

Monitool: Strategies to enable the use of DGTs in a regulatory context

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Vienna, DGT2019, September 2019



Overview

- 1. Why do we want to use DGTs in a regulatory environment?
- 2. What indicators do we have that regulatory bodies are prepared to consider their use?
- 3. What are the current impediments to using them in this way?
- 4. What strategies to enable their use are we currently examining in Monitool?
- 5. What lessons have we learned so far in Monitool?
- 6. Where to next?









1. Why do we want to use DGTs in a regulatory environment?





Shortcomings of current spot sampling for regulatory monitoring

- Spot sampling→ represents metal concentration at the exact sampling time (over/sub estimation the contamination of the system)
- Missing of episodic contamination and/or decisions taken based on transient peak of contaminants
- Metal concentrations below the detection limits
- Toxicological relevance of dissolved concentrations ???







European Water Framework Directive (WFD;2000/60/EC) <u>Aim:</u> to achieve a "Good Ecological and Chemical Status" for all European Union waters (including transitional/estuarine and coastal waters)



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Environmental Quality Standards

- chemical quality refers to the determination of environmental quality standards (EQSs)
- EQS can be defined as the concentration of a chemical in the environment below which there is not expected to be an adverse effect on the specific endpoint being considered, e.g. the protection of aquatic life.
- EQSs in the WFD for Cd, Cr, Cu, Pb, Ni, Zn, As and Hg refer to the dissolved concentration (i.e., obtained after filtration of the water sample through a 0.45-µm filter), and as far as possible for Pb and Ni to the bioavailable concentrations.





EQS for metals

- naturally found in the aquatic environment, but certain metals are also considered to pose aquatic hazard
- their toxicity to aquatic life is not fixed, but instead depends on the chemical form in which the metal exists (metal speciation), as well as a range of environmental parameters (such as pH, calcium concentration, alkalinity, and the presence of dissolved organic ligands (estimated by dissolved organic carbon (DOC) measurements)
- concentrations of total metal in waters have limited relevance to potential environmental risk (e.g. Campbell 1995; Niyogi and Wood 2004)





What about coastal and transitional waters?

- freshwater and saltwater systems provide very different environments for metal ions, which significantly impacts on their bioavailability
- What about transitional (e.g. estuarine) waters, which are intermediate in salinity and can vary on a diurnal cycle?



The impact on salinity, and indeed change of salinity, on dissolved metal concentration, and by extension therefore on bioavailable metal concentration, Osté, 2013





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- DGTs can provide information on "the concentration of a chemical in the environment below which there is not expected to be an adverse effect on the specific endpoint being considered" (i.e. EQS)
- DGTs are already widely used in investigative monitoring
- So, if can elucidate a relationship between data obtained with DGTs and current EQSs, this should enable the use DGTs for regulatory monitoring.





Overview

1. Why do we want to use DGTs in a regulatory environment?



2. What indicators do we have that regulatory bodies are prepared to consider their use?





Technical Report - 2009 - 025

"While checking compliance with the WFD provisions is currently based on chemical analysis of spot samples taken in a defined frequency, it is desirable to introduce other techniques [...complementary methods...] for improving the quality of the assessment and to benefit from resource saving developments, as they become available" "Complementary methods can be used in surveillance and operational monitoring provided that they meet the requirements "

COMMON IMPLEMENTATION STRATEGY FOR THE WATER FRAMEWORK DIRECTIVE (2000/60/EC)

Guidance Document No. 19

GUIDANCE ON SURFACE WATER CHEMICAL MONITORING UNDER THE WATER FRAMEWORK DIRECTIVE





Overview

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- 2. What indicators do we have that regulatory bodies are prepared to consider the use?

3. What are the current impediments to using them in this way?





Technical Report - 2009 - 025

"Difficulties encountered include bio-fouling, backcalculating to water concentration and calibration. Thus, further research and validation is required before using this technology for compliance checking. Passive samplers sample the freelydissolved bioavailable water concentrations. Results may, therefore, deviate from the total water concentrations measured in spot samples"

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We're figuring this out right now, and have overcome already many of these challenges calculating to water concentration and calibration. This is literally why we're here using this technology for compliance checking. Passive samplers sample the freelydissolved bioavailable water concentrations. Results may,

This is not a bad thing, in fact there are many advantage to this! *measurea in spot samples* COMMON IMPLEMENTATION STRATEGY FOR THE WATER FRAMEWORK DIRECTIVE (2000/60/EC)



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Metal measurement in aquatic environments by passive sampling methods: Lessons learning from an *in situ* intercomparison exercise

CrossMark

A. Dabrin ^{a, *}, J.-P. Ghestem ^b, E. Uher ^c, J.-L. Gonzalez ^d, I.J. Allan ^e, M. Schintu ^f, N. Montero ^g, J. Balaam ^h, E. Peinerud ⁱ, C. Miège ^a, M. Coquery ^a

- estimation of measurement uncertainties
- Data dispersion of TWA concentrations was mainly explained by uncertainties generated during DGT handling and analytical procedure steps





Trends in Environmental Analytical Chemistry November 2015, Volume 8, Pages 20-26 <u>http://dx.doi.org/10.1016/j.teac.2015.07.001</u> <u>http://archimer.ifremer.fr/doc/00275/38606/</u> © 2015 Elsevier B.V. All rights reserved

Achimer http://archimer.ifremer.fr

Position paper on passive sampling techniques for the monitoring of contaminants in the aquatic environment -Achievements to date and perspectives

Miège Cécile ^{1, *}, Mazzella Nicolas ², Allan Ian ³, Dulio Valeria ⁴, Smedes Foppe ^{5, 6}, Tixier Céline ⁷, Vermeirssen Etienne ⁸, Brant Jan ⁹, O'toole Simon ¹⁰, Budzinski Hélène ¹¹, Ghestem Jean-Philippe ¹², Staub Pierre-François ¹³, Lardy-Fontan Sophie ¹⁴, Gonzalez Jean-Louis ¹⁵, Coquery Marina ¹, Vrana Branislav ⁵

"Indeed, regulatory implementation of PS requires decisionmakers to be convinced of the need to globally change the current monitoring and compliance checking concept under the WFD. The relevance of the signal obtained by passive sampling (integrative sampling, relation of TWA concentrations with the environmental risk to aquatic organisms) should be stressed."





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Interreg Atlantic Area Transnational Cooperation Programme 3 years (2017-2020) Total cost: 1.92 M€



Main objectives:

- To define Environmental Quality Standards and protocols for the use of DGTs in chemical monitoring within the European Water Framework Directive
- To develop a network of laboratories focused on the use of DGTs within the European Water Framework Directive





Full Partners







Associated Partners (Stakeholders and Endusers)







The Plan!









WP5: Monitool sampling strategy

- 8 European regions
- 4 sampling sites per region (estuary or coast)
- In 2018: 2 sampling campaigns (wet and dry seasons)



Atlantic Area

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WP5: Monitool Sampling Sites



WP5: Monitool sampling strategy



IN SITU PHYSICO-CHEMICAL PARAMETERS (at DGTs Depth)



Temperature, salinity, DO (mg/L and %), pH, turbidity, depth, specific conductivity, biofouling

WP4: Database and statistical analysis

Published/ unpublished data



Environmental quality standard (EQS) adaptation for DGT

- Concentration of metal (DGT)
- Concentration of metal (water)
- Physico-chemical parameters in water (DOC, turbidity, SPM, temperature, salinity, disolved
 - oxygen, biofouling)







Concentration of metal (ng L⁻¹)





WP6: EQS Adaptation

Study how EQS
have been
developed

Common Implementation Strategy for the Water Framework Directive	
Environmental Quality Standards (EQS) Substance Data Sheet	
Priority Substance No. 6 Cadmium and its Compounds	
CAS-No. 7440-43-9	
Final version Brussels, 31 July 2005	

 Identify technical barriers to EQS adaptation

NORMAN

Joint Programme of Activities 2013

TOPIC: PASSIVE SAMPLING

"Linking Environmental Quality

Standards and Passive Sampling" Expert group meeting

nce laboratories and related organisations for

ormar

 Develop methodology for adaptation



• Data validity range





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- Site selection is critical
- Standardising language (is D1 th 24 hours after deployment?)
- Beware DGT thieves!
- The weather can wreck the best^{420 × 315}
- Shipping gremlins can cause havoc....
- Integrity of raw data input







Preliminary results (from wet season)

Volt. vs ICPMS vs DGTs – Basque Country estuaries





D: day HT: high tide LT: low tide





Preliminary results (from wet season)







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Publish the protocols



Sample processing and analysis protocol Sampling protocol / Interreg Atlantic Area + + MONITOOL MONITOOL new tools for water quality monitor Sampling Protocol Sample processing and analysis 13 December 2017 13 December 2017 No. version: 3 No. version: 3 rivate document vate document -Cefas -Cefas







Dive into the data to develop a framework for adapted EQS

- Results from both sampling periods (wet and dry season)
- Results from all Partners regions
- Statistical analysis with all data
- Develop adapted EQS-DGT !





Expand beyond Monitool



- Adapt EQS for more substances
- Investigate the relationship between the metal fraction captured by DGT and bioavailability
 - Alternative to saline BLMs?









NANY THANKS FORYOUR ATTENTION!!

https://www.monitoolproject.eu/ https://es-es.facebook.com/monitoolproject/ @MonitoolProject

MONITOOL

MONITOOL PROJECT







Associated Partners













AGENCE FRANÇAISE POUR LA BIODIVERSITÉ ÉTABLISSEMENT PUBLIC DE L'ÉTAT







Chemcatcher[®] and DGT passive sampling devices for regulatory monitoring of trace metals in surface water[†]

Ian J. Allan,^{*ab} Jesper Knutsson,^c Nathalie Guigues,^d Graham A. Mills,^e Anne-Marie Fouillac^d and Richard Greenwood^b

Received 14th February 2008, Accepted 18th April 2008 First published as an Advance Article on the web 23rd May 2008 DOI: 10.1039/b802581a

"The range of concentrations measured by spot and passive sampling, for exposures up to 28 days, demonstrated **that both modes of monitoring were equally reliable**. Passive sampling provides information that cannot be obtained by a realistic spot sampling frequency and this may impact on the ability to detect trends and assess monitoring data against environmental quality standards when concentrations fluctuate."



