USE OF DGT PASSIVE SAMPLERS FOR URANIUM MONITORING IN MINING SITES AND ACTIVE NUCLEAR SITES: WHAT DO WE MEASURE WITH DGT?

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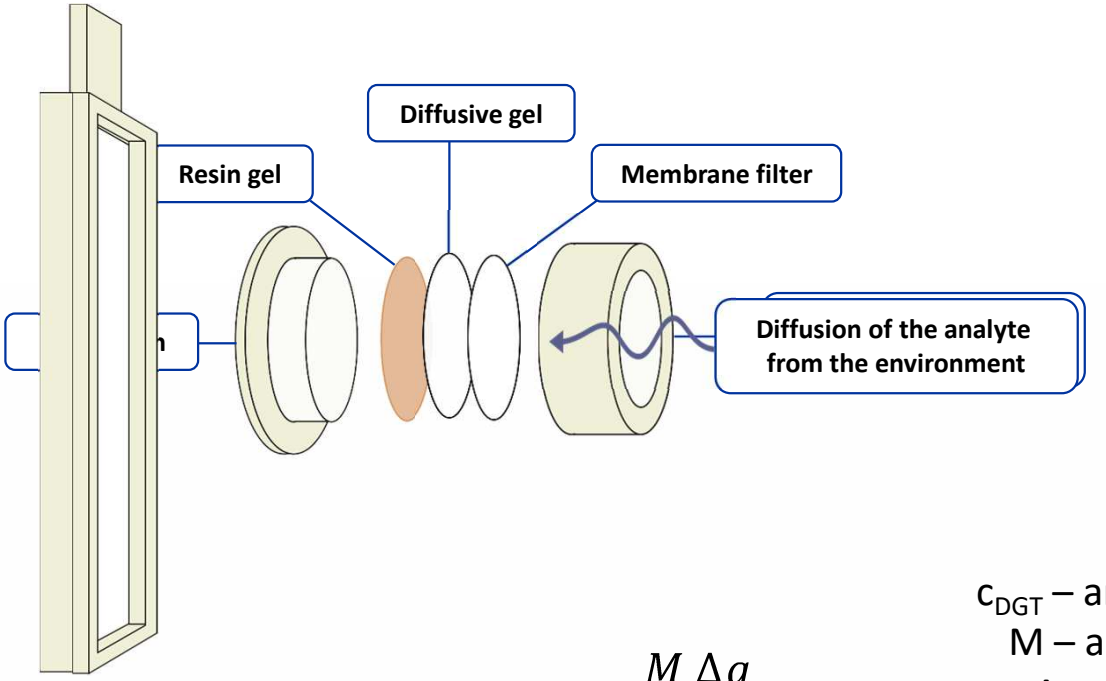
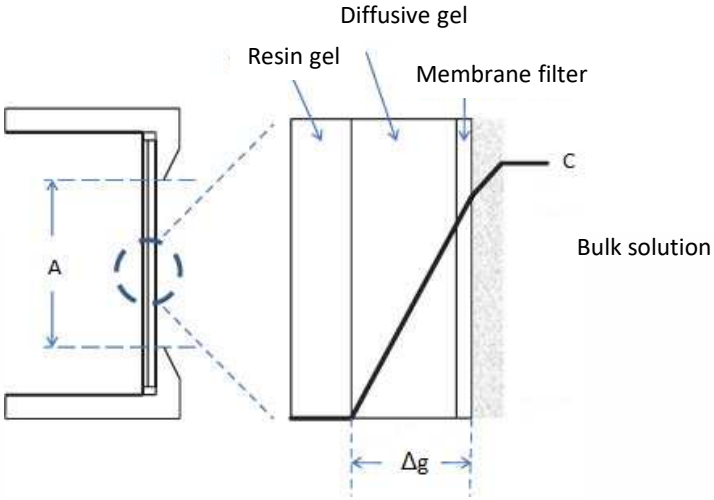
Diffusive Gradients in Thin Films (DGT)

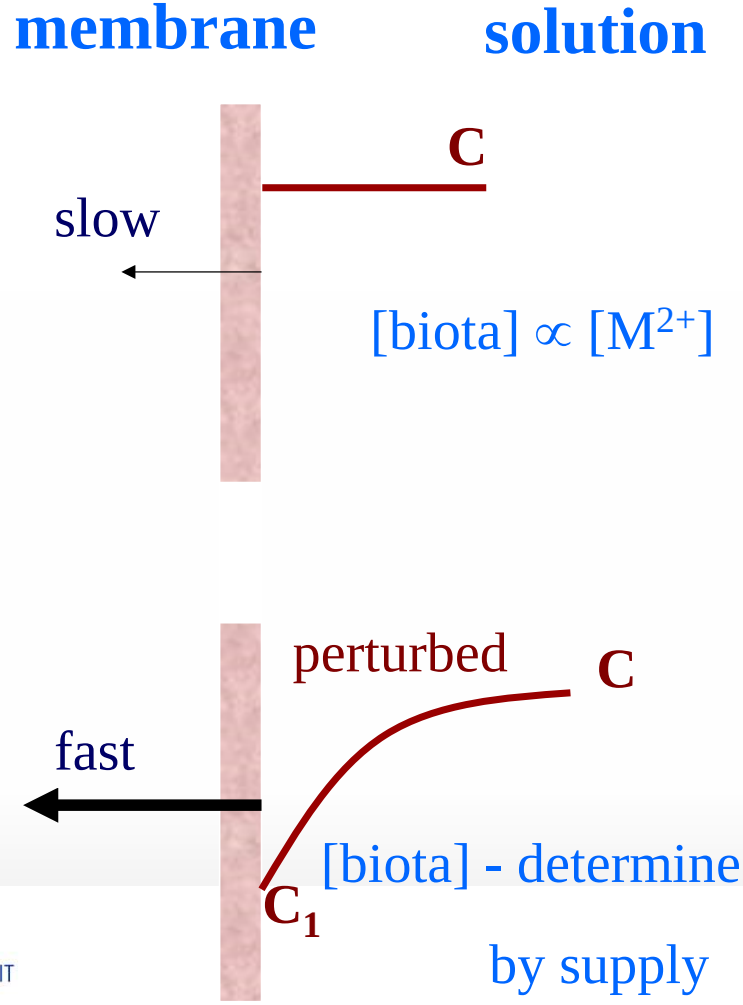




$$c_{DGT} = \frac{M\ \Delta g}{D\ A\ t}$$

c_{DGT} – analyte concentration in solution (µg L^{-1})
M – analyte mass eluted from resin gel (ng)
Δg – thickness of the diffusive layer (cm)
D – diffusion coefficient of the analyte ($cm^2\ s^{-1}$)
A – exposure area (3.14 cm^2)
t – deployment time (s)

Biouptake and Chemical Equilibrium



Equilibrium

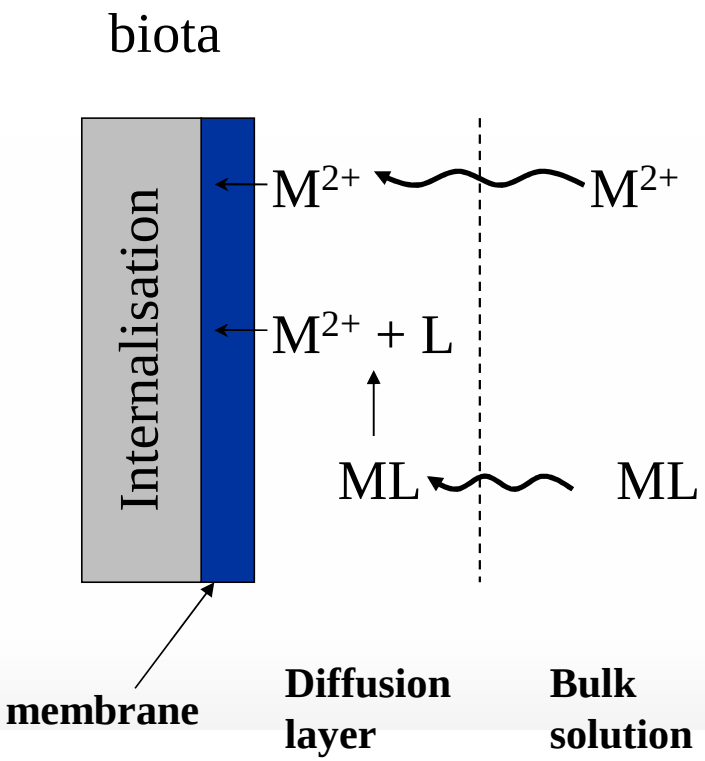
Free Ion Activity Model (FIAM)

Biotic Ligand Model (BLM) applies

Non-equilibrium

Kinetics of supply may be important?

Metal Uptake by Biota



in bulk solution

$C_b = [M] + [ML]$

What concentration do biota experience?

i) $[M^{2+}]$ (fast)

ii) $[M^{2+}]$ +?[ML] (slow)

It depends on the lability and the mobility of the metal species

DGT AND BIOAVAILABLE METAL FRACTION

WHAT DOES THIS MEAN FOR URANIUM

Bioavailable fraction?

-define as sum: UO_2^{2+} , $UO_2(OH)^+$, $UO_2(OH)_2$, UO_2CO_3?
No DGT resin suitable

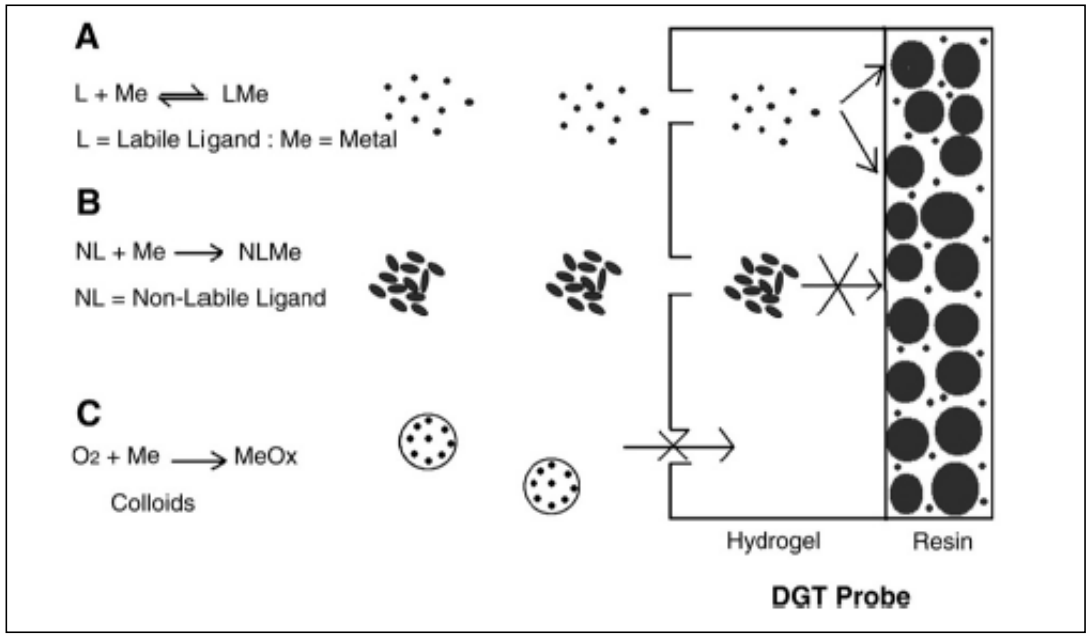
-truly dissolved species (<1nm)?

pore size diffusive gel: 5-10nm

- inorganic U complexes
- small humic and fulvic acid fraction

➢ Effective binding on resin gel will depend on:

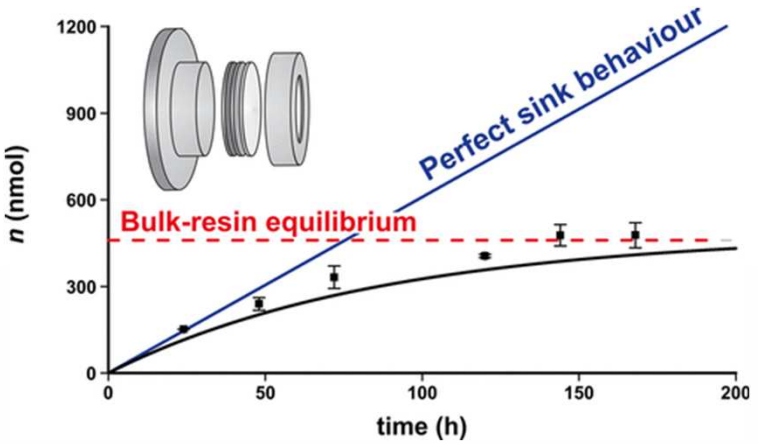
- ➢ resin gel used
- ➢ sample matrix
- ➢ Deployment time



DGT URANIUM

UNCERTAINTIES

$$c_{DGT} = \frac{M\,\Delta g}{D\,A\,t}$$



2 main uncertainties:

- Diffusion coefficient

- Possible non-linear accumulation

Commonly used resins:

-Chelex 100
-Metsorb
-Diphonix: requires elution in **1 M 1-hydroxyethane-1, 1-diphosphonic acid (HEDPA)**

(Dow Piwpa): requires elution in **concentrated HNO_3**
(Lewatit FO 36)
(new resins in development)

DIFFUSION COEFFICIENT URANIUM

DETERMINED BY DIFFUSION CELL OR DGT in 10 mM NaNO3 at 25°C (10^{-6} cm^2 s^{-1})

pH	D_{DGT}[a]	D_{DGT}[b]	D_{DGT}[c]	D_{DGT}[d]	D_{DGT}[d]	D_{DGT}[d]	D_{DGT}[e]	D_{DGT}[i]	D_{cell}[f]	D_{cell}[d]	Dcell[h]
	Chelex	Spheron Oxin	Metsorb	Chelex	Metsorb	Diphonix	DOW PIWBA	Lewatit FO 56			
3.0			2.67	4.07	4.97	4.55	5.02		6.13	7.20	
4.0			3.14	4.42	4.65	4.66	5.37		5.81	7.37	
5.0	4.7		4.53	3.89	4.13	3.90	4.63		4.96	4.88	
6.0	3.4	4.39	3.61	4.25	4.81	4.56	4.05		3.27	3.88	
7.0			3.03	4.34	5.03	3.83	4.95	4.38	2.53	2.99	1.5
8.0			4.32	4.63	4.82	4.19	5.13		2.01	2.44	
9.0				4.13	4.35	4.22	5.15		1.8	1.90	

Average 4.40

a: Garmo et al. 2003 b. Gregusova and Docecal, 2011c. Hutchins et al. 2012 d. Drozdzak et al, 2015
e. Drozdzak et al., 2016f. Li et al.2006 g. Kerist and Liu. 2010 h. Zhao et al. 2020, i. Smolikova et al. 2021
* for a solution of 0.01M NaNO3/0.9mM NaHCO3

DGT URANIUM

GENERAL FINDINGS

Good performance of Chelex at pH<7

General good agreement between Chelex, Metsorb, Dow, Diphonix in natural waters

Better performance of Dow and Diphonix in high matrix mining waters (Drozdzak et al., 2015, 2016)

Long term monitoring of uranium using Metsorb: need to analyse diffusion boundary layer for each water course (Turner, 2014)

Impairment of performance of Chelex, Metsorb, Lewatit, Dow-PIWBA in seawater for longer deployment times (only Diphonix able to accumulate linearly up to 1 month) (Smolikova et al., 2022)

DGT PROJECT AT THE ORANO TRICASTIN SITE

Industrial Activities

Chemical processes and uranium enrichment activities preceding the final stage of fuel assembly fabrication for nuclear power plant reactors.

Environmental protection

Hydraulic barrier (10m deep steel wall) to protect surrounding groundwater and surface water (Gaffiere River)

hundreds of piezometers for environmental monitoring

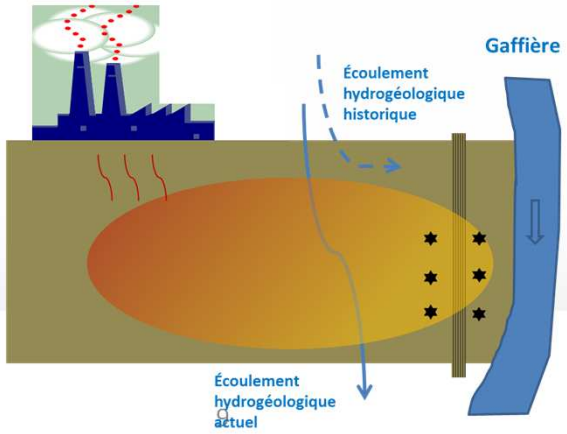
Orano Tricastin site

Environmental monitoring

Environmental monitoring network on and around the site

over 1000 U analysis yearly

Daily, weekly or monthly sampling



DGT PROJECT

1. Can DGT be used as a long-term monitoring tool (up to 1 month) for uranium in ground water and river water, in order to obtain time integrated averaged concentrations?

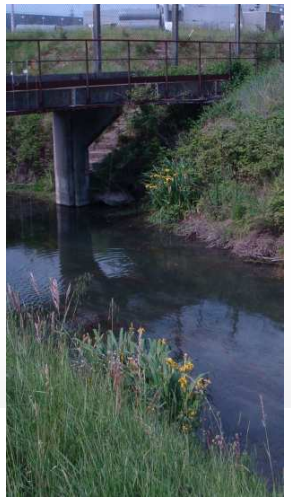
Ideally:

-DGT resins should be readily available or easy to produce

-elution and analysis procedure should be compatible with routine monitoring analysis

2. Will the DGT be able to measure concentration changes during an accidental spill (specific water composition: high F, metals, etc)

Orano Tricastin site



Gaffière river and protective structures

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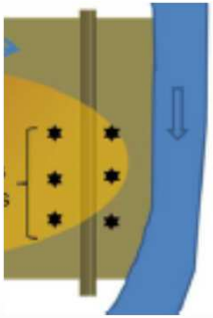
Preliminary expedition

Deployment in groundwater (5 piezometers) and river water (1 station) using Chelex resin
-groundwater: 24h
-river water: 24h, 2d, 7d, 14d, 21, 30d

- Chelex resin impaired for deployments >2 days
- Diffusion coefficient 4.4 E-6 cm^2/s may not be suitable for carbonate rich waters
- Diffusion boundary layer in piezometers need to be assessed
- Perform lab tests using Tricastin surface water using Chelex, Diphonix and Dow resins and double resin layers



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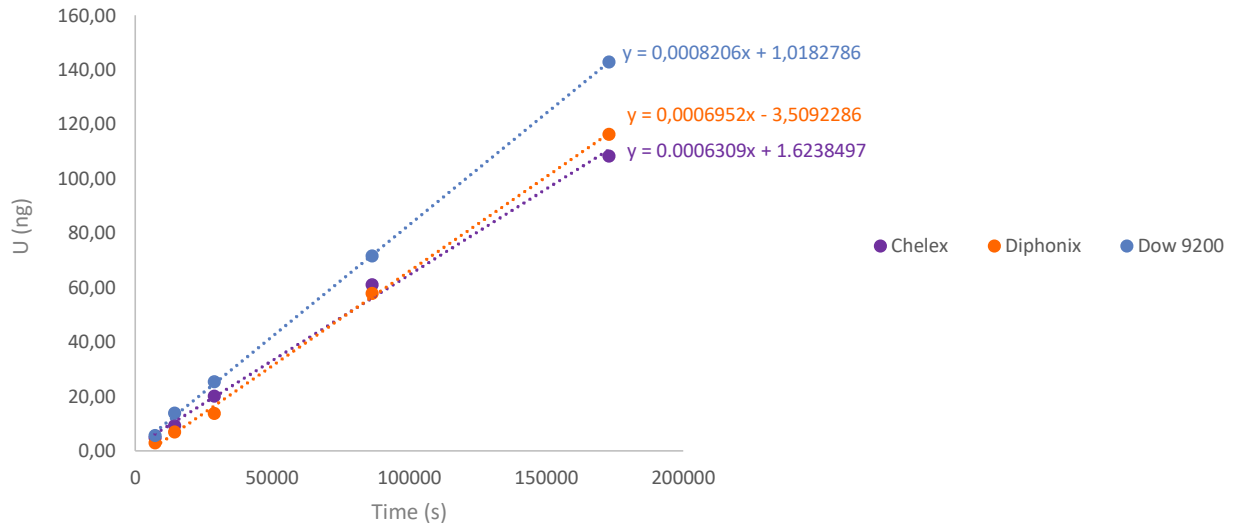
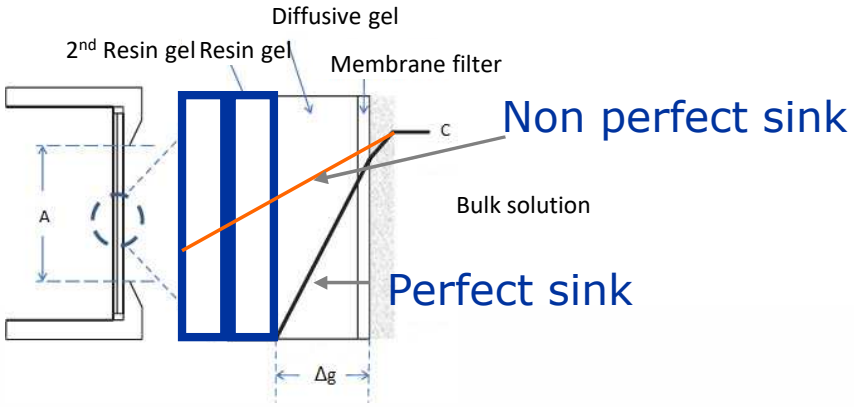
Diffusion coefficients in Tricastin water

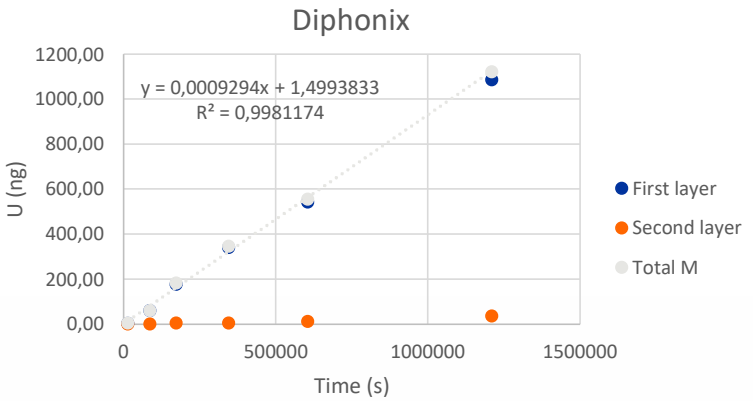
Uptake of U on single resin after 48 hours

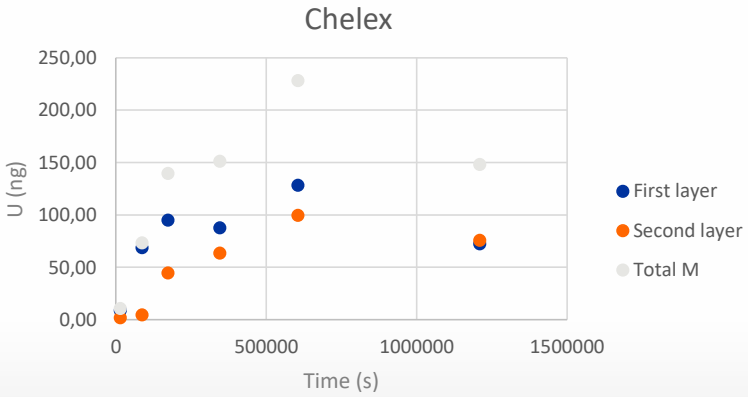


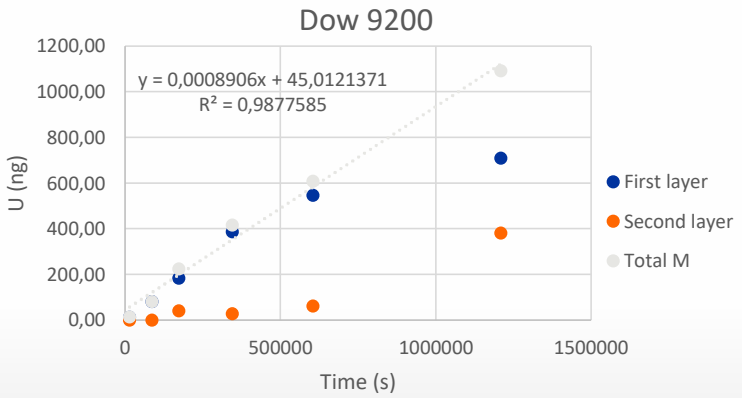
25 °C	Chelex	Diphonix	Dow 9200
D [$cm^2\ s^{-1}$]	3,3 x 10^{-6}	3,9 x 10^{-6}	4,1 x 10^{-6}

Uptake of U on double resins – 14 days-Tricastin water

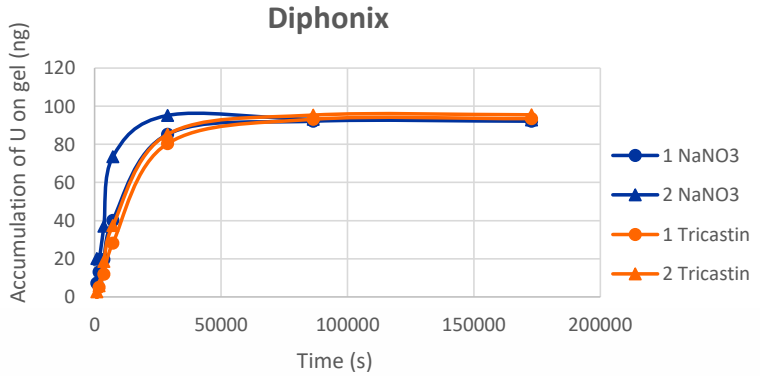


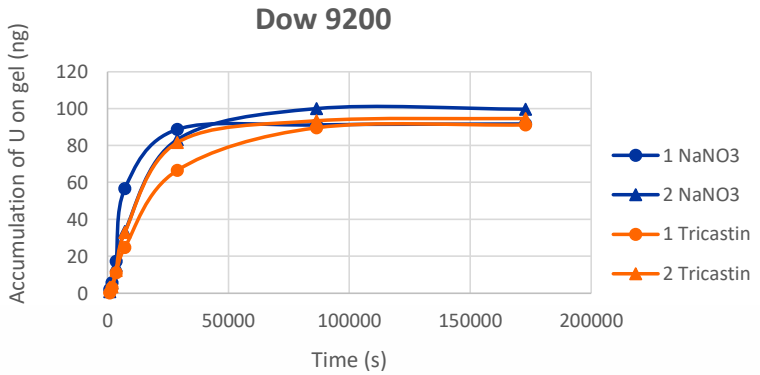


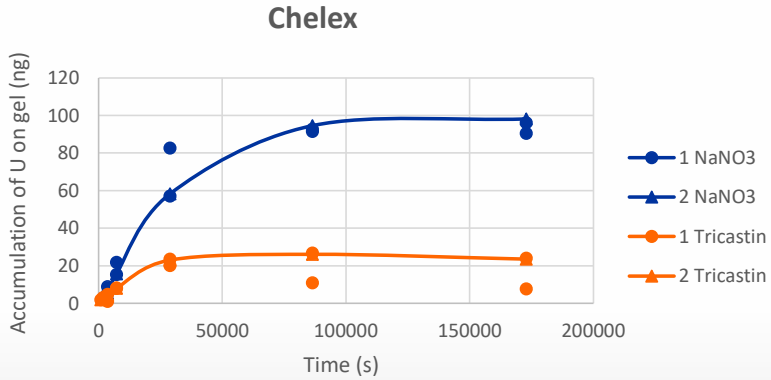




Uptake kinetics of U on resin gels







100 ppb U solution in $NaNO_3$ matrix and Tricastin water matrix

Diffusion boundary layer (DBL) in well mixed solutions

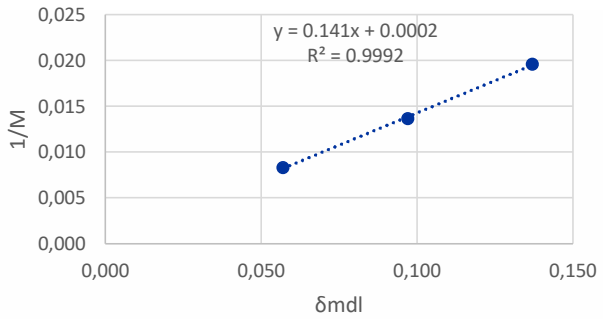
Use 3 different diff layers thickness

$$\frac{1}{M} = \frac{1}{c_{DGTe} A_E t}\left(\frac{\delta^{mbl}}{D^{mdl}} + \frac{\delta^{dbl}}{D^{w}}\right)$$

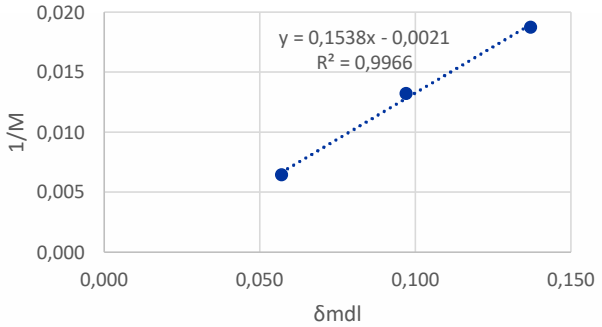
$$s = \frac{1}{c_{DGTe} A_E D^{mdl} t}$$

$$y = \frac{\delta^{dbl}}{c_{DGTe} A_E D^{w} t}$$

Diphonix



Dow 9200

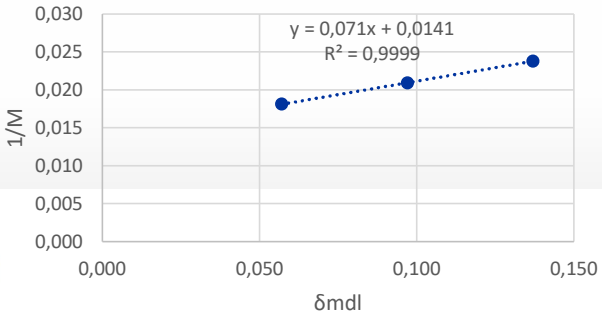


$$\delta^{dbl} = \frac{y D^{w}}{s D^{mdl}}$$

$$c_{DGTe} = \frac{1}{s D^{mdl} A_E t}$$

DBL=0- 0.0014mm: neglegible

Chelex



Not fully labile:
DBL cannot be calculated with Chelex!!
-provides information on lability of U complexes, not DBL

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Second expedition

Diphonix, Dow 9200 and Chelex resin

Two sampling sites - Gaffière river and piezometer ET538

Sampling times – 1, 2, 7, 14, 21, 28/30 days

Determination of DBL (24 h) with Diphonix at both sampling sites

Temperature logger for whole experiment in Gaffière river

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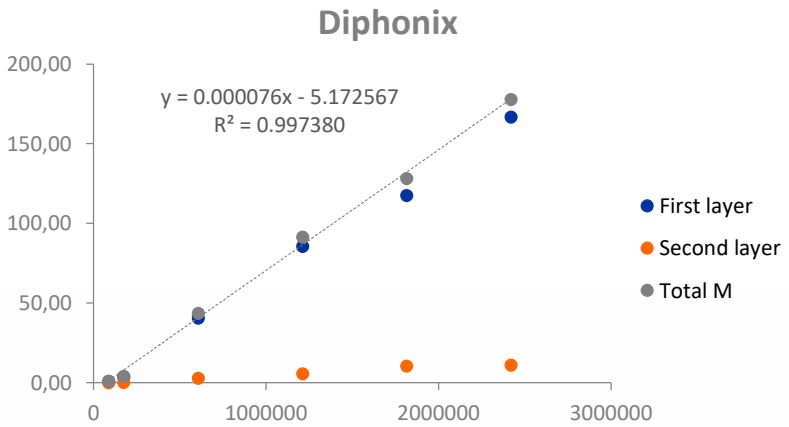
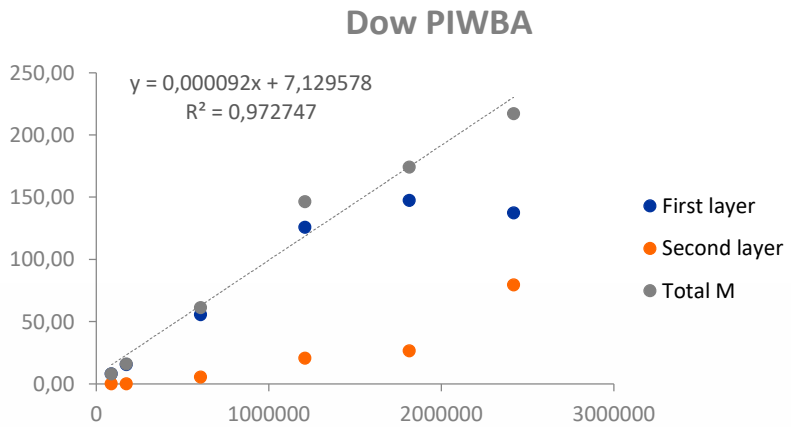
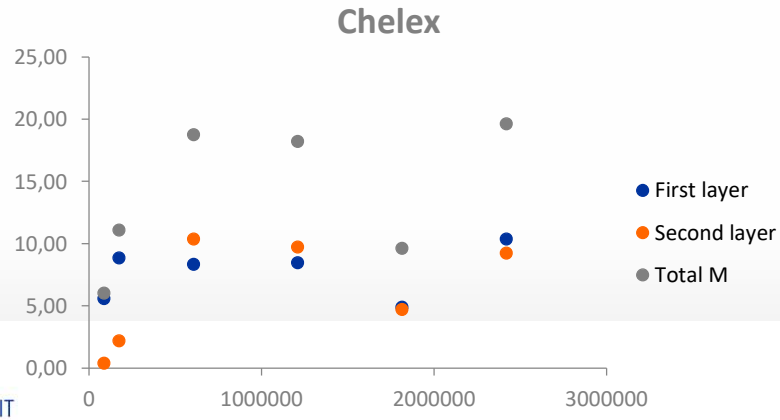
Gaffiere River

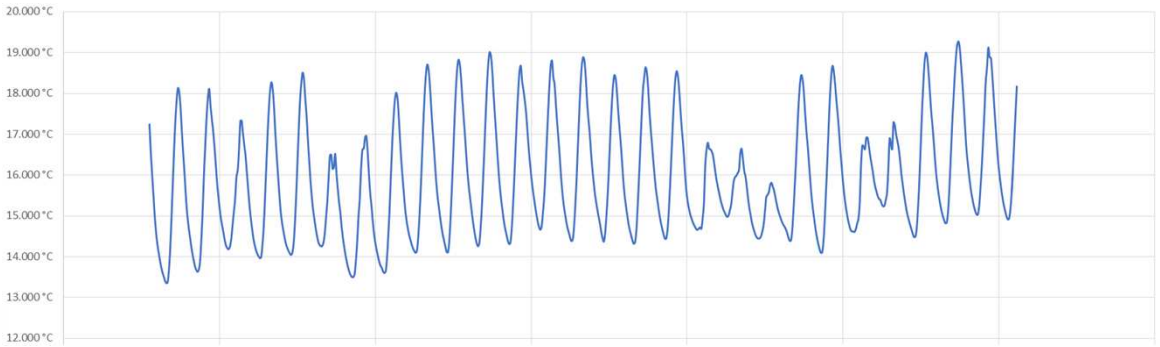




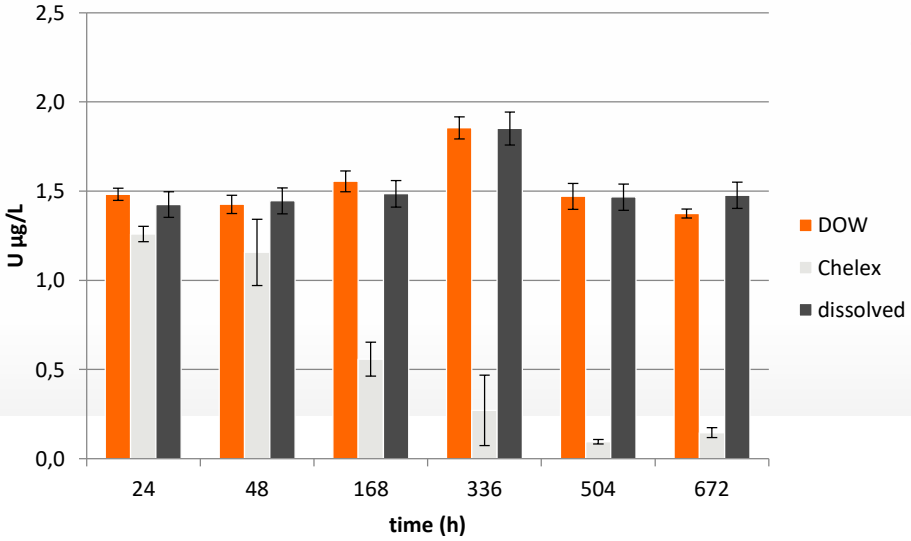


- DBL neglegible
- No more accumulation on Chelex resins after 1 week
- U accumulation on 2nd resin starts after 2 weeks for DOW PIWBA
- Only very small fraction on 2nd resin for Diphonix
- Sum of two resins used in DGT calculations
- Calibration problem with Diphonix extractions: no DGT calculations made

Gaffiere River

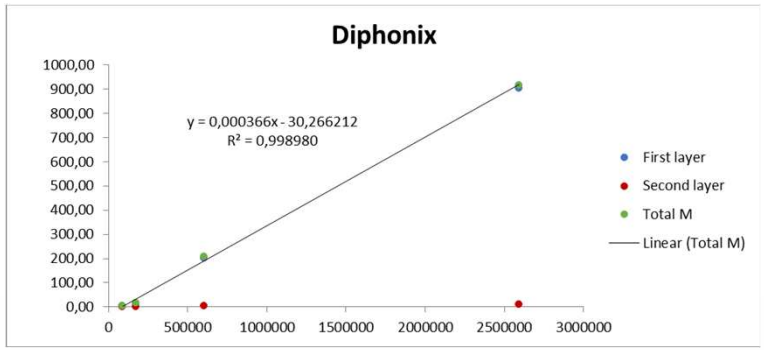


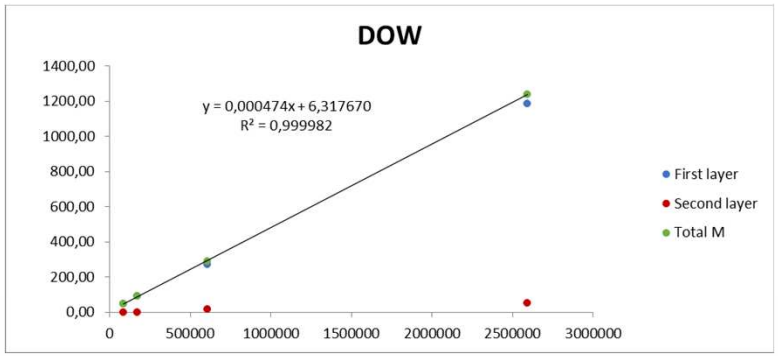
Average temperature obtained with temperature data logger

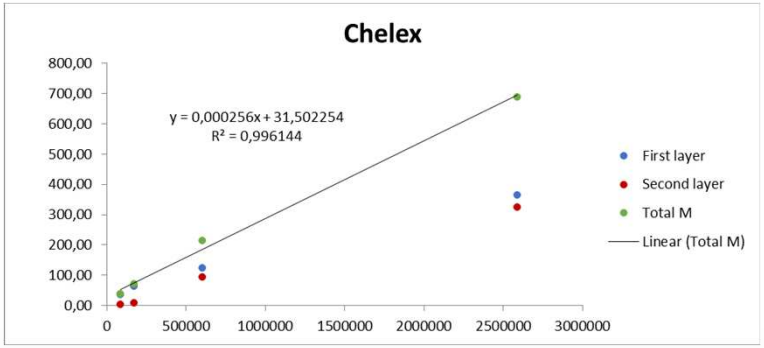


- Good agreement between dissolved concentrations and C-DGT using DOW resin

Groundwater: piezometer

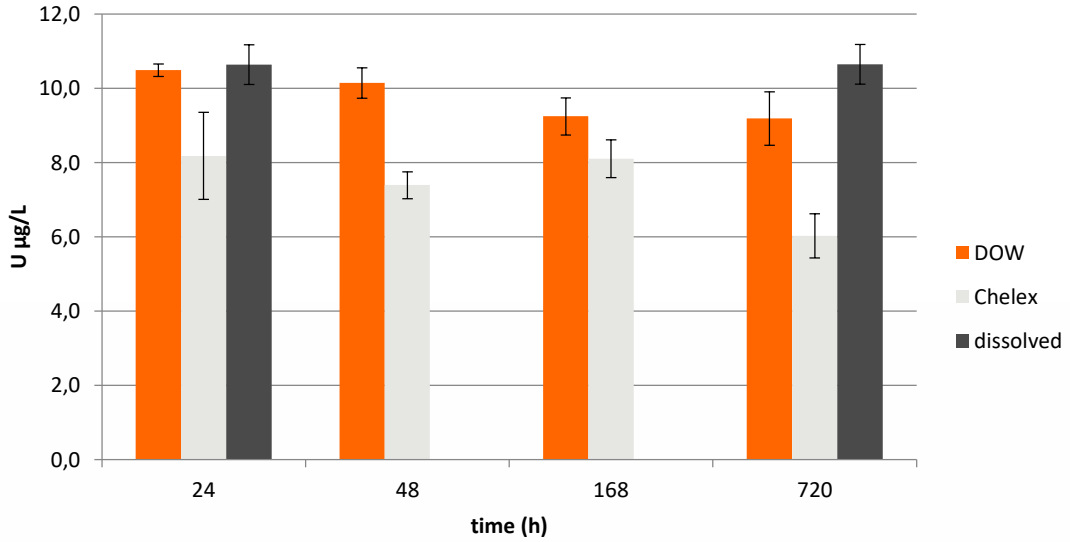






- DBL=0,024cm
- Lower fraction on 2nd resin for DOW in comparison to river water
- Accumulation on Chelex gels continues

Groundwater: piezometer



- DBL must be taken into account for groundwater samples (very low water flow)
- Good correspondence between C DGT DOW and grab samples
- Relatively better performance of Chelex compared to river water

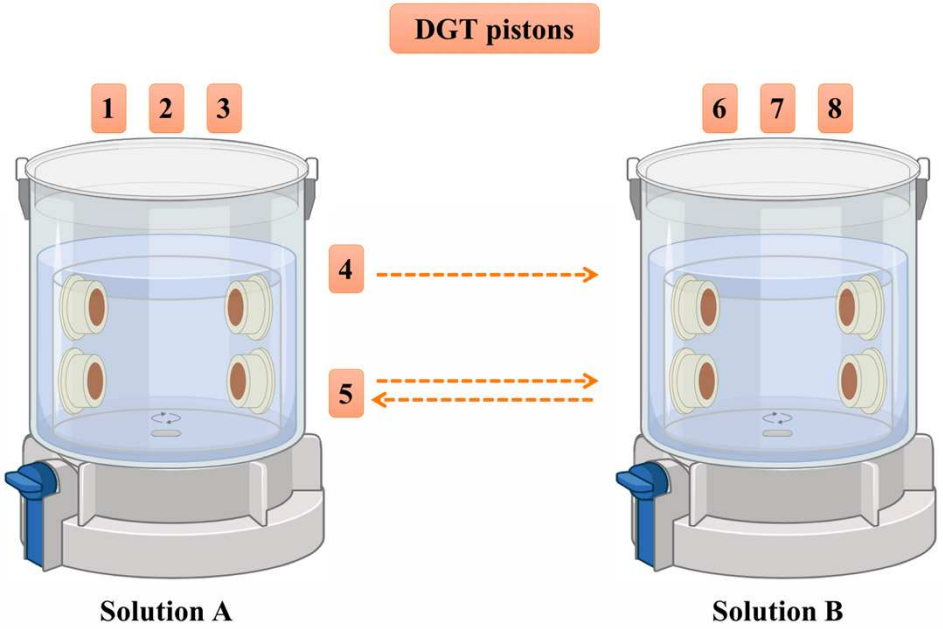
TIME-WEIGHTED AVERAGE CONCENTRATIONS MEASURED WITH THE DIFFUSIVE GRADIENTS IN THIN-FILMS TECHNIQUE FOR URANIUM IN RESPONSE TO SIMULATED POLLUTION EVENTS

1. 6 hours in sol. A
2. 22 hours in sol. A
3. 28 hours in sol. A

Control Diff coeff

4. 6 hours in sol. A and 16 hours in sol. B
5. 6 hours in sol. A, 16 hours in sol. B and 6 hours in sol. A
6. 6 hours in sol. B
7. 22 hours in sol. B
8. 28 hours in sol. B

Control Diff coeff



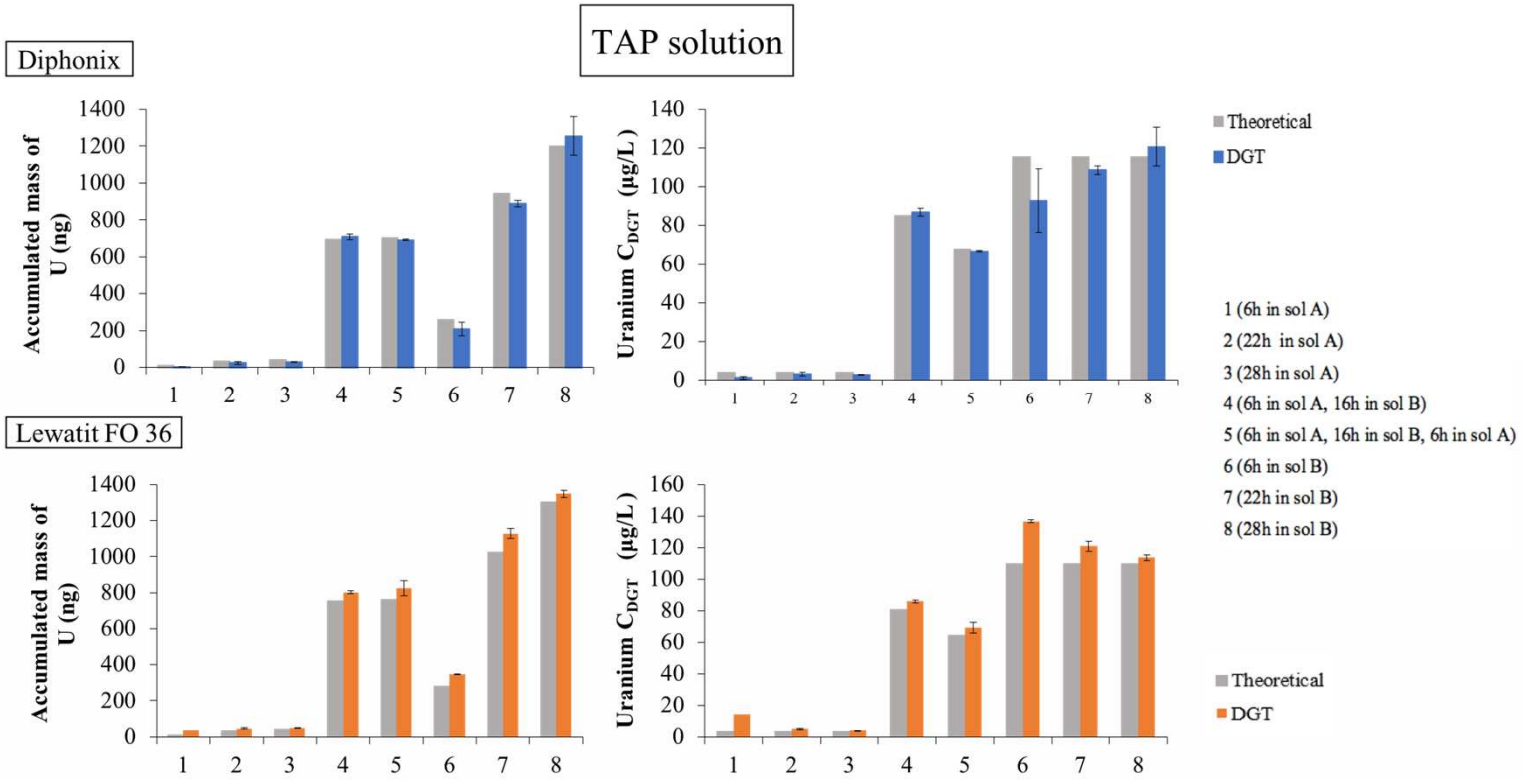
Performed in diluted tap water with high carbonate content
Diphonix and Lewatit FO 36 as resins
Diffusion coefficients determined
- Diphonix = 3.48 * 10^{-6} cm^2/s
- Lewatit = 3.97 * 10^{-6} cm^2/s

tapwater

Spill: dil 1/100 in tapwater

EVALUATION OF PJ6 SPILL EXPERIMENT (TAP WATER)

PJ6 spill composition (mg/L)	
U	1
F	250
Fe	80
NO_3	250

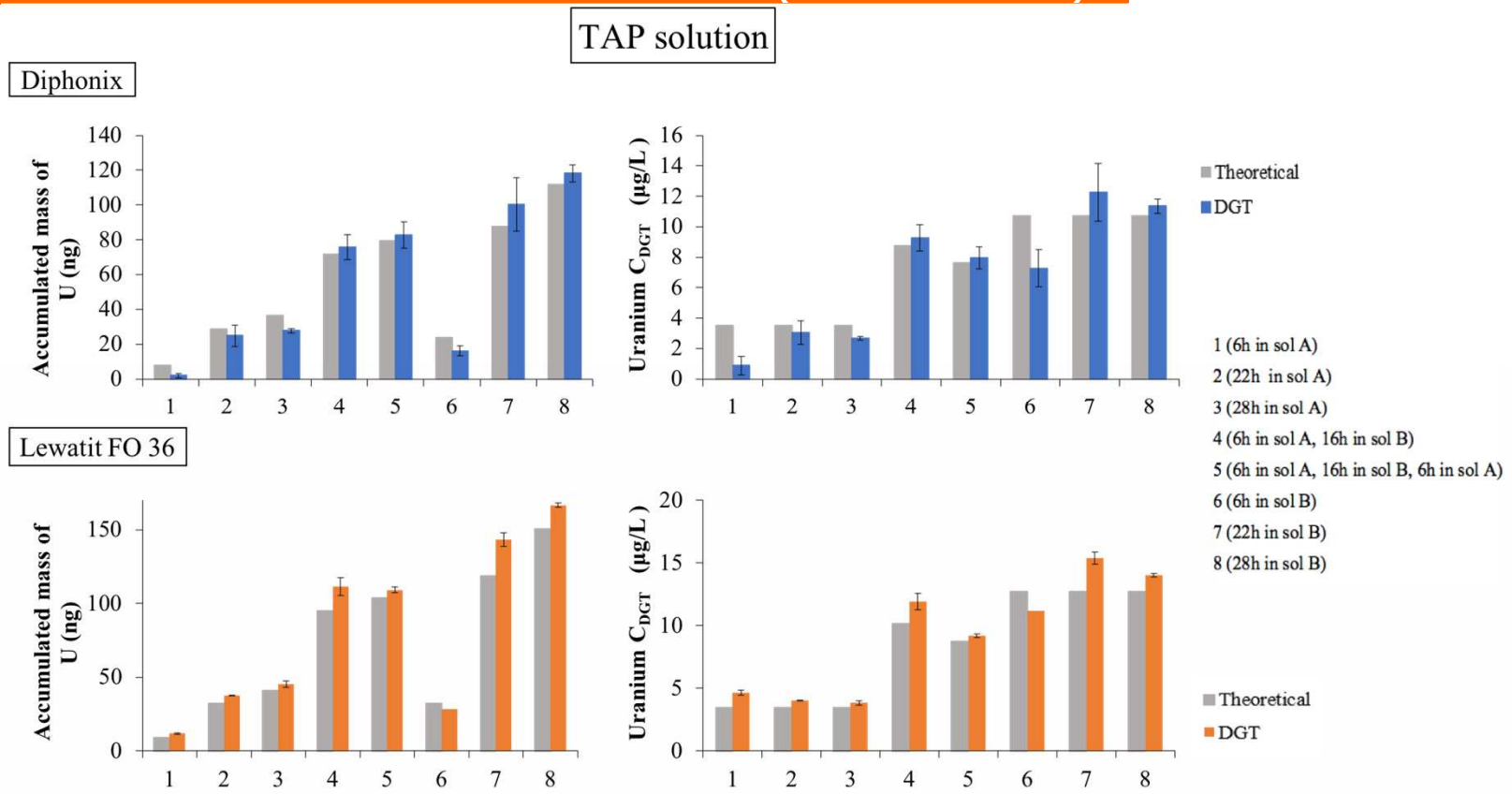


Graph 8: Accumulated mass of uranium on the resin gel (left) and uranium DGT-determined concentrations (right) determined by Diphonix or Lewatit FO 36 vs. theoretical values during the PJ6 experiment in diluted tap water (TAP).

- Good agreement between theoretical and experimentally obtained values with low SDs (<10%)
- Robust performance of both resin, even during changes between sol A and sol B (pistons 4 and 5)
- In presence of carbonates in solutions, the spill has minimal effect on the U complexation and its lability towards DGTs

EVALUATION OF PJ5 SPILL EXPERIMENT (TAP WATER)

PJ5 spill composition (mg/L)	
U	1
F	25
Fe	5
N	300
P	10
As	2
Cu	0.5
Cr	0.1
Mn	0.5
Al	5

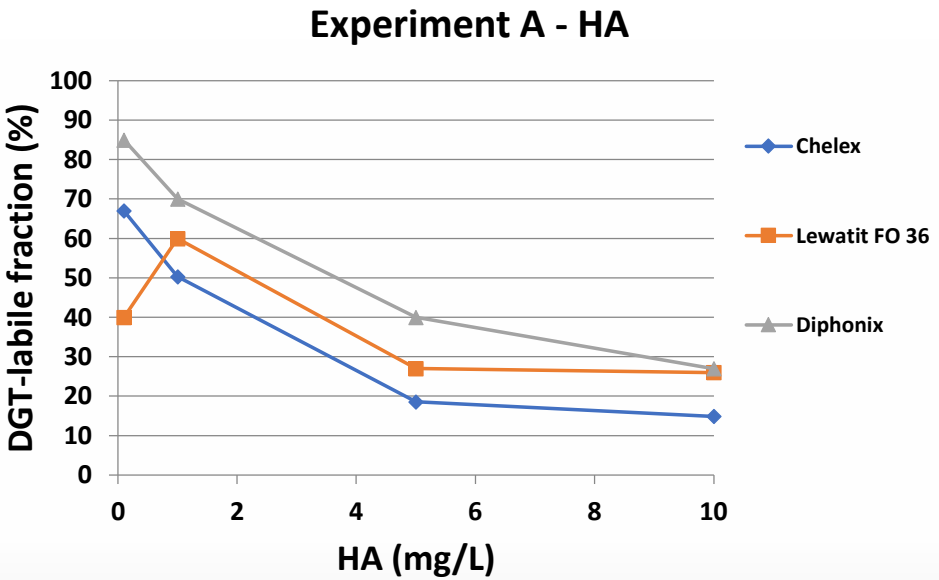


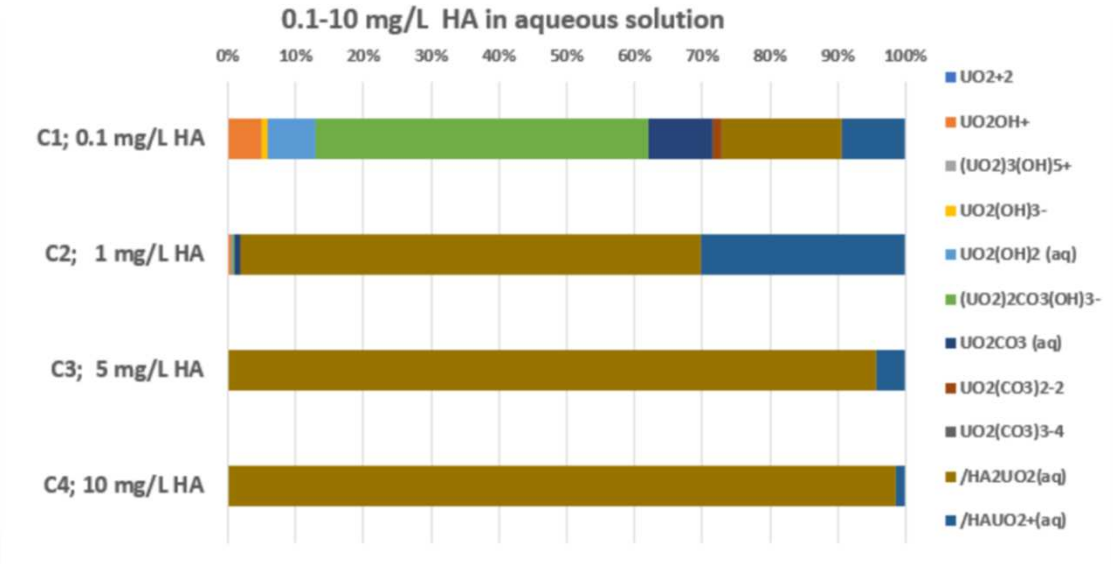
Graph 9: Accumulated mass of uranium on the resin gel (left) and uranium DGT-determined concentrations (right) determined by Diphonix or Lewatit FO 36 vs. theoretical values during the PJ5 experiment in diluted tap water (TAP).

- Good agreement with theoretical values, except for short deployment periods of Diphonix (pistons 1, 6)
- Robust performance of both resin, even during changes between sol A and sol B (pistons 4 and 5)
- Similarly to PJ6 in TAP, the PJ5 spill has minimal effect on U lability towards DGTs in presence of carbonates in solutions

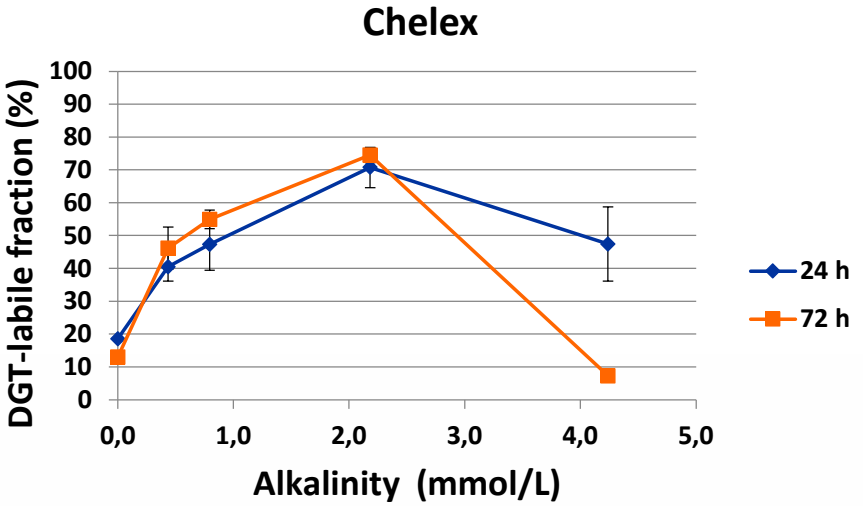
INFLUENCE OF HUMIC MATTER ON DGT LABILITY OF URANIUM

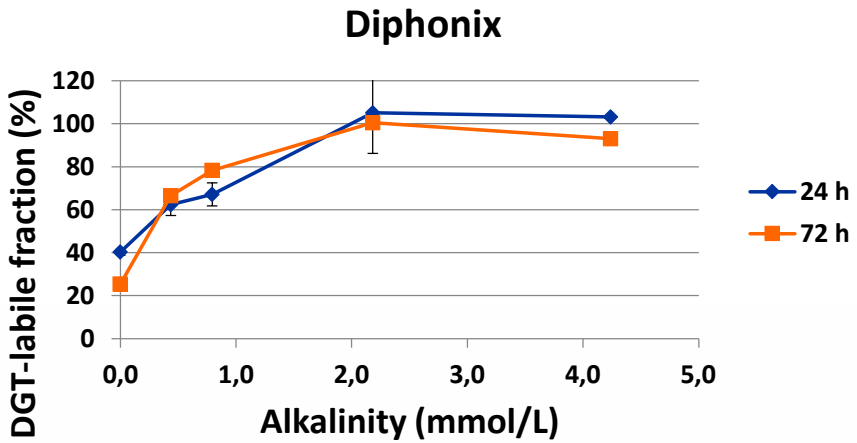
HA solutions made from technical humic acid (Aldrich)
HA added to U solutions in 0.1M $NaNO_3$

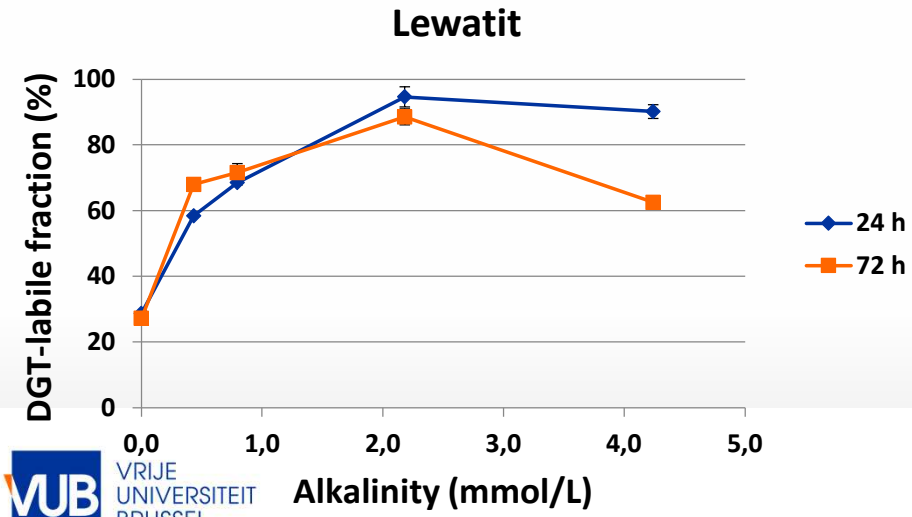


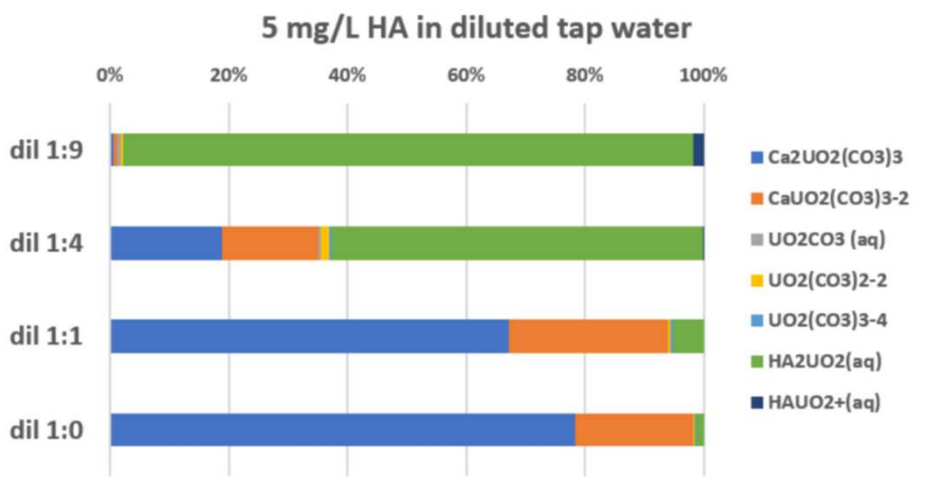


INFLUENCE OF CARBONATE CONCENTRATIONS ON DGT LABILITY OF 5 mg/l HA SOLUTIONS









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CONCLUSIONS

- Under perfect sink conditions DGT will measure truly dissolved inorganic fraction and labile humic and fulvic fractions
- Care must be taken when using Chelex resin for U in carbonate rich waters
- Diphonix can be used for long term deployments even in carbonate rich waters

HOW CAN WE IMPROVE DGT AS A MONITORING TOOL FOR U?

1. reduce uncertainties on diffusion coefficient

   conditional diffusion coefficient (pH, alkalinity, Ca)?

2. Interlaboratory comparison needed

THANK YOU FOR YOUR ATTENTION