DGT as a research tool
its impacts on science and regulation

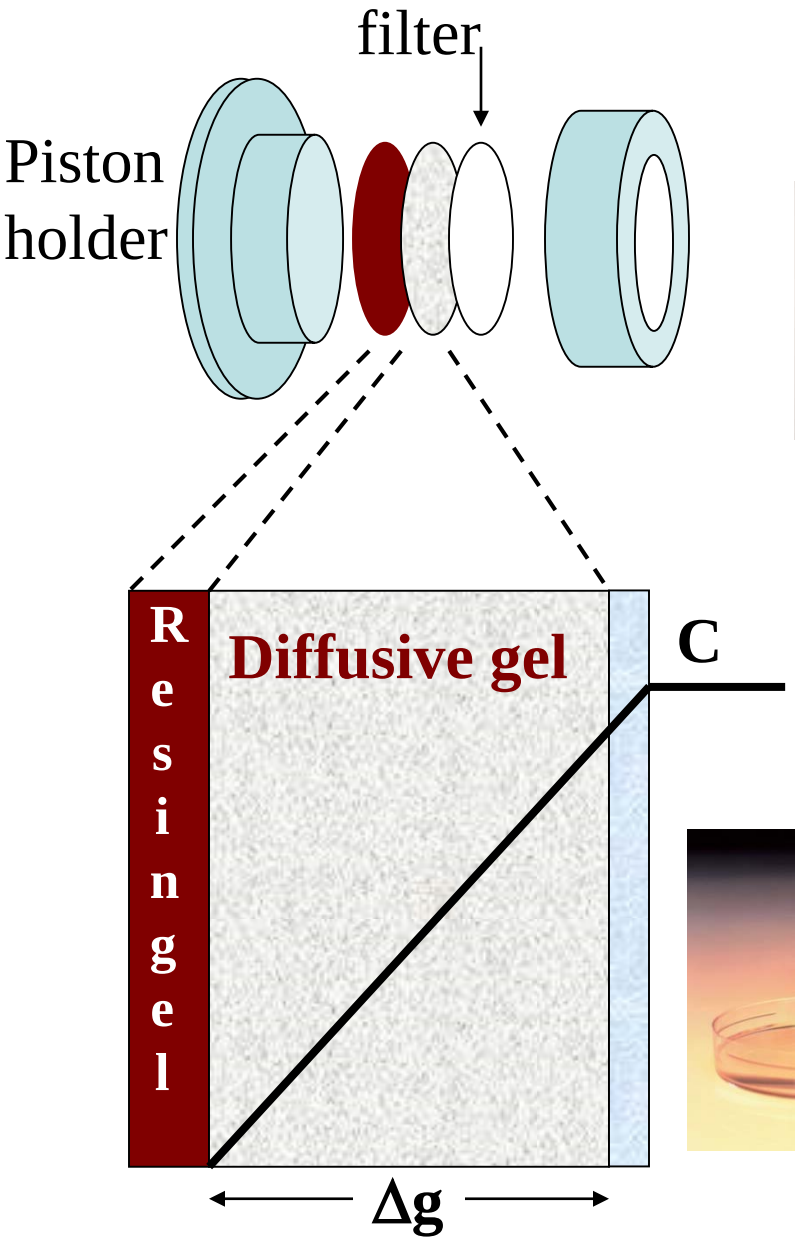
Hao Zhang

LEC, Lancaster University, UK

The Lancaster Environment Centre

Lancaster University

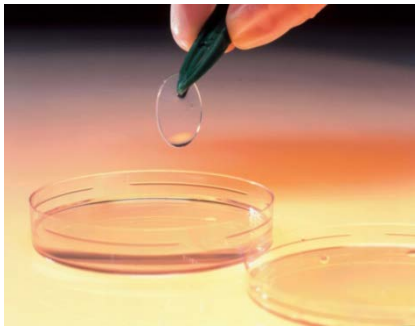
Diffusive Gradients in Thin-films



$$F = M/At$$

$$F = DC/\Delta g$$

$$C = M\Delta g/DAt$$

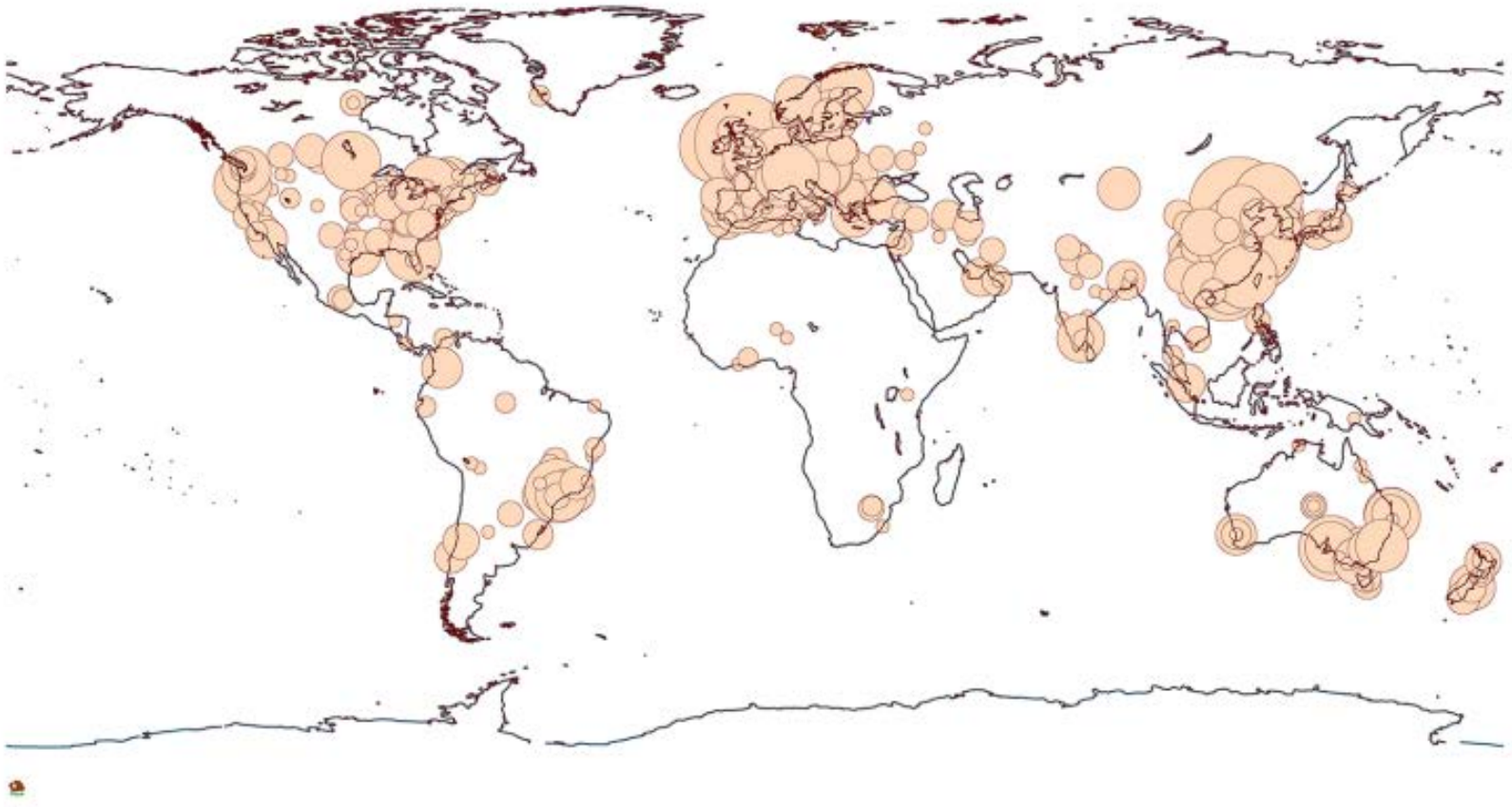


- Simple device
- Simple calculations
- More accurate
- In situ TWA

About DGT

- Invented in Lancaster in 1993
- Patented worldwide in 1994
- First publication in 1994 (Nature)
- DGT Research Ltd established in 1997
- Used in >400 labs/organisations in over 70 countries
- Publications: > 1500 in waters, soils and sediments
- **南京维申环保科技有限公司** 2014, DGT®

Distribution of labs using DGT around the world



What Can DGT Measure?

> 60 inorganic elements; > 170 polar organics

Metals (Al, Cr, Cd, Cu, Co, Ni, Zn, Pb, Fe, Mn, Ca, Mg, REEs
Mo, As, Se, W, V, Sb, Au, Hg)

Radionuclides (Cs, Sr, Tc, U, Cm, Pu)

Nutrients (K^+, PO_4, NO_3^-, NH_4^+)

Others (S^{2-})

Organics: antibiotics, PCPs, illicit drugs, pesticides, antipsychotic drugs etc.

On-going and planned development:

Organics (POPs, PAHs, anti-cancer drugs, Pharmaceuticals)

Nutrients (SO_4^{2-})

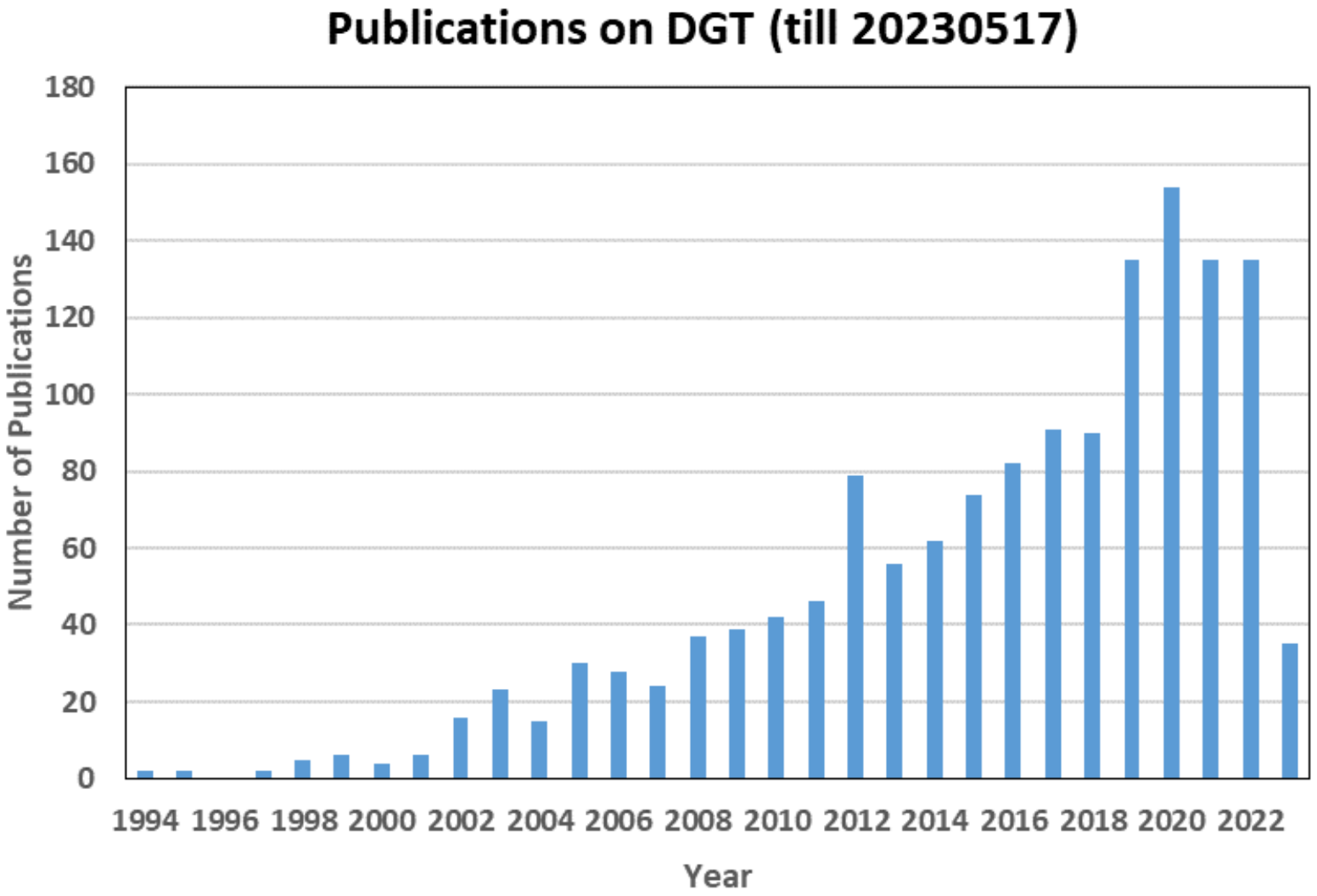
Others (Ra, Am)

Organic Chemicals Can Be Measured by DGT Devices

>170 compounds in published studies

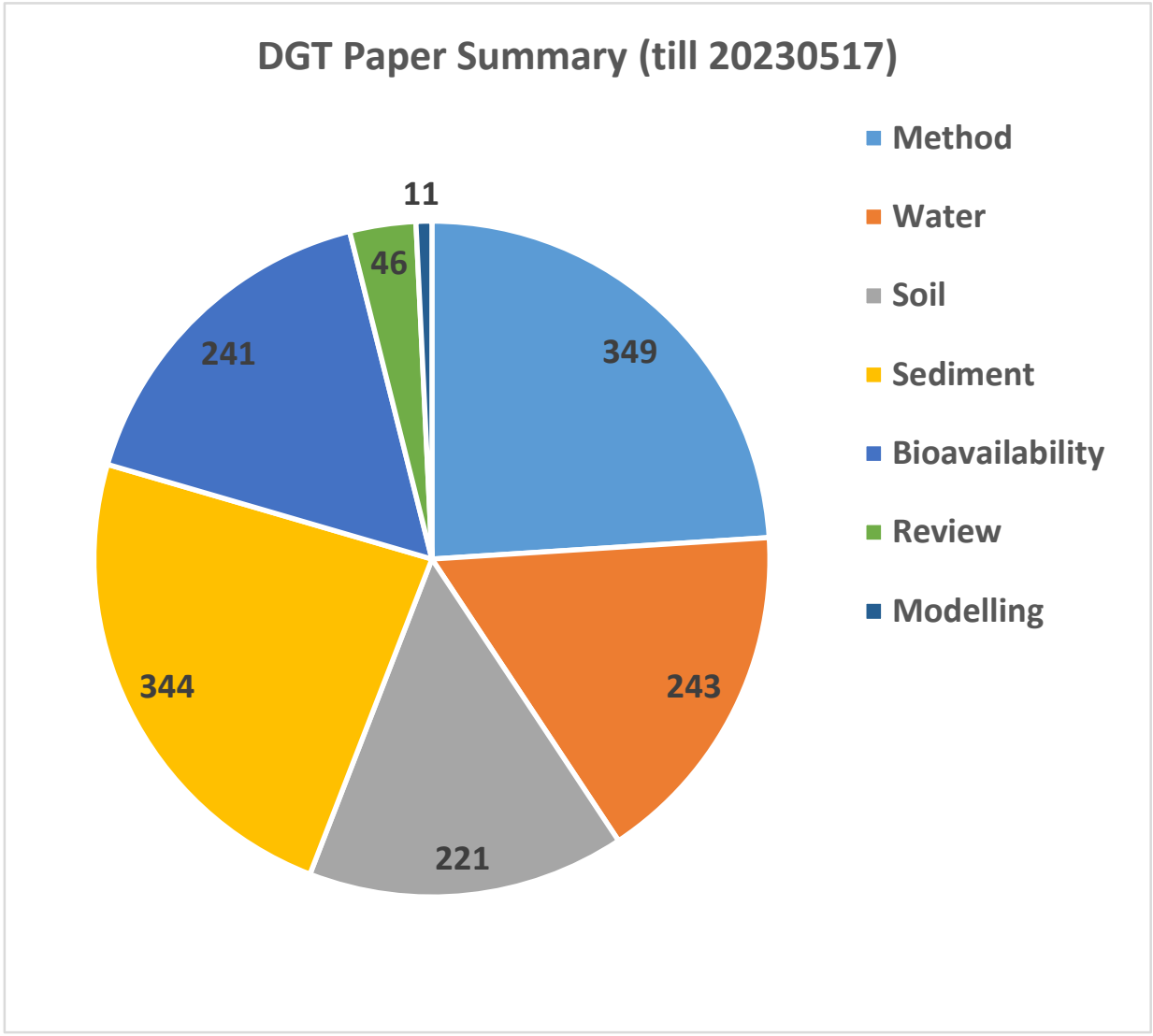
• Antibiotics	JEM 2012; ES&T 2013
• Phenols and bisphenols	ACA, CL 2014; AC 2015
• Pesticides	AC 2015; 2016; 2017; ACA 2017; ES&T 2018
• Other pharmaceuticals	AC 2016; 2017; ES&T 2018; ES&T 2019
• Illicit drugs	ES&T 2017
• Personal care products	ES&T 2017;
• Pesticides	JAFC 2018; EI 2019
• Organophosphate esters	AC 2018; 2019
• Endocrine disrupting chemicals	AC 2017; Water Res 2018; EI 2019
• Perfluorinated compounds	AC 2018; 2020
• Antipsychotic drugs	STOTEN 2022

Peer-Reviewed DGT Papers



Total: >1500 Organics: 77

DGT papers in different research fields



2021 and 2022, Total: 270 Water: 40 Monitoring: 25

Monitoring Organic Chemicals in Waters by DGT

Comparing with POCIS and Chemcather

Sampling rates per unit ($R_{S/A}$, mL $(d \cdot cm^2)^{-1}$)
for neonicotinoid insecticides (NNIs) target compounds

Sampler	*T*/°C	IMI	CLO	TMX	DIN	THI	ACE	NIT	FLO	IMIT
DGT	25	5.41	5.41	6.10	5.10	5.41	5.41	4.78	5.41	4.78
	23	4.52	4.14	4.14	-	-	-	-	-	
POCIS	22	1.14	0.70	0.61	-	1.16	1.77	-	-	-
	25	2.10	1.44	1.33	-	2.55	1.92	-	-	-
	20	5.61	5.28	4.41	2.31	4.67	5.22	-	-	-
Chemcatcher	20	0.57	0.50	-	-	0.94	-	-	-	-
	15	3.33	2.89	3.33	-	4.10	-	-	-	-

Chen W. et al. submitted to ES&T

DGT in groundwaters and wastewaters

Recent Review Comparing Different Passive Samplers

Chemosphere Volume 299, July 2022, 134448

The study of polar emerging contaminants in seawater by passive sampling: A review

Henry MacKeown, Barbara Benedetti, Marina Di Carro, Emanuele Magi

- As far as reliability is concerned, o-DGTs seem promising for future marine applications. In fact, they can be applied without calibration, unlike polar Chemcatcher and POCIS samplers.
- Compared to the other integrative passive samplers for polar compounds, o-DGT sampling rates are less influenced by flow variations. Therefore, the o-DGT has a great potential for monitoring a large class of organic pollutants in the marine environment.

Applications in Waters

Speciation - various lab studies

- **in situ** (comparison with total dissolved or $\mathbf{C^{dyn}_{max}}$)

Kinetics - in situ rate constant determination

Bioavailability

- metal uptake in periphyton and macrophytes
- toxicity in fish
- biological analogue (mussels)

Monitoring

- rivers, lakes and oceans
- effluents
- storm events
- harbours (metals from protective paints)

Trace Metals and REY Speciation in Deep-Sea Water

TrAC Trends in Analytical Chemistry, Volume 155, October 2022, by Katja Schmidt et al.

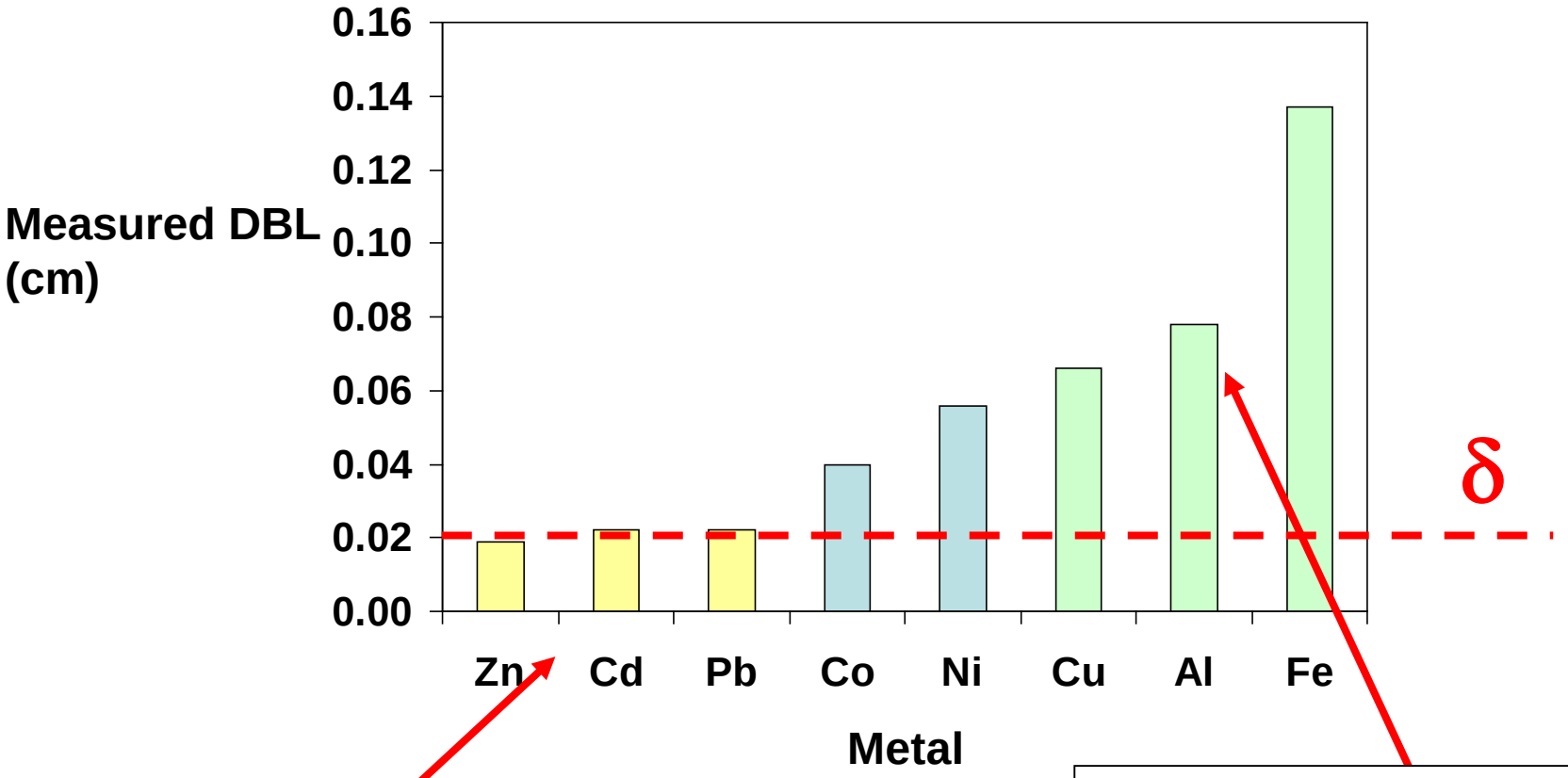
First deep-water in situ study of DGT lability, in bottom waters of the central NE Pacific (>5000m).

Area	Probe-ID Chelex	Cd	Cu	Mn	Ni	Probe-ID Metsorb	V	As
		nmol kg^{-1}					nmol kg^{-1}	
60km SSE of "Dredge Site"	PS-4-NM1	0.798	1.29	0.418	7.31	PS4-NT1	32.5	12.2
	PS-4-NM2	0.757	1.43	0.304	7.23	PS4-NT2	33.2	10.5
	PS-4-NM3	0.662	1.46	0.462	6.32	PS4-NT3	31.9	11.4
	PS-4 Av	**0.739**	**1.39**	**0.395**	**6.96**	**PS-4 Av**	**32.5**	**11.3**
	PS-4 RSD	9.39	6.84	20.7	7.9	PS-4 RSD [%]	2.01	7.57
Blank Av (n = 6)	**5E-04**	**0.054**	**0.043**	**0.055**		**Blank Av**	1.17	2.87
Blank RSD [%]	101	68.5	68	29		Blank RSD [%]	22.2	24.5
LOQ	*9E-04*	*0.06*	*0.007*	*0.014*		*LOQ*	*0.02*	*0.01*

In the dissolved fraction (<0.2 µm), 70% to 100% of Cd, Ni, V, and REY, but only 25% of Cu and < 50% of As were determined.

Interpreting Kinetic Signatures

River Wyre, Garstang, 2004 (Warnken *et al*., EST, 2007)



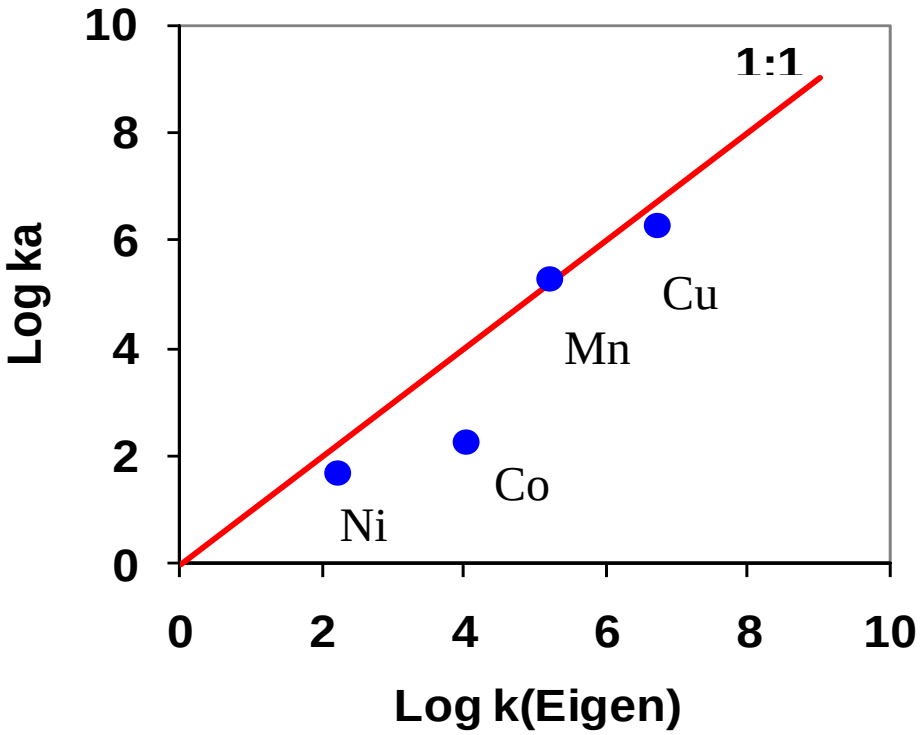
For these metals:

Measured DBL ≈ physical DBL governed by water flow past DGT surface

For these metals, DBL in presence ligands is governed by dissociation of metal from ML complex

Measured DBL >> physical DBL

Obtaining Kinetic Rate Constants



$$\mathrm{M} + \mathrm{FA} \underset{k_d}{\rightleftharpoons} \mathrm{M\text{-}FA}$$

$$1/M = \frac{(\Delta g + \delta + g_{kin})}{(D_M C_M + C_{MFA} D_{MFA}) A t}$$

$$g_{kin} = D_{M\text{-}FA}\sqrt{(K[FA]/(k_d D_{M\text{-}in}))}$$

Eigen: association rate constant is determined by the rate of water loss

Warnken et al., 2009, , *Environ. Sci. Technol,* 41, 3179-3185.

DGT for Metal speciation and kinetics

CSIRO PUBLISHING

Research Paper

Environ. Chem. **2011**, *8*, 517–524

www.publish.csiro.au/journals/env

Using diffusive gradients in thin films to probe the kinetics of metal interaction with algal exudates

Jacqueline Levy,[A,C] *Hao Zhang,*[A] *William Davison*[A] *and Rene Groben*[B]

frontiers in Chemistry

REVIEW

published: 06 April 2021

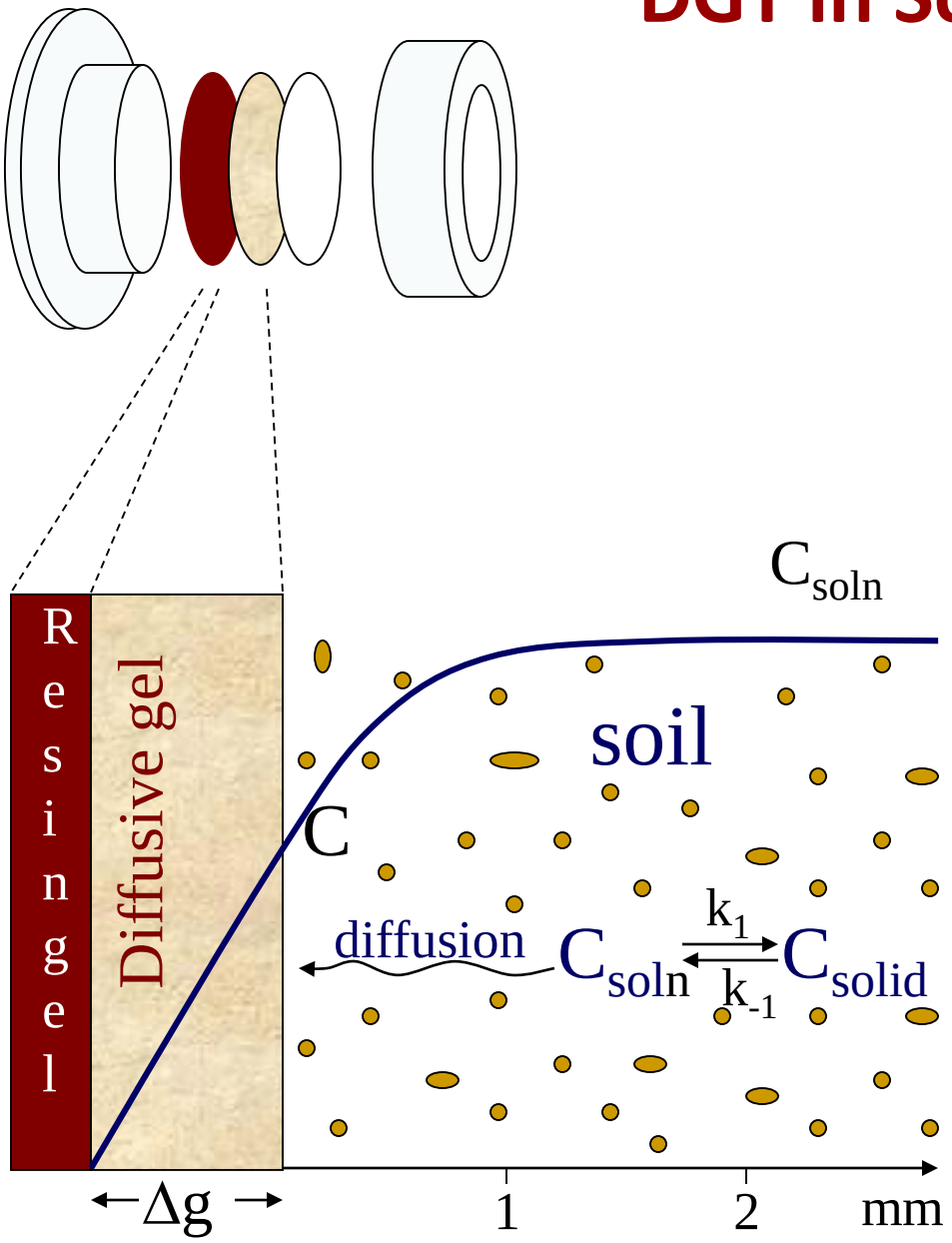
doi: 10.3389/fchem.2021.624511

Speciation of Inorganic Compounds in Aquatic Systems Using Diffusive Gradients in Thin-Films: A Review

Josep Galceran[1]*, Yue Gao*[2*]*, Jaume Puy*[1]*, Martine Leermakers*[2]*, Carlos Rey-Castro*[1]*, Chunyang Zhou*[2] *and Willy Baeyens*[2]

[1] *Departament de Química, Universitat de Lleida and AGROTECNIO-CERCA, Lleida, Spain,* [2] *Analytical, Environmental and Geo-Chemistry Department, Vrije Universiteit Brussel, Brussels, Belgium*

DGT in Soils or Sediments



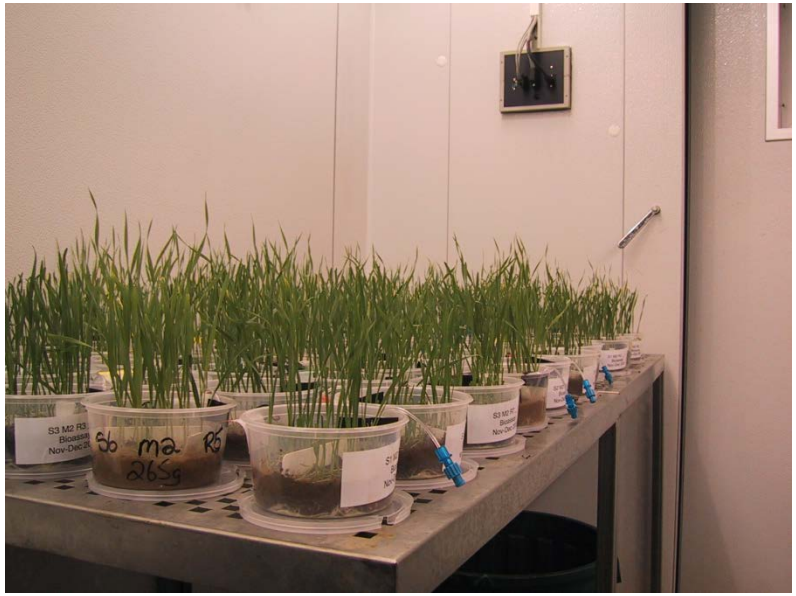
$$C = \frac{M\Delta g}{D_d t A}$$

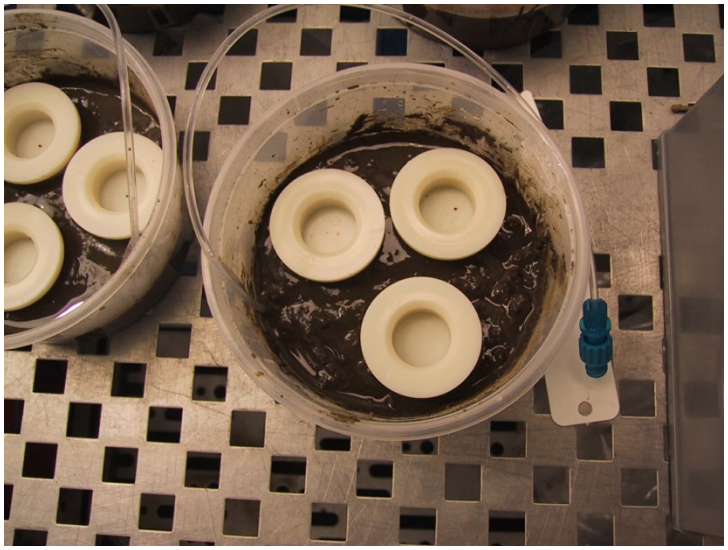
$R = C/ C_{soln}$

R depends on:

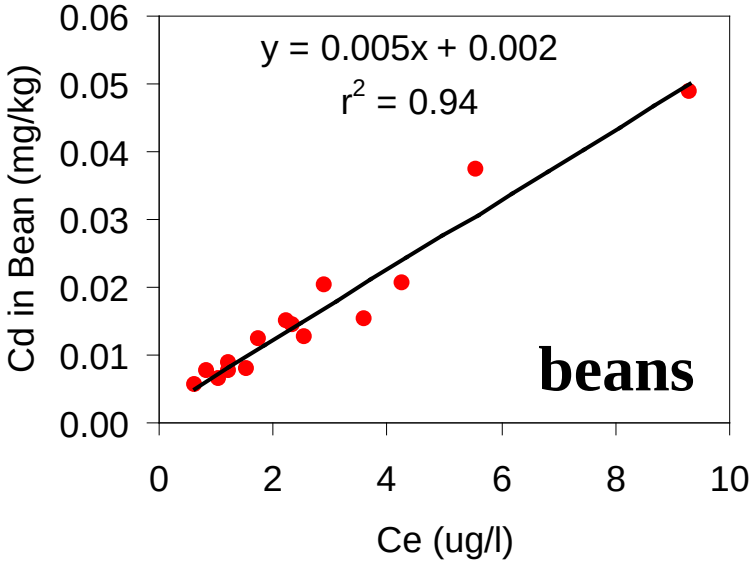
- Capacity of solid phase reservoir
- Kinetics of resupply processes

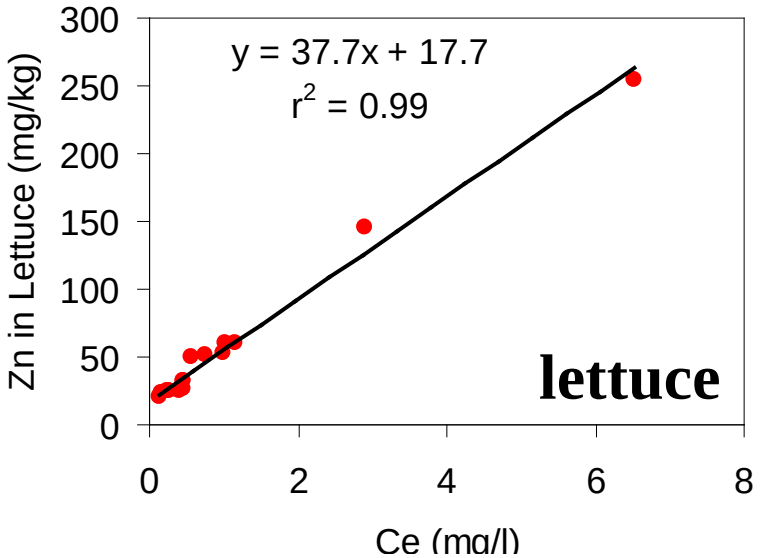
DGT Research in Soils

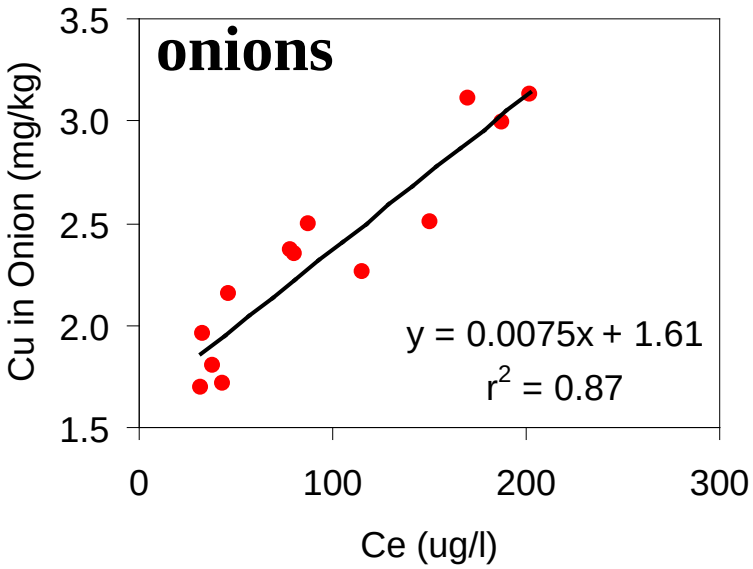


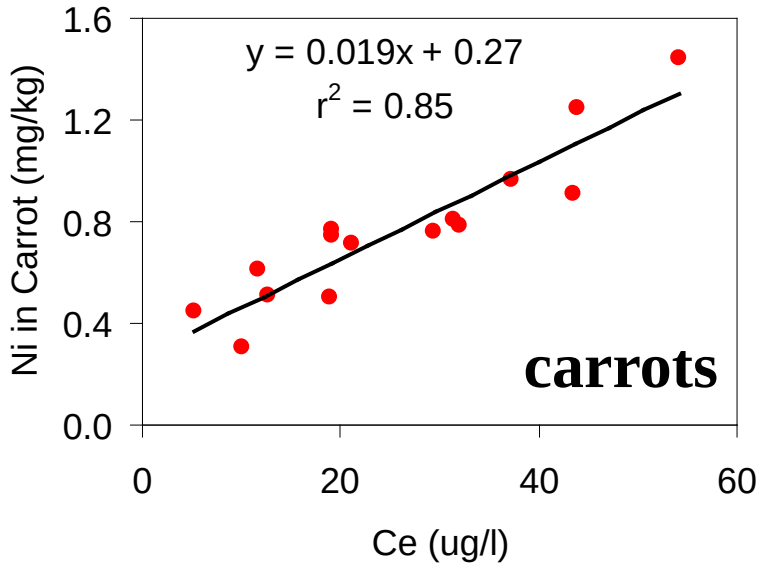


DGT and Vegetables



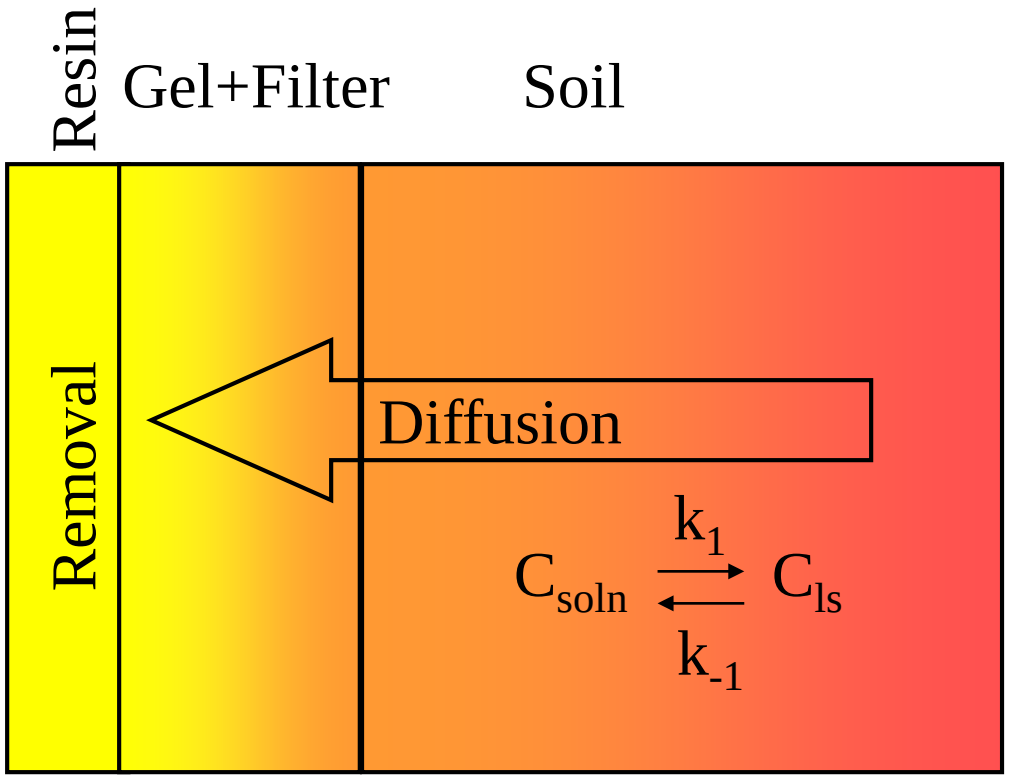






Zhang et al., 2023, in preparation

DGT induced fluxes in soil or sediments - DIFS



$$\text{labile } K_{dl} = \frac{C_{ls}}{C_{soln}}$$

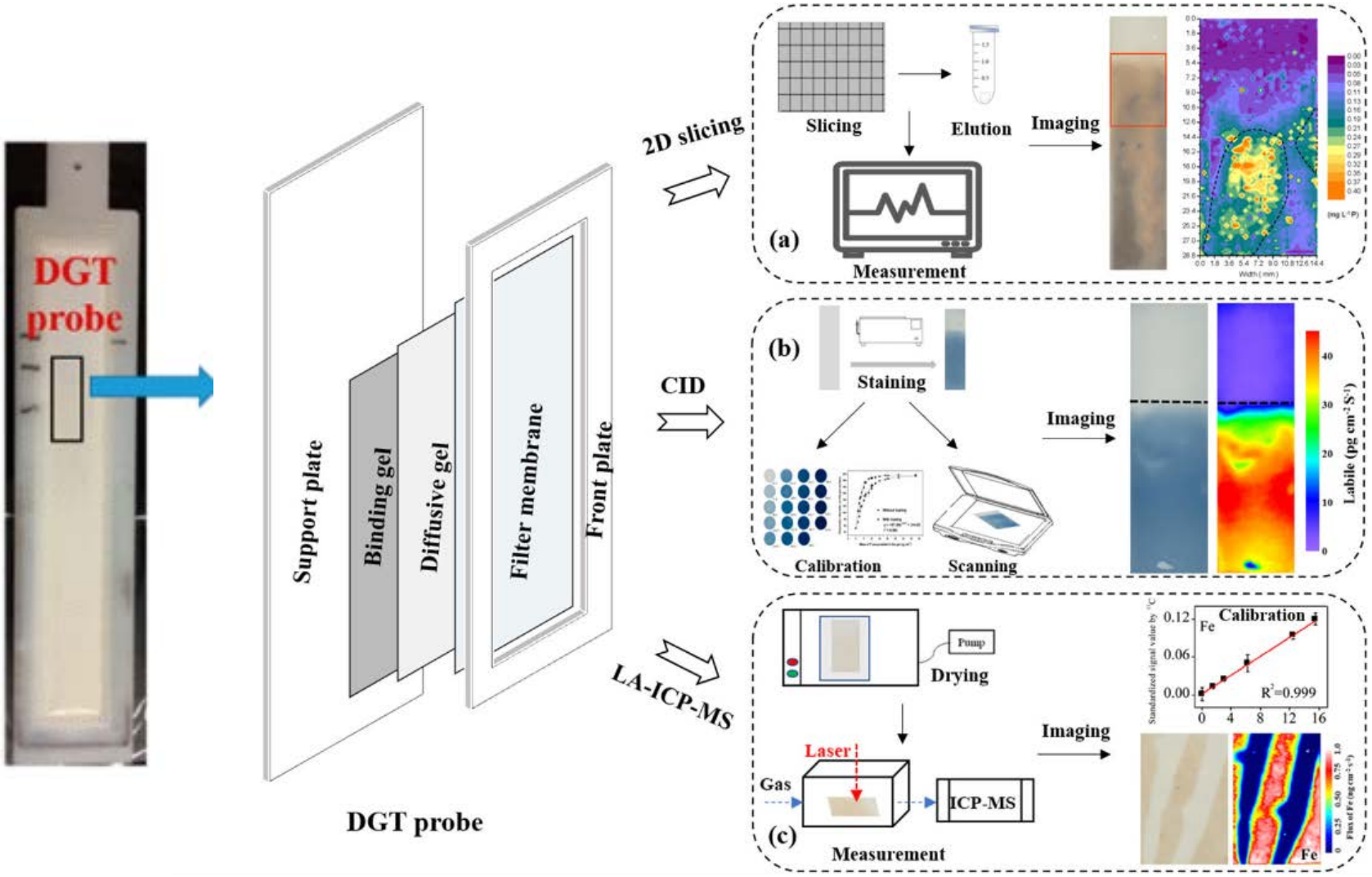
Response time

$$T_c = \frac{1}{k_1 + k_{-1}}$$

Large T_c - slow response
Small T_c - rapid response

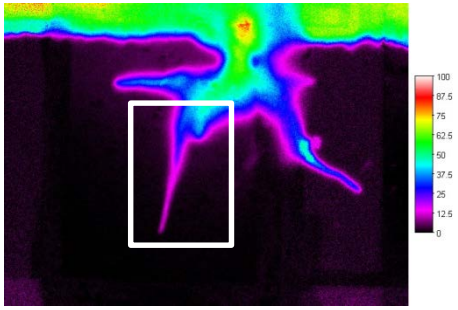
A numerical model mimicing DGT uptake, diffusion transport and exchange

DGT Research in Sediments

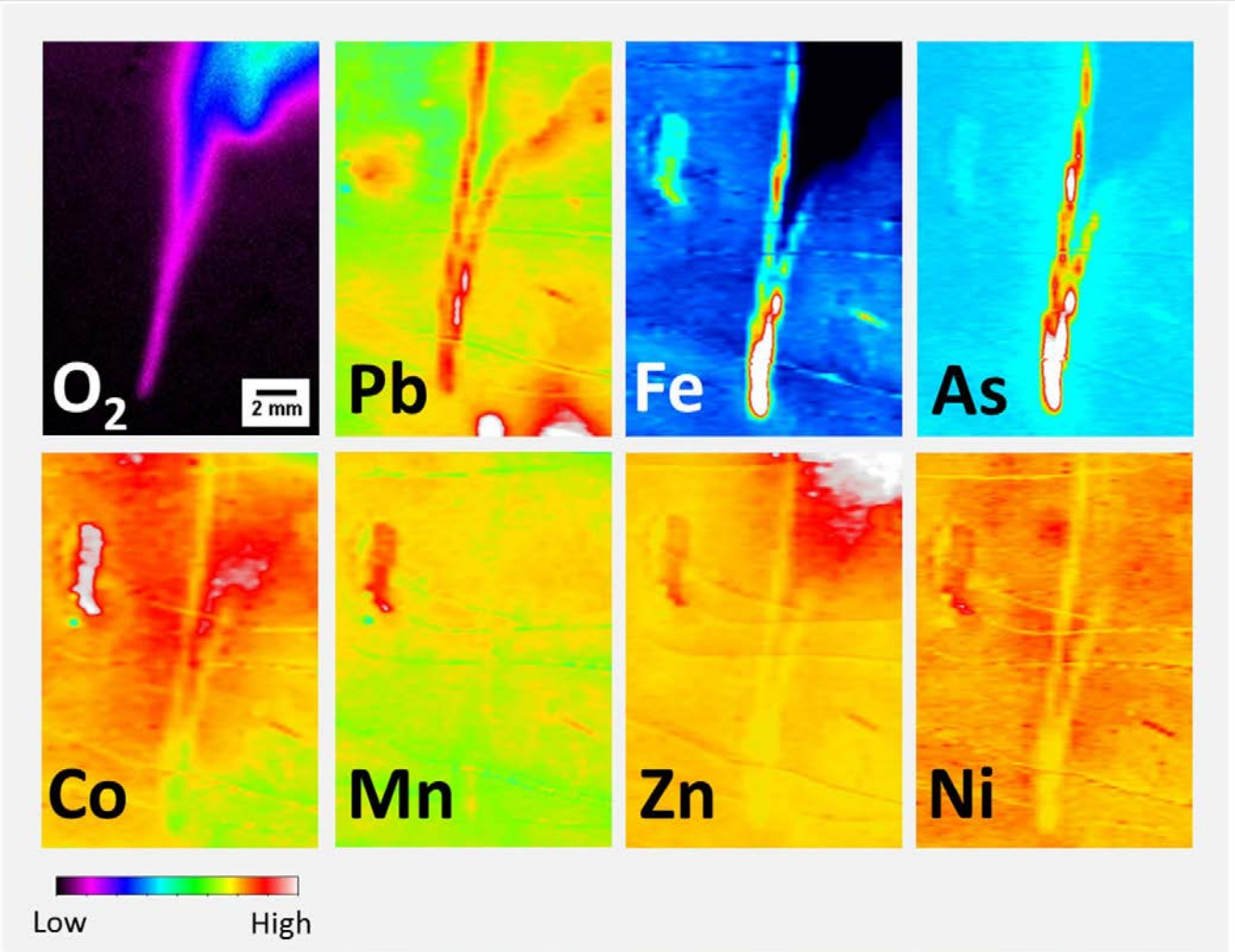


CRITICAL REVIEWS IN ENVIRONMENTAL SCIENCE AND TECHNOLOGY 2023, VOL. 53, NO. 12, by Cai Li et al.

Visualisation of O_2, Pb, Fe, As, Co, Mn, Zn and Ni around a set of rice roots



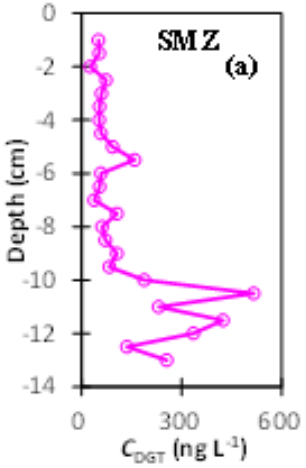
PO (Planar Optode)
DGT-ICPMS-Laser

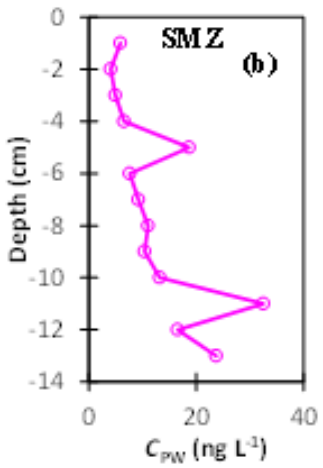


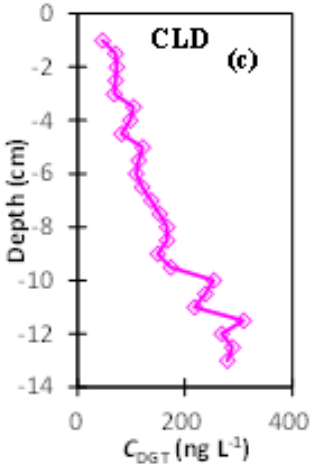
Williams, Paul et al. *Environ. Sci. Technol.*, 2014, *48* (15), pp 8498–8506.

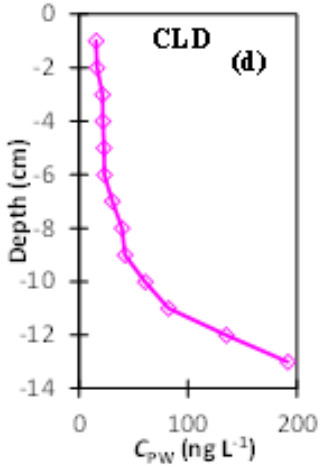
$$4Fe^{2+} + O_2 + 6H_2O = 4FeOOH + 8H^+$$

First High Spatial Resolution Measurement of Antibiotics in Sediments









Yanying Li et al. Submitted to ES&T

Summary of DGT Impacts

- **Some big steps in sciences**

- **First step on solid ground for regulation**
  - *** Monitool**
  - * standard methods/guidelines for water, soil and sediment quality control in China, Australia and New Zealand

Impacts

- **Monitoring in different environments**
- **Forensics (illicit drugs)**
- **Precision Agriculture (K, P, N)**
- **High quality Aquaculture (metals and antibiotics)**
- **Risk assessment (water treatment and soil remediation)**
- **New standards and new regulations**

Cutting Edge Research

- **Chemical Speciation (including nano)**
- **Bioavailability**
- **Toxicity**
- **Dynamic Models**
- **Biogeochemical processes in soils and sediments**

  (DGT-isotopes, PO/DGT-ICPMS-Laser, DGT-Colorimetry-Scanning)

- **Rhizosphere processes**
- **New types of DGT**

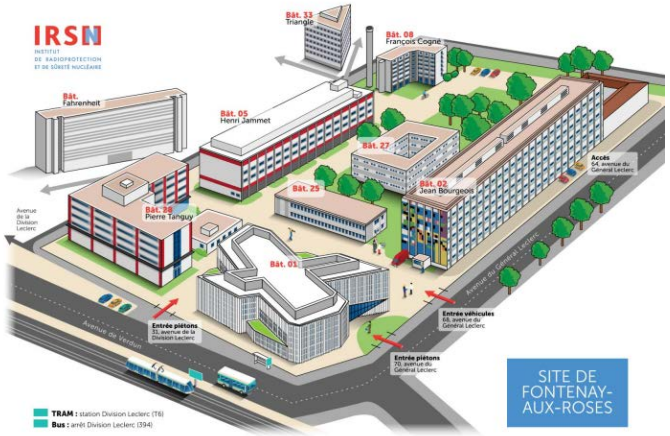
Thank You

You are all very welcome to:

The 7th international DGT conference (11-13 October 2023)

(IRSN, Fontenay-aux-Roses, Paris, France)

Place



Meeting room

Gala dinner in "Ciel de Paris".

53rd floor in Montparnasse tower

Organised by Dr. Josselin Gorny and Dr. Laureline Fevrier

Website: www.dgt2023.fr, deadline for abstracts: 31 May.