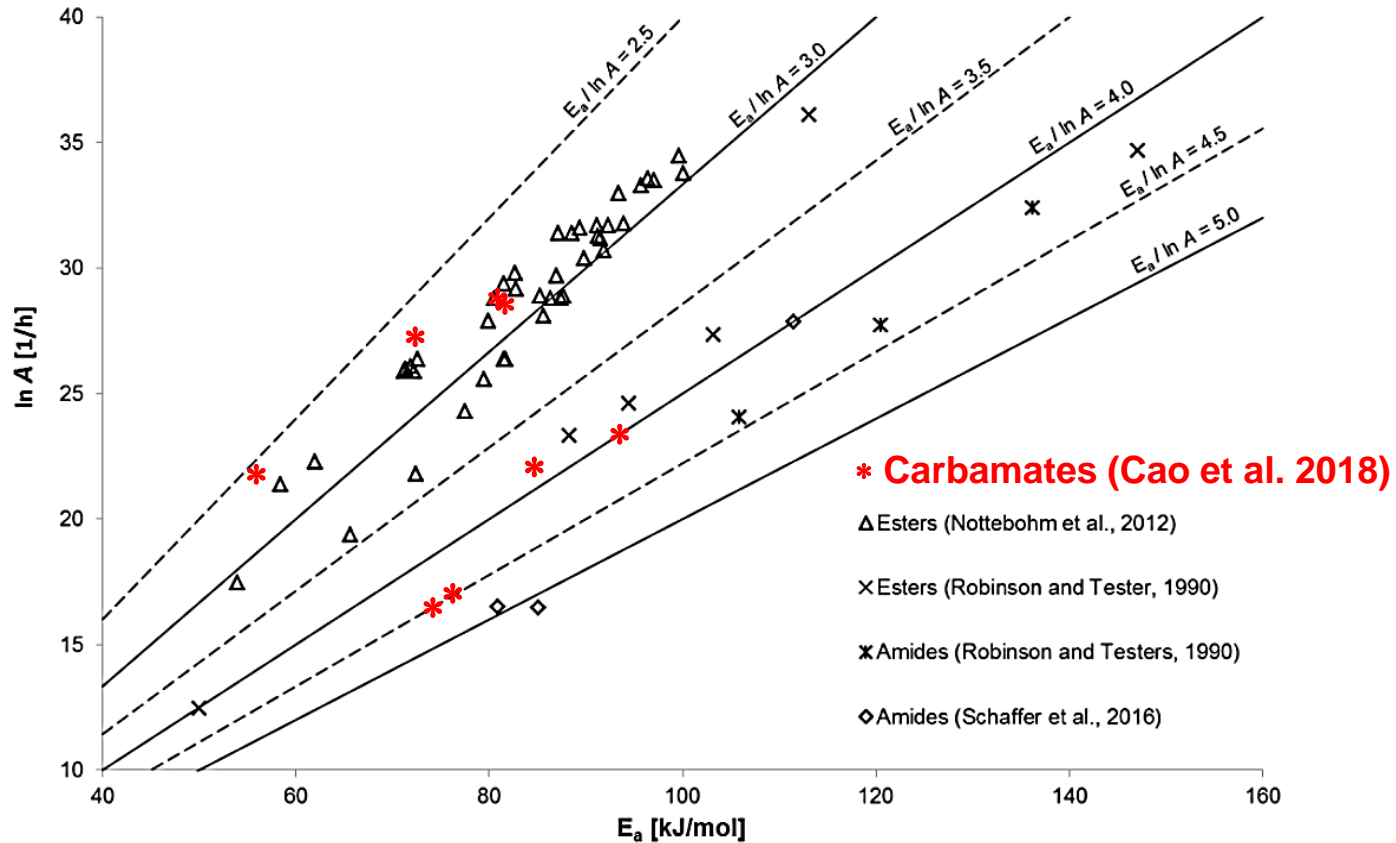


⇒ Broad range of the rate constant k_h

⇒ The structure of the acid part controls the speed of hydrolysis

Dependence of reaction rate constant (k_h) on temperature (2)

Plummer et al. 2010: $E_a / \ln A$ are too close to measure thermal drawdown



Source: Jin et al. (2017)

$\Rightarrow E_a / \ln A$ of carbamates from 2.5 to 5

\Rightarrow Carbamates cover the range the for esters and amides

Compound classes

Carbamates are promising thermo-sensitive tracers

Molecular structure and the temperature have a significant influence on the reaction rate.

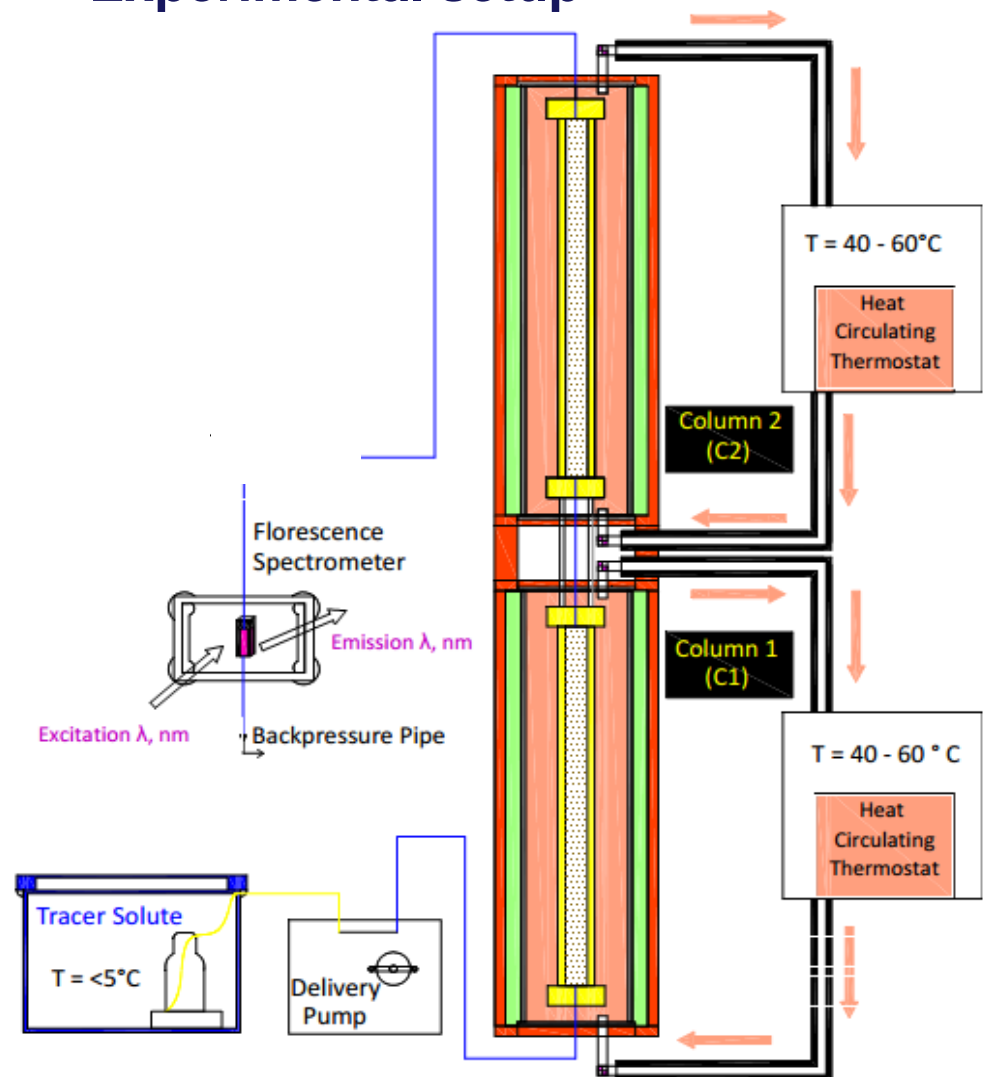
<i>Temperature</i>			
40°C	80°C	150°C	350°C
Carbamates hydrolysis			Thermodecay of Classical tracers
Esters hydrolysis	Amides hydrolysis		

Transferability to field needed

- Thermal gradient with different injection methods
 - ✓ Continuous injection
 - ✓ Moving front
 - ✓ Push-Pull
 - ✓ Pulse injection
- Defined temperature is applied (T -target) and compared to the temperature calculated from the tracer breakthrough curve (T -obtained).

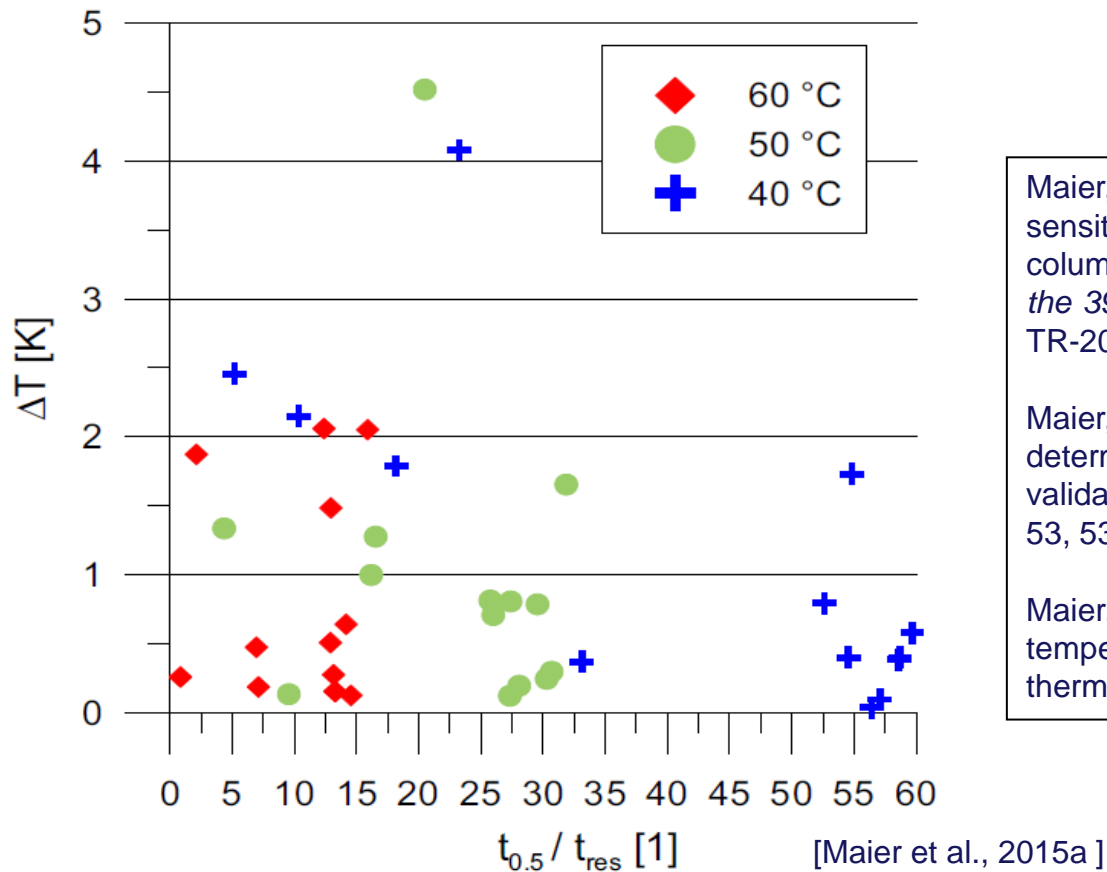
(Maier et al., 2015a und b)

- Experimental setup



Flow-through experiments

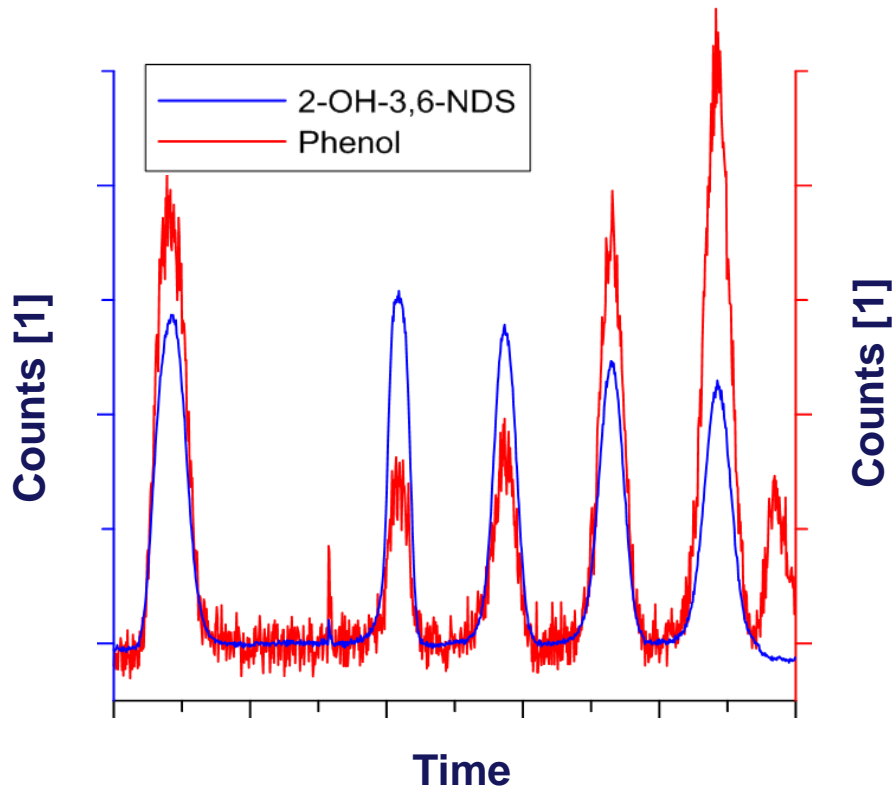
Successful application demonstrated in lab columns for the first time
(Maier et al., 2014; Maier et al., 2015a, b)



Maier, F., Schaffer, M., Licha, T., 2014. Ability of thermo-sensitive tracers for precisely estimating system temperatures in column experiments with thermal gradient. In: *Proceedings of the 39th Stanford Geothermal Workshop*, Stanford, USA, SGP-TR-202.

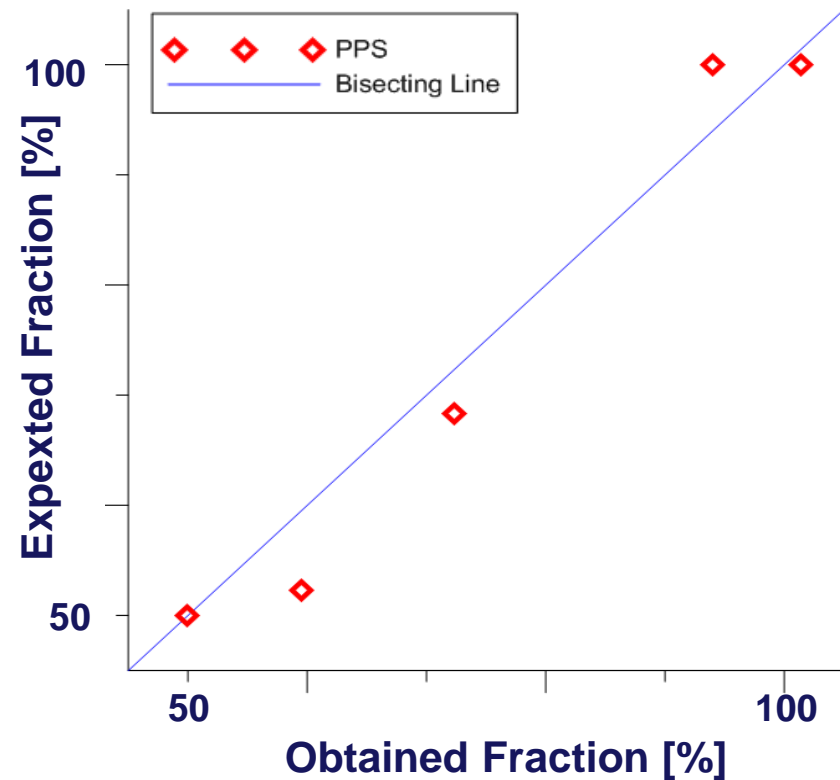
Maier, F., Schaffer, M., Licha, T., 2015a. Temperature determination using thermo-sensitive tracers: Experimental validation in an isothermal column heat exchanger. *Geothermics* 53, 533–539.

Maier, F., Schaffer, M., Licha, T., 2015b. Determination of temperatures and cooled fractions by means of hydrolyzable thermo-sensitive tracers. *Geothermics* 58, 87–93.



- Phase 1: 5 pulses injected in 2h
- Phase 2: Stop flow for 20 min
- Phase 3: Reversed flow

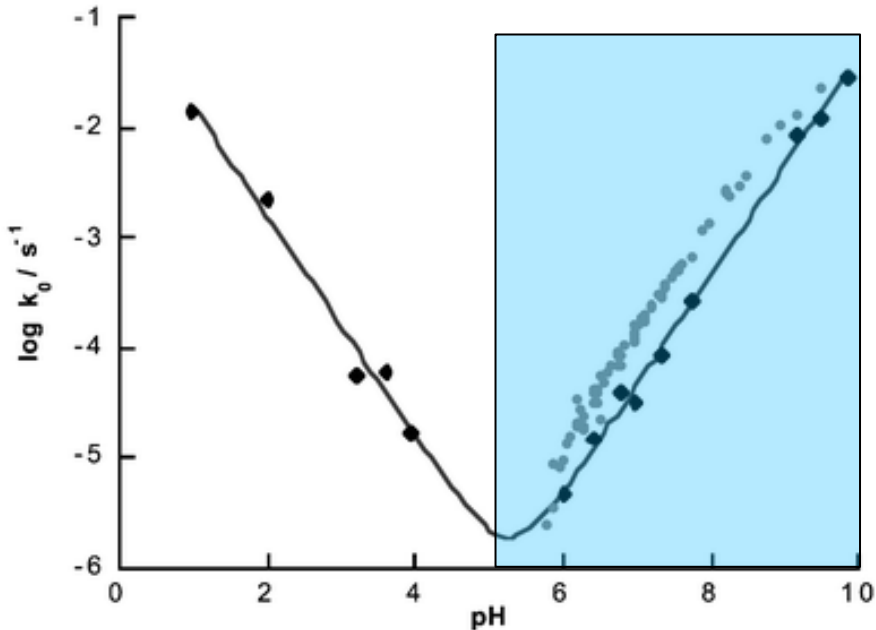
T_{eff}	T_{mean}	cooled fraction
54	50	0,50
43	40	1,01
45	41	0,94
50	46	0,72
52	48	0,60



Compound classes: boundary conditions

reservoir pH: 2–7.5 (depends on reservoir temperature)

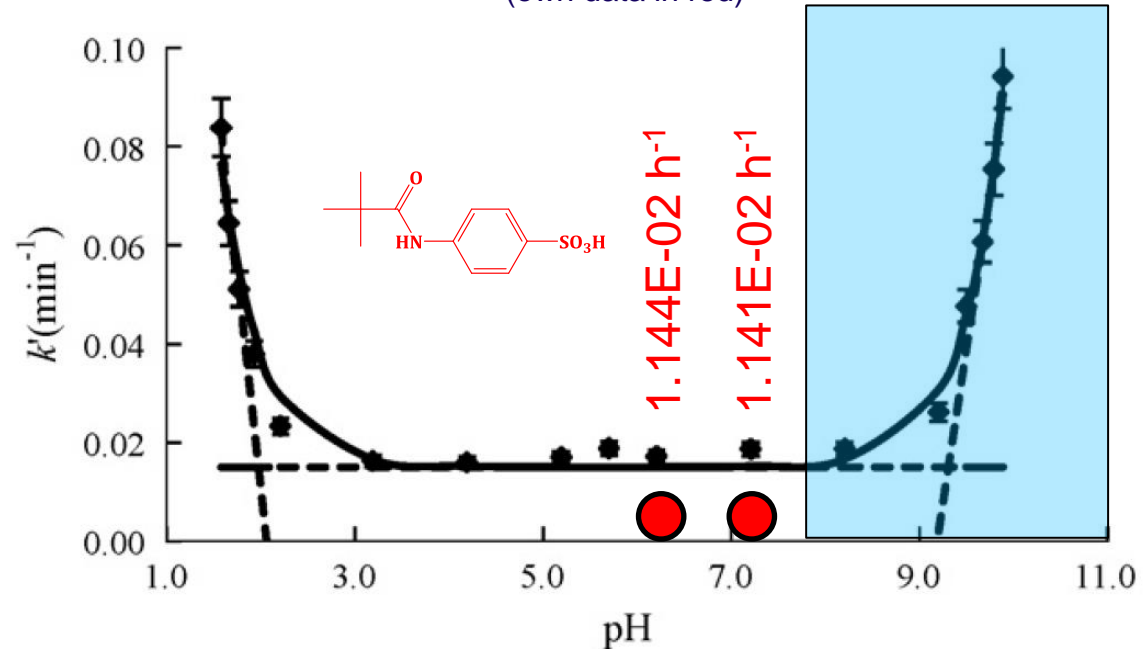
Esters



[Kirby and Marriott, 2002]

Amides

(own data in red)



[Duan et al., 2010]

Carbamates: reaction rate constant for primary pH 0–7, secondary pH 2–9

OH⁻ catalyzed reaction field,
depends on pOH,
pH+pOH=pK_w, pK_w= f(T)

further drawback of esters:

- naturally occurring enzymes (hydrolase) catalyse the reaction
- this speeds up reaction by factor of 10
- may/will give unreliable temperatures in natural low temperature systems

☞ catalysis by natural enzymes not (yet) observed for amides and carbamates

Organic Molecules as Sorbing Tracers for the Characterization of Fracture Surface Areas in Enhanced Geothermal Systems (EGS)



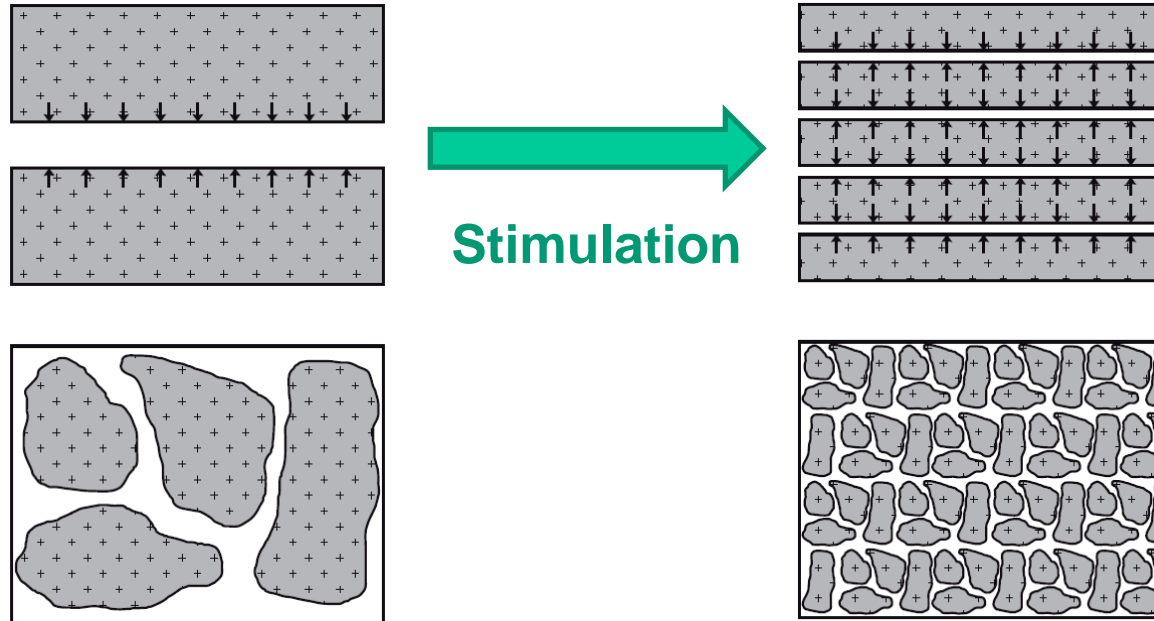
Fracture Surface Area

A_{frac} related to heat exchange area (A_{heat})

lower A/V ratio

higher A/V ratio

same
bulk
porosity



➔ Increase of A_{frac} due to hydraulic reservoir stimulation

Area available for Sorption is proportional to A_{frac}

➡ Retardation factor (R) is measure for A_{frac}/V :

$$R = 1 + \frac{A_{frac}}{V} K_{fw}$$

➡ Sorption affinity K_{fw} (fracture-surface/water partitioning coefficient) depends on **molecular structure** and **boundary conditions**

Schaffer M, Warner W, Kutzner S, Börnick H, Worch E, Licha T (2017): Organic molecules as sorbing tracers for the assessment of surface areas in consolidated aquifer systems. Journal of Hydrology 546: 370–379.

State of Art: Sorbing tracers

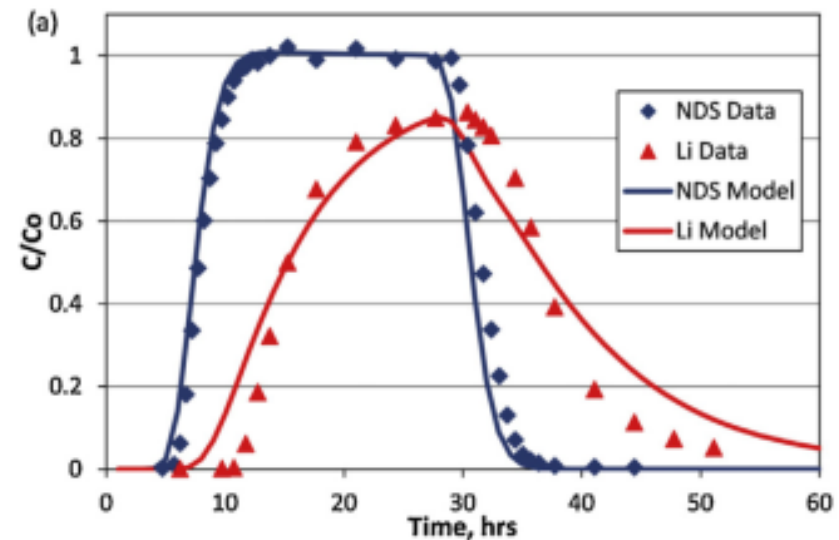
Reservoir surfaces have negative charge (quartz, clay coatings, etc.)

➔ Use of cations (+)

Inorganic cations

Li^+ , Cs^+ (Dean et al., 2012; 2015)

“cation-exchanging tracers”



[Dean et al., 2015, *Geothermics*]

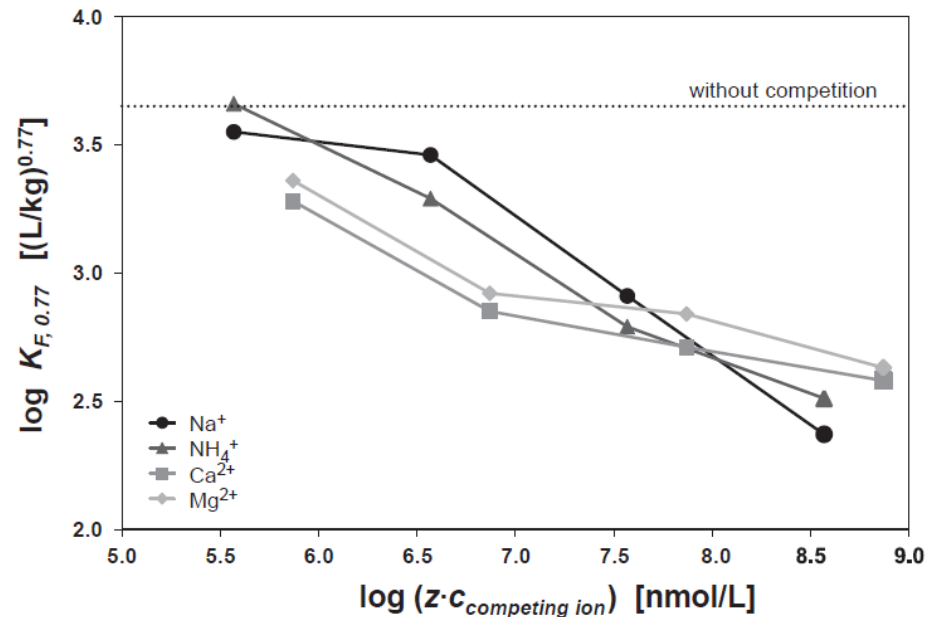
Advantages: thermally stable, low toxicity, inexpensive

Disadvantages: limited number of ion types, analysis in trace concentrations, irreversible fixation in clay interlayers (Cs^+ , K^+ , NH_4^+), no additional sorptive interactions possible, potential geogenic background

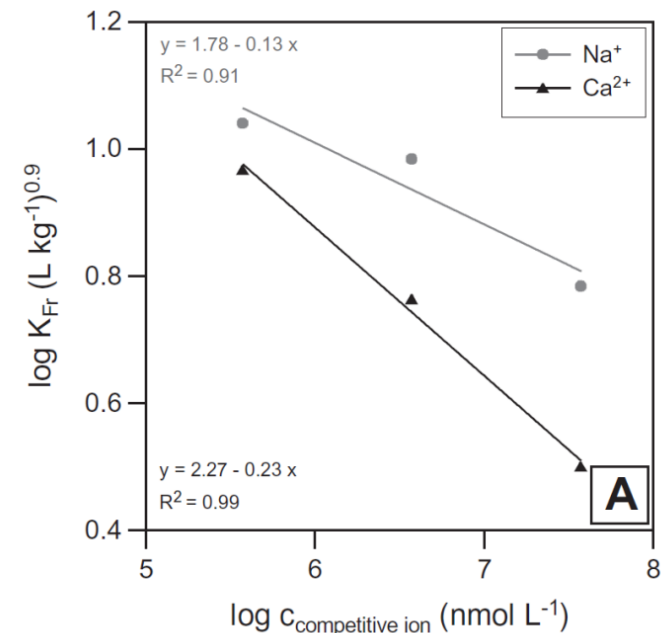
Organic cations: Competition with Other Ions

Sorption of metoprolol onto silica gel and aquifer sediment:

- Predictable within a certain concentration range
- Competing ions of same valence have similar effects



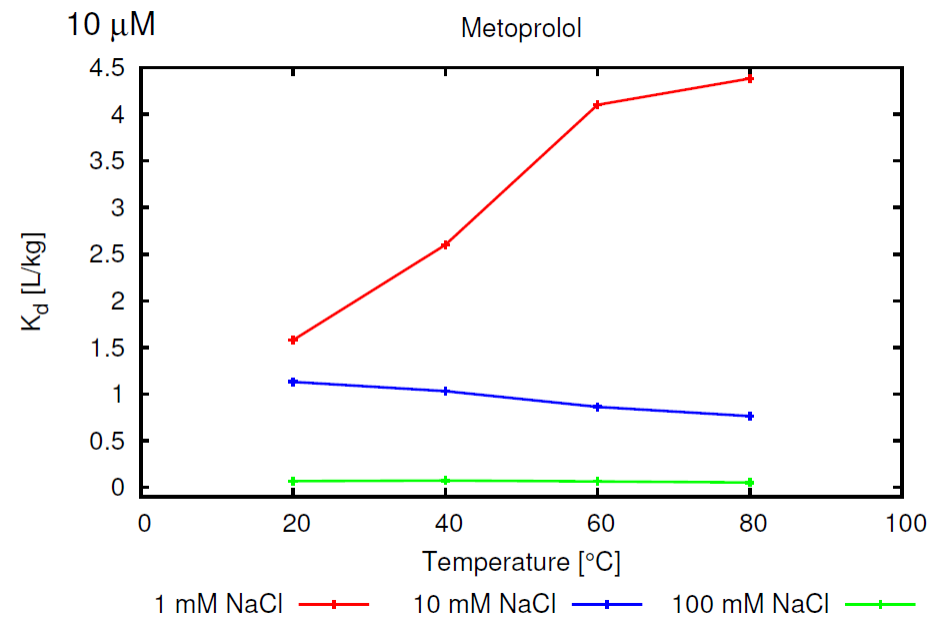
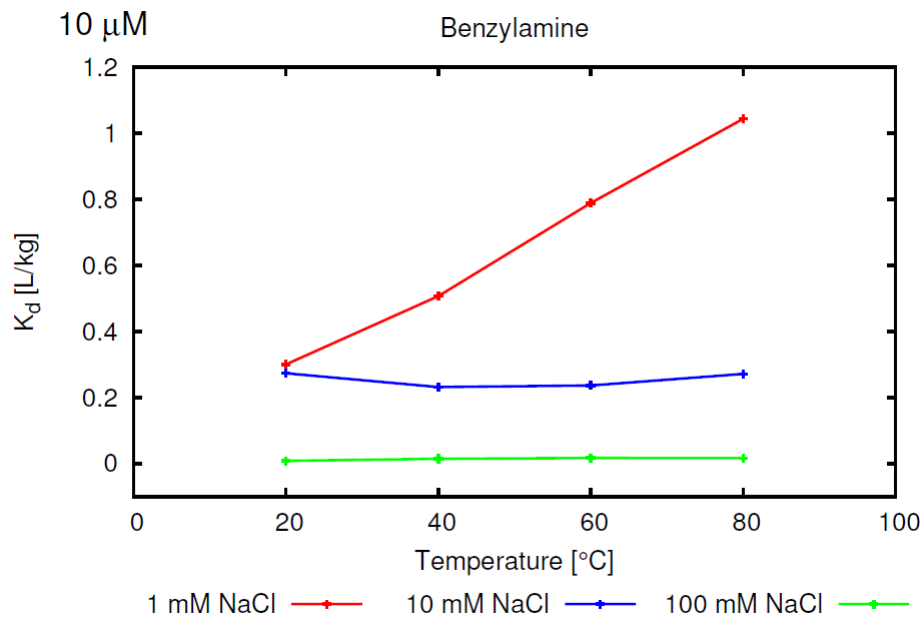
Kutzner S, Schaffer M, Börnick H, Licha T, Worch E (2014): Sorption of the organic cation metoprolol on silica gel from its aqueous solution considering the competition of inorganic cations. *Water Research* 54: 273–283.



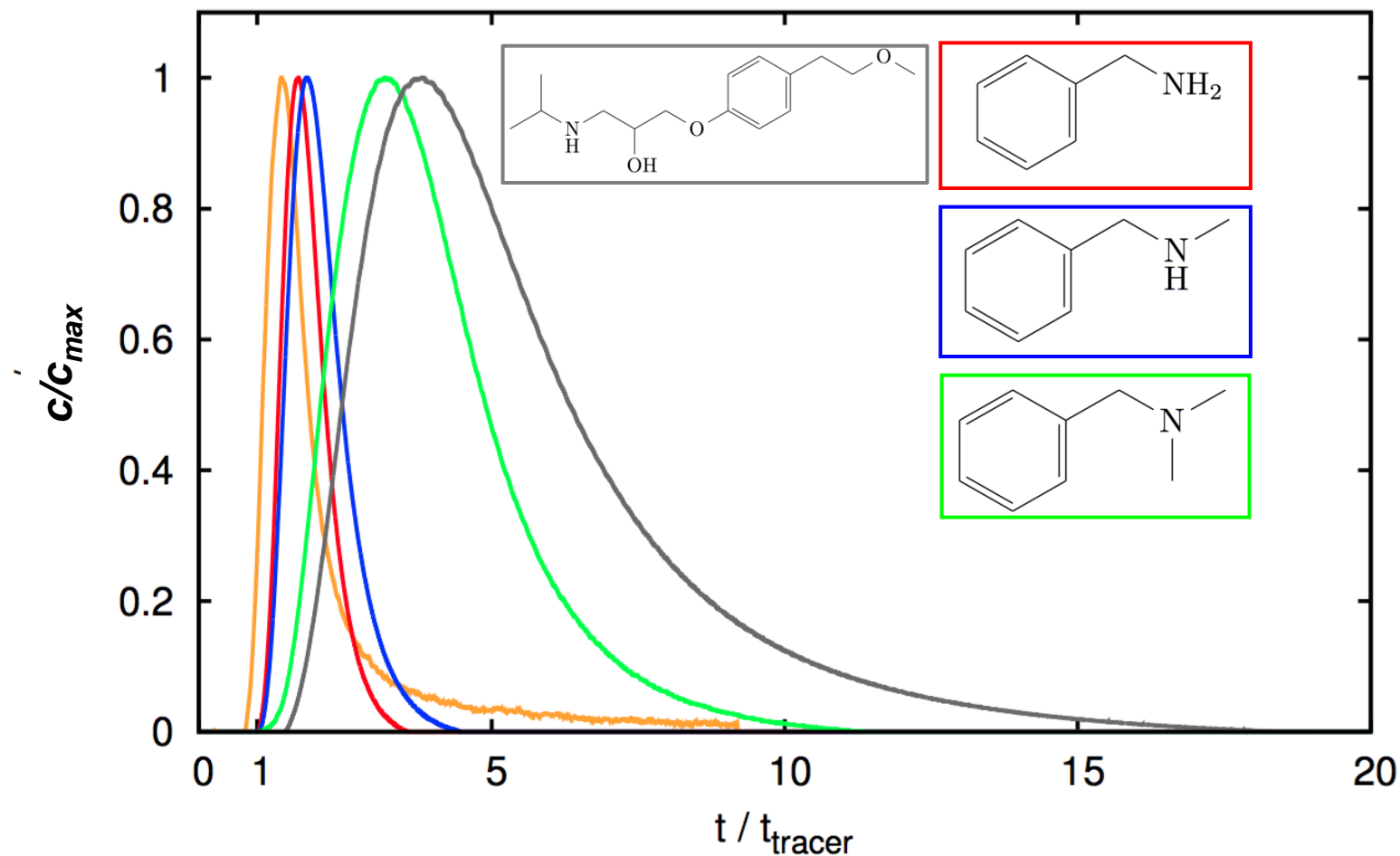
Niedbala A, Schaffer M, Licha T, Nödler K, Börnick H, Ruppert H, Worch E (2013): *Chemosphere* 90(6): 1945–1951.

Influence of Temperature

- No temperature-dependence for salt concentrations $>0.5\text{g/L}$
- Higher retardation with higher temperatures only for low salinity

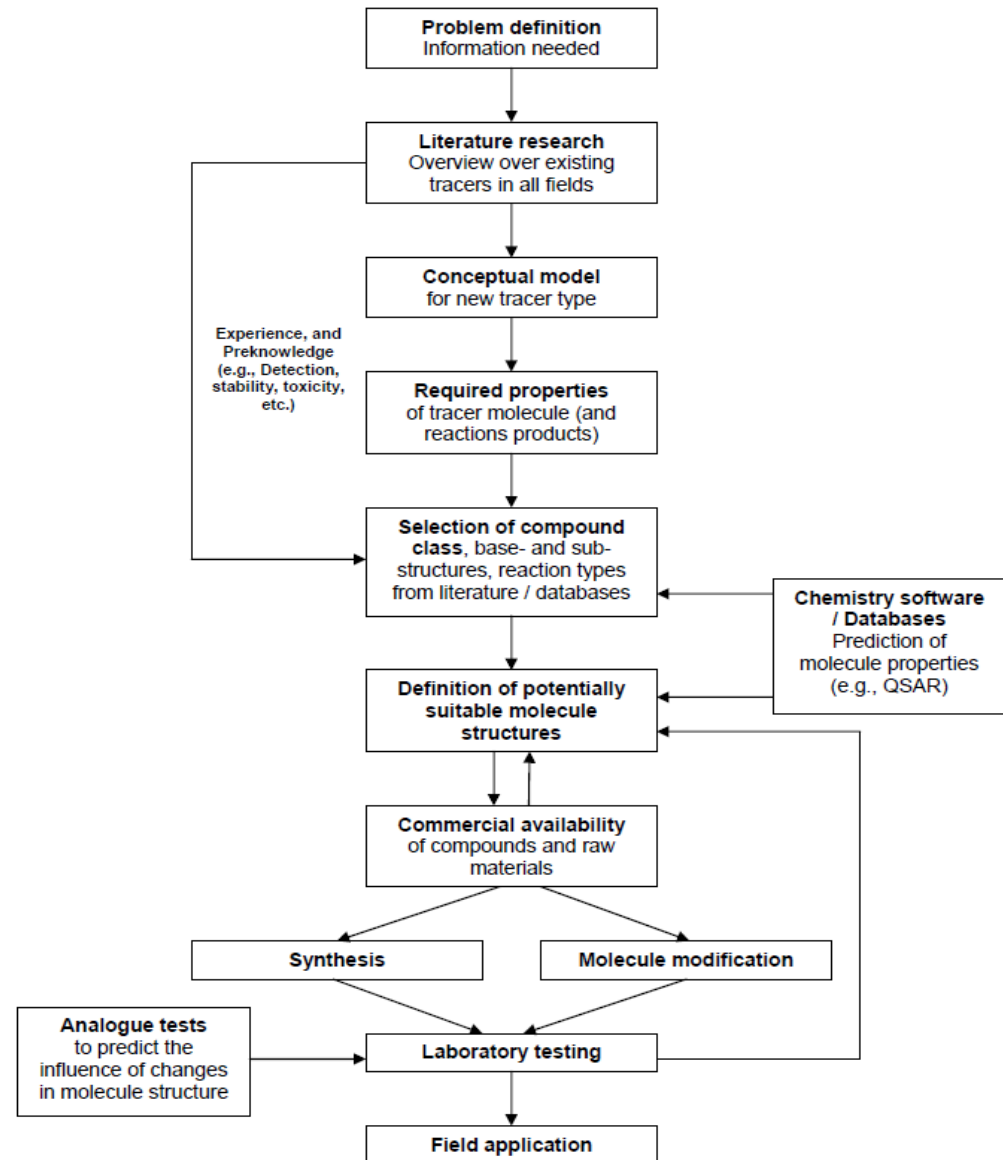
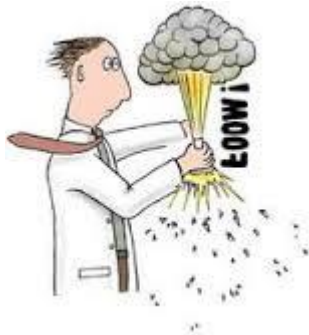


20 °C, 10 mM NaCl, 10 μM



Tracer design

- Molecular design to support tailor and problem-oriented tracer cocktails.



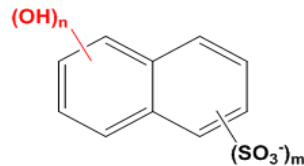
Non-conservative tracer design

Conservative tracer molecule

Non-Conservative tracer molecule



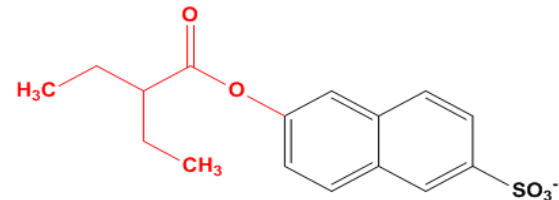
Base molecule



n-Hydroxynaphthalene-m-sulfonate

Molecular design

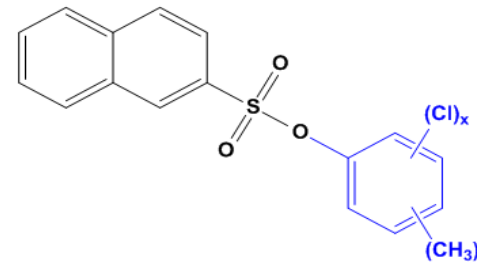
Thermo-sensitive compound



2-Ethylbutyryl-2-hydroxynaphthalene-6-sulfonate

Molecular design

Interface-sensitive compound



x-Chloro-y-methylphenylnaphthalene-2-sulfonate

Thank you



Bundesministerium
für Umwelt, Naturschutz
und Reaktorsicherheit

DFG Deutsche
Forschungsgemeinschaft

Bundesministerium für Umwelt (BMU, 0325417)

Deutsche Forschungsgemeinschaft (DFG, LI 1314/3-1 and 2)

Mechthild Rittmeier, Anke v. Gaza, Lothar Laake, Reiner Schulz

Peter Rose (University of Utah)

Mitchell Plummer (Idaho National Laboratory)



***And of course you, the audience
for your attention and interest!***