USE OF ARTIFICIAL TRACERS AS TOOL TO QUANTIFY CONTAMINATION OF DEEP GROUNDWATER SAMPLES BY DRILLING FLUID
IN THE FRAME OF THE NAGRA DEEP DRILLING PROJECT

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Introduction

Ten artificial tracers were tested in lab experiments as tool to quantify contamination of deep groundwater samples by four drilling fluids (experiment 1) in regard to recovery rate (0, 3, 5, 101 days). Additionally, the five best tracers were added in powdered Opalinus Clay (OC) suspensions (10, 20, 50 g ad 100 ml demin. water) in order to simulate the uptake by solids in the drilling fluid (experiment 2, recovery rate). The tracers were analyzed by HPLC-FLD using silica columns or a graphite column depending on the used tracer. For the choice of tracer, the following properties must be considered: heat stability, sorption affinity, solubility and low detection limit.

Detection and quantification limits of the used tracers.

	limit of detection [µg/l]	limit of quantification [µg/l]
Uranine	0.0009	0.003
EOY	0.008	0.024
SRB	0.004	0.014
SRG	0.002	0.006
PYR	0.01	0.03
1368PTSA	0.002	0.006
NaN	0.01	0.03
1NSA	0.02	0.05
15NDSA	0.01	0.03
136NTSA	0.1	0.3

Experiment 1: Tracer-Drilling Fluid-Interaction

Drilling Fluids
- High Performance Water-Based Mud (HPWBM)
- Pure-Bore Drilling Fluid
- Polymer Drilling Fluid
- Potassium Silicate Drilling Fluid

Tracers:
UR, EOY, SRB, PYR, 1368 PTSA, NaN, 136NTSA, 1NSA, 15NDSA

Experimental set-up:
UR, PTSA 10 ng Tracer + 10 ml Drilling Fluid → 1µg/l
Other Tracers 100 ng Tracer + 10 ml Drilling Fluid → 10 µg/l

Sampling intervals

Polymer Drilling Fluid

start	3 days	5 days	7 days	26 days	101 days
100 µl	100 µl	100 µl	10 µl	10 µl	10 µl

Pure-Bore Drilling Fluid

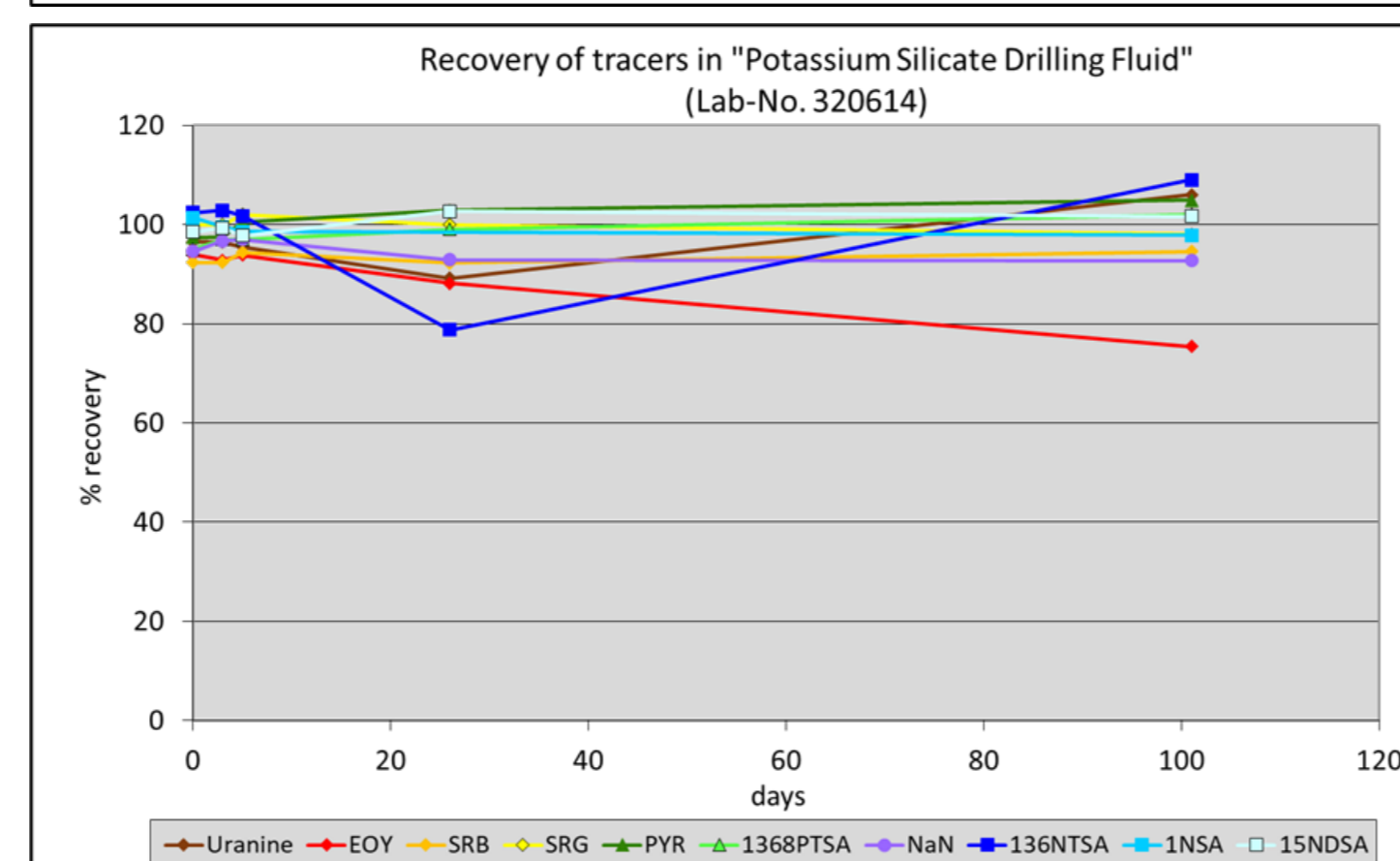| start	3 days	5 days	26 days	101 days
100 µl	100 µl	100 µl	100 µl	100 µl

"High Performance Water Based Mud" (HPWBM)

start	3 days	5 days	6 days	26 days	101 days
100 µl	100 µl	100 µl	100 µl	100 µl	100 µl

Potassium Silicate Drilling Fluid

start	3 days	5 days	26 days	101 days
100 µl	100 µl	100 µl	100 µl	100 µl

Filtration of drilling fluids has shown adsorption effects, therefore sampling and dilution of homogenised sample in water demin. for analysis is recommended.

Recovery of tracers in "Polymer Drilling Fluid" (Lab-No. 320611) without pH adjustment

Recovery of tracers in "High Performance Water Based Mud" (Lab-No. 320613)

Recovery of tracers in "Pure-Bore Drilling Fluid" (Lab-No. 320612) without pH adjustment

Recovery of tracers in "Potassium Silicate Drilling Fluid" (Lab-No. 320614)
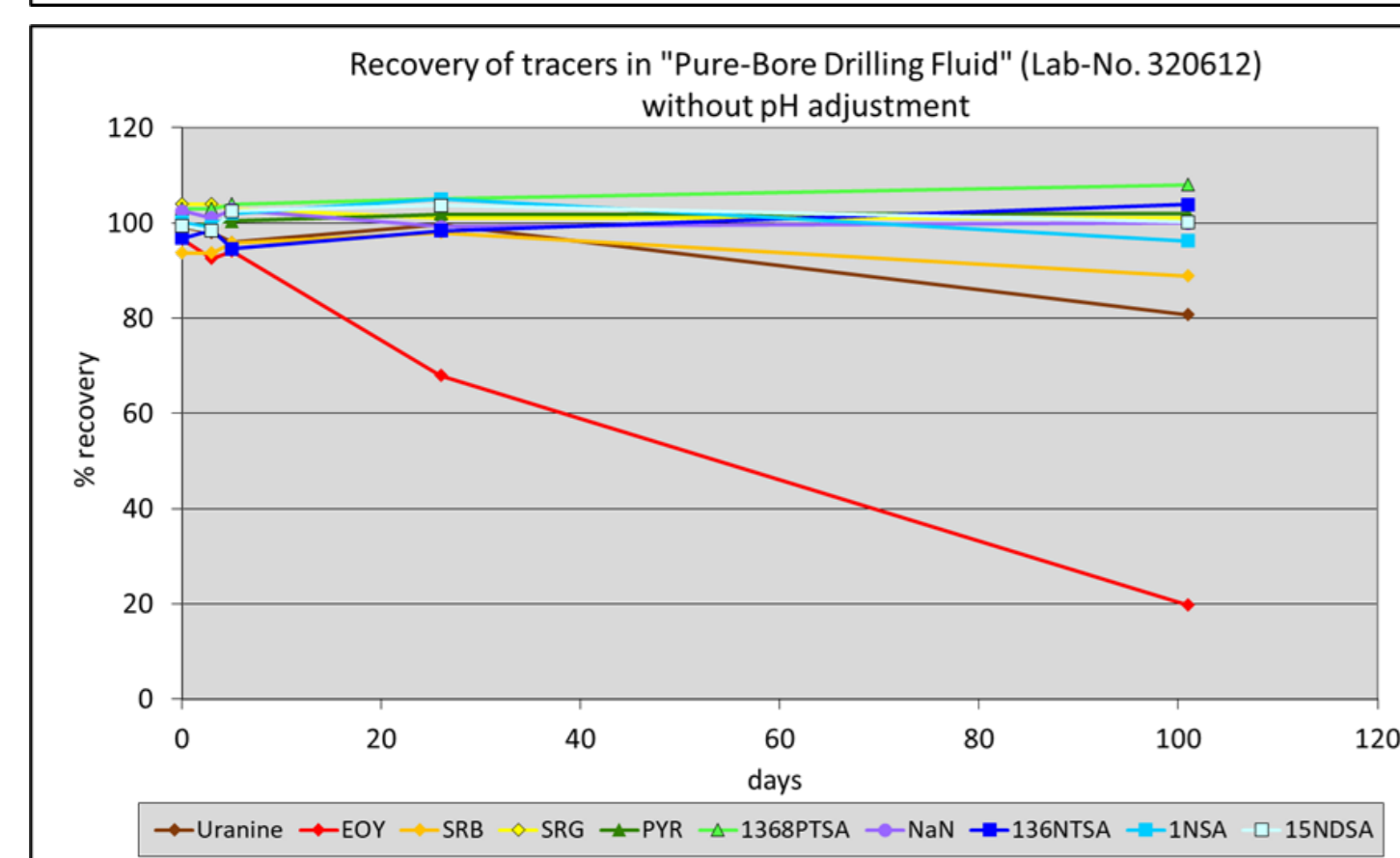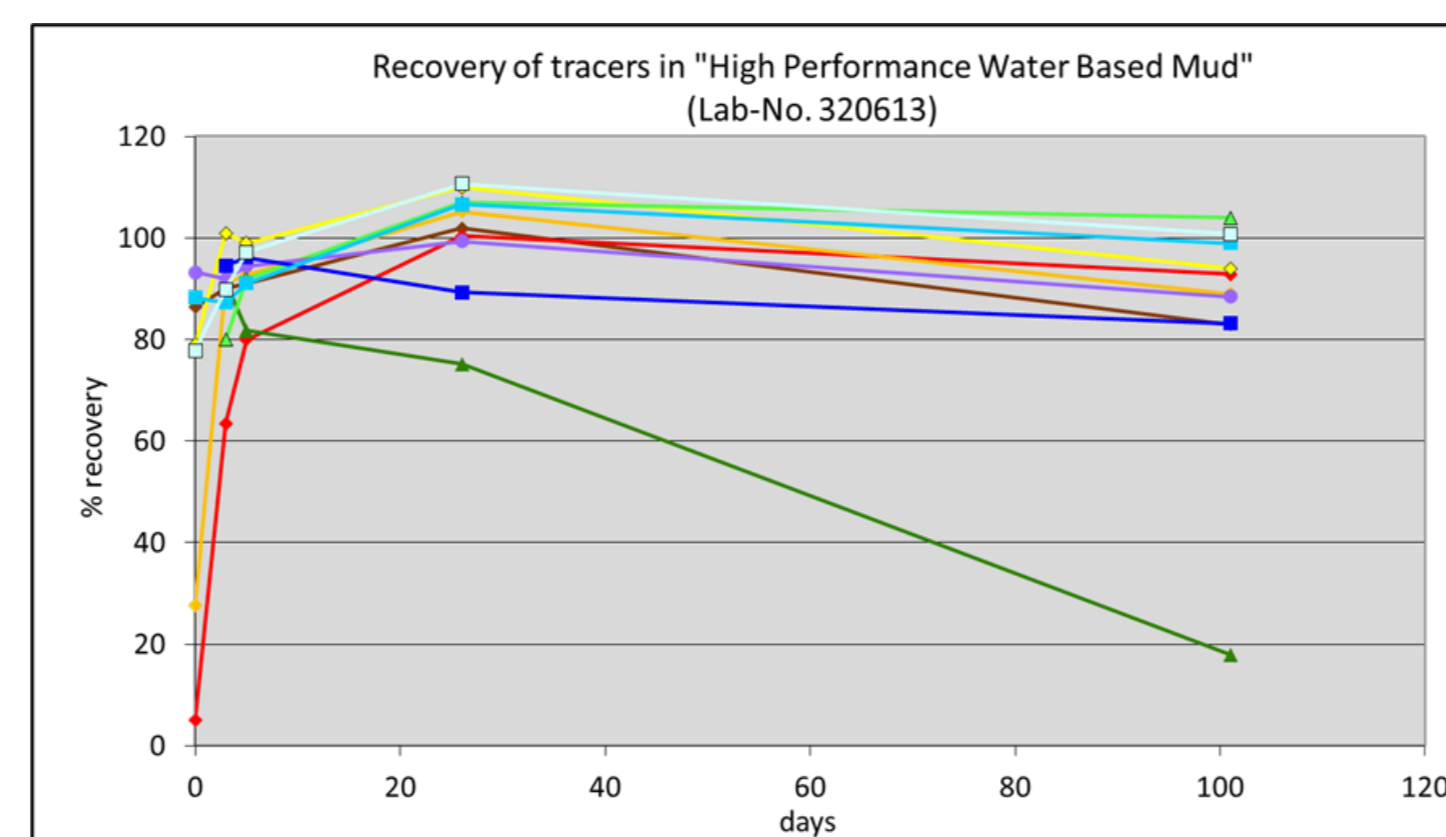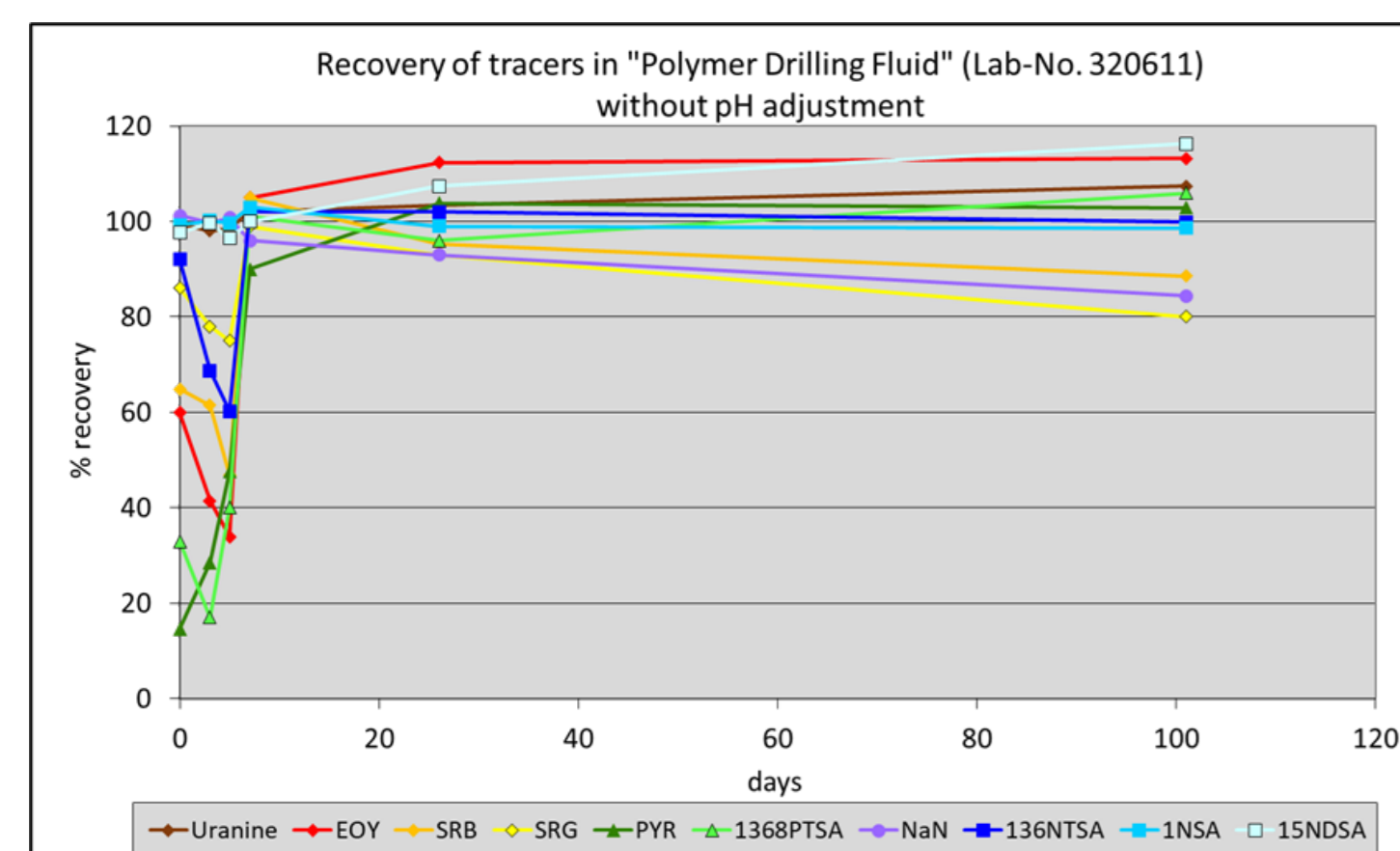
Conclusion

Evaluation of 10 tracers for use in different drilling fluids

	Polymer Drilling Fluid	Pure-Bore Drilling Fluid	High Performance Water Based Mud	Potassium Silicate Drilling Fluid
Uranine	1	1	3	2
EOY	7	9	8	10
SRB	6	3	6	9
SRG	5	2	4	1
PYR	9	8	10	7
1368PTSA	8	6	9	8
NaN	4	4	1	5
136NTSA	10	10	7	6
1NSA	2	5	2	3
15NDSA	3	7	5	4

- good stability
- low detection limit
- low interaction
- low sorption affinity

→ good recovery rate
→ usable tracers:
  → **Uranine**
  → **SRG**
  → **1NSA**
  → **NaN**

➢ not recommendable: EOY, SRB, 1368PTSA (maybe in higher concentrations)

Experiment 2: Tracer – Rock-Interaction

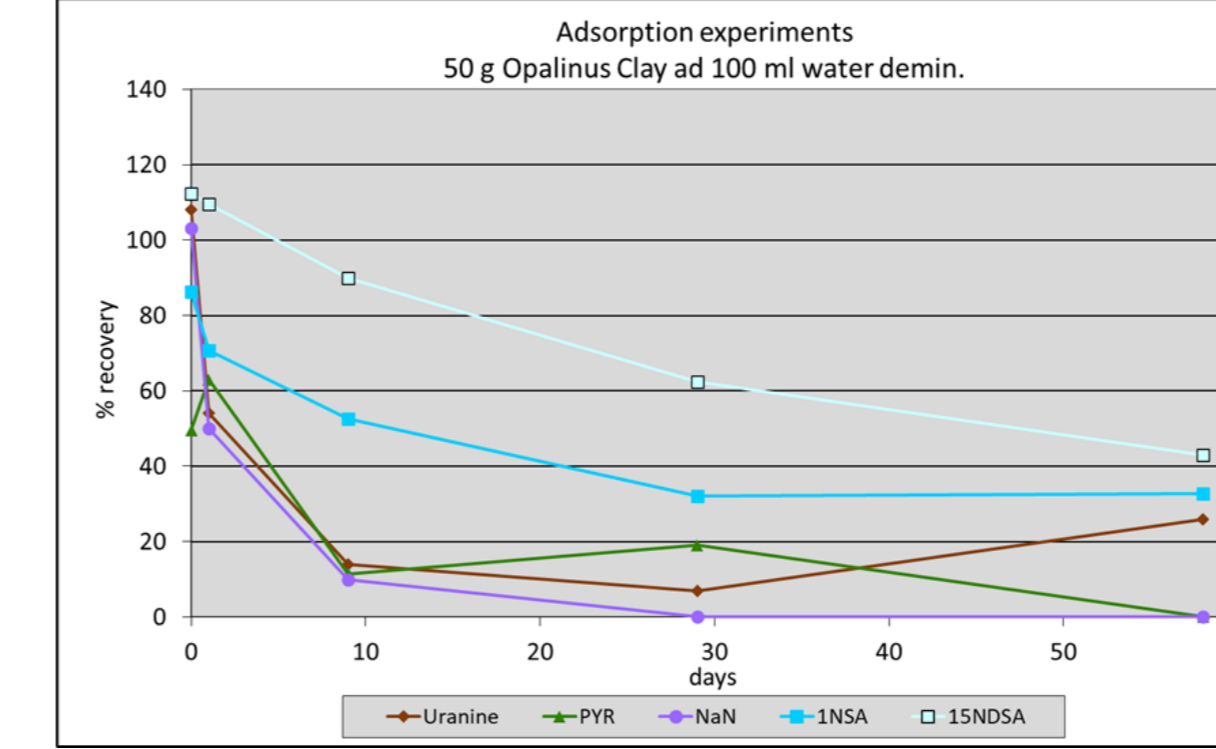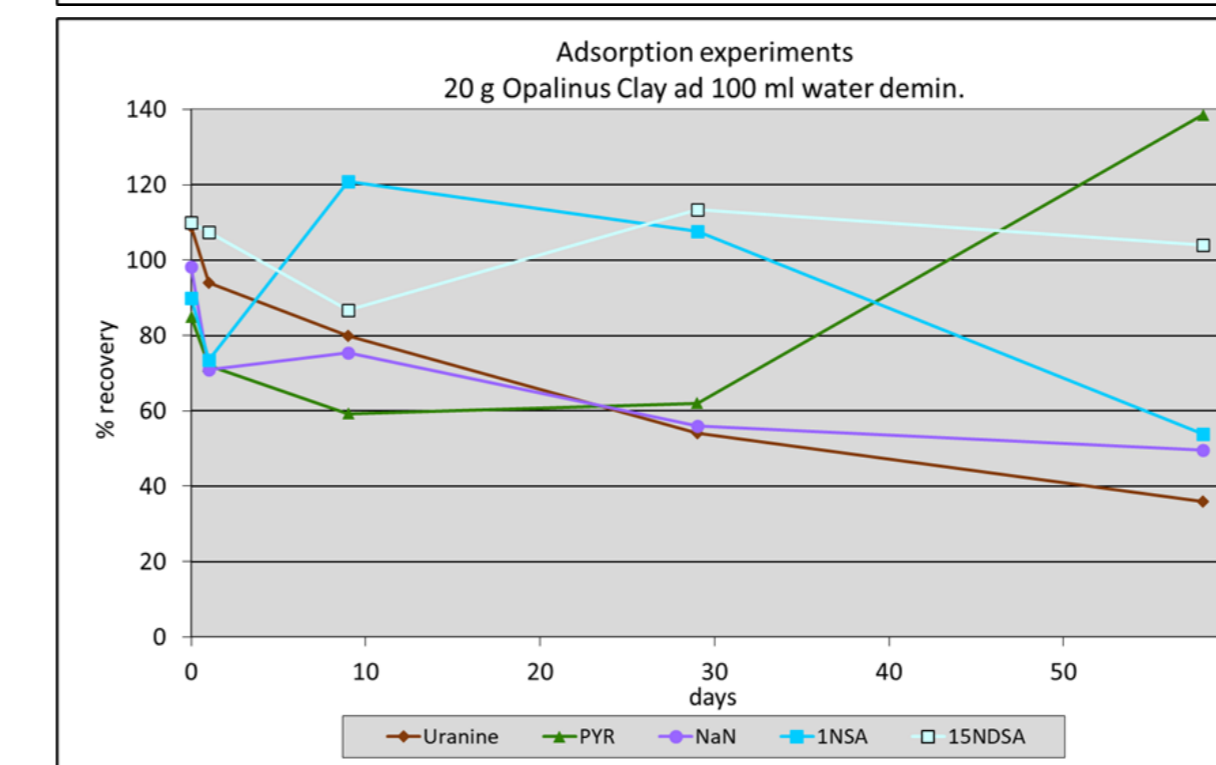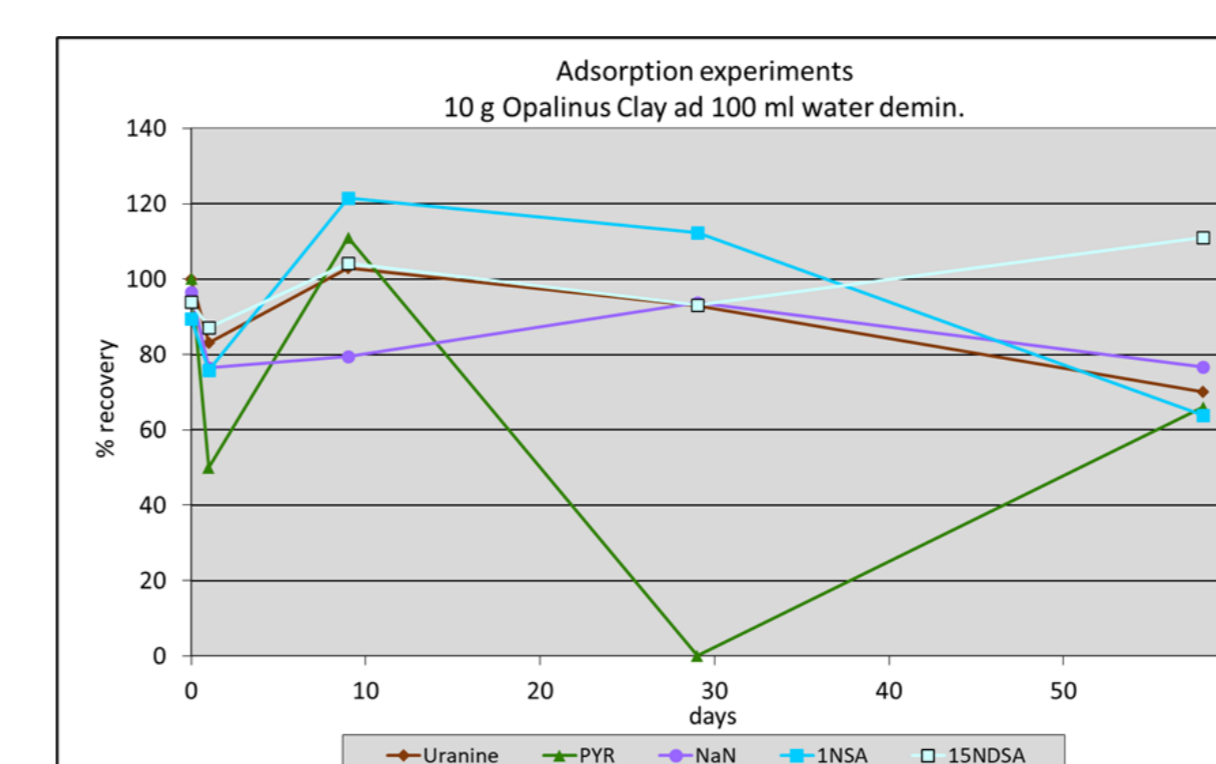### Rock-material: Opalinus Clay

Tracers:
UR, PYR, NaN, 1NSA, 15NDSA

Experimental set-up:

mass of ground rock material [g]	water volume [ml]	total volume [ml]	density [g/cm³]	Tracer Concentration [µg/l]
10	96.5	100	1.06	10 (UR 1)
20	92.5	100	1.14	10 (UR 1)
50	81.0	100	1.36	10 (UR 1)

Sampling intervals

start	1 days	9 days	29 days	58 days
10 µl	10 µl	10 µl	10 µl	10 µl

Adsorption experiments 10 g Opalinus Clay ad 100 ml water demin.

Adsorption experiments 20 g Opalinus Clay ad 100 ml water demin.

Adsorption experiments 50 g Opalinus Clay ad 100 ml water demin.

Conclusion

Opalinus Clay Evaluation of 5 tracers for use in different rock solutions

15NDSA	1
UR	2
1NSA	3
NaN	4
PYR	5

The same experiments were performed under the equal conditions with sandstone and limestone.

Outlook

The analyses can be done very selective in the laboratory by HPLC-FLD with a graphite column without filtration. The tracers showing a good recovery in the presence of OC and drilling fluids may be added in starting concentrations of 0,1-1 mg/L for specific drilling sections, increasing the reliability of the determination of ground- or porewater sample contamination.
Further details about the groundwater campaigns interested people can refer to Emiliano Stopelli and to Armin Pechstein (both Nagra).

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