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DGT for organics monitoring and research: development and applications

Kevin C Jones and Hao Zhang

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Lancaster Environment Centre, UK

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Talk structure

- Brief Introduction
- Organics and DGT – progress so far
- DGT for organics – application case studies
- DGT for organics – the future

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Trace organics group – our 'dream' to reality

- Quantify and apportion sources (ultimately reduce sources)
- Monitor and regulate the environment effectively
- Understand chemical fate and behaviour - in the environment and through controlled studies and models
- Therefore – determine concentrations and fluxes
- *Passive sampling has many uses and can help make our dreams come true!*

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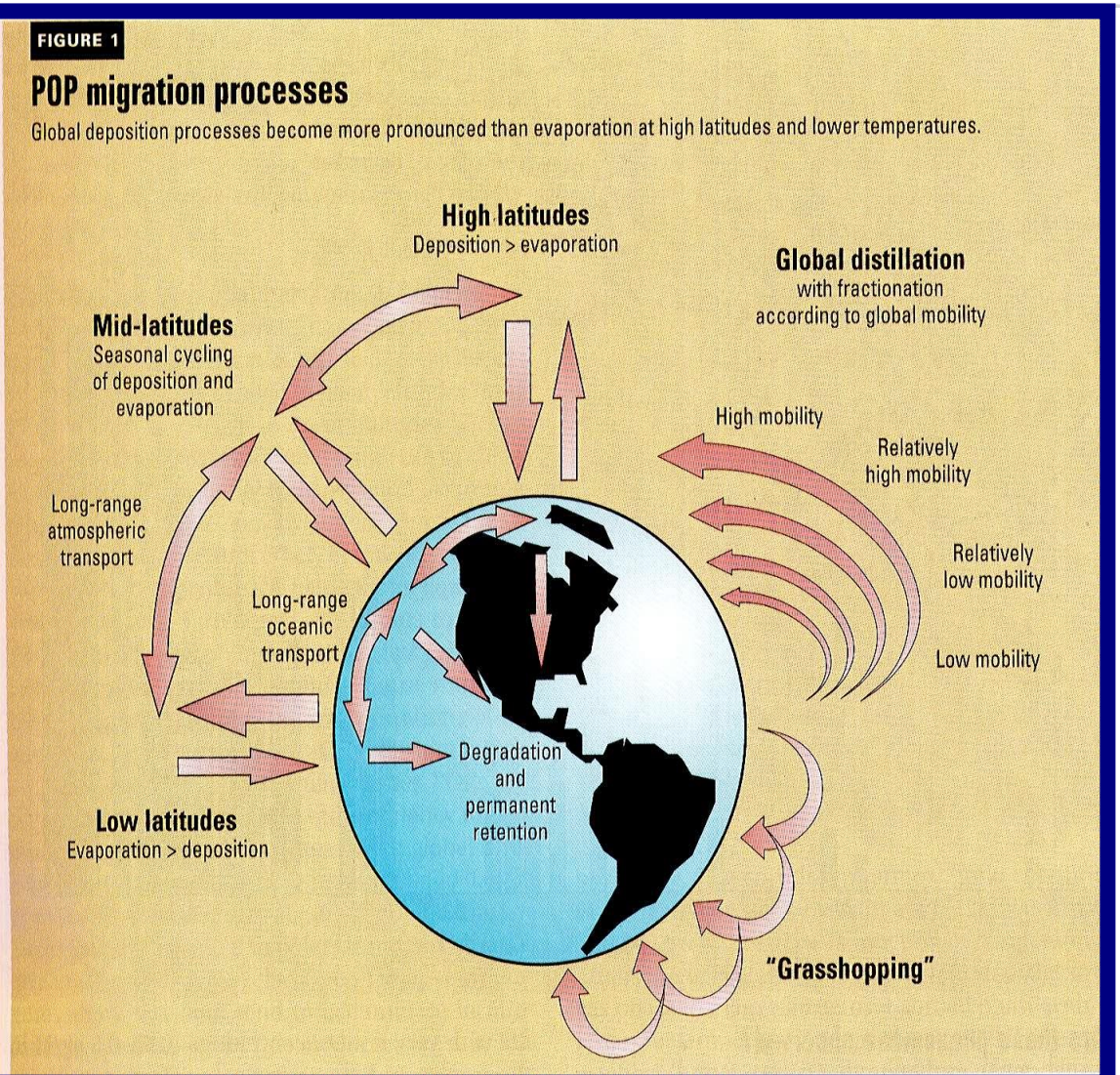
My starting interest…



~1990

Global cycling of POPs

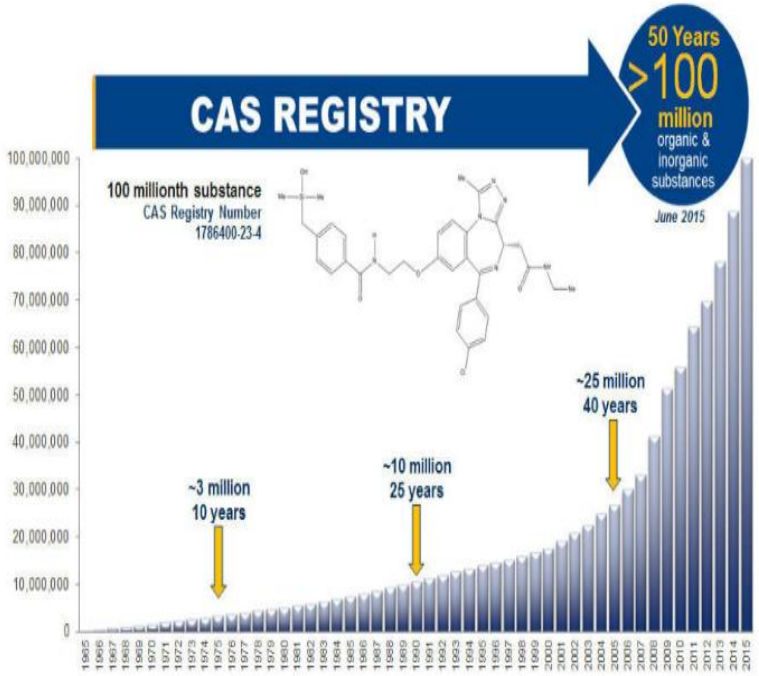
Hypothesis – cold condensation, distillation, fractionation

How to test?

Need to measure different places simultaneously for long time…

WATER/SOIL - CURRENT FOCUS – why?

- Many classes and sources/uses; number constantly growing
- Often poor treatment (e.g. WWTPs not designed to remove)
- Ubiquitous in the environment e.g. *Science* >600 pharmaceuticals in waters
- Effects at low levels (e.g. endocrine, hormonal, resistance genes…)
- How to prioritise? Regulation, screening, monitoring tools
- Physical-chemical property range – solubilities, partitioning…



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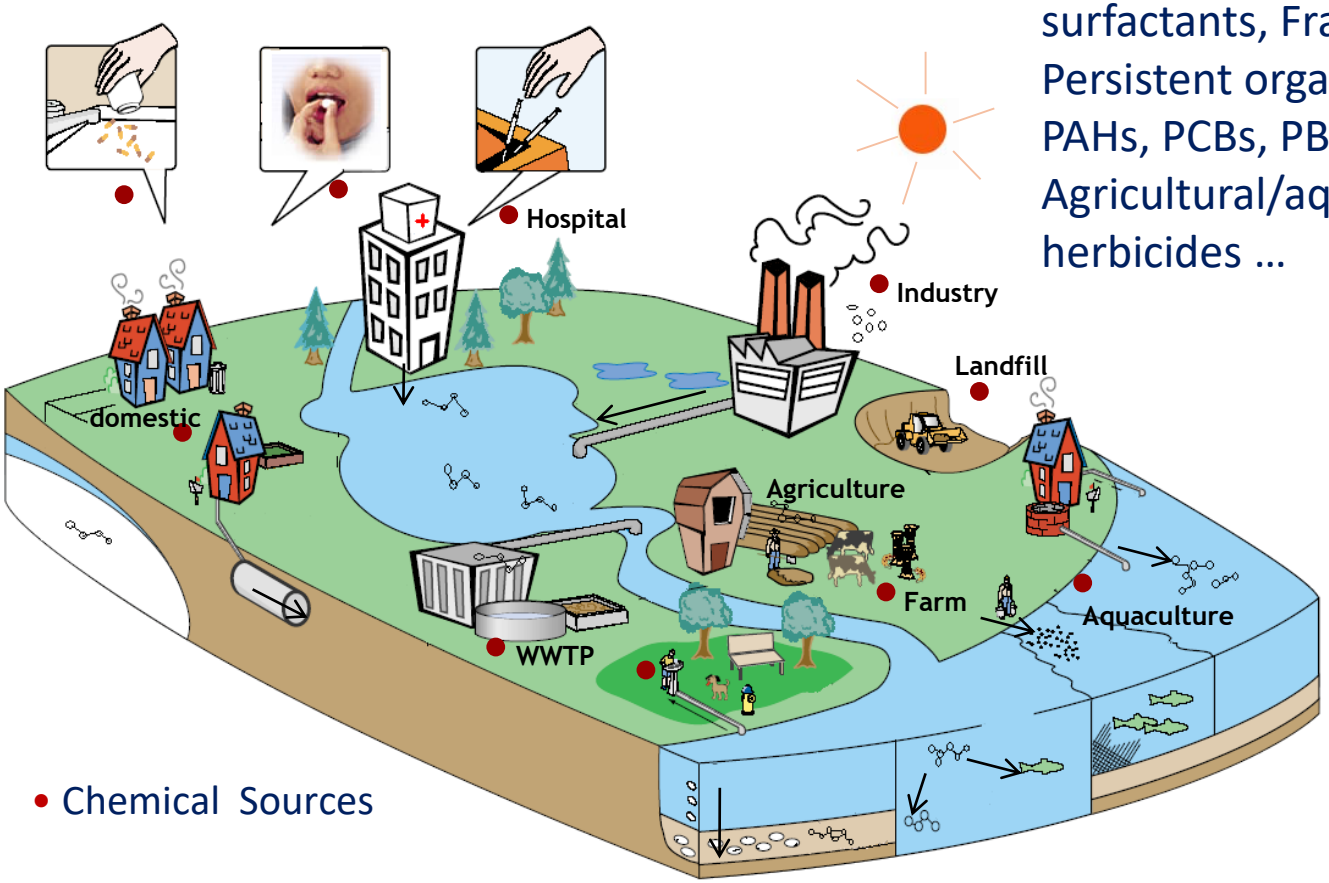
Organic contaminants – what and where?



- Chemical Sources

Pharmaceuticals and personal care products (PPCPs): antibiotics, UV filters…
Household products: detergents, surfactants, Fragrances …
Persistent organic pollutants (POPs): PAHs, PCBs, PBDEs, dioxins…
Agricultural/aqua-cultural - pesticides, herbicides …

Monitor discharges and the environment

Couple with models - ‘measure everything everywhere’

DGT – inherent advantages for organics

- Organics developments started ca 2008…
- **Prof Hao Zhang – this morning – inorganics/nutrients - 800 papers, >250 labs, 30 countries, strong community, shared practice**
- No calibration needed in the field
- Simple, robust, cheap
- Pre-concentrate & pre-clean during deployment.
- Combine with highly sensitive LC-MS, GC-MS.
- Different configurations possible:
  - Varying surface area and exposure time – to suit purpose
  - Different analytes (different resins, sampler materials)
- Derive bioavailable, free and relevant forms of substance

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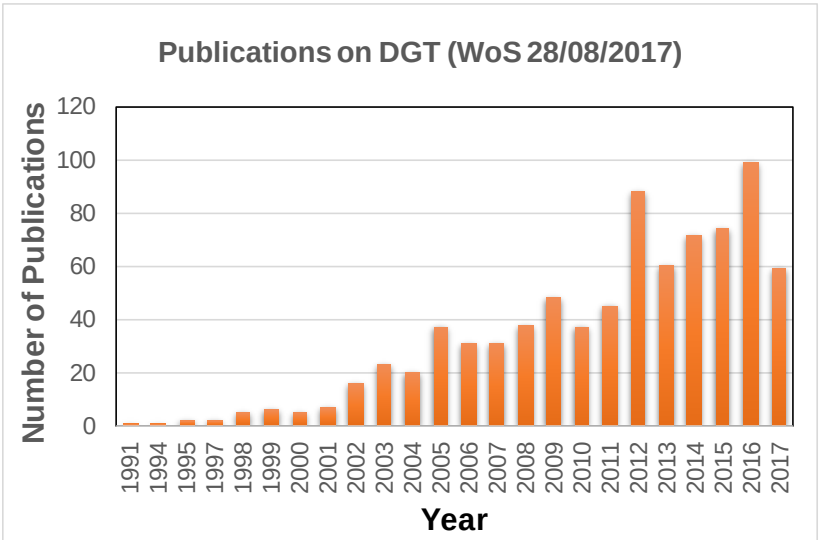
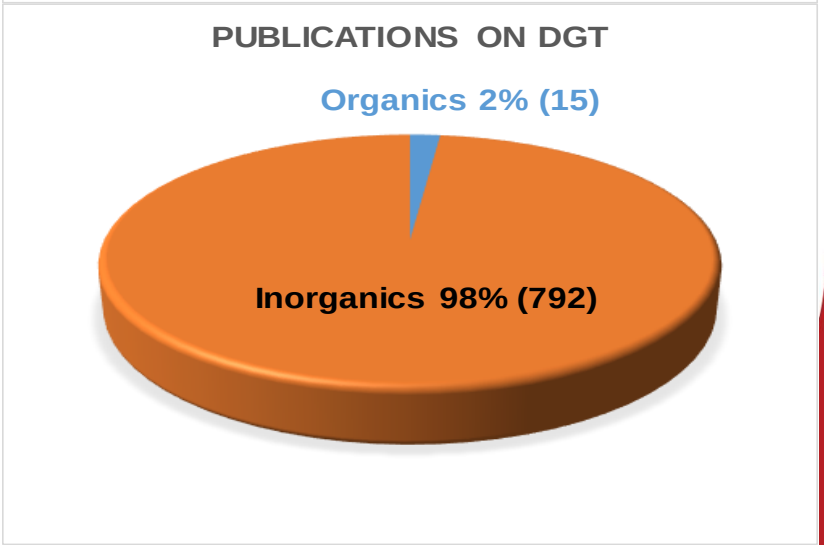
DGT – organics…new line of research

Field: Web of Science Categories	Record Count	% of 807	Bar Chart
ENVIRONMENTAL SCIENCES	427	52.912 %	
CHEMISTRY ANALYTICAL	224	27.757 %	
ENGINEERING ENVIRONMENTAL	130	16.109 %	
SOIL SCIENCE	50	6.196 %	
WATER RESOURCES	47	5.824 %	
CHEMISTRY MULTIDISCIPLINARY	46	5.700 %	
PLANT SCIENCES	31	3.841 %	
AGRONOMY	29	3.594 %	
TOXICOLOGY	29	3.594 %	
MARINE FRESHWATER BIOLOGY	26	3.222 %	
GEOCHEMISTRY GEOPHYSICS	24	2.974 %	
GEOSCIENCES MULTIDISCIPLINARY	23	2.850 %	
OCEANOGRAPHY	21	2.602 %	
METEOROLOGY ATMOSPHERIC SCIENCES	18	2.230 %	
BIOCHEMICAL RESEARCH METHODS	16	1.983 %	
MATERIALS SCIENCE MULTIDISCIPLINARY	12	1.487 %	
ECOLOGY	10	1.239 %	
CHEMISTRY PHYSICAL	9	1.115 %	
ENGINEERING CHEMICAL	9	1.115 %	
MECHANICS	9	1.115 %	
PHYSICS APPLIED	9	1.115 %	
MULTIDISCIPLINARY SCIENCES	7	0.867 %	
POLYMER SCIENCE	6	0.743 %	
SPECTROSCOPY	6	0.743 %	
THERMODYNAMICS	6	0.743 %	





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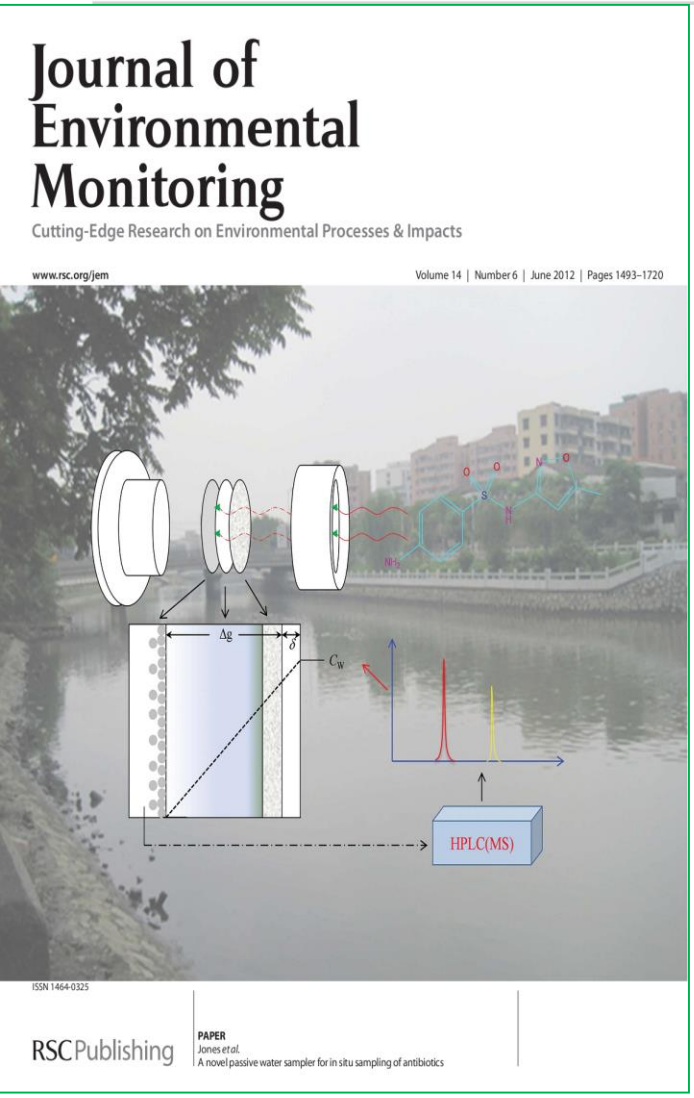
DGT development steps for organic compounds



Chen et al JEM, 2012

First paper on DGT for organics - a guideline based on antibiotics

Gel and resin performance (capacity)	LAB
Investigate key parameters – pH, IS, DOM	LAB
Check sample materials for contamination/adsorption	LAB
Measure precise diffusion coefficients in test cell	LAB
Optimise extraction, clean-up, recoveries	LAB/FIELD
Investigate storage/stability/handling	LAB/FIELD
Investigate exposure time, detection limits	FIELD

Current situation – chemicals studied

About 120 compounds in published studies

• Antibiotics	Chang'er Chen et al; ES&T 2013
• Phenols and bisphenols	ACA 2014
• Pesticides	AC 2015; 2017; ACA 2017
• Other pharmaceuticals	AC 2017
• Illicit drugs	ES&T 2017; CRAES team in Beijing
• Personal CPs/oestrogens	Wei Chen; ES&T 2017; WR 2018

In press/submitted/development

• Pesticides	Yanying Li
• Anticancer drugs	Helena Franquet-Griel
• Perfluorinated compounds	Nanjing team
• Organophosphate esters (Kow range)	Runmei Wang
• **More on the way from several groups….**	

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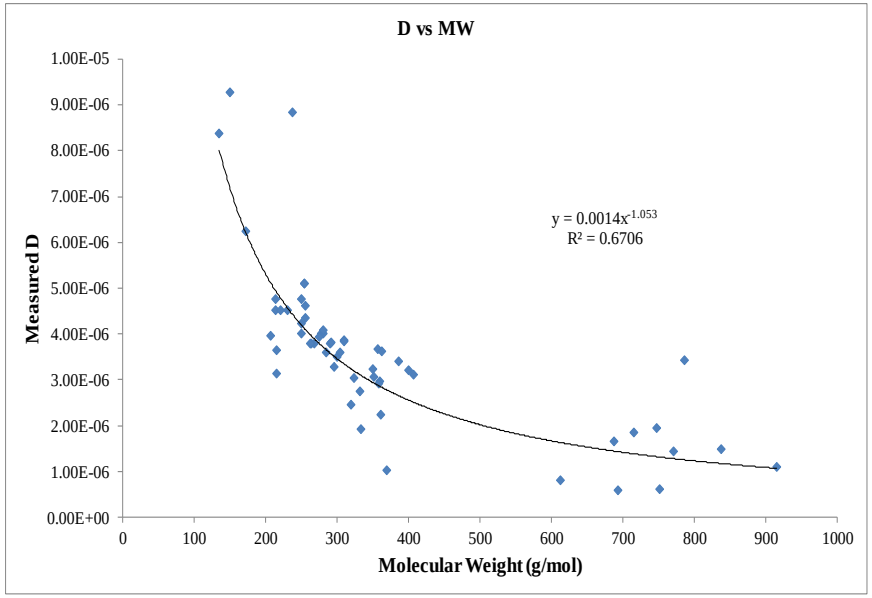
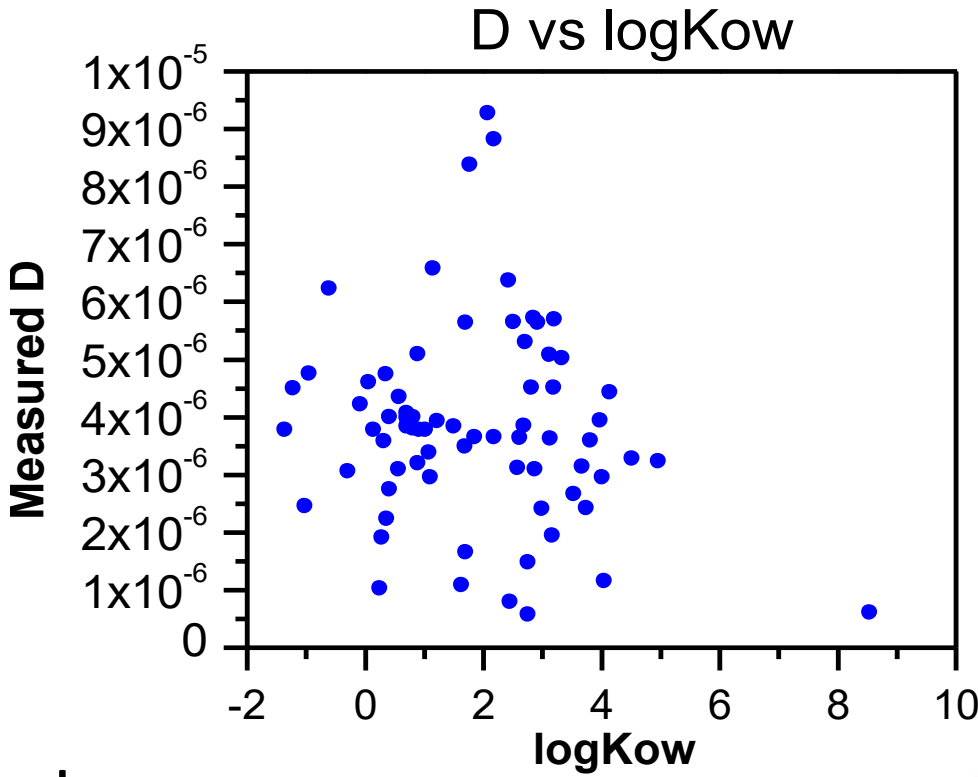
Current situation – chemicals studied

MW spans 100 - 900





Relationships with properties being explored

Prediction of DC – measurements really needed; protocols/guidelines

Challenges with high Kow, low aqueous solubility compounds

So far – studies use the existing DGT configuration. Where is the 'limit'?

Current situation – binding phases; diffusive phases and filters

Binding phases **desirable properties = high capacity; fast; some selectivity**

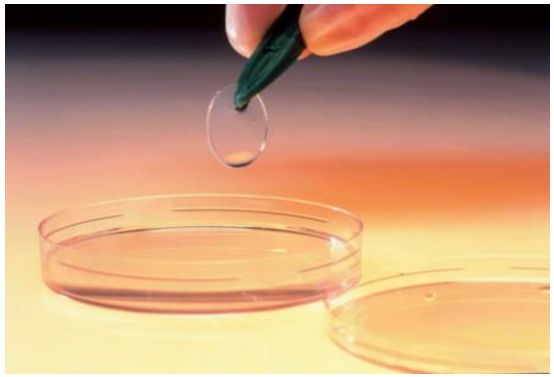
HLB; XAD-18; SXLA; activated charcoal; molecularly imprinted polymers; nano-TiO2

Diffusive phases **desirable properties = no significant retention**

Polyacrylamide; agarose

Filters **desirable properties = protective role; minimal retention**

Hydrophilic PTFE; hydrophilic polyethersulfone (PES); hydrophilic polypropylene



Exploring limits of normal DGT configuration – Runmei Wang

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Literature:

- 4 types of membrane filters;
- 7 types of binding layers;
- 116 compounds so far…

Using organophosphate esters (OPEs): Kow range from 0.8 – 9.5

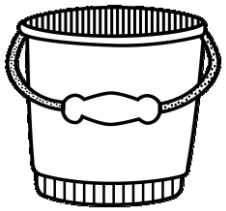
DGT moldings and gels:

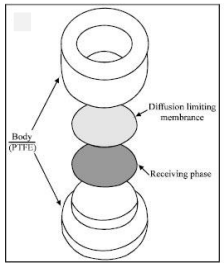
- <1% sorption; sorption equilibrium – few hours

Membranes:

- Compounds Kow < 4 minimal delay in permeation; > 4 can be days

Current situation - validation, comparisons





Chem-catcher

POCIS

DGT **'GRAB'** **AUTO-SAMPLER** **OTHER PASSIVE SAMPLERS**

e.g. Environment Agencies; water treatment plants

The benefits: **Time weighted average concentrations; many studies for inorganics**

In situ, not subject to change in transport and storage

Freely available forms (i.e. will NOT be the same as total)

Chen et al. **Better than grab; comparable to auto (much cheaper; multi-site)**

Challis et al. **DGT favoured**

Some applications and case studies…

Environmental Science & Technology

Article

47, 13587-13593

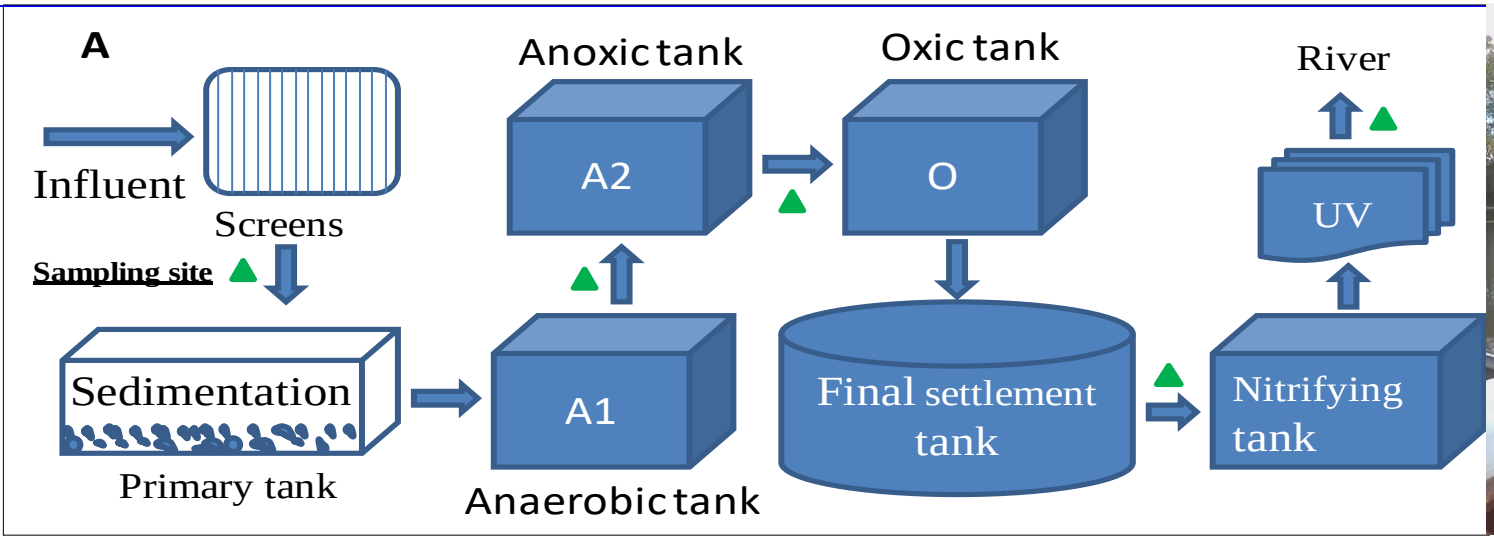
pubs.acs.org/est

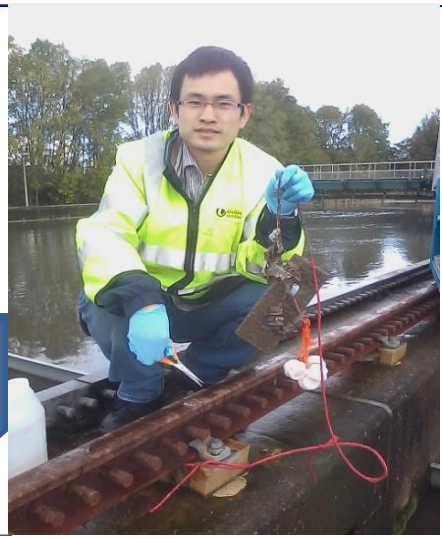
Evidence and Recommendations to Support the Use of a Novel Passive Water Sampler to Quantify Antibiotics in Wastewaters

Chang-Er Chen,[†] Hao Zhang,[†] Guang-Guo Ying,[‡] and Kevin C. Jones*,[†,‡]

[†]Lancaster Environment Centre, Lancaster University, Lancaster, LA1 4YQ, United Kingdom

[‡]State Key Laboratory of Organic Geochemistry, Guangzhou Institute of Geochemistry, Chinese Academy of Science, Guangzhou, 510640, China





- Validated sampler against grab and auto-samplers – typical sampling 1-4 weeks
- Plant efficiencies can quickly and easily be determined…
- Treatment steps and their performance can be identified…
- ABs generally poorly removed; Some transformations e.g. sulfonamides
- New urban Chinese WWTPs working better than UK
- New work on PCP removal in China

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Environmental Forensics
e.g. illicit drugs use and sources

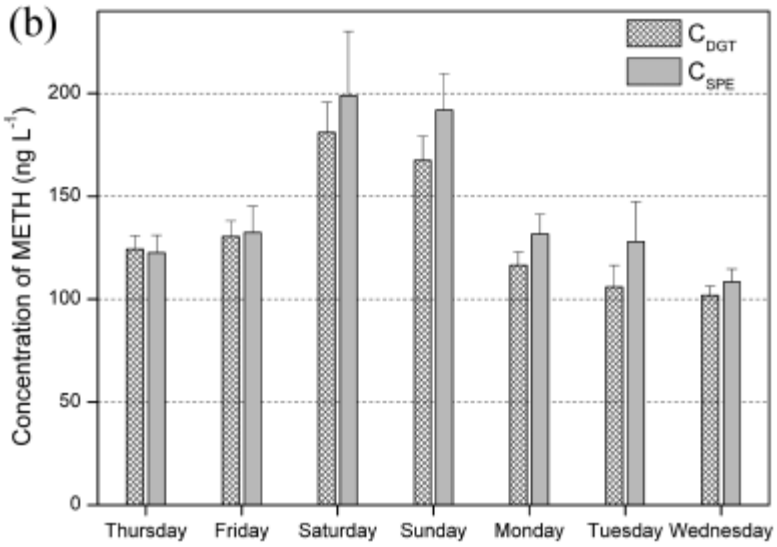
Environmental Science & Technology

Article

pubs.acs.org/est

Investigation and Application of a New Passive Sampling Technique for in Situ Monitoring of Illicit Drugs in Waste Waters and Rivers

Changsheng Guo,[†] Tingting Zhang,[‡] Song Hou,[†] Jiapei Lv,[†] Yuan Zhang,[†] Fengchang Wu,[†] Zhendong Hua,*[‡] Wei Meng,[†] Hao Zhang,[§] and Jian Xu*[,†]



Amphetamine in Beijing WWTP influent

Tracking tool for police in urban areas

Comparison between countries/cities

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Soils and sediments

Environmental Science & Technology

Article

pubs.acs.org/est

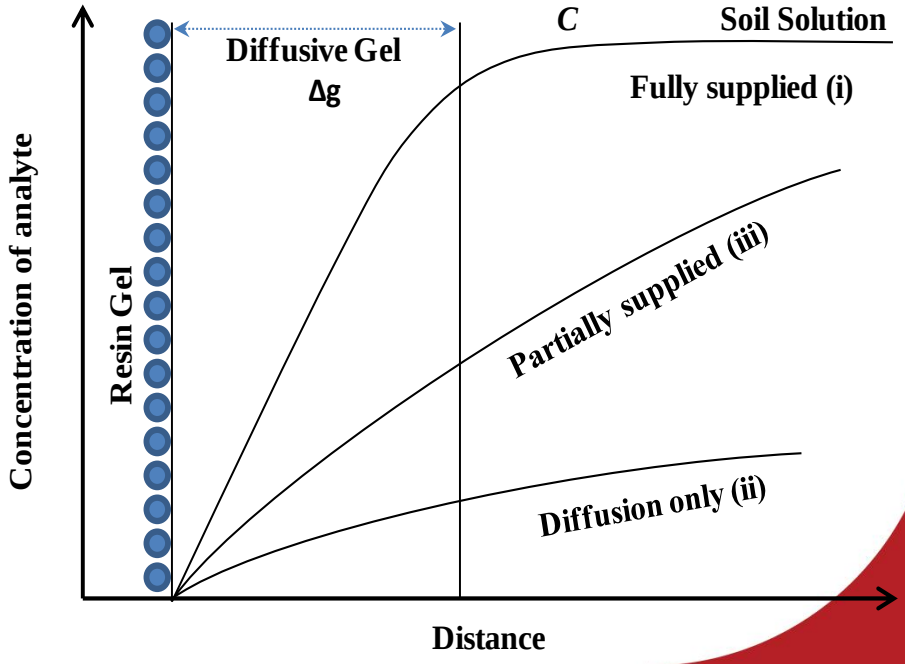
Desorption Kinetics of Sulfonamide and Trimethoprim Antibiotics in Soils Assessed with Diffusive Gradients in Thin-Films

Chang-Er Chen,[†] Kevin C. Jones,[†,‡] Guang-Guo Ying,[‡] and Hao Zhang*[,†]

$R = C_{DGT}/C_{soln}$

indicator of the extent of depletion of pore water concentrations at the DGT interface.

Technique – giving in situ kinetic parameters for modelling



Bioavailability, degradation, predicting maize uptake

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Shoot

Root

Soil

Atrazine Degradation

HA

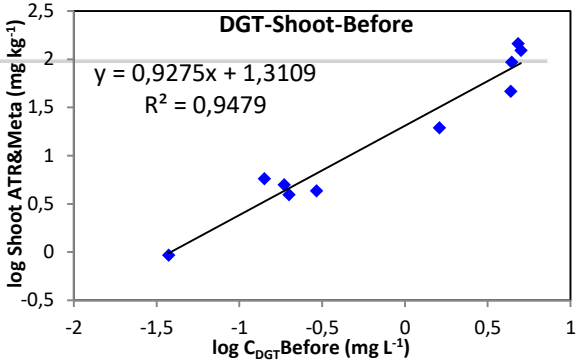
ATR

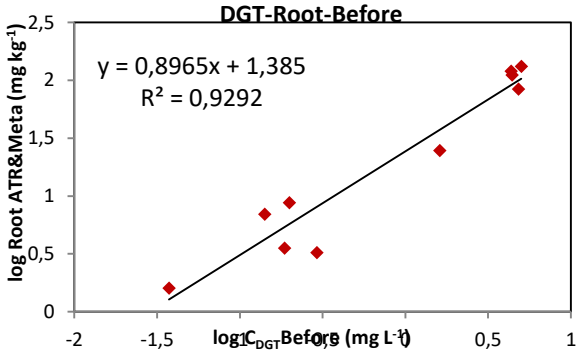
CYA

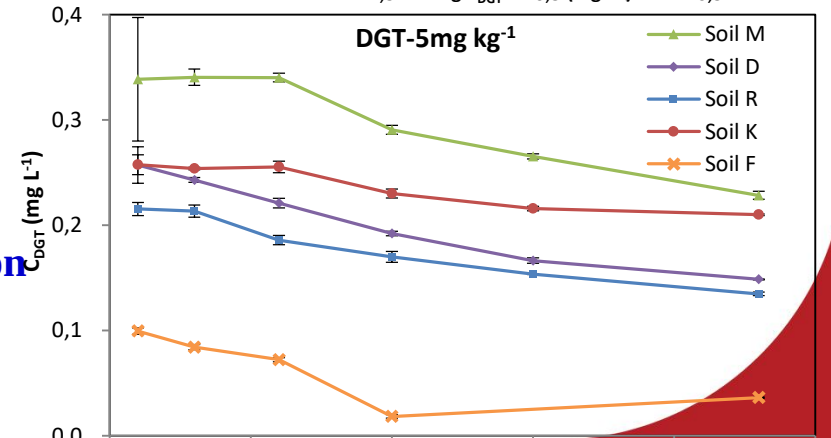
DIA

DEA

Atrazine Translocation Pathway

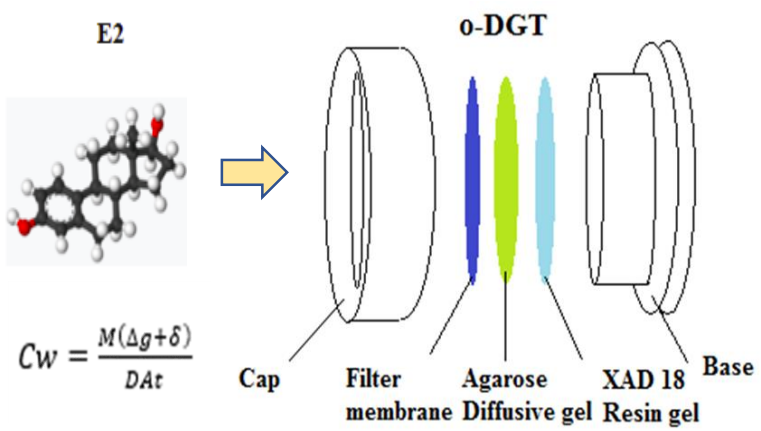




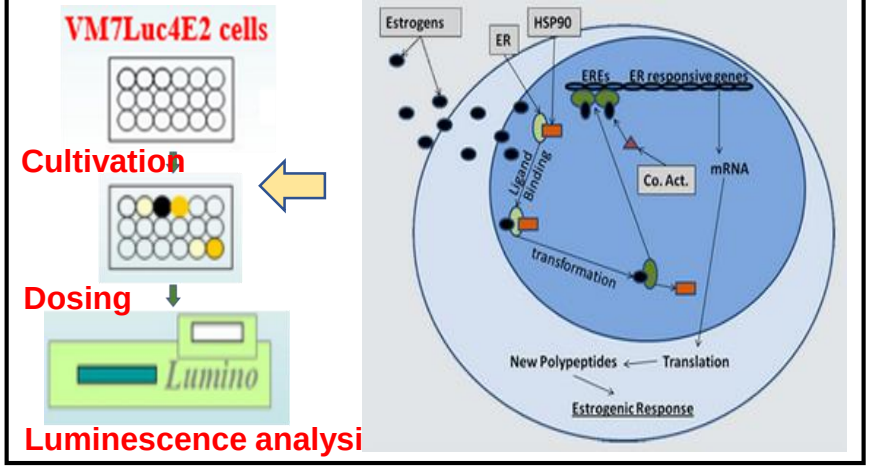


DGT coupled with bioassays e.g. estrogen screening

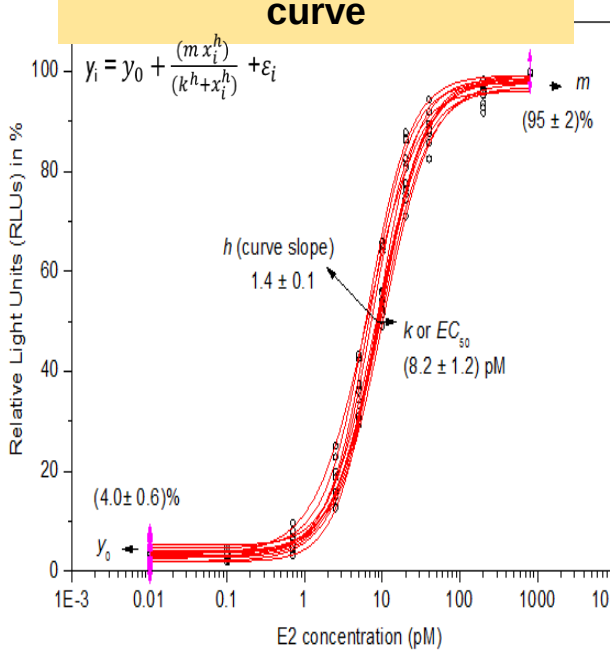
Pre-concentrated by DGT



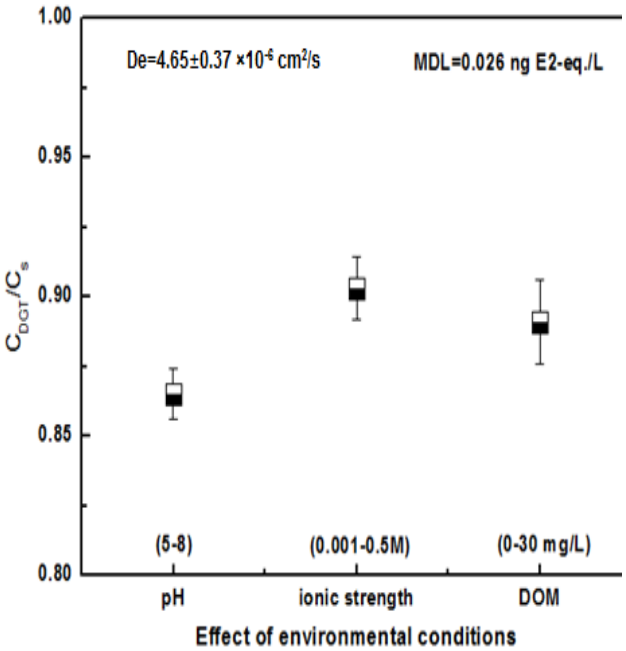
ERE-CALUX bioassay



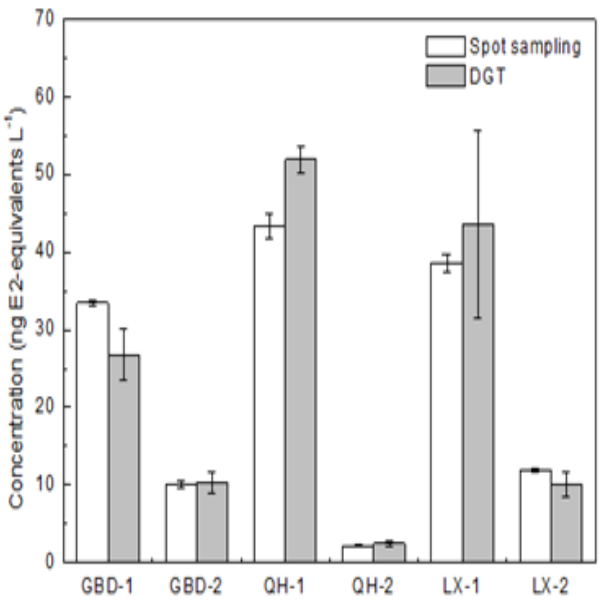
Concentration-response curve



o-DGT performance



Field work



Sampling station in WWWPT in Beijing

The Future 1 – developing DGT for organics

- Known principles - extend to organic chemicals
- Many diverse compounds – no universal ‘sampler phases’

- Already samplers for many compound classes; easiest being addressed first…

- In future, a ‘family’ of DGTs needed
- How far can the compound range/limits be extended?
- Can new DGT designs be developed?

- Need experiments on degradation/losses; then clear protocols

The Future 2 – monitoring and screening

- Routine monitoring of target analytes (with GC-MS; LC-MS)
- Routine screening for unknowns/non-target analytes

- This will partly be driven by low cost, and the power of coupling multiple measurements to catchment-based models

- This will greatly improve knowledge and management of sources and water quality

The Future 3 – science applications

- DGT as a ‘Scientific tool’ for *in situ* understanding

- Increasing applications to process-based understanding e.g.
  - Sorption/desorption soils/sediments
  - Interactions with DOM
  - Sediment-water interface processes

- Mimicking bioavailability/bioaccumulation – risk assessment

- Combine with effects-based analysis to improve toxicological and eco-toxicological testing

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Dr Hao Cheng, DGT Research Ltd

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Prof Yue Gao, Vrije University, Brussels

Thank you – we welcome collaborative opportunities

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