



**UNIVERSITY OF  
PORTSMOUTH**

**Professor Gary R. Fones**



**MONITOOL Stakeholder Conference  
Cagliari, Italy 19<sup>th</sup> May 2023**

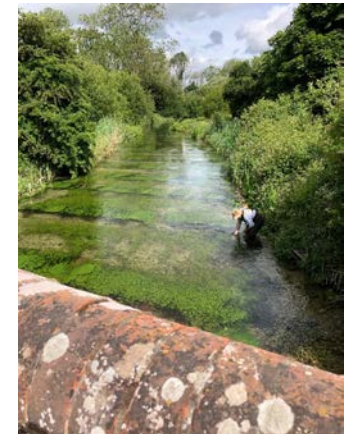
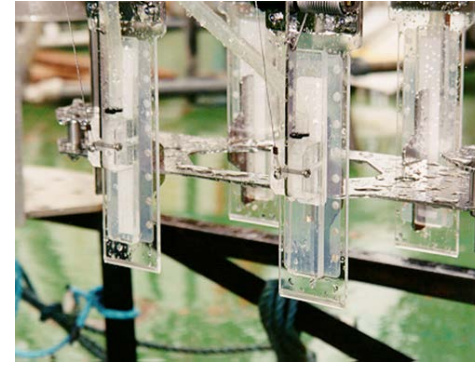
**30+ Years of Passive Sampling- What's Next?**



# 30+ Years of Passive Sampling- What's Next?

## Presentation Outline:

- Background history
- Passive sampling devices
- Examples of DGT use
- Examples of Chemcatcher use
- The future?





# 30+ Years of Passive Sampling- What's Next?

## Background and history

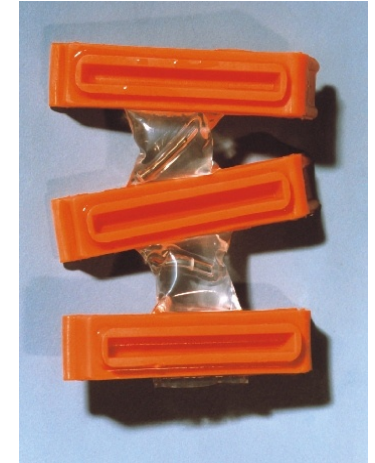
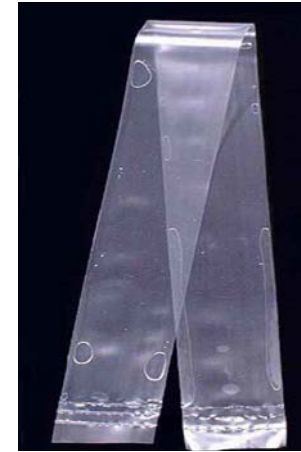
- Passive samplers have been used since the 1920's (biomonitoring)
- Air monitoring in the 1970's
- Water and sediment in the 1990's
  - DET, DGT, POCIS, SPMDs, SLMDs, Chemcatcher
- **1<sup>st</sup> March 1995** – my introduction to passive sampling
- DGT/DET in sediments - Lancaster
- DGT in the water column - WHOI
- DGT & Chemcatcher - Portsmouth



# Types of passive sampling devices by pollutant class

- **Monitoring non-polar organic contaminants** - partition/absorption

- Semi-Permeable Membrane Devices (SPMD)
- Low-density polyethylene membrane and silicone rubber strips/sheets
- Membrane Enclosed Sorptive Sampler (MESCO)
- SPME fibres – using various phases (like air monitoring)
- Chemcatcher® (Non-polar version)
- Naked bound chromatographic disks (e.g.  $C_{18}$ ,  $C_8$ )



- **Monitoring polar organic contaminants** - adsorption

- Polar Organic Compound Integrative Sampler (POCIS)
- Chemcatcher® (Polar version)
- Naked bound chromatographic disks (e.g. SDB- and Oasis-based phases)
- Ion-exchange resins (anionic and cationic)
- Organic Diffusive Gradient in Thin films (o-DGT)



- **Monitoring metals** – chelating and other mechanisms

- Diffusive Gradient in Thin films Device (DGT)
- Chemcatcher® (Metals/organo-metals version)
- Ecoscope (ALcontrol AB)
- Various permeation devices (e.g. for mercury)



- **Monitoring nutrients**

- DGT
- Chemcatcher® (anion exchange disk)



# Passive samplers for non-polar pollutants



Critical Reviews in Analytical Chemistry



ISSN: (Print) (Online) Journal homepage: <https://www.tandfonline.com/loi/batc20>

## Applications for Passive Sampling of Hydrophobic Organic Contaminants in Water—A Review

Adam C. Taylor, Gary R. Fones, Branislav Vrana & Graham A. Mills

To cite this article: Adam C. Taylor, Gary R. Fones, Branislav Vrana & Graham A. Mills (2021) Applications for Passive Sampling of Hydrophobic Organic Contaminants in Water—A Review, Critical Reviews in Analytical Chemistry, 51:1, 20-54, DOI: [10.1080/10408347.2019.1675043](https://doi.org/10.1080/10408347.2019.1675043)

To link to this article: <https://doi.org/10.1080/10408347.2019.1675043>

### Partition-based samplers

Now a well established technology using strips or large sheets (e.g. 10 x 20 cm) of pre-cleaned low density polyethylene (LDPE) or silicone rubber (PDMS).

Typically 2-4 week deployments or longer.

High sampling rates 1-20 L/day water cleared, function of sampler size.

Soxhlet extracted and concentrated for GC/MS.

Low LoD (~ pg/L) achieved over long deployments.

Useful to trying to reach very low WFD-EQS for some substances.

High potential for acceptable use in WFD routine compliance monitoring.



***LDPE/PDMS sheets fixed to deployment cage.  
Use several sheets for different analyses.***

# Sediments – DET and DGT

- Metals, organometallics, nutrients and major cations



The Science of the Total Environment 221 (1998) 127–137

the Science of the  
Total Environment

An International Journal for Scientific Research  
into the Environment and its Relationship with Man

Development of constrained DET for measurements of  
dissolved iron in surface sediments at sub-mm resolution

Gary R. Fones<sup>a</sup>, William Davison<sup>a,\*</sup>, Geoff W. Grime<sup>b</sup>

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Lancaster LA1 4YQ, UK

<sup>b</sup>Scanning Proton Microbe Unit, Department of Nuclear Physics, University of Oxford, Oxford OX1 3RH, UK

Received 29 May 1998; accepted 24 June 1998

## Dissolved metals in surface sediment and a microbial mat at 100- $\mu$ m resolution

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<sup>\*</sup>Environmental Science Division, Institute of Environmental and Biological  
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Keble Road, Oxford OX1 3RH, UK



Available online at [www.sciencedirect.com](http://www.sciencedirect.com)

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Continental Shelf Research 24 (2004) 1485–1504

CONTINENTAL SHELF  
RESEARCH

[www.elsevier.com/locate/csr](http://www.elsevier.com/locate/csr)

## The fine-scale remobilization of metals in the surface sediment of the North-East Atlantic

Gary R. Fones<sup>1</sup>, William Davison<sup>\*</sup>, John Hamilton-Taylor

Environmental Science Department, Institute of Environmental and Natural Sciences, Lancaster University, Lancashire, LA1 4YQ, UK

Received 17 October 2003; received in revised form 30 April 2004; accepted 14 May 2004

Talanta 178 (2018) 670–678



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journal homepage: [www.elsevier.com/locate/talanta](http://www.elsevier.com/locate/talanta)



Development and evaluation of a new diffusive gradients in thin-films  
technique for measuring organotin compounds in coastal sediment pore  
water



Russell F. Cole<sup>a</sup>, Graham A. Mills<sup>b</sup>, Michelle S. Hale<sup>a</sup>, Ruth Parker<sup>c</sup>, Thi Bolam<sup>c</sup>,  
Peter R. Teasdale<sup>d,e</sup>, William W. Bennett<sup>f</sup>, Gary R. Fones<sup>a,\*</sup>

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# DGT – water column

- Metals, nutrients, radionuclides

Environmental  
Science  
Processes & Impacts



PAPER

## Evaluation of DGT as a long-term water quality monitoring tool in natural waters; uranium as a case study†

Cite this: Environ. Sci.: Processes Impacts, 2014, 16, 393

Geraldine S. C. Turner,<sup>a</sup> Graham A. Mills,<sup>b</sup> Michael J. Bowes,<sup>c</sup> Jonathan L. Burnett,<sup>d</sup> Sean Amos<sup>d</sup> and Gary R. Fones<sup>a,\*</sup>

Analytica Chimica Acta 854 (2015) 78–85



Contents lists available at ScienceDirect

Analytica Chimica Acta

journal homepage: [www.elsevier.com/locate/aca](http://www.elsevier.com/locate/aca)



## Evaluation of diffusive gradients in thin-films using a Diphonix<sup>®</sup> resin for monitoring dissolved uranium in natural waters



Geraldine S.C. Turner<sup>a</sup>, Graham A. Mills<sup>b</sup>, Jonathan L. Burnett<sup>c</sup>, Sean Amos<sup>c</sup>, Gary R. Fones<sup>a,\*</sup>

<sup>a</sup> School of Earth and Environmental Sciences, University of Portsmouth, Burnaby Building, Burnaby Road, Portsmouth, Hampshire PO1 3QL, UK

<sup>b</sup> School of Pharmacy and Biomedical Sciences, University of Portsmouth, St. Michael's Building, White Swan Road, Portsmouth, Hampshire PO1 2DT, UK

<sup>c</sup> AWE Aldermaston, Reading, Berkshire RG7 4PR, UK



## Evaluation of DGT techniques for measuring inorganic uranium species in natural waters: Interferences, deployment time and speciation

Geraldine S.C. Turner<sup>a</sup>, Graham A. Mills<sup>b</sup>, Peter R. Teasdale<sup>c</sup>, Jonathan L. Burnett<sup>d</sup>, Sean Amos<sup>d</sup>, Gary R. Fones<sup>a,\*</sup>

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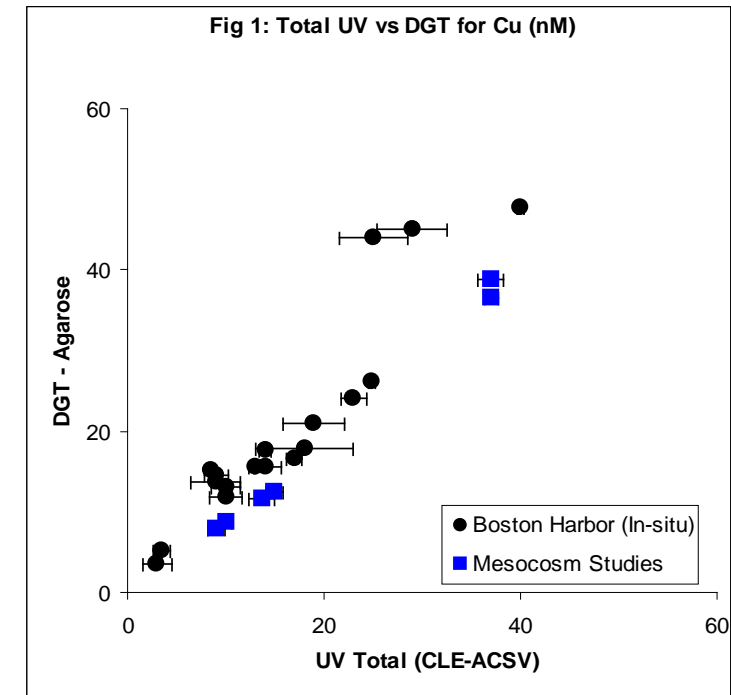
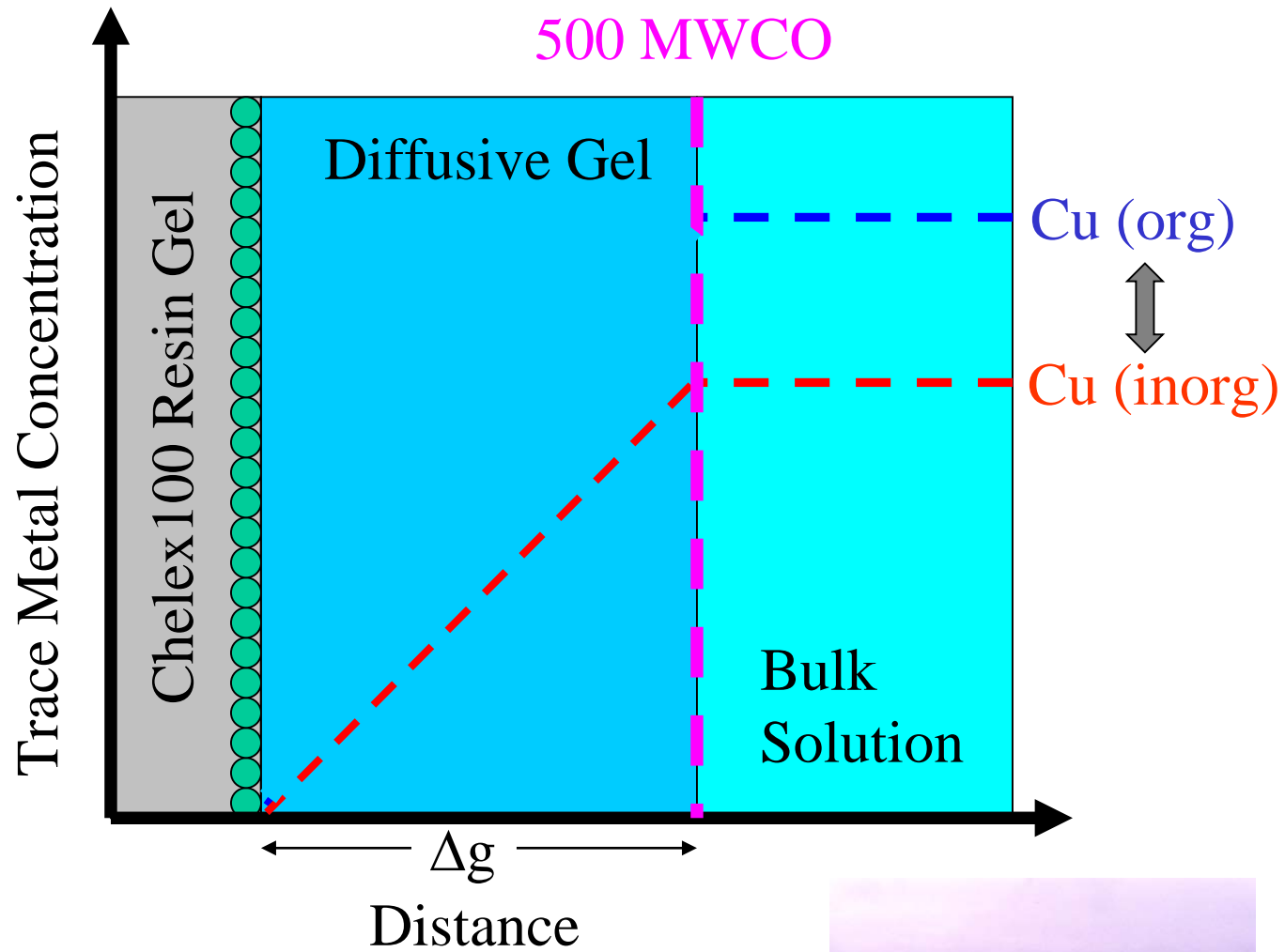
<sup>b</sup> School of Pharmacy and Biomedical Sciences, University of Portsmouth, St Michael's Building, White Swan Road, Portsmouth, Hampshire, PO1 2DT, UK

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# Woods Hole Oceanographic Institute (WHOI)





# The Chemcatcher® passive sampler

3 part **PTFE body** (Active sampling surface area ~ 20 cm<sup>2</sup>)

**Different membranes** (50 mm diameter)

Polyethersulphone, Low density polyethylene, Cellulose acetate

**Receiving phase** (47 mm)

**3M Empore™ disks**

C<sub>18</sub>/C<sub>8</sub>

SDB-XC

SDB-RS

Anion & Cation

Chelating

Carbon



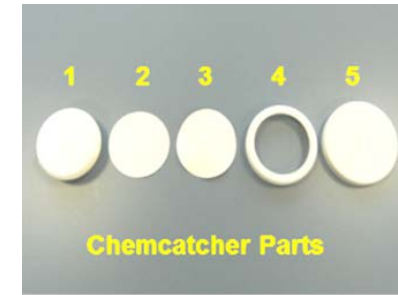
Phases bound into PTFE matrix – high loading/capacity

Or more recently:

**Horizon Atlantic® disks**: polymeric HLB (Hydrophilic/Lipophilic Balanced) -  
as used in the POCIS or DVB media bound in a glass fibre matrix.

Both disks used for extraction chemicals from water in the laboratory.

High quality analytical chemistry SPE products, available worldwide.  
Their use gives highly reproducible, simple passive samplers.



Chemcatcher Parts



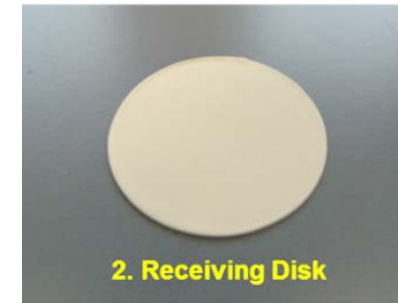
3. Protective Membrane (PES)



1. Base Plate



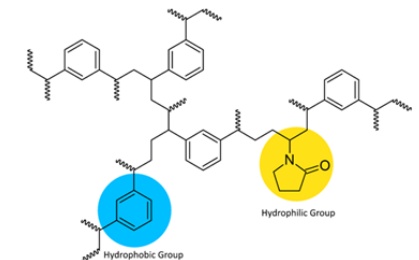
4. Retaining Ring



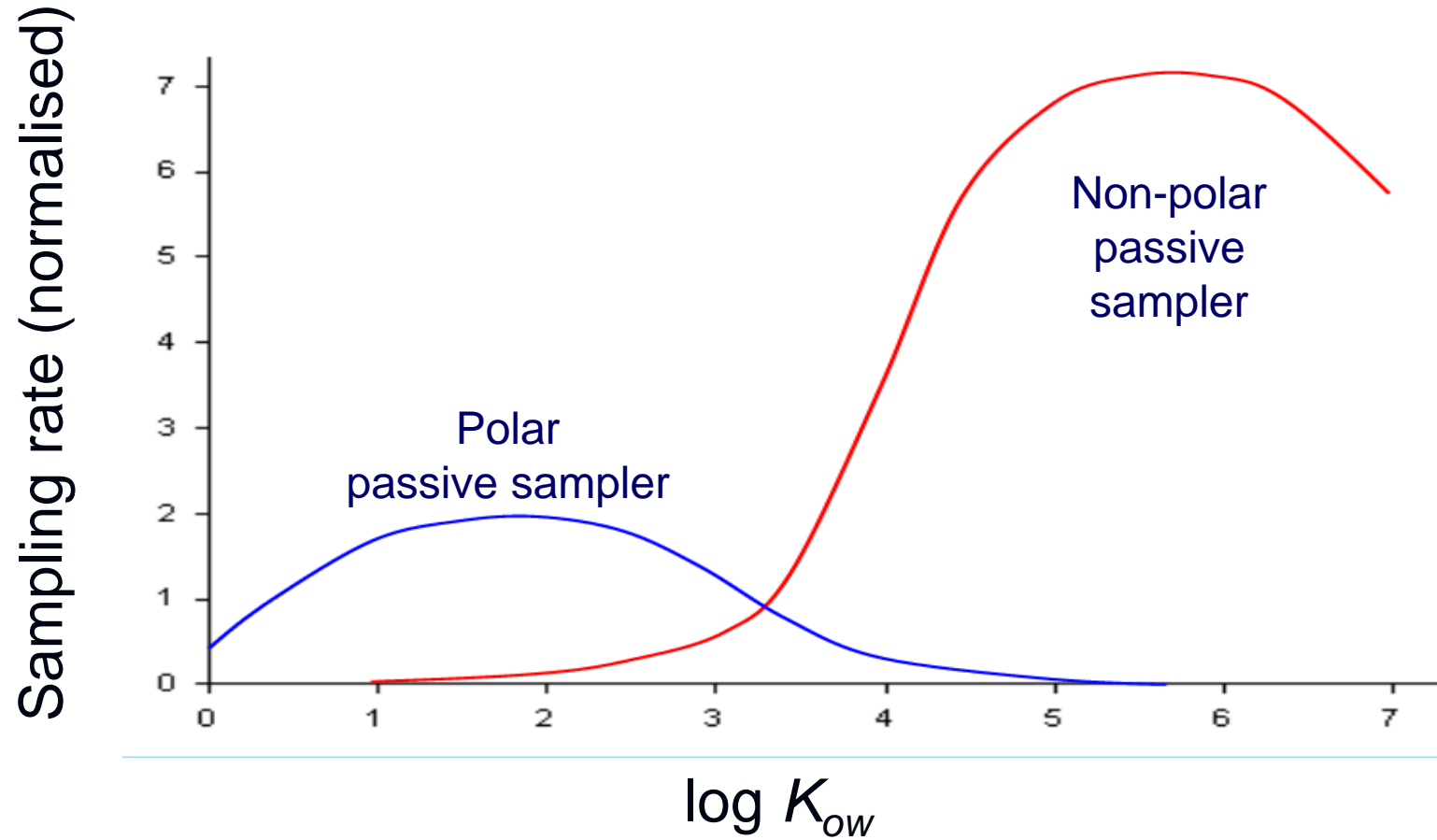
2. Receiving Disk



2 & 3  
1  
4  
Fully Assembled Sampler



# Sampler selectivity





# Polar and emerging (non-regulated) pollutants

Wide range of **polar pesticides** used in high volumes

Pollutants of emerging concern arise from a plethora of product types and cover a wide range of chemical classes.

**Human medicines** – 10,000 plus drugs currently in use

**Hormones** such as synthetic and natural estrogens and androgens

**Human personal care products** such as essential oils, herbal medicines, anti-bacterials and fragrances

**Veterinary medicines** such as antibiotics and anti-parasitic agents

**Per- and polyfluoroalkyl substances (PFAS)** – 15,000 plus chemicals

**Metabolites** and environmental **transformation** products of man-made chemicals that are produced from biological, chemical and physical breakdown reactions – e.g. waste water treatment plants.

Several of these classes are now on WFD Watch List and expected to be fully regulated in future revisions of the List of Priority Substances.

# 30+ Years of Passive Sampling- What's Next?

## What do we currently do?

- Chemcatcher passive sampler
- 1D LC-MS (LC-QqQ, Q-TOF, Orbitrap)
- Targeted analysis of polar pollutants
- Non-target and suspect screening of polar pollutants in surface waters
- Multivariate analysis to provide solutions for catchment management

Environmental Science and Pollution Research (2018) 25:25130–25142  
<https://doi.org/10.1007/s11356-018-2556-3>

### RESEARCH ARTICLE



## Calibration and application of the Chemcatcher® passive sampler for monitoring acidic herbicides in the River Exe, UK catchment

Ian Townsend<sup>1</sup> · Lewis Jones<sup>1</sup> · Martin Broom<sup>1</sup> · Anthony Gravell<sup>2</sup> · Melanie Schumacher<sup>2</sup> · Gary R. Fones<sup>3</sup>  · Richard Greenwood<sup>4</sup> · Graham A. Mills<sup>5</sup>

Talanta 179 (2018) 57–63



Contents lists available at ScienceDirect

Talanta

journal homepage: [www.elsevier.com/locate/talanta](http://www.elsevier.com/locate/talanta)



## Calibration and field evaluation of the Chemcatcher® passive sampler for monitoring metaldehyde in surface water



Glenn D. Castle<sup>a</sup>, Graham A. Mills<sup>b</sup>, Adil Bakir<sup>a</sup>, Anthony Gravell<sup>c</sup>, Melanie Schumacher<sup>c</sup>, Ian Townsend<sup>d</sup>, Lewis Jones<sup>d</sup>, Richard Greenwood<sup>e</sup>, Stuart Knott<sup>f</sup>, Gary R. Fones<sup>a,\*</sup>

Science of the Total Environment 787 (2021) 147519



Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: [www.elsevier.com/locate/scitotenv](http://www.elsevier.com/locate/scitotenv)



## Passive sampling with suspect screening of polar pesticides and multivariate analysis in river catchments: Informing environmental risk assessments and designing future monitoring programmes



Adam C. Taylor<sup>a</sup>, Graham A. Mills<sup>b</sup>, Anthony Gravell<sup>c</sup>, Mark Kerwick<sup>d</sup>, Gary R. Fones<sup>a,\*</sup>

<sup>a</sup> School of the Environment, Geography and Geosciences, University of Portsmouth, Burnaby Road, Portsmouth PO1 3QL, UK

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# 30+ Years of Passive Sampling- What's Next?

## What do we currently do?

- Chemcatcher passive sampler
- Pesticides, pharmaceuticals and personal care products
- UK Rivers (Arun, Avon, Itchen, Rother, Test)
- Drinking water supply
- International – South Africa, Thailand, Israel (Ministry of Agriculture)



Environ Monit Assess (2019) 191:388  
<https://doi.org/10.1007/s10661-019-7515-z>

## Use of the Chemcatcher® passive sampler and time-of-flight mass spectrometry to screen for emerging pollutants in rivers in Gauteng Province of South Africa

Cornelius Rimayi · Luke Chimuka · Anthony Gravell · Gary R. Fones · Graham A. Mills

Water Research 222 (2022) 118965



Contents lists available at ScienceDirect

Water Research

journal homepage: [www.elsevier.com/locate/watres](http://www.elsevier.com/locate/watres)



Pesticide fate during drinking water treatment determined through passive sampling combined with suspect screening and multivariate statistical analysis

Adam C. Taylor<sup>a</sup>, Graham A. Mills<sup>b</sup>, Anthony Gravell<sup>c</sup>, Mark Kerwick<sup>d</sup>, Gary R. Fones<sup>a,\*</sup>

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<sup>b</sup> School of Pharmacy and Biomedical Sciences, University of Portsmouth, White Swan Road, Portsmouth PO1 2DT, United Kingdom

<sup>c</sup> Natural Resources Wales, Faraday Building, Swansea University, Singleton Campus, Swansea SA2 8PP, United Kingdom

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MethodsX 10 (2023) 102054



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MethodsX

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Method Article

Monitoring of polar organic compounds in fresh waters using the Chemcatcher passive sampler

Rosamund F.A. Robinson<sup>a</sup>, Graham A. Mills<sup>b</sup>, Gary R. Fones<sup>a,\*</sup>

<sup>a</sup> School of the Environment, Geography and Geosciences, University of Portsmouth, Burnaby Road, Portsmouth, PO1 3QL, UK

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# 30+ Years of Passive Sampling- What's Next?

What do we currently know and what don't we know?

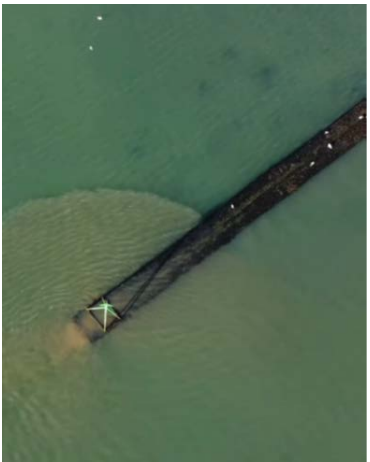
- **Passive samplers have been used for:**
- Metals, nutrients, cations, anions, organometallics, radionuclides and a wide range of organic contaminants (non-polar and polar)
- Sediments, surface water, drinking water, groundwater, wastewater
- Regulatory work, investigative work, EQs,
- **What's missing and challenges**
- Full chemical profiling – are we sequestering everything and able to analyse it?
- Why are we using passive samplers?



# 30+ Years of Passive Sampling- What's Next?

## Take advantage of new analytical techniques

- Two-dimensional liquid chromatography with high resolution ion mobility mass spectrometry
- Waters SELECT SERIES Cyclic IMS – based at Southampton University (GCxGC as well)
- “The lack of serially hyphenated separation capability hinders the complete chemical profiling of surface water and the currently unknown breakdown products”
- Identify polar compounds in more complex matrices (e.g., wastewater, leachates)
- Identify previously undetected transformation products and metabolites



# The use of passive sampling devices and 2D LC-MS for identification and quantification of polar pollutants in surface waters

## What will we be able to do

- Research into using novel receiving phases
  - 2D can enable more polar compounds to be identified
- Complex mixtures and impact on aquatic life
  - New work with the Environment Agency (England)



# 30+ Years of Passive Sampling- What's Next?

## What can we do in the future

- New contaminants and compounds
  - Full chemical profiling for polar organic contaminants
  - Per- and polyfluoroalkyl substances (PFAS)
  - Explosives
  - Wider range of anti-biotics for AMR research
  - Sediments?

## What should we continue to do

- Strengths of passive sampling
  - TWA concentrations and EQs
  - Areas difficult to obtain high resolution spot sampling
  - Pre-concentration to lower detection limits

