ORGANIZED BY:

azti tecnalia
Transforming
Science into
Business

Environment
Centre
Lancaster
University

SUPPORTED BY:

ura
ur agentzia
agencia vasca del agua

DGT®

EUSKADI
BASQUE COUNTRY

28th September to 1st October - Donostia-San Sebastián (Spain)

DGTConference2015

“From DGT Research to Environmental Assessment”

www.azti.es/dgtconference

CONTENTS

FOREWORD

María J. Belzunce-Segarra

AZTI

Hao Zhang

LANCASTER UNIVERSITY

We warmly welcome you to the DGT Conference 2015 that takes place on the Campus of the Basque Country University, in the beautiful city of San Sebastian, from 28 September to 1 October 2015.

On this occasion we have titled the conference From DGT Research to Environmental Assessment with the aim of stimulating discussions and initiatives to move the DGT technique forward to be used in environmental monitoring programs under the framework of national and international legislations.

We know that contamination of the environment is one of the most important problems that affect organisms and human health. Even now, it is still a challenge to measure many substances that are present in the environment in very low concentrations, as their detection using traditional analytical techniques is difficult. During the last two decades, the diffusion-based passive samplers have been widely used for trace metals measurement in natural waters, soils and sediments. While the advantages of passive samplers compared to traditional sampling and analytical techniques have been well reported, there are several uncertainties and limitations that need to be addressed and discussed.

The DGT Conference program contains six different sessions that cover different aspects of the DGT technique (advantages, weaknesses, latest advances and novelties….) in various environments: aquatic systems, sediments and soils. There is also a session on Bioavailability to encourage contributions discussing the relationship between DGT measurements and effect on biota; a session on Environmental Assessment and Legislation to debate the use of this technique to meet quality objectives set by the environmental legislations; and the Addendum session to sum up discussions, hopefully reach some conclusions and make some final remarks.

We really hope that the DGT Conference 2015 will provide a unique and high quality forum for knowledge interchange and debate with experts from all around the world. We also expect that the DGT Conference 2015 will be an occasion that stimulate interactions and collaborations between scientists working in a wide range of environments.

And finally, but none the less important, we wish you to enjoy the wonderful city of San Sebastian and its surroundings, and we invite you to discover the unique Basque Country traditions and customs.

Welcome to you all!!. Looking forward to meeting you.

Sincerely,

Hao & Maria J.

ORGANISING AND SCIENTIFIC COMMITEES

ORGANIZING COMMITTEE:

International:

Hao Zhang, Lancaster University, UK (chairperson)

Local:

Maria J Belzunce-Segarra, AZTI, Spain (co-chairperson)

Meritxel González, AZTI, Spain

Mercedes Fernández, AZTI, Spain

Iratxe Elso, AZTI, Spain

Javier Franco, AZTI, Spain

SCIENTIFIC COMMITTEE:

Hao Zhang, Lancaster University, UK (chairperson)

Maria J Belzunce-Segarra, AZTI, Spain (co-chairperson)

Javier Franco, AZTI, Spain

Jun Luo, Nanjing University, China

Jean-Louis González, Ifremer, France

Marco Schintu, University of Cagliari, Italy

Dianne Jolley, University of Wollongong, Australia

Peter Teasdale, Griffith University Gold Coast, Australia

Natalia Montero, Ikerbasque, Spain

AGENDA

28 SEPTEMBER 2015

19:00 – 21:00 **Welcome Reception**
Palacio MIRAMAR
Paseo de Miraconcha, 48
San Sebastián

A beautiful mansion built by the royal family as a summer holiday home in about 1887. It has impressive views of the bay and Santa Clara Island. Miramar Palace is now owned by the city of Donostia-San Sebastián

29 SEPTEMBER 2015

8:00 – 9:00 **Registration**

9:00 **Opening remarks.**
Dr. Hao Zhang. Lancaster University. UK.
Dr. María J. Belzunce-Segarra. AZTI. Spain

9:15 **Plenary Lecture**
"Exploring the versatility of passive samplers for (nano)contaminant risk assessment". Enzo Lombi. University of South Australia.

WATER SOLUTIONS AND AQUATIC ENVIRONMENTS (CONTINENTAL, BRACKISH AND MARINE WATERS)

Chairs: **Dr. Jaume Puy. University of Lleida. Spain.**
Dr. Gary Fones. University of Portsmouth. United Kingdom.

10:00 **Keynote lecture.**
"DGT, a simple and efficient tool for environmental studies?. A few examples on Hg". Olivier Clarisse. Université de Moncton, Canada

10:40 **Coffee break**

11:10 "What information can we extract from DGT data?". Josep Galceran. Departament de Química, Universitat de Lleida. Spain.

11:30 "Evaluating the performance of DGT with a Chelex-Metsorb mixed binding layer for measurement of trace metals and oxyanions in natural seawater". Amir Houshang Shiva. Environmental Futures Research Institute, School of Environment, Griffith University. Australia.

11:50 “Trace Metals Speciation in Crude Oil Contaminated Seawater Using DGT with Different Membranes”. Mohammed. M. Al Kasbi. The Lancaster Environment Centre, Lancaster University. United Kingdom.

12:10 “Evaluation of a zirconia oxide-DGT for the determination of Cr(III) and Cr(VI) through selective elution”. Delphine Devillers. Research Group on Water, Soil and Environment (GRESE - EA 4330), University of Limoges. France

12:30 “Determination of methylmercury concentrations in low contaminated rivers by passive sampling method and isotopic dilution GC-ICP-MS”. Aymeric Dabrin. Irstea. France

12:50 **Lunch**

Chairs: **Dr. Josep Galceran. University of Lleida. Spain.**
Dr. Fiona Regan. Dublin City University. Ireland.

14:00 “In situ selective determination of methylmercury in river water by diffusive gradient in thin films technique using baker’s yeast immobilized in agarose gel as binding phase”. Amauri Antonio Menegário. Centro de Estudos Ambientais, Univ. Estadual Paulista. Brazil.

14:20 “Evaluating the diffusive gradients in thin-films technique for the measurement of dissolved uranium in natural waters”. Gary R. Fones. University of Portsmouth. United Kingdom.

14:40 “Can DGT be used to elucidate uranium speciation in natural waters?”. Laureline Février. IRSN/PRP-ENV/SERIS/L2BT. France.

15:00 “Using DGT to determine representative dissolved inorganic nitrogen and phosphorus concentrations in natural freshwaters”. Jianyin Huang. Environmental Future Research Institute, School of Environment, Griffith University.Australia.

15:20 **Coffee break**

15:50 “First applications of DGT technology to groundwater monitoring in Hungary”. Tamás Madarász. University of Miskolc. Hungary

16:10 “Monitoring of heavy metals in sewage systems by use of passive sampler, DGT”. Ø. Mikkelsen. Norwegian University of Science and Technology (NTNU) Department of Chemistry. Norway.

POSTER SESSION

Chairs: **Dr. Jaume Puy, University of Lleida. Spain**
Dr. Gary Fones, University of Portsmouth. UK
Dr. Josep Galceran. University of Lleida. Spain
Dr. Fiona Regan. Dublin City University. Ireland

16:30-16-45 **Brief Introduction**

16:45-17:45 **Posters forum**

19:00 **Sailing Tour. Included in the registration fee.** The “Ciudad de San Sebastian” catamaran will treat you to a compleately different view of the city. 1 hour sailing tour to enjoy delightful views of the city from the sea. Max 80 people.

30 SEPTEMBER 2015

SEDIMENTS

Chairs: Dr. Peter Teasdale and Dr. William Bennet. Griffith University. Australia.

9:00 **Keynote lecture**
“From environmental assessment to DGT: advancing the methods for risk assessment of metals in sediments”. Stuart L. Simpson. Centre for Environmental Contaminants Research, CSIRO Land and Water. Australia.

9:40 **“**Determination of As speciation in river sediment using DGT techniques”. Josselin Gorny. Laboratory LASIR. France.

10:00 “Assessing contaminant biogeochemistry: a new view using DGT and DET”. William Bennett. Environmental Futures Research Institute and Griffith School of Environment, Griffith University. Australia.

10:20 “Resolving biogeochemical controls of arsenic and antimony mobility in contaminated sediments using DGT and DET”. Maja Arsic. Environmental Futures Research Institute, Griffith University. Australia.

10:40 **Coffee break**

Chairs: Dr. Peter Teasdale and Dr. William Bennet. Griffith University. Australia.

11:10 “Use of DGTs to estimate release of metals from re-oxygenating Baltic Sa sediments”. Martin M. Larsen. Aarhus University, Dept. of Bioscience. Denmark.

11:50 “Trace metal capacities of suspended particulate reagent-iminodiacetate (microchelex) resin using diffusive gradients in thin films”. Yue Gao. Analytical Environmental and Geochemistry, Faculty of Science, Vrije Universiteit Brussel. Belgium.

12:10 “Two-dimensional imaging of oxyanions in sediments by a high-resolution precipitated zirconia based-DGT technique”. Dong-Xing Guan. State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University. China.

12:30 “In situ, high-resolution monitoring of labile phosphorus distribution and mobilization in sediments of a large eutrophic lake”. Shiming Ding. State Key Laboratory of Lake Science and Environment, Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences. China.

12:50 “Measurement of mercury and methylmercury in sediment porewater using DGT ”. Yue Gao. Analytical Environmental and Geochemistry, Faculty of Science, Vrije Universiteit Brussel. Belgium.

13:10 **Lunch**

RELATING BIOAVAILABILITY AND EFFECTS TO DGT DATA

Chairs: Dr. Stuart Simpson. CSIRO. Australia.

14:20 “An Evaluation of Arsenic and Antimony Bioavailability in Historically Contaminated Soil”. Lien K. Ngo. School of Chemistry, University of Wollongong. Australia.

14:40 “Assessing impacts of jellyfish carrion on sediment redox conditions using diffusive in situ samplers”. Ariella Chelsky. Australian Rivers Institute – Coasts and Estuaries, Griffith School of Environment, Griffith University. Australia.

15:10 “Assessment of Diffusive Gradient in Thin Film Samplers for Measurement of Bioavailable Hg”. Danny Reible. Texas Tech University. United States of America

15:30 “Passive samplers and biomarkers to assess metal labile concentrations and the associated biological effects: case studies in the North-Médoc salt marshes (Gironde estuary, France) and in the Oiartzun estuary (Spain)”. Javier Franco. AZTI. Spain

POSTER SESSION

16:20-17:35 **Poster Forum**

20:00 **Conference Dinner. Included in the registration fee.** Dinner in a Typical basque Cider House. Bus included.

1 OCTOBER 2015

SOILS AND PLANTS

Chairs: Dr. Jun Luo. Nanjing University
Dr. Jakob Santner. University of Natural Resource and Life Sciences. Austria.

9:00 **Keynote lecture.** "Ion Mapping of the Rhizosphere: Arsenic & Rice". Paul N. Williams. Queen´s University Belfast. United Kingdom.

9:40 "Soil phosphorus mobility and solid-to-solution phase resupply studied by DGT". Daniel Menezes-Blackburn. Lancaster University, Lancaster Environment Centre. United Kingdom.

10:00 "The localisation of phosphorus solubilisation, uptake and release in the rhizosphere of plants with differential nutrient mobilisation strategies". Jakob Santner. Institute of Soil Research, University of Natural Resources and Life Sciences, Vienna. Austria.

10:20 "Measurement of sulfur stable isotope variations in bioavailable sulfate in soils by DGT MC ICP-MS". Ondrej Hanousek. University of Natural Resources and Life Sciences, Vienna. Austria.

10:40 **Coffee break**

11:10 "Predicting the Uptake of 10 Metals by 5 Vegetables Using DGT". Hao Zhang. Lancaster Environment Centre, Lancaster University, United Kingdom.

11:30 "Merging DGT and planar optodes into single-layer probes for simultaneous, co-localized chemical imaging of metals and pH in the rhizosphere". Christoph Hoefer. Department of Forest and Soil Sciences, Institute of Soil Research, University of Natural Resources and Life Sciences, Vienna. Austria.

ENVIRONMENTAL ASSESSMENT AND LEGISLATION

Chairs: Dr. Marco Schintu. University of Cagliari. Italy
Dr. Trang Huynh, University of Queens land. Australia

11:50 **Keynote lecture.** "Use and assessment of passive samplers by the French water national and regional authorities to improve the WFD implementation". Pierre-François Staub. ONEMA-DAST. France.

12:30 "Assessment of the Production of Diffusive Gradient Thin Films (DGT) and Associated Quality Control Protocols in a University Laboratory Setting". Julia Caprio. Geosyntec Consultants, Knoxville Tennessee. United States of America.

12:50 **Lunch**

14:00 "Large scale" application of the passive sampling techniques: Evaluation of DGT technique as a monitoring tool for the assessment of the chemical status of water bodies". M.J. Belzunce-Segarra. AZTI. Spain.

14:20 "Monitoring bioavailability of metals and metalloids in river water receiving mine water discharge using DGT". Trang Huynh . Centre for Mined Land Rehabilitation, Sustainable Minerals Institute, The University of Queensland. Australia.

14:40 "Mobile passive sampling with DGTs for the measurement of trace metals in seawater". Marco Schintu. Università di Cagliari. Italy.

15:00 "DGTs, a complementary tool towards more efficient biomonitoring practices". Jonathan Richir. STARESO SAS. France.

15:20 "An in-depth assessment into simultaneous monitoring of dissolved reactive phosphorus (DRP) and low-molecular-weight organic phosphorus (LMWOP) in aquatic environments using diffusive gradients in thin films (DGT)". Christian

Wilhelm Mohr. Department of Chemistry,
University of Oslo. Norway.

15:40 Coffee break

ADDENDUN

Chairs: **Hao Zhang, Lancaster University, UK**
Peter Teasdale, Griffith University Gold Coast, Australia
Jun Luo, Nanjing University, China
Marco Schintu, University of Cagliari, Italy
Maria J. Belzunce-Segarra, AZTI, Spain
Javier Franco, AZTI, Spain

16:10 Discussion Forum

17:10 Future issues

17:30 Closing remarks

SPEAKERS AND ABSTRACTS

PLENARY SPEAKER

Enzo Lombi. University of South Australia

"Exploring the versatility of passive samplers for (nano)contaminant risk assessment"

Passive samplers, including DGT, provide a versatile set of tools for the investigation of contaminant (and nutrient) availability and transformation at both bulk and spatially-resolved level. This presentation will provide examples of such applications and will also discuss the role that passive samplers can play in relation to the risk assessment of engineered nanoparticles.

Professor Enzo Lombi is based at the University of South Australia. His main area of research is the biogeochemistry of trace elements and environmental fate of engineered nanomaterials. He has a special interest in synchrotron-based techniques for the investigation of biological and soil processes.

KEYNOTE SPEAKERS

Olivier Clarisse. Université de Moncton, Canada

"DGT, a simple and efficient tool for environmental studies?. A few examples on Hg

In this presentation, Olivier Clarisse will focus on DGTs for monomethylmercury (MMHg), the major organic form of Hg. The considerable interest in this neurotoxin is due to its wellknown toxicity, its accumulation in biota and its biomagnification in the aquatic food chain. By providing detailed information on MMHg concentration, speciation and production, DGTs may contribute to complete our knowledge of this pollutant biogeocycle. We will discuss more specifically DGT potentials to determine MMHg bioavailability as a surrogate for biosentinel organisms, to establish MMHg speciation in the dissolved phase, and to predict mercury methylation rate in sediment. Leaving the lab to real field conditions (i.e. Ontario pristine stratified freshwater lake, Alberta's oil sand impacted watershed, San Francisco Bay sediment), we will present new insights from DGT on Hg biogeochemistry.

Dr. Olivier Clarisse is an environmental chemist teaching analytical chemistry at Université de Moncton (Canada). His research aims to understand the aquatic ecosystem response to human perturbation and natural variations and especially the fate and effects of heavy metals. Using a full range of analytical methods and original integrated environmental approaches, he has focused his interest lately on mercury developing DGT to monitor this pollutant in the environment and exploring its applications in water, sediment and snow.

Stuart Simpson. CSIRO, Australia

"From environmental assessment to DGT: advancing the methods for risk assessment of metals in sediments"

In this presentation traditional approaches to predict metal exposure or effects to benthic organisms will be compared to DGT-based predictions for benthic amphipod, bivalve and copepod species in field and laboratory exposures to field-collected metal-contaminated freshwater and marine sediments. The need to estimate metal concentrations in sediment pore waters from DGT-induced metal fluxes will be discussed, along with methods for predicting toxicity when multiple metals exist with differing toxicities to aquatic organisms.

Dr Stuart Simpson is a Senior Principal Research Scientist with the CSIRO Land and Water Flagship. He has more than 20 years of research experience covering water and sediment quality assessment in freshwater and marine environments. His main research interests include establishing relationships between contaminant forms, bioavailability and exposure and observed biological/ecological effects, and the development and application of sediment quality guidelines and advanced assessment tools. He applies this research through a wide range of consultancy projects for industry and government. His research on sediment quality assessment methods, and factors influencing contaminant bioavailability and effects, led to the award, with Graeme Batley and Jenny Stauber, of the Land and Water Australia Eureka Prize for Water Research in 2006. He is author of some 200 scientific research publications.

Paul Williams. Queen´s University Belfast, United Kingdom

"Imaging and Characterization of the Temporospatial Availability of Arsenic in the Rhizosphere"

Plants have evolved a range of ingenious mechanisms to alter their root-soil environment to both liberate and capture essential trace elements as well as limit their exposure to harmful contaminants, all within a wide range of chemistries. This talk will focus on how DGT can offer new perspectives on plant-soil interactions, and the processes that influence this dichotomy between the mobilisation of mineral nutrients and also their toxic analogues.

Paul N. Williams, Lecturer in Soil & Environmental Biogeochemistry at Queen's University Belfast, obtained his Ph.D. degree in Biological Sciences from the University of Aberdeen in 2007. Previous to working at Queen's he has held Research Fellowships with the Chinese Academy of Sciences, Lancaster University and a Lectureship with the University of Nottingham. His research interests are orientated around the role of soils in global food security, and in particular arsenic assimilation by rice in South & East Asia.

Pierre-François Staub. ONEMA-DAST, France

"Use and assessment of passive samplers by the French water national and regional authorities to improve the WFD implementation"

He will present the scope of the recent applications of the passive samplers in water environment which have been supported through national and basin policy, especially in the frame of the WFD implementation, including developpement & assessment exercises.

Pierre-François Staub has got his PhD in chemistry since 1995, specialty in analytical chemistry (microanalysis), and more recently (2008) joined the water community to act as a scientific officer at Onema, coordinating national R&D efforts to meet the WFD objectives in the domain of chemical status and pollution issues.

Exploring the versatility of passive samplers for (nano) contaminant risk assessment

E. Lombi, M. Khaksar, H. Zhang, R. Sekine, E. Donner, G. Brunetti, K.G. Scheckel and K. Vasilev

Future Industries Institute, University of South Australia, Mawson Lakes, South Australia
enzo.lombi@unisa.edu.au

ABSTRACT

Passive samplers, including DGT, provide a versatile set of tools for the investigation of contaminant (and nutrient) availability and transformation at both bulk and spatially-resolved level. This presentation will provide examples of such applications and will also discuss the role that passive samplers can play in relation to the risk assessment of engineered nanoparticles (NPs).

Rapid development of nanotechnology leads to dramatic increase in production, distribution and release of engineered nanoparticles into the environment. Nevertheless, human and environmental risk assessment procedures for these materials are still in their early stage of development. Among the various NPs released to the environment AgNPs are the most commonly present in consumer products. The chemistry of Ag in the environment is extremely complex with transformations to chloride and sulphides greatly reducing the solubility of Ag and with the ionic Ag considered as the main driver of toxicity. A newly developed 'nano' Diffusive Gradients in Thin Films (DGT) device was designed specifically to avoid confounding effects when measuring element lability in the presence of nanoparticles. However, NPs concentrations are so low in the environment that, at present, their detection is extremely challenging if not impossible. Therefore, we developed a system to study NPs transformations in situ through the immobilisation of NPs onto a charged surface. In this sense, these devices, called nano in situ deployment devices (nIDDs), are able to sample the environmental conditions and the transformation products of NPs. Plasma polymerization is used to create a charged layer to which NPs of opposite charge are attached. Nanoparticles are the analysed upon exposure and retrieval in/from different complex environmental compartments. These devices can be constructed and in a variety of ways to cater for the research question of interest. In particular, the nature of the substrate can be chosen to best fit the requirement of the analytical technique being utilized; the surface polymer applied can carry positive or negative charge to provide anchoring to NPs with various surface functionalization; the shape and size of the device can be tailored to allow the exploration of heterogeneous environments.

One of the major limitations of nIDDS is related to the fact that dissolution processes are not covered by this method. To overcome this issue we are developing a combined nIDD-DGT device that should be able to simultaneously assess transformation and dissolution of NPs when analysed using ICP-MS and synchrotron-based X-ray Absorption Spectroscopy

KEY WORDS

DGT, a simple and efficient tool for environmental studies? A few examples on Hg biogeochemistry investigation.

Olivier Clarisse

Département de chimie et de biochimie. Université de Moncton. Nouveau-Brunswick, E1A 3E9 - Canada
olivier.clarisse@umoncton.ca

ABSTRACT

Integrated in monitoring programs, passive sampler such as DGTs (Diffusive Gradient in Thin film) should represent a powerful tool to assess a pollutant impact on the ecosystem. However, despite an apparent simplicity, interpretation of the mass of pollutant accumulated by the device could be tricky as several environmental factors affect the DGT devices. On the other hand, if handled properly, DGTs may provide valuable information on a pollutant biogeochemical transformation, speciation and bioavailability.

In this presentation, we will focus on DGTs for monomethylmercury (MMHg), the major organic form of Hg. The considerable interest in this neurotoxin is due to its well-known toxicity, its accumulation in biota and its biomagnification in the aquatic food chain. By providing detailed information on MMHg concentration, speciation and production, DGTs may contribute to complete our knowledge of this pollutant biogeocycle. We will discuss more specifically DGT potentials to determine MMHg bioavailability as a surrogate for biosentinel organisms, to establish MMHg speciation in the dissolved phase, and to predict mercury methylation rate in sediment. Leaving the lab to real field conditions (i.e. Ontario pristine stratified freshwater lake, Alberta's oil sand impacted watershed, San Francisco Bay sediment), we will present new insights from DGT on Hg biogeochemistry.

KEY WORDS

methylmercury, speciation, bioavalibaility, Hg methylation

What information can we extract from DGT data?

Josep Galceran[a*], Martín Jiménez-Piedrahita[a], Alexandra Altier[a], Sara Cruz-González[a], Calin A. David[a], Joan Cecilia[b], Carlos Rey-Castro[a], and Jaume Puy[a]

[a]*Departament de Química*
[b]*Departament de Matemàtica, Universitat de Lleida. Spain.*
** galceran@quimica.udl.cat*

ABSTRACT

Strictly speaking, a single DGT measurement only provides the accumulated **mass** of the analyte. However, we access to other relevant information when we gather different accumulations and interpret the results within a theoretical framework. For instance, if the accumulations are proportional to the deployment times, it is reasonable to ignore the transient period, and we can obtain the **flux** along the steady-state regime.

This presentation will focus on aqueous solutions where a metal binds to a ligand and forms a complex. In such a system, one can compute the **lability degree**, provided the diffusion coefficient of the complex is known. This lability degree (ranging from 1 for fully labile complexes to 0 for inert complexes), results from the interplay of reaction and diffusion. From the flux, assuming a well-known model and values for key geometrical and physical parameters, one can also compute the virtual concentration, c_{DGT}, which can be interpreted as the free metal concentration in bulk solution (without any ligand) that would produce the same accumulation. c_{DGT} has been successfully correlated with bioaccumulation. It will be shown that, for a mixture of complexes, c_{DGT} (which is practically always greater than the free metal concentration) is a summation of the labile contributions weighted by the diffusion coefficients(*1*). So, in extreme cases, c_{DGT} can even be larger than the total metal concentration.

By working with DGT devices with diffusive gels of different thicknesses one can get access to the thickness of the diffusive boundary layer (**DBL**) and to the **kinetic signature** of the mixture. The extraction of accurate DBL thicknesses relies on taking into account the penetration of complexes inside the resin gel(*2*).

By working with DGT devices with resin gels of different thicknesses (or better still with stacks of resin layers) one can get information about the **kinetic characteristics** of the various bindings in the system metal-ligand-resin.

By working with solutions at different ionic strengths and pH-values one can get access to information on the **electrostatic effects** that impact on accumulation. For instance, Ni accumulation from a Ni+NTA system can dramatically increase when moving from low to high ionic strength(*3*).

These examples illustrate the importance of developing and checking sound interpretative frameworks. A challenging endeavour where contributions from different expertise fields meet.

REFERENCES

1. Galceran, J.,Puy, J. Interpretation of diffusion gradients in thin films (DGT) measurements: a systematic approach. *Environ.Chem.* **2015,** *12*, 112-122
2. Levy, J. L.; Zhang, H.; Davison, W.; Galceran, J.; Puy, J. Kinetic Signatures of Metals in the Presence of Suwannee River Fulvic Acid. *Environ.Sci.Technol.* **2012,** *46*, 3335-3342.
3. Puy, J.; Galceran, J.; Cruz-Gonzalez, S.; David, C. A.; Uribe, R.; Lin, C.; Zhang, H.; Davison, W. Metal accumulation in DGT: Impact of ionic strength and kinetics of dissociation of complexes in the resin domain. *Anal.Chem.* **2014,** *86*, 7740-7748.

KEY WORDS

lability degree, low ionic strength, interpretative framework

Evaluating the performance of DGT with a Chelex-Metsorb mixed binding layer for measurement of trace metals and oxyanions in natural seawater

Amir Houshang Shiva*, Peter R. Teasdale, William W. Bennett, David T. Welsh

Environmental Futures Research Institute, School of Environment, Griffith University, Gold Coast campus, QLD 4222, Australia
**amir.shiva@griffithuni.edu.au +61401186488*

ABSTRACT

The performance of Chelex-Metsorb as a new DGT mixed binding layer (DGT-MBL) for simultaneous measurement of a wide range of cations (Al, Cd, Co, Cu, Mn, Ni, Pb, Zn) and oxyanions (As, Mo, Sb, V, W) in natural seawater using both open (ODL) and restricted (RDL) diffusive layers was investigated. The results were separately compared with the measurements of DGT-Chelex and DGT-PAMPAA (polyacrylamide-acrylic acid copolymer) for cations and DGT-Metsorb for oxyanions. The thickness of the diffusive boundary layer (DBL) was also measured using DGT-MBL with different thicknesses of ODL. The uptake and elution efficiencies of several cations were measured for the PAMPAA binding gel for the first time. The concentrations of analytes were measured by DGT equation, using diffusion coefficients measured separately in ODL and RDL for each analyte. Good agreement was observed between C_{MBL} and C_{Chelex} for measurement of Cd, Co, Cu, Ni, Pb and Zn, with the C_{MBL}/C_{Chelex} values between 0.92 and 1.16 and with no statistical differences. However, the DGT-MBL measured higher concentrations for Mn which was significantly different ($p<0.05$) from DGT-Chelex measurements. Compared to both DGT-MBL and DGT-Chelex, the DGT-PAMPAA measured significantly lower concentrations for Co, Mn and Ni (between 7-52%), but relatively higher concentrations for Cu and Pb (74-81% and 66-70%, respectively), indicating this binding gel may have had a higher degree of selectivity for these metal species. The concentrations measured by DGT-MBL and DGT-Metsorb were consistent for As, Sb and V with no statistical differences ($p > 0.05$) and the ratios of $C_{MBL}/C_{Metsorb}$ between 0.85 and 1.12. However, DGT-MBL measured higher concentrations for Al compared to the DGT-Metsorb with the ratios of C_{MBL}/C_{Ms} between 1.23-1.33, likely due to the uptake of minor cationic Al species by Chelex. Interestingly, DGT-Chelex measured only 6-8% of Al species measured by DGT-MBL or DGT-Metsorb. None of the DGT binding gels showed statistical differences between measured concentrations by restricted (C_{RDL}) and open (C_{ODL}) diffusive layers for Cd, Co, Mn, Ni, Pb, Zn, As, Sb and V. However, speciation measurements for Cu and Al were significantly different ($p < 0.05$) with the ratios of C_{RDL}/C_{ODL} between 0.68-0.75 for Cu and 0.73-0.79 for Al.

KEY WORDS

Diffusive gradients in a thin film; DGT mixed binding layer (Chelex-Metsorb); DGT-PAMPAA; open diffusive gel; restricted diffusive gel; speciation

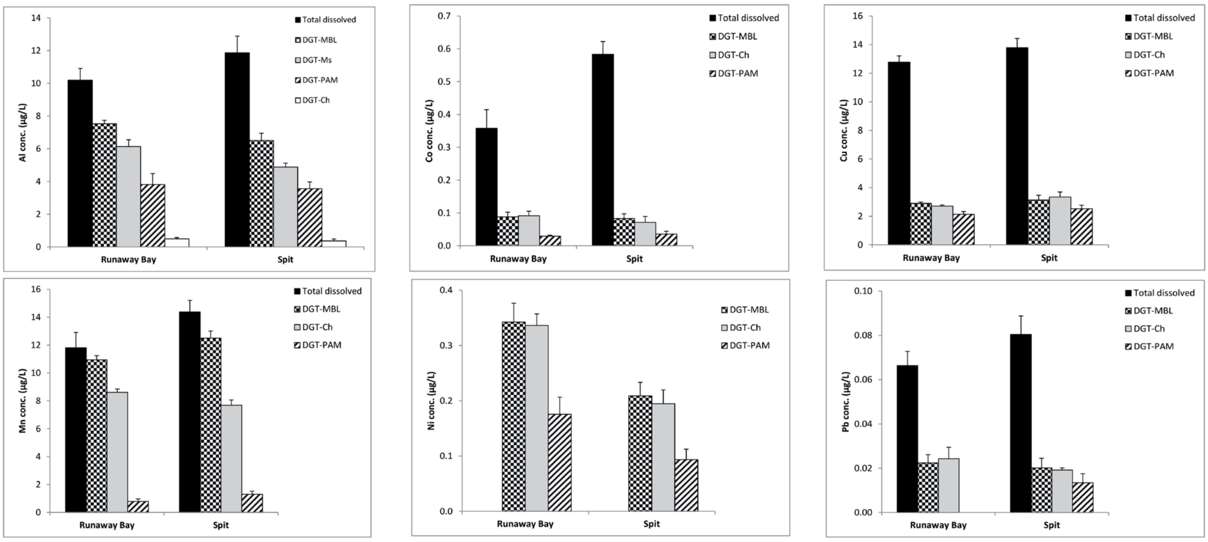

Figure 1. Comparison of DGT labile concentrations for cations using different binding gels (MBL = mixed binding layer, Ch =Chelex, PAM = polyacrylamide-acrylic acid, Ms = Metsorb) at two selected natural seawaters.

Trace Metals Speciation in Crude Oil Contaminated Seawater Using DGT with Different Membranes

Mohammed. M. Al Kasbi*, Hao. Zhang,

The Lancaster Environment Centre, Lancaster University, Lancaster, LA1 4YQ, United Kingdom.
** m.alkasbi@lancs.ac.uk*

ABSTRACT

Crude oil refineries, mining and industrial activities often produce point sources of primary trace metals pollution in marine environments. The determination of trace metal concentrations and speciation is challenging due to oil organic complex matrix, high salinity and low background concentrations. Current study has been focused on the development of the diffusive gradients in thin films (DGT) method for the concentration and speciation measurements of trace metals in the crude oil contaminated Oman's aquatic environment. Five types of DGT devices were used, OP-DGT, RG-DGT, 1000 and 3500 MWCO-DGT and Nafion-112-DGT, were evaluated for the simultaneous measurements of labile trace metal (Co, Ni, Cu, Cd, and Pb, Zn, Fe, Mn, Al and Cr) concentrations in synthetic seawater treated with different levels of crude oil 1% and 4% oil water ratios (OWR), after 48 hours of mixing time. Diffusion coefficients of metals were measured through diffusive gel, dialysis and Nafion-112 membranes in synthetic seawater at pH of 5.8 using diffusion cell. The measured D values (21ºC) for the above metals in the dialysis membrane were ≈ 11-16 times lower than the D values for OP (open pore) diffusive gels. Whereas, the diffusion coefficients of metals through Nafion-112 were ≈18-42 times lower than the D values for OP diffusive gel. At 1 and 4% of OWR, all metals except Cu and Cd did not show any significant difference in different DGT devices, due to the low molecular weight of complexed metals comparing to the pore size of the diffusion layers. The DGTs-labile fractions of Cu were between 11 - 61.2%. Only 14-20 % of Cd fractions were unable to diffuse through DGT devices with RG, dialysis (1000 and 3500 MWCO) and Nafion112 gels. The (1000 MWCO dialysis)-DGT labile metals concentrations were compared with measured concentrations in 1000 MWCO equilibrium microdialysis. Concentrations of Pb and Zn measured by (1000 MWCO)-DGT were similar to the concentrations measured in equilibrium microdialysis samples, may be due to the weak complexes with the organics released from oils. Whereas, the measured concentrations of Co, Cu, Ni and Cd in the dialysis higher than the DGT-labile concentrations. It is possible that their complexes exist at low molecular weight species, small enough to pass through the 1000 MWCO microdialysis pores but not labile enough to be measured by (1000 MWCO)-DGT devices. *In situ* field evaluations in seawater and groundwaters around refineries and industrial areas in Oman confirmed that the Nafion-DGT only measures free ionic metals due to the sulfonic group in the membrane, the dialysis-DGT measures small labile metal complexes and OP-DGT measures larger labile metal complexes according to the size difference.

KEY WORDS

DGT, speciation, Nafion, crude oil, seawater, contamination, Oman.

Evaluation of a zirconia oxide-DGT for the determination of Cr(III) and Cr(VI) through selective elution

Delphine Devillers*, Stéphane Simon, Adeline Charriau, Gilles Guibaud, Rémy Buzier

Research Group on Water, Soil and Environment (GRESE - EA 4330), University of Limoges, 123 Avenue Albert Thomas, 87060 Limoges Cedex, France
**delphine.devillers@etu.unilim.fr*

ABSTRACT

Chromium in natural waters can be present as two oxidation states: Cr(III) and Cr(VI). It is of interest to quantify them separately, as Cr(VI) is more toxic than Cr(III). This quantification is commonly performed from spot water samples and is only representative of the concentration at the time of sampling. The Diffusive Gradient in Thin film (DGT) technique allows overcoming this limit by the integration of the contamination during the deployment period and provides time-weighted average concentrations. Although DGT has already been proposed to determine a single chromium species (Cr(III) or Cr(VI)), the determination of chromium speciation would require two different probes.

In this work, a DGT system based on zirconia oxide binding layer was investigated and was proven to bind both Cr(III) and Cr(VI) species, and thus allows the determination of total labile chromium. Furthermore, Cr(III) and Cr(VI) were selectively recovered to give access to labile chromium speciation. The combination of a zirconia-DGT device and selective elutions enables the individual quantification of Cr(III) and Cr(VI) with a single device. The different steps of the development and validation of this methodology will be presented.

Selective elution consists in elution of Cr(VI) by NaOH followed by elution of Cr(III) with HNO_3. Its selectivity and efficiency were evaluated. With the first elution step of the binding gel with NaOH, 98±3% of Cr(VI) was recovered whereas eluted Cr(III) was not quantifiable (<0.5%). This proves the selectivity and quantitativity of the elution of Cr(VI). Cr(III) was then recovered with the HNO_3 elution step with a 55±3% efficiency. Although elution efficiency was repeatable, acid digestion of the gel could be advised for a complete recovery of Cr(III).

The robustness of the method was evaluated through the study of the effect of pH, ionic strength and interference of ions. The performances of the methodology were assessed by the evaluation of its repeatability and the determination of the effective binding capacity. Results showed that DGT system could accumulate at least 20 µg of Cr(III) or Cr(VI), which would enable a maximum deployment time higher than 2 years in waters containing 1 µg L^{-1} of labile chromium, a typical concentration in rivers, or one week for more concentrated waters (100 µg L^{-1}) like industrial effluents. Finally spiked natural samples were used for validation of the methodology.

KEY WORDS

Diffusive Gradient in Thin film (DGT), Chromium, Speciation, Selective elution

Determination of methylmercury concentrations in low contaminated rivers by passive sampling method and isotopic dilution GC-ICP-MS

Aurélie Magnier, Aymeric Dabrin*, Ghislaine Grisot, Marina Coquery

Irstea, UR MALY, 5 rue de la Doua-CS70077, F-69626 Villeurbanne cedex, France
** aymeric.dabrin@irstea.fr*

ABSTRACT

Diffusive gradient in thin film (DGT) samplers have been widely used as water quality monitoring tools to study cationic trace metals of the Water Framework Directive (WFD) (e.g. lead, cadmium or nickel). However, these samplers based on a polyacrylamide diffusive gel and a Chelex resin do not allow trapping methylmercury (MeHg) and inorganic mercury (Hg(II) which is also a priority substance of the WFD. The most common DGTs developed for these two mercury species are based on a 3-mercaptopropyl functionalized silica gel (3M) resin, with a diffusive gel either in polyacrylamide or in agarose. However, until now, studies have been mainly focused on the application of such DGTs in relatively contaminated surface waters (total Hg in dissolved phase; HgTD > 5 ng/L or MeHg in dissolved phase; MeHgTD > 0.25 ng/L).

The aim of this study was to develop a home-made passive sampler combined with analysis by gas chromatography-inductively coupled plasma-mass spectrometry (GC-ICP-MS) to measure low levels of MeHg in surface waters. Consequently, our work has focused on the control of Hg contamination mainly via the control of blank DGT, which could influence the measured concentrations of total mercury (HgTOT) and MeHg at very low levels. Moreover, we developed and adapted an analytical method by isotopic dilution GC-ICP-MS, allowing the extraction, derivatization and quantification of the mass of MeHg trapped by the home-made/3M DGT at environmental levels. Then, triplicates of home-made samplers were deployed in a low contaminated river from France (Bourbre River; HgTD ~ 0.5 ng/L) at three sites and we assessed time-weighted average (TWA) concentrations for HgTD and MeHgTD

Basically, our home-made/3M DGT resins presented low total mass of Hg (HgTOT) level (<LQ = 0.03 ng) compared to commercial DGTs based on a spheron-thiol resin. Our results clearly demonstrated that initial mass of Hg in commercially available DGTs was masking Hg accumulation after deployment in a low contaminated river. Thus, in these environmental conditions, commercial DGTs are not well adapted or they would require a longer deployment time. Oppositely, our home-made/3M DGTs were suitable to assess TWA concentration of HgTD in a low contaminated river. Then the quantification of MeHg trapped in the home-made/3M resin was achieved by isotopic dilution (ID), extraction with acidic thiourea solution and derivatization before measurement by GC-ICP-MS. This optimized, sensitive and reproducible developed method, combining passive sampling method (10 days deployment) and ID-GC-ICP-MS, allowed the measurement of low level of MeHg in the Bourbre River, corresponding to a MeHg TWA concentration of 90-130 pg/L.

KEYWORDS

Methylmercury, speciation, monitoring, freshwater, blanks

In situ selective determination of methylmercury in river water by diffusive gradient in thin films technique using baker's yeast immobilized in agarose gel as binding phase

Amauri Antonio Menegário[a*], Makenly Tafurt Cardona[a], Carlos Eduardo Eismann[a], Carlos Alfredo Suarez[a], Karen Luko Silva[a], Ézio Sargentini Junior[b]

a Centro de Estudos Ambientais, Univ. Estadual Paulista, Rio Claro, SP, Brazil.
b Instituto Nacional de Pesquisas da Amazônia (INPA), Manaus, AM, Brazil
** amenega@rc.unesp.br*

ABSTRACT

Saccharomyces cerevisiae immobilized in agarose as binding phase and polyacrylamide as diffusive layer in the diffusive gradient in thin films technique (DGT) was used for selective determination of methylmercury (MeHg). Deployment tests showed linearity in mass uptake up to 48 h (3276 ng). When coupling the DGT technique with Cold Vapor Atomic Fluorescence Spectrometry, the analysis had a limit of detection of 0.0004 ng mL^{-1} (pre concentration factor of 11 for 48 h deployment). Diffusion coefficient of $7.03 \pm 0.77 \times 10^{-6}$ cm2 s^{-1} at 23 °C was obtained. Effect of ionic strength (from 0.0005 mol L-1 to 0.1 mol L^{-1} NaCl) and pH (from 3.5 to 8.5) on MeHg uptake were evaluated. For these range, recoveries of 84 - 105% for ionic strength and 84 - 98% for pH were obtained. Potential interference due to presence of Cu, Fe, Mn, Zn was also evaluated showing good recoveries (70-87%). The selectivity of the proposed devices was evaluated by deployments in solutions containing MeHg and Hg(II). DGT devices containing the proposed binding agent and polyacrylamide hydrogel as diffusive layer showed recoveries of 102 - 115 % for MeHg and 10.4 - 11.3% for Hg(II). The *in situ* performance of the devices was evaluated in Negro River (Manaus-AM, Brazil), which indicated that the developed technique can be successfully employed for *in situ* measurements.

KEY WORDS

S. cerevisiae; mercury; river water

Evaluating the diffusive gradients in thin-films technique for the measurement of dissolved uranium in natural waters

Gary R. Fones*, Geraldine S.C. Turner and Graham A. Mills

University of Portsmouth, Portsmouth, Hampshire, PO 3QL, UK
** gary.fones@port.ac.uk*

ABSTRACT

The UKs existing nuclear infrastructure, as well as proposed new generation reactors, is committed to provide assurance that it is not impacting the aquatic environment. To achieve this, extensive monitoring regimes are implemented to detect actinide materials in a range of natural waters – from surface and groundwater to the open oceans. Passive samplers have several advantages over conventional methods for monitoring radionuclides in the dissolved phase, including simplicity, provision of time-weighted average concentrations, and *in situ* pre-concentration of the analytes. Diffusive Gradient in Thin Films (DGT) device has been identified as one type of passive sampler that can effectively measure dissolved concentrations of uranium, thereby providing information on the bioavailability and speciation of this actinide. Four adsorbents (Chelex-100, manganese dioxide [MnO_2], Metsorb and Diphonix resin (TrisKem International) were evaluated as a receiving phase for the measurement of inorganic uranium species in synthetic and natural waters both in the laboratory and in field trials. In laboratory experiments using the actinide specific resin Diphonix, uptake of uranium (all 100% efficiency) was unaffected by varying pH (4–9), ionic strength (0.01–1.00 M, as $NaNO_3$) and varying aqueous concentrations of Ca^{2+} (100–500 mg L^{-1}) and HCO3- (100–500 mg L^{-1}). Due to the high partition coefficient of Diphonex, several elution techniques for uranium were evaluated. The optimal eluent mixture was 1 M NaOH/1 M H_2O_2, eluting 90% of the uranium from the resin. Uptake of uranium was linear ($R^2 = 0.99$) over time (5 days) in laboratory experiments using artificial freshwater showing no saturation effects of the resin. In field deployments (River Lambourn, UK) the devices quantitatively accumulated uranium for up to 7 days. DGT validation experiments (5 days) gave linear mass uptake over time ($R^2 \geq 0.97$) for the other three adsorbents in low ionic strength solution (0.01 M $NaNO_3$). Field deployments in fresh water (River Lambourn, UK) gave linear uptake for up to 7 and 4 days for Metsorb and MnO_2 respectively. The ability of the DGT devices to measure U isotopic ratios with no isotopic fractionation was shown by all four resins, thereby proving the usefulness of the technique for environmental monitoring purposes. Diffusive boundary layer (DBL) measured in the field showed that the DBL-corrected U concentration was half that determined when the effect of the DBL was not considered, highlighting the need for this to be taken into consideration when undertaking field deployments.

KEY WORDS

Actinides, Uranium, Diphonix resin, Natural waters, Water monitoring, Chelex-100, Manganese dioxide, Metsorb, Titanium dioxide

Can DGT be used to elucidate uranium speciation in natural waters?

L. Février[a*], L. Carasco[a], B. Porterat[b], O. Simon[a], L. Pourcelot[b], R. Gilbin[a]

[a] *IRSN/PRP-ENV/SERIS/L2BT – B.P.3, 13 115 Saint Paul-lez-Durance Cedex*
[b] *IRSN/PRP-ENV/SERIS/LERCM – B.P.3, 13 115 Saint Paul-lez-Durance Cedex*
* *laureline.fevrier@irsn.fr*

ABSTRACT

Uranium is a radioactive contaminant of concern for the aquatic environment, with potential releases to freshwaters due to mining, processing and waste disposal. It can be accumulated in living organisms (after waterborne or trophic exposure) leading to chemical and radiological damages. The toxicity of uranium in freshwater depends on its speciation, and is therefore influenced by the physico-chemical conditions of the water, such as pH, water hardness, dissolved organic carbon (DOC) and alkalinity. Researches involving DGT have been developed so far either to monitor uranium in freshwater or to estimate the bioavailable fraction of uranium. The objective of this study was to evaluate the ability of the DGT technique to give insight of uranium speciation in natural freshwaters. Two complementary strategies were developed, using DGT with (1) different resins able to sorb different uranium species or with (2) different diffusive gels able to differentiate the uranium complexes based on their size.

On one hand, Metsorb and Chelex DGT with a 0.8 mm diffusive gel thickness were deployed for 3 different times in four French rivers, exhibiting contrasted physico-chemical conditions. On the other hand, Chelex DGT with open or restricted diffusive gels of 0.4, 0.8 and 2 mm thickness were deployed for 3 different times in an acidic freshwater lake. Uranium speciation in these aquatic media was simulated by VMinteq based on the main measured physico-chemical parameters of the waters.

The uranium concentration measured by the Chelex resin was always lower than that measured by the Metsorb resin. However, the magnitude of this difference varied with the DOC concentration, the pH and the concentration of calcium. This result may be explained by the presence of calco-uranyl-carbonate ($Ca_2UO_2(CO_3)_3$) and fulvic uranium complexes which are either inert or partially labile in DGT. The comparison of the uranium concentration measured with restricted gels and different gel thicknesses to the one measured with open pore gels showed that uranium measured with the Chelex resin is mainly regulated by the kinetics of dissociation of such partially labile complexes.

Taken together this result suggested that deploying a set of DGT that combines different gels (pore size and thickness) and different resins might give insight of uranium speciation in natural waters.

KEY WORDS

uranium, speciation, restricted pore, open pore, kinetics

Using DGT to determine representative dissolved inorganic nitrogen and phosphorus concentrations in natural freshwaters

Jianyin Huang*, William W. Bennett, David T. Welsh, Peter R. Teasdale

Environmental Future Research Institute, School of Environment, Griffith University, Gold Coast campus, QLD 4222, Australia
** Jianyin. huang@griffithuni.edu.au*

ABSTRACT

Nitrogen (nitrate and ammonium) and phosphorus (phosphate) are major nutrients that determine the productivity and quality of aquatic ecosystems. Nutrient concentrations can differ from place to place because of differences in climate, catchment geology and land use, water flow regimes and the presence or absence of major point sources, such as wastewater treatment plants. However, nutrients may also change considerably due to shorter term processes such as rainfall events and diurnal cycles. The use of infrequent grab sampling as the basis of environmental monitoring is therefore likely to be unrepresentative of water quality within a waterway and is likely to miss important contamination events. The *in situ* DGT technique provides time weighted-average concentrations that are highly representative of the analyte concentrations over the deployment time. DGT techniques have recently been developed for NO3-N and NH4-N (described in another presentation). This presentation describes the results of a study in which DGT-reactive nitrate, ammonium and phosphate were determined in several freshwater streams in south-east Queensland and compared with the concentrations in grab samples collected over the deployment period. To date DGTs have been deployed in Loders Creek - a small, highly-modified catchment (≈10 km^2) dominated by urban and light industrial land use – during the summer wet season (Figure 1). The grab sample results showed that all nutrient concentrations varied considerably over time. Nitrate and phosphate tended to increase with during rainfall events, although nitrate peaked more quickly. Ammonium also increased but only after a time-lag and were quite low during the actual rainfall events. The DGT results were very similar to the average grab sample concentrations for nitrate and phosphate and showed the same general trends. However, the results for ammonium seemed to be quite different at times. Further analysis of these results will be provided and along with results of similar studies in other catchments.

KEY WORDS

dissolved inorganic nitrogen, dissolved phosphorus, time-weighted average concentrations, freshwater flows and diurnal cycles.

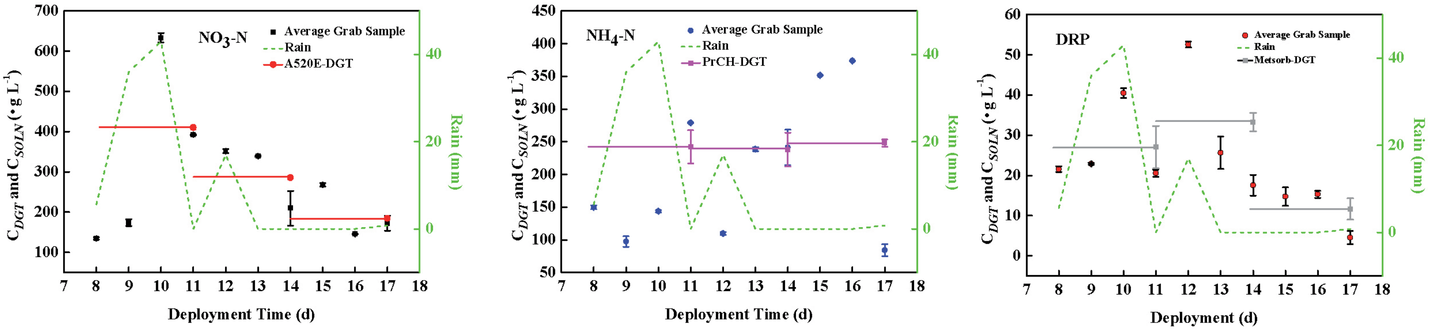

Figure 1 Values of average grab sample and DGT results for NO$_3$-N, NH$_4$-N and DRP at Loders Creek from 8th Dec to 17th Dec 2014

First applications of DGT technology to groundwater monitoring in Hungary

Tamás Madarász*, Andrea Kolencsikné Tóth, István Székely

University of Miskolc, Hungary
** hgmt@uni-miskolc.hu*

ABSTRACT

The University of Miskolc, Department of Hydrogeology and Engineering Geology is a leading research entity in hydrogeology Eastern Europe. In its recent research project (titled WELLaHEAD) the team has dedicated its effort to a complex research agenda related to various quantitative and qualitative groundwater management issues. The test areas are research sites from North – East Hungary, one of Europe’s least developed regions. One of the focus areas of the research is related to heavy metal contamination of former ore mines, industrial sites and the groundwater quality monitoring in drinking water source areas.

Besides lab activities (testing DGT technology) and conventional monitoring methods (groundwater sampling and lab analysis) we have deployed DGT passive samplers on three test sites for the detection on TWA concentration of heavy metals and arsenic. The diffuse gel technology passive samplers are new to monitoring practice in Hungary. Our aim is to obtain high quality data and offer a new technology option for using it in groundwater monitoring systems and in health risk assessment. One of our test site was a karstic aquifer providing drinking water for the city of Miskolc, an other test site was a former ore mine, having issues with AMD contamination, the third area was an industrial disposal site. All three sites represent different geological/hydrogeological environment, some of them having extreme environmental conditions. Deployment in the karstic aquifer DGT proved no heavy metal contamination that would cause health risk to receptors of the drinking water supply. At the acid mine site the DGT samplers, were installed at 4 locations along the treatment technology, and it proved the efficiency of a newly installed pilot reactive barrier, however at extremely low pH level, the sampler was not useful.

At the industrial waste disposal site, the DGT samplers were installed in monitoring wells, proving contamination plumes and main trajectories of the contamination from mobilized from the disposal site to groundwater, and surface water.

Our team is dedicated to continue with DGT monitoring campaigns, and to convince relevant Hungarian technical and legislative actors about the applicability and benefits of DGT technology, especially in contaminated site monitoring and health risk assessment.

KEY WORDS

DGT, Acid mine drainage site, industrial waste disposal site, extreme pH conditions, monitoring remediation technology

Monitoring of heavy metals in sewage systems by use of passive sampler, DGT

T. Hosking[a], T. M. Muthanna[b], Ø. Garmo[b], Ø. Mikkelsen[a*]

[a] *Norwegian University of Science and Technology (NTNU) Department of Chemistry, N-7491 Trondheim, Norway*
[b] *Norwegian University of Science and Technology Department of Hydraulic and Environmental Engineering, N-7491 Trondheim, Norway*
[c] *Norwegian Institute for Water Research (NIVA), P.O. Box 173 Kjelsaas, NO-0411 Oslo, Norway*
**oyvind.mikkelsen@chem.ntnu.no*

ABSTRACT

Reducing the supply of metals in the sewage systems is of great importance within governmental water treatment. High concentrations of such environmental toxicants increase the costs for the water treatment, and could also cause problems with e.g. discharge of sludge for further use. The most effective process to reduce the environmental problem in wastewater would be to remove or lower the use of products that contribute to the discharges. To be able to regulate and control the supply of heavy metals to the sewage systems, easy to use monitoring tools are needed. Passive samplers like DGT (Diffusive Gradients in Thin films), is strong candidates for being implemented in such monitoring activity. However, up to present, the use of DGT in sewage systems is rare, and more research is need for quality assurance of such samplers for use in sewage water. Several issues arise when using passive samplers in typical sewage systems. The possible deposition of sludge and particles on the surface of the filter, and the possible lack of sample medium from time to time in the system are both issues that could affect the accumulation of the metals in the sampler. Further, e.g. the ion strength of the sewage water and the temperature could vary over shorter or longer periods of time. This project was collaboration between Trondheim Municipality, NIVA and NTNU. The purpose of this study has been to investigate the possible use of DGT's in sewage systems, especially as a potential tool for source tracking. Experiments were conducted both in real samples in sewage streams, and in artificial samples for quality assurance. Samples collected manually and by DGT´s were analyzed by ICP-MS for a number of elements like zinc, lead, cadmium, copper, chromium, cobalt, manganese, nickel and iron. The results indicate that a possible dehydration of the DGT affects the precision, though the average concentration of a number of samplers still might give a useful estimation of the metal levels for monitoring and source tracing purpose. Results indicated that dried samplers were more prone to contamination. The passive sampler indicates to be particularly affected by suspended solids after few days of exposure. It appears to be an increasing fouling with increased exposure time and increased presence of sludge/particulate in the sewage in water. Turbidity could be used for a possible indirect correction. For the metals cadmium, nickel, cobalt, manganese, zinc and iron, a good correlation was found for results obtained with DGT and results from frequent conventional sampling (bottle samples). The total concentration of copper and lead, however, was often considerably higher than concentrations measured with DGT, this might indicate that these metals were largely bound particles or strongly complexed in the sewage water. Somewhat lower accuracy was observed for samples with high turbidity, however this does not impair the potential of the passive samplers as tools for e.g. source tracking, but there is a disadvantage that the total concentration of lead and copper in the wastewater might be somewhat under estimated in samples with high turbidity.

KEY WORDS

sewage, metals, environmental toxicant, passive sampler

From environmental assessment to DGT: advancing the methods for risk assessment of metals in sediments.

Stuart L. Simpson

Centre for Environmental Contaminants Research, CSIRO Land and Water, Sydney, Australia
** stuart.simpson@csiro.au*

ABSTRACT

The quantification of the risk posed by contaminated sediments is critical for regulators. This process considers the concentrations and forms of sediment contaminants, and the likelihood that the contaminants may cause adverse effects to selected receptors in the environment. For many contaminants, the assessment of bioavailability is crucial to the prediction of toxicity effects to benthic organisms. However, while many regulatory frameworks now promote the use of procedures for assessing the bioavailability of contaminants in sediments, the current methods suffer from many inadequacies. The use of inappropriate or inadequate tools for assessing contaminant bioavailability in sediments can result in incorrect assessment decisions, e.g. 'finding no impact' when effects are occurring to benthic organisms.

This presentation will consider current approaches for the assessment of bioavailability of metals in sediments, and how DGT stands as a step forward in suite of tools available. Traditional approaches to estimate the bioavailable metal fraction include pore waters analyses, the use of acid-volatile sulphide-simultaneously extractable metal (AVS-SEM) relationships or other non-exhaustive metal extraction procedures. The ability of these techniques to predict metal exposure or effects to benthic organisms will be compared to DGT-based predictions for benthic amphipod, bivalve and copepod species in field and laboratory exposures to field-collected metal-contaminated freshwater and marine sediments. The need to estimate metal concentrations in sediment pore waters from DGT-induced metal fluxes will be discussed, along with methods for predicting toxicity when multiple metals exist with differing toxicities to aquatic organisms. The evidence provided by the collective studies should now be leading environmental assessors to DGT, as a technique that provides excellent forms of information on the bioavailability and potential toxicity of metals in sediments.

ACKNOWLEDGMENTS

Dianne Jolley, Elvio Amato, Maria Belzunce-Segarra for collaboration in the DGT studies. I thank Helen Price for assistance for DGT preparation, David Spadaro and Ian Hamilton for assisting with toxicity tests, Robert Jung, Chad Jarolimek and Josh King for assisting with metal analyses, and Chamani Wadige for assisting with field work.

Determination of As speciation in river sediment using DGT techniques

Josselin Gorny[a], Ludovic Lesven[a], Gabriel Billon[a], David Dumoulin[a], Catherine Noiriel[b], Caroline Pirovano[c] and Benoît Madé[d]

[a] Laboratory LASIR; UMR CNRS 8516 – University Lille 1, Sciences and technologies, Villeneuve d'Ascq, France
[b] Laboratory Géosciences Environnement Toulouse, Observatoire Midi-Pyrénées, UMR 5563 – University Paul Sabatier, CNRS, IRD, Toulouse, France
[c] Laboratory UCCS; UMR 8012 CNRS – University Lille 1, Villeneuve d'Ascq, France
[d] French National Radioactive Waste Management Agency (Andra), Research and Development Division (DRD), Châtenay-Malabry, France

ABSTRACT

Both toxicity and bioavailability of arsenic are strongly dependent on its chemical speciation, which must be closely considered when studying contamination of surface waters and sediments. The different species also have their own physical and chemical characteristics, resulting in various degrees of mobility according to the biogeochemical properties of the matrix. More particularly, in sediments where strong redox gradients occur within the first cm below the water-sediment interface, the geochemical behavior of As is still not fully understood. The study of the aqueous speciation of As in pore waters is still challenging since the sediment matrix is anoxic and complex, and the concentrations of As are low (a few µg L^{-1} or less).

Diffusive Gradient in Thin film (DGT) technique appears to be an interesting alternative in order to determine *in situ* speciation of arsenic. The methodology for determining As speciation by the DGT techniques (combination of two DGT probes with different selectivities, here Zn-ferrite and 3MP resins) which has been fully validated by HPIC-ICP-MS in synthetic solutions, will be described. In conclusion and perspective, we will present an application of a DGT exposition in sediments to show that this technique should be soon fully operational.

KEY WORDS

arsenic, DGT, redox speciation, river sediment

Assessing contaminant biogeochemistry: a new view using DGT and DET

William Bennett*, Maja Arsic, David Welsh and Peter Teasdale

* w.bennett@griffith.edu.au

ABSTRACT

The sediments of aquatic systems can be both a source and a sink for environmental contaminants. Understanding the biogeochemical cycling of contaminants within aquatic systems relies on obtaining accurate measurements of porewater concentrations at relevant spatial scales. Conventional methods, which typically rely on coring and porewater extraction by squeezing or centrifugation, fail to meet either of these requirements. Conversely, passive sampling methods such as DGT and DET can provide a better approach to obtain accurate measurements of porewater solutes at high resolution, in one or two dimensions. This approach is much more effective in dealing with the confounding effects of sediment heterogeneity.

Here we present various examples of the application of DGT and DET methods to investigating contaminant biogeochemistry in sediments. These examples range from the study of background concentrations of arsenic in marine sediment, to the measurement of elevated concentrations of antimony in the freshwater sediment of a contaminated wetland. A variety of methods are discussed, including the Chelex-Metsorb mixed binding layer DGT for measuring trace cations and oxyanions, the 3-mercaptopropyl functionalised silica DGT for the selective measurement of As^{III} and Sb^{III}, and the colorimetric iron(II) DET method for the measurement of high-resolution porewater iron(II) concentrations. The use of mesocosm experiments for resolving mechanistic controls on poorly studied contaminants is also evaluated - this approach is particularly effective at investigating contaminant responses to changing redox conditions, which is often hard to assess in the field.

The research to date in this field has clearly demonstrated the power of applying DGT and DET porewater samplers to investigating contaminant biogeochemistry in sediment systems. This approach results in measurements at higher spatial resolution than conventional techniques (mm vs. cm), which is essential when the oxic and sub-oxic zones in productive sediments are often <1 cm deep. Furthermore, advances in DGT methodology have enabled *in situ* speciation measurements to be made in sediments (e.g. As^{III} and Sb^{III}), an important step forward in understanding the biogeochemical processes behind contaminant mobilization and sequestration. Finally, we discuss the challenges in applying these methods to the routine assessment of contaminated sediments, and how the DGT community might begin addressing these issues into the future.

KEYWORDS

contaminant, biogeochemistry, arsenic, antimony, iron

Resolving biogeochemical controls of arsenic and antimony mobility in contaminated sediments using DGT and DET

Maja Arsic*, Peter Teasdale, David Welsh and William Bennett

Environmental Futures Research Institute, Griffith University, Gold Coast, QLD 4222, Australia
**Presenting author: maja.arsic@griffithuni.edu.au*

ABSTRACT

Antimony is an emerging global contaminant with chemical characteristics and speciation similar to arsenic, as they are adjacent elements in Group IV. Consequently, these two metalloids have been assumed to behave similarly in the environment, although data to support this is limited. Recent studies have suggested that these elements actually respond differently to changes in pH and redox conditions. While arsenic mobility has been clearly linked to the reductive dissolution of iron(III) oxyhydroxide minerals, the nature and extent of the relationship between antimony mobility and iron biogeochemistry is unclear. As toxicity varies with speciation, it is critical to understand the biogeochemical controls on the mobility and binding of antimony species.

In order to investigate the differences in arsenic and antimony mobility, contaminated sediments were exposed to changing redox conditions (oxic-anoxic-oxic) in a mesocosm, which was compared to a control mesocosm (oxic conditions only). As^{III}, As^{V}, Sb^{III}, Sb^{V} and Fe^{II} concentrations were measured in the water column to observe relationships between element fluxes across the sediment-water-interface. High-resolution concentration profiles (1-3 mm) were obtained using DGT and DET techniques. The total porewater concentrations for all elements were determined using a mixed binding layer (Chelex-100 and Metsorb MBL), while 3-mercaptopropyl functionalized silica gel was used as the binding phase for measuring reduced inorganic arsenic and antimony (As^{III} and Sb^{III}). The diffusive gel of the 3-mercaptopropyl functionalized silica gel DGT probe was used as a DET gel for the colorimetric determination of Fe^{II}, allowing the co-distributions of As^{III}, Sb^{III} and Fe^{II} to be measured. Deployment of these two probe types allowed for the calculation of As^{V} and Sb^{V} by difference in the homogenised sediment.

The joint release of inorganic arsenic and ferrous iron was observed with the onset of anoxic conditions in the water column. As expected, arsenic mobilization was strongly related to the reductive dissolution of iron(III) oxyhydroxides in the sub-oxic zone of the sediment. This was visible due to the high spatial resolution capabilities of coupled DET-DGT techniques to examine the concomitant relationship between these two elements in the sediment pore water. Conversely, there was no relationship between iron(III) oxyhydroxide dissolution and antimony mobility or speciation. Antimony displayed the opposite behaviour to arsenic; anoxic conditions decreased antimony mobility in the water column and increased concentrations within the sub-oxic zone of the sediment. While the selective measurement of the MBL- and mercapto-silica-DGT samplers indicated that As^{III} was the dominant species supplied from the solid phase to the sediment pore water, there was no such distinction between antimony species. These findings demonstrate the potential for diffusive sampling techniques to investigate and compare the effects of changing redox conditions on the speciation and mobility of arsenic and antimony, as well as resolve their relationships with other elements such as iron. Importantly, these results show a clear difference between the mobility of arsenic and antimony despite their other chemical similarities, which has considerable consequences sfor the remediation and management of contaminated sites.

KEY WORDS:

Antimony; arsenic; biogeochemistry; iron; speciation; mixed binding layer (MBL); Diffusive gradients in thin-films (DGT); Diffusive equilibrium in thin-films (DET)

Use of DGTs to estimate release of metals from re-oxygenating Baltic Sa sediments

Martin M. Larsen*, Gitte Jacobsen

* mml@bios.au.dk

ABSTRACT

The Baltic Sea have large areas of anoxic or periodically anoxic sediments, and large efforts have been put into re-oxygenation of bottom water and hence the sediments.

To investigate the effect of re-oxygenation on the release of metals from sediments, sediment cores from the Bornholm Deep was sampled, and triplicate cores was treated in three cases: Anoxic surface water, re-oxygenated surface water and re-oxygenated surface water + mudcrabs. The sediment profiles was followed with DGT-sticks, and at the end of the 12 days experiment, pore water was sampled from two or three depths in the sediment core after crabs and DGT sticks was removed from the cores. Sediment metal content in the profiles was also measured.

The addition of mudcrabs seemed to give an increasing effect of some metals (Ni, Cd) in the porewater, despite lower sediment concentrations. In the waterphase, mudcrabs significantly (t-test, 0.05) increased the concentration of Co, Ni and V, whereas Cu was lower. Cd showed the highest concentration in re-oxygenated water phase, wheras Pb, Fe and Mn showed no effect of the treatments. The difference in cores with anoxic and oxygenated sediments was not significant for most metals. Results from the DGT are being processed and will be presented at the conference.

This project was in part sponsored by EU project VECTORS: FP7- Ocean-2010 grant Agreement no. 266445 and internal AU-DCE project "passive samplers in monitoring hazardous substances".

KEY WORDS

Porewater, Baltic Sea, Sediment, Metal release, Anoxia

Improving our understanding of heterogeneity and biogeochemical processes in coastal sediment habitats with two-dimensional, high-resolution measurements of iron(II) and sulphide

Nadeeka Rathnayake Kankanamge*, Peter Teasdale, David Welsh and William Bennett

Environmental Futures Research Institute, Griffith University, Gold Coast campus, Queensland, Australia,
** Nadeeka.rathnayakekankanamge@griffithuni.edu.au*

ABSTRACT

Coastal zone sediments are very complex, dynamic and diverse ecosystems. They have typically high microbial productivity that is disturbed by the presence of burrowing macro- and micro-invertebrate populations and benthic plants in some locations, which induce heterogeneity. Obtaining representative measurements of pore water solute concentrations in heterogeneous sediments remains a major challenge, especially with conventional coring techniques that provide one-dimensional profiles at cm-resolution and often require a mixing step as part of the sample processing. However, the development and application of inexpensive, thin-film passive samplers that measure two-dimensional, high-resolution distributions of pore water solutes have facilitated investigation of this spatial heterogeneity within sediments and the role such heterogeneity plays in biogeochemical processes. The DET (diffusive equilibration in a thin film) and DGT (diffusive gradients in a thin film) measure iron(II) and sulphide, respectively, and can be combined in a way that has been particularly useful for obtaining co-distributions of the major biogeochemical zones (iron(III)-reduction in the sub-oxic, sulphate-reduction in the anoxic zone) in coastal sediments. Replicate measurements of iron(II) and sulphide co-distributions allows heterogeneous features and the interaction of major biogeochemical zones to be observed readily. Our study has attempted to observe the degree of heterogeneity present in various benthic habitats (seagrass, mangrove and mudbanks) and to establish whether these techniques can be used to describe a 'typical' biogeochemical distribution. Seagrass meadows have a complex rhizosphere and mangroves are surrounded by pneumatophores. This study has confirmed that the measured sediments exhibit a high degree of heterogeneity; especially the seagrass sediment for which no overall idea of the sediment biogeochemistry could be deduced. The mangrove and mudbank habitats also had a high degree of heterogeneity, although patterns in the distribution of iron(II) and sulphide were more apparent than with the seagrass sediment. Recent results to characterize the biogeochemistry of other estuarine sediments will also be presented.

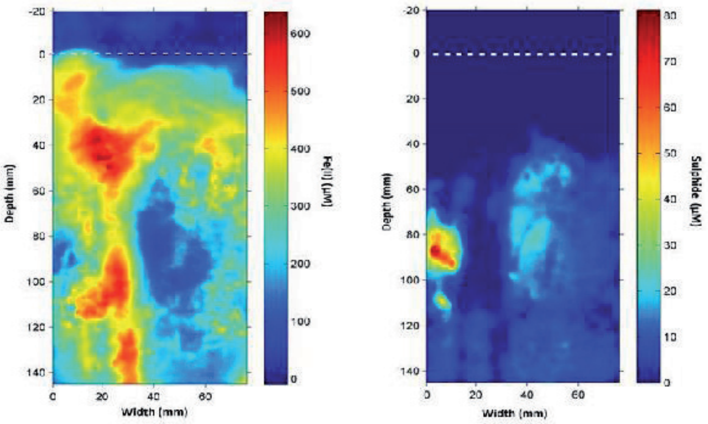

Figure 1. Heterogeneous distribution of Fe(II) (left) and sulphide (right) in mangrove forest site adjacent to Coombabah Lake catchment, Gold Coast, Australia

KEYWORDS

Coastal sediments; biogeochemical processes; sediment heterogeneity; high-resolution, two-dimensional measurements; thin film diffusive techniques (DET & DGT)

Two-dimensional imaging of oxyanions in sediments by a high-resolution precipitated zirconia based-DGT technique

Dong-Xing Guan[a], Jun Luo[a], Paul N. Williams[b]

[1]*State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Jiangsu 210023, China,*
[2]*Institute for Global Food Security, School of Biological Sciences, Queen's University Belfast, Belfast BT9 7BL, United Kingdom, D.X. G. dxguan1789@163.com, J. L. (corresponding author) esluojun@nju.edu.cn, P.N W. p.williams@qub.ac.uk*

ABSTRACT

Sub-mm scale gradients need to be determined if fluxes and cycling of oxyanions, such as phosphorus, are to be fully quantified and understood in wetland systems. High-resolution diffusive gradients in thin-films (HR-DGT) is one of only a limited number of techniques that can measure the fine distribution of oxyanions in sediments and waters. However, to be an effective HR-DGT method the analyte binding agents within the sampler, must be homogeneously distributed in the binding layer, have an adequate sorption capacity and possess a very fine particle size (≤10 µm). In the present study, we prepared a novel DGT binding layer by direct precipitation of zirconia phase into a precast hydrogel and investigated the performance of this precipitated zirconia (PZ) for measuring six oxyanions (P, V, As, Se, Mo, Sb) simultaneously, both in laboratory and field settings (Guan *et al.* 2015). Ultrathin PZ gels (60 µm) were also fabricated and trialled in conjunction with planar optodes for simultaneous capture of oxyanion and oxygen fluxes in sediment mesocosms.

PZ HR-DGT was validated for a wide range of environmental conditions, i.e. pH 4-8, ionic strength, 1-100 mmol L^{-1} $NaNO_3$, and anion competition. Compared with ferrihydrite HR-DGT, sorption capacities for oxyanions were significantly higher and the storage life of the gel was an order of magnitude longer. Compared to slurry gels prepared by incorporating binding particles within a solidifying polymer, the PZ gel was not only quicker and easier to prepare, but the gel was stronger. Furthermore, the particle size ≤0.2 µm of zirconia in the PZ gel was at least 50 times smaller than that of conventional slurry zirconia (SZ) gel. Importantly for high–resolution analysis using laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS), PZ gel discs showed little horizontal shrinkage when dried, which was in contrast to the SZ gel discs. The flexibility and cost effectiveness of the presented technique and its ability to be measured by LA-ICP-MS and used with other chemical imaging approaches makes it a useful addition to a growing range of HR-DGT techniques and applications (Williams *et al.* 2014).

REFERENCES

Guan, D. X., P. N. Williams, J. Luo, J. L. Zheng, H. C. Xu, C. Cai, and L. Q. Ma. 2015. Novel precipitated zirconia-based DGT technique for high-resolution imaging of oxyanions in waters and sediments. Environ. Sci. Technol. 49: 3653-3661.

Williams, P. N., J. Santner, M. Larsen, N. J. Lehto, E. Oburger, W. Wenzel, R. N. Glud, W. Davison, and H. Zhang. 2014. Localized flux maxima of arsenic, lead, and iron around root apices in flooded lowland rice. Environ. Sci. Technol. 48: 8498-8506.

KEY WORDS

oxyanions, high-resolution DGT, precipitated zirconia gel, sediment-water interface, oxygen, planar optode

In situ, high-resolution monitoring of labile phosphorus distribution and mobilization in sediments of a large eutrophic lake

Shiming Ding*, Qin Sun, Di Xu, Yan Wang, Chaosheng Zhang

State Key Laboratory of Lake Science and Environment, Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, Nanjing 210008, China
**smding@niglas.ac.cn*

ABSTRACT

Eutrophication is a major environmental issue for lakes in the world. Understanding the labile status of phosphorus (P) in sediments is crucial for managing a eutrophic lake, but it is hindered by lacking *in situ* data particularly on a catchment scale. Diffusive gradients in thin films (DGT) is an *in situ*, dynamical, and high-resolution technique which has the potential to satisfy the accurate measurement of labile P in sediments, while it is seldom tested *in situ* on a large spatial scale.

In this study, we for the first time characterized *in situ* labile P in sediments at a two-dimensional (2D), submillimeter resolution with the Zr-oxide diffusive gradients in thin films (Zr-oxide DGT) technique on a large-lake scale. The partitioning of horizontal heterogeneity of labile P showed a likely active layer at the depths of 0-30 mm. Calculation of the apparent diffusion flux of P across the SWI showed that the sediments tended to be a source and sink of overlying water P in the algal- and macrophyte-dominated regions, respectively. The DGT-labile P in the 0-30 mm active layer showed a better correlation with overlying water P than the labile P measured by *ex situ* chemical extraction methods. It implies that *in situ*, high-resolution profiling of labile P with DGT is a more reliable approach in *in situ* monitoring of the labile P in sediments in the field.

Another Zr-oxide based DGT (ZrO-Chelex DGT) was further employed to *in situ* obtain labile Fe and P being weakly absorbed onto sediment solids in Lake Taihu. The measurement recorded a coincident distribution between them at the one- and two- dimensional, 1.0 mm spatial resolution, which was a result of the reduction of oxyhydroxides Fe(III) and a simultaneous release of Fe(II) and P as theoretically predicted. The dominant role of Fe cycling in controlling the release of P was further supported by the poor correlations between labile P and other P-associated metals (Al, Ca and Mn). Moreover, there was a coherent resupply of P and Fe from sediment solids, which was reflected by a similar extent of solid resupply between them. Therefore, it provided a strong evidence for the theory of the Fe redox-driven release of P in sediments.

KEY WORDS

Eutrophication, diffusive gradients in thin film, phosphorus

Trace metal capacities of suspended particulate reagent-iminodiacetate (microchelex) resin using diffusive gradients in thin films

Yue Gao*, and Sebastiaan van de Velde

** yuegao@vub.ac.be Laboratory of Analytical, Environmental and Geochemistry (AMGC)*
Faculty of Sciences, Vrije Universiteit Brussel. Pleinlaan 2, 1050 Brussels, BELGIUM

ABSTRACT

The technique of Diffusive Gradients in Thin Films (DGT) was used to assess Fe, Mn, Cd, Co, Cu and Ni mobilization in anoxic sediment porewaters. Two types of DGT probes including the classic Chelex-100-DGT and microchelex-DGT (suspended particulate reagent-iminodiacetate) were deployed, but for some of the metals results from those 2 types of DGT were very different. Therefore, experiments in ground water samples spiked with the afore mentioned metals were performed. While the difference in Cd, Co, Cu, Ni and Fe concentrations between both DGT probes was small, it was not the case for Mn. To understand the observed discrepancies, further experiments assessing the capacity of both resins for Fe and Mn as well as binding competition experiments between Fe or Mn and Cu or Cd were carried out in an oxygen free atmosphere in order to mimic an anoxic sediment situation.

Fe and Mn binding capacities on microchelex-DGTs are around 20-25 µg, which means that they are by far lower than on chelex-100 DGTs and about 5 times lower than literature values assuming Fe and Mn have equivalent capacities as Cd on the microchelex resin. Moreover, trace metals which are found in a preferential place in the selectivity list of iminodiacetate based resins, such as Cu but also Cd, will compete strongly with Fe and Mn when they are present in the same environment and will replace them because they have a much stronger affinity for this type of resin. These findings are very important because microchelex is for the moment the only resin that can be used for 2-D image mapping of trace metal hotspots in sediment pore waters with DGTs.

KEY WORDS

chelex, microchelex, DGT, capacity, Fe, Mn, binding competition

An Evaluation of Arsenic and Antimony Bioavailability in Historically Contaminated Soil

Lien K. Ngo[a*], Dianne F. Jolley[a], Benjamin M. Pinch[a], William W. Bennett[b], Peter R. Teasdale[b]

[a] *School of Chemistry, University of Wollongong, NSW 2522, Australia*
[b] *Griffith School of Environment, Griffith University, 4222, QLD, Australia*
** kln881@uowmail.edu.au*

ABSTRACT

The accumulation of toxic elements, such as arsenic (As) and antimony (Sb), emitted from mining activities is putting increasing pressure on the environment and human health. Currently there is very little known about the biogeochemical behaviour of Sb and its uptake mechanisms by plants, and it is generally assumed to be the same as that of As. The aim of this study was to investigate the ability of the diffusive gradients in thin films (DGT) to predict the bioavailability of As and Sb to the radishes (Raphanus sativus) from historically contaminated soil, in comparison to conventional soil-analysis techniques. The cherry belle and long white icicle radishes were grown in pots containing a soil concentration series, in which the historically contaminated soil was mixed with uncontaminated control soil at different ratios. Soils were fully characterised for metal concentrations, particle size, organic carbon content, nutrients (nitrogen and phosphorus), water holding capacity, and pH.

The bioavailabile fractions of As and Sb in the soils were determined using various analytical approaches: DGT (as CDGT), soil solution concentrations, and sequential extraction procedure (SEP). These were then compared with As and Sb accumulation in various compartments of the plant tissues. All of the 'bioavailable' fractions, irrespective of the analytical approach, showed that both As and Sb were tightly bound to the solid phase, and that As was more mobile than Sb, even though the concentrations of total soil As were significantly lower than total soil Sb. There were dose-dependent linear relationships identified between As and Sb in radish tissues and their concentrations measured by DGT, soil solution, and labile fractions obtained from SEP. These realtionships were stronger for As and Sb accumulation by the cherry belle radish (the correlation coefficients, $R^2 = 0.94 – 0.99$) than for the white icicle radish ($R^2 = 0.81 – 0.97$). For the white icicle radish, As in the plant roots were more highly correlated with the 'bioavailable' fractions than in plant shoots, while the opposite was true for Sb.

It can be concluded that DGT-labile, soil solution, and SEP-labile fractions are comparable surrogate techniques in measuring bioavailability of As and Sb in the historically contaminated soil. It is likely that their predictive capacity will depend on the particular element and plant cultivar. This study provides a greater understanding of the biogeochemistry of As and Sb in long-term contaminated soil and thier bioavalability (as metal uptake) to root vegetables.

KEY WORDS

Arsenic, Antimony, Radish, Diffusive gradients in thin films, Sequential extraction

Assessing impacts of Jellyfish Carrion on sediment redox conditions using diffusive *in situ* samplers

Chelsky, A.[a*], Pitt, K.A.[a], Ferguson, A.J.P.[b], Bennett, W.W.[c], Teasdale, P.R.[c], D.T. Welsh[c]

[a] *Australian Rivers Institute – Coasts and Estuaries, Griffith School of Environment, Griffith University, Gold Coast Campus, Queensland 4222, Australia*
[b] *New South Wales Office of Environment and Heritage, Sydney, New South Wales 2000, Australia*
[c] *Environmental Futures Research Institute, Griffith School of Environment, Griffith University, Gold Coast Campus, Queensland 4222, Australia*
* *ariella.chelsky@griffithuni.edu.au*

ABSTRACT

The collapse of jellyfish blooms may cause significant ecosystem perturbations, due to the oxygen demand and nutrient release associated with the decomposition of jellyfish carrion. This study investigated the biogeochemical effects of the decomposition of jellyfish *in situ*. Gelatinous carrion was added to sandy sub-tidal sediment in a shallow coastal lagoon and porewater solute concentrations were quantified over three days using diffusive gradients in thin films (DGT) and diffusive equilibration in thin films (DET) samplers. Chemical fluxes and changes to the macrofaunal community were also measured. Sediment redox conditions became more reduced in plots with jellyfish compared to controls, as indicated by an increase in porewater concentrations of iron (II) and sulfide. Chamber incubations of the sediment showed an increase in sediment oxygen demand and the efflux of dissolved organic carbon and organic and inorganic nitrogen in jellyfish plots, compared to control plots. The macrofaunal community shifted in sediment cores collected from the jellyfish plots relative to controls, with a decreased abundance of some taxa. The migration of toxic sulfide towards the sediment-water interface, coupled with low oxygen conditions, may explain the change in the macrofaunal community. When jellyfish blooms collapse, and large amounts of carrion sink to the benthos, they could therefore cause significant ecosystem perturbations. The DGT/DET samplers enabled fine scale measurements of changes to sediment porewater solutes as jellyfish detritus decomposed and this study thus demonstrates the utility of DGT/DET to assess important biogeochemical processes.

KEY WORDS

Bacterial decomposition, gelatinous zooplankton, nutrient flux, remineralization, iron (II), sulfide

Assessment of Diffusive Gradient in Thin Film Samplers for Measurement of Bioavailable Hg

Danny Reible*, Balaji Rao

Civil and Environmental Engineering, Texas Tech University
** danny.reible@ttu.edu*

ABSTRACT

Mercury (Hg) and methylmercury (MeHg) are of substantial concern in sediment environments. Diffusive gradient in thin films (DGT) provide a means of measuring labile mercury (Hg) species in pore-waters. However, questions regarding what forms of Hg can pass through a DGT and how they are related to true bioavailable Hg fractions species is still not understood. For instance, studies comparing the net methylation rate in contaminated sediments indicate that not all Hg forms will be available for microbial conversion to methylmercury. Particulate Hg (> 0.45 µm) is not expected to be bioavailable and is inaccessible by DGTs, whereas, the truly dissolved (< 1 nm) are readily accessible by both biota and DGT. However, the transport through DGTs of potentially bioavailable colloidal bound forms of Hg (~1– 450 nm) has not been specifically evaluated. To address this gap, studies were conducted by preparing different molecular sizes of organic Hg complexes (from 'dissolved' to high molecular weight colloids) followed by measurement of the Hg uptake by DGTs at multiple time intervals. The Hg-organic colloids were made from natural organic matter and synthetic polymers containing strong Hg binding sites (e.g., thiolated polyethylene glycols). The uptake of these colloidal-Hg in the DGT were evaluated by comparing their measured diffusion coefficient through the DGT gel layers. The results from these studies were used to better interpret the biological relevance (e.g., microbial methylation potential) of different Hg size forms taken up by DGTs. The predicted bioavailability was compared to measurements of methylation rates and biological uptake in deposit feeding benthic organisms. Results suggest that the DGTs provide a useful measure of bioavailability compared to traditional measures such as bulk solid concentration or filtered/centrifuged porewater concentrations.

KEY WORDS

Mercury, Colloids, Methylation potential

Passive samplers and biomarkers to assess metal labile concentrations and the associated biological effects: case studies in the North-Médoc salt marshes (Gironde estuary, France) and in the Oiartzun estuary (Spain)

N Montero[a,b,c], Magalie Baudrimont[d], Javier Franco[a*],1 P González[d], P-Y Gourves[d], MJ Belzunce[a]

[a] *Marine Research Division, AZTI-Tecnalia. Herrera kaia, Portualdea z/g 20110 Pasajes, Spain*
[b] *National Research Centre for Environmental Toxicology, ENTOX/University of Queensland, 39 Kessels Road, Coopers Plains, Queensland 4108, Australia*
[c] *IKERBASQUE, Basque Foundation for Science, María Díaz de Haro 3, 48013 Bilbao, Spain.*
[d] *Marine Station of Arcachon, University of Bordeaux, UMR CNRS EPOC 5805, Aquatic Ecotoxicology. Place du Dr Peyneau, 33120 Arcachon, France*
**jafranco@azti.es*

ABSTRACT

The European Water Framework Directive (WFD; 2000/60/EC) and the Marine Strategy Framework Directive (MSFD; 2008/56/EC) refer to contaminants bioavailability and ecotoxicological effects. However, current methods to measure bioavailability suffer from many inadequacies(1) and, besides, traditional spot sampling does not adequately represent the fluctuations of contaminants and their potential toxicity in variable systems. These issues that can lead to incorrect assessment decisions have resulted in greater demand for new in situ testing approaches. The passive sampler Diffusive Gradient in Thin-films (DGT) enables the in situ measurement of labile metal concentrations in waters(2), which is a better proxy to potential biological adverse effects than the routinely measured dissolved metal concentrations. On the other hand, the use of bivalves is widely extended because metals accumulated in their tissues reflect environmental concentrations and the associated biochemical and physiological alterations (i.e. biomarkers) can be used as early indicators of the effects of the chemical compounds on the biota.

This study is a collaborative project that combines for the first time in the Aquitania-Euskadi region the use of in situ DGTs with bioaccumulation and biomarker studies in transplanted oysters (Crassostrea gigas), in estuarine and port waters located in the Basque-French coast. The objective is to establish cause-effect relationships between labile metal concentrations and biological effects for an integrated evaluation of the ecosystem health.

Metal analyses (Al, Cd, Co, Cr, Cu, Ni, Mn, Pb and Zn) of DGTs and oyster tissues were performed by ICP-MS and ICP-OES, respectively. The mercury accumulated in DGTs and in oyster tissues was measured by CV-AAS (AMA 254). The toxicological responses were studied at three levels: physiological impacts (growth, state of reproduction and the condition index of oysters), biochemical responses (metallothioneins (MTs) concentrations: detoxification proteins scavenging metals ; malondialdehyde (MDA) production: final product of lipid peroxydation), and transcriptomic responses (by Quantitative PCR: to quantify the expression of several genes implied in different cellular functions. Three organs were studied: gills, digestive gland and the rest of tissues.

Differences in contamination in both areas of study were detected by means of DGTs, which is in accordance with the different contamination sources present at each site. Also, different bioaccumulation patterns in oysters and specific toxic responses at different levels were observed. The results show higher concentrations of Pb, Zn, Al, Hg and Co in port waters which are related with higher bioaccumulation in the oysters' gills. The protein and genetic responses also show larger alteration in oysters exposed to the port waters.

This study demonstrates that the DGT technique provides excellent information on the bioavailability and potential toxicity of metals. In overall, the integration of chemical and biological tools allowed a comprehensible water quality assessment of these complex systems.

REFERENCES

[1] Simpson, S. L.; Yverneau, H.; Cremazy, A.; Jarolimek, C. V.; Price, H. L.; Jolley, D. F. DGT-induced copper flux predicts bioaccumulation and toxicity to bivalves in sediments with varying properties. Environ. Sci. Technol. 2012, 46, 9038-9046.

[2] Davison, W., Zhang, H., 1994. In situ speciation measurements of trace components in natural waters using thin-film gels. Nature 367:546-548.

KEY WORDS

labile metals, bioaccumulation, biomarkers, oysters

Ion Mapping of the Rhizosphere: Arsenic & Rice

Paul N. Williams[a,b,*], Jakob Santner[c], Morten Larsen[d], Niklas Lehto[e], Eva Oburger[c], Walter Wenzel[c], Ronnie N. Glud[d], William Davison[b], Hao Zhang[b], Yue Gao[f], Dong-xing Guan[g], Gang Li[h], Jun Luo[g]

[a] *Institute for Global Food Security, Queen's University Belfast, David Keir Building, Malone Road, Belfast, Northern Ireland.*
[b] *Lancaster Environment Centre, Lancaster University, UK.*
[c] *Rhizosphere Ecology & Biogeochemistry Group, University of Natural Resources & Life Sciences, Tulln, Austria.*
[d] *Institute of Biology and Nordic Centre for Earth Evolution (NordCEE), University of Southern Denmark, Odense M. Denmark.*
[e] *Faculty of Agriculture & Life Sciences, Lincoln University, New Zealand.*
[f] *Analytical, Environmental & Geochemistry, Vrije Universiteit Brussels, Belgium.*
[g] *School of the Environment, Nanjing University, China.*
[h] *Institute of Urban Environment, Chinese Academy of Sciences, Xiamen, China.*
**Email: p.williams@qub.ac.uk*

ABSTRACT

"Rice is the dominant source of inorganic arsenic in the human diet. If we can fix the rice problem, we can more or less fix arsenic exposure from food. It would make a huge difference." The toxic side of rice (Nature 2014).

Paddy soil biogeochemistry leads to high mobility of the carcinogen inorganic arsenic (iAs). Rice roots are highly efficient at assimilating this toxin, ultimately resulting in rice grain having much higher iAs concentrations compared to other crops. Currently there is grave concern in SE Asia regarding iAs exposures. From the mobilisation of iAs sequestered in soil minerals to it's unloading into the grain, the pathways for iAs speciation are complex, interacting with numerous other elemental cycles (P, Si, C, S, Fe). But despite, the considerable advances made in the last decade in understanding the uptake of iAs by rice, perhaps the largest gap in our knowledge lies with rhizosphere biogeochemical cycling.

Oxygen leaking from submerged rice root surfaces causes a discontinuous covering of ferrous iron to develop on all but the newly emerged root tips. While, affected rhizosphere soils become enriched in iAs by the coupled processes of diffusion and oxidation. However, the role of this rhizoplane 'iron-plaque' remains an enigma. It is not fully known whether root epidermal cells access nutrients (Fe, Mn, Zn) and toxicants (iAs, Cd) directly from these 'iron-plaques'? Or what happens to localised oxyhydroxide accretions when aerobic conditions are no longer sustained? Does the plant actively control their pulsed remobilisation? These questions, and more, remain largely unanswered due to the lack of suitable techniques that can capture the key elemental parameters required to decipher the underlying geochemical processes: i) in situ ii) in two dimensions iii) at appropriate scales (spatial & time) iv) and simultaneously. However, recent advances in DGT ion mapping provide perhaps a new vantage point from which to measure/explore the mercurial chemistries of the rice rhizosphere.

REFERENCES

Rice. Contamination: the toxic side of rice, Nature, 2014, 514, S62-S63.

KEY WORDS

arsenic, rice, rhizosphere, element mapping

Soil phosphorus mobility and solid-to-solution phase resupply studied by DGT

Daniel Menezes-Blackburn[a*], Hao Zhang[a], Courtney D. Giles[b], Timothy S. George[b], Charles Shand[b], David Lumsdon[b], Pat Cooper[b], Renate Wendler[b], Lawrie Brown[b], Marc Stutter[b], Martin Blackwell[c], Tegan Darch[c], Catherine Wearing[a], Philip M. Haygarth[a]

[a] *Lancaster University: Lancaster Environment Centre, Lancaster, LA1 4YQ, UK.*
[b] *James Hutton Institute: The James Hutton Institute, Aberdeen, AB15 8QH and Dundee, DD2 5DA, Scotland, UK.*
[c] *Rothamsted Research: North Wyke, Okehampton, Devon, EX20 2SB, UK.*
** d.blackburn@lancaster.ac.uk*

ABSTRACT

The mobility and resupply of inorganic phosphorus (P) from the solid phase was studied in 32 representative soils from UK. Diffusive gradients in thin films (DGT), diffusive equilibration in thin films (DET) and the DGT-induced fluxes in sediments model (DIFS) were used as tools for exploring solid-to-solution desorption kinetics. On average and across soil types, the inorganic P maximum distance of depletion was 0.42±0.10 cm, the equilibration time (T_c) was 3.63 h, the desorption rate constant (k^{-1}) was 0.0046 h^{-1}, and the desorption rate was 4.71 nmol l^{-1} s^{-1}. Previously characterized physicochemical properties from Stutter *et al.* (2015) of the same soils were used for correlation analysis. The correlation between P_{Olsen} with P_{DGT}, P_{DET} and phosphorus effective concentration (P_E) was enhanced when similar soils were isolated and used in the comparison, clearly showing that these parameters respond differently to different soil types. The P_E was better correlated to most of soil P tests than P_{DGT}, indicating that this parameter may be a better representation of P availability across soil types than P_{DGT}. While the relative DGT-induced inorganic P flux responses in the first hour is mainly a function soil wetting properties and % C_{org}, at longer times it is a function of the resupply capacity (R-R_{diff}) of the soil solid phase. In general, resupply from solid phase was considered low comparing to othercchemichal elements, as shown by high T_c and low K_{-1} values. Desorption rates and resupply from solid phase were fundamentally influenced by P saturation status as reflected by their high correlation with P concentration in water, FeO strips, Olsen and NaOH-EDTA extracts. Despite our previous expectations, soil pH and particle size distribution showed little or no effect on the evaluated parameters. The DGT and DET techniques, along with the DIFS model, were considered accurate and practical tools for studying parameters related to soil P desorption kinetics.

KEY WORDS

DGT, Phosphorus, Nutrient availability, Plants, Soil.

The localisation of phosphorus solubilisation, uptake and release in the rhizosphere of plants with differential nutrient mobilisation strategies

Jakob Santner[a,b,*], Andreas Kreuzeder[a,c], Vanessa Scharsching[a], Rainer Muehlbacher[a], Eva Oburger[a], Christoph Hoefer[a] and Walter W. Wenzel[a]

[a] *Institute of Soil Research, University of Natural Resources and Life Sciences, Vienna, Konrad-Lorenz-Strasse 24, 3430 Tulln, AT*
[b] *Division of Agronomy, University of Natural Resources and Life Sciences, Vienna, Konrad-Lorenz-Strasse 24, 3430 Tulln, AT,*
[c] *Land Salzburg, Abteilung 5 - Natur- und Umweltschutz, Gewerbe, Michael-Pacher-Straße 36, 5020 Salzburg, Austria*
* *jakob.santner@boku.ac.at*

ABSTRACT

Although the mechanisms involved in nutrient uptake by plant roots and plant-mediated mobilization of labile nutrient fractions in soil are well understood, their localization is experimentally challenging. Many previous efforts to investigate nutrient turnover at this small spatial scale suffer from highly artificial growth and sampling conditions, potentially contorting the results and their interpretation. Recent advances in DGT and planar optode chemical imaging techniques offer the unique possibility to obtain data on the localization of plant root nutrient acquisition, solubilization and release around roots growing in soil at high spatial resolution.

In an extensive experimental campaign we investigated the distribution of P around plant roots of buckwheat (*Fagopyrum esculentum* MOENCH), wheat (*Triticum aestivum L.*) and lupine (*Lupinus albus L.*). Simultaneously, the distribution of DGT-labile Ca, Mg, Al and Fe was monitored, as increases in their solubility may indicate the dissolution of phosphate sorbents as well as phosphate minerals in the rhizosphere. These data were complemented by parallel imaging of the rhizosphere pH. In a second study we used a ^{33}P radiotracer technique in combination with DGT sampling and autoradiography to elucidate the sites of P efflux from maize (*Zea mays L.*) roots.

Our results show pronounced P mobilization at the root tips of buckwheat and lupine, which acidify their rhizosphere, while no such P hotspots were found for wheat. P depletion was observed alongside buckwheat roots in acidic soil, as well as along wheat roots in acidic and calcareous soil. Interestingly, zones of P solubilization along up to 10 mm long sections of buckwheat roots in calcareous soils were found. Similarly, such elongated zones of high Mn solubility were found on calcareous soil for buckwheat, wheat and lupine roots. While efflux was previously hypothesized to be evenly distributed across the whole root system surface, our results indicate a strong localization to apical root zones.

This work is the first to study the sub-mm localization of root P uptake and related mechanisms in detail in soil. Our data provide new insight into the spatial distribution of P acquisition and release, and also into the localization of Mn solubilisation by plant roots.

KEY WORDS

Phosphorus, efflux, uptake, rhizosphere, chemical imaging

Measurement of sulfur stable isotope variations in bioavailable sulfate in soils by DGT MC ICP-MS

Ondrej Hanousek[a,b], Jakob Santner[c,d], Torsten W. Berger[b], Sean Mason[e] and Thomas Prohaska[a]

[a] University of Natural Resources and Life Sciences Vienna, Department of Chemistry - VIRIS Laboratory, 3430 Tulln, AT
[b] University of Natural Resources and Life Sciences Vienna, Institute of Forest Ecology, 1190 Vienna, AT
[c] University of Natural Resources and Life Sciences Vienna, Institute of Soil Research, 3430 Tulln, AT
[d] University of Natural Resources and Life Sciences, Vienna, Division of Agronomy, 3430 Tulln, AT
[e] School of Agriculture, Food and Wine, University of Adelaide and The Waite Research Institute, SA 5064, Australia
** ondrej.hanousek@boku.ac.at*

ABSTRACT

Sulfur is an essential plant nutrient and can be found as part of amino acids, proteins or lipids. The main sulfur form taken up by plants is sulfate. Sulfur may undergo various biogeochemical processes in soil, many of which are affecting its bioavailability. Moreover, these processes are known to influence the isotopic composition of SO_4-S. Therefore, analysis of stable sulfur isotopes is a tool to follow biological activity and geochemical processes, which affect the availability of sulfate to plants in soils.

A classical method to analyze the content and isotopic composition of bioavailable SO_4-S in soil is soil extraction (e.g. using NH_4NO_3) followed by precipitation ($BaCl_2$) and mass spectrometric analysis using isotope ratio mass spectrometry (IRMS). However, sulfate precipitation is sample consuming and/or demands high contents of sulfate in the sample. Multi collector inductively coupled plasma mass spectrometry (MC ICP-MS) allows for the direct measurement of S isotopes in a solution even in the sub-mg/g range (only limited by the S background concentration). The measurement is however limited due to effects of co-extracted matrix elements (K, Ca etc.) on the measurement precision and accuracy. Therefore, an alternative method is required combining the extraction of sulfate from soil and the high sensitivity and isotope ratio measurement accuracy of MC ICP-MS.

We present a DGT method for direct sampling of bioavailable sulfate from soil, even at low concentrations and small amounts of sample. The sampled sulfate can be leached from the resin gel easily in 1 mol L^{-1} HNO_3. The eluate is then directly measured by MC ICP-MS without the need for further matrix element separation. Method parameters (diffusion coefficient in APA2 gel, elution efficiency from resin gel) were determined using ^{35}S as radiotracer. Isotope ratio analysis was optimized using the high resolution capabilities of MC ICP-MS and effects of the sampling procedure on the isotope ratio were investigated in order to ensure that an unbiased isotopic composition of bioavailable S can be assessed.

KEY WORDS

Sulfur, stable isotopes, DGT, MC ICP-MS

Predicting the Uptake of 10 Metals by 5 Vegetables Using DGT

Hao Zhang*, Mark Bescoby, Nigel Paul and Bill Davison

Lancaster Environment Centre, Lancaster University, Lancaster, LA1 4YQ, UK
** h.zhang@lancaster.ac.uk*

ABSTRACT

A potential health risk to humans posed by metal contaminated soils is through uptake of metals to food crops. Many studies have demonstrated that the concentration of metal in the plant is determined by the bioavailability of metal in the soil rather than the total concentration. DGT (diffusive gradients in thin-films), which measures an effective concentration (CE), has so far predicted metal uptake with considerable success. However, very limited work has been reported on using DGT to assess metal concentrations in common vegetables. A comprehensive study was undertaken to establish the relationship between CE and metal concentrations in 5 vegetable species for 15 UK allotment soils representing a range of conditions including contamination with metals.

Soils were collected from 102 allotments. Measurements of CE, soil solution concentration, CaCl2 extractable and total metal concentrations were made in all the soils. On the basis of these measurements, 15 soils that represented a wide range of characteristics and metal concentrations were selected for plant growth experiments. Lettuce, cabbage, carrots, beans and onions were grown in each soil and metals measured in the harvested part of the plant. Metal concentrations, including Al, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb were analysed by ICP-MS (X7, Thermo Elemental).

CE, as measured by DGT, was systematically related to metals in plants for all 10 metals and all plant species. All data for Zn, Cd, Cu and Ni could be fitted by a linear regression. An example is shown in Figure 1. All Al and Cr data were fitted best by a regression based on the equation $y = a \ln x + b$. For Mn, Fe, Co and Pb the best regression equation depended on plant species.

For some metals good fits to the concentration in plants were obtained for concentrations of metals measured in soil solutions (Zn, Pb and Ni) and in CaCl2 extracts (Zn and Ni), but in many cases there was no apparent relationship. The fits were generally less good than for DGT. Cu was the only metal for which the concentration in plants varied systematically with total metal in soils.

This study of the predictive capability of DGT for metals in vegetables confirms that CE measured by DGT is able to predict metal concentrations in plants better than other measurements of metal in soils. Metals measured in both soil solution and in CaCl2 extracts could be used to predict the concentration of some metals in some plants growing in these soils. However, only CE, as measured by DGT, can be used to predict the concentrations of all 10 metals in all 5 plant species tested.

KEY WORDS

metals, bioavailability, vegetable, effective concentrations, soils.

Merging DGT and planar optodes into single-layer probes for simultaneous, co-localized chemical imaging of metals and pH in the rhizosphere

Christoph Hoefer[a*], Jakob Santner[a], Sergey M. Borisov[b], Walter W. Wenzel[a], Markus Puschenreiter[a]

[1]Department of Forest and Soil Sciences, Institute of Soil Research, University of Natural Resources and Life Sciences, Vienna (BOKU), Konrad-Lorenz-Strasse 24, A-3430, Tulln, Austria.
[2]Institute of Analytical Chemistry and Food Chemistry, Graz University of Technology, Stremayrgasse 9, A-8010, Graz, Austria
**christoph.hoefer@boku.ac.at*

ABSTRACT

In rhizosphere research, passive and diffusion-based sampling techniques such as diffusive gradients in thin films (DGT) and planar optode sensors (POS) are emerging tools.

Recently, a high resolution mixed binding gel (HR-MBG) was developed for simultaneous imaging of anionic and cationic species. This gel is urethane-based (Hydromed D4) and contains a mix of Zr-hydroxide and suspended particulate reagent-iminodiacetate (SPR-IDA) as binding agents.1 After solute sampling, the gel is analysed by laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS) and an image is derived from the acquired data.

POS are thin films of an analyte-specific fluorophore-hydrogel cocktail, coated onto a polyester support foil. Fluorescent colour-ratiometric imaging is based on (i) excitation of the fluorophore at a specific wavelength, (ii) emission of fluorescent light by the excited fluorophore in response to the analyte concentration and (iii) capture of the raw RGB camera signal.2 After calibration of the RGB data, the image is plotted using image analysis software.

Here we attempt to merge DGT and POS in a single gel layer for simultaneous, co-localized imaging of dissolved anions and cations and pH. We investigate different combinations of anion and cation resins previously used for DGT imaging in combination with DCIFODA (2´,7´-dichloro-5(6)-N-octadecyl-carboxamidofluorescein) as pH indicator.

Preliminary results indicate interferences of anion binding materials with DCIFODA protonationfor both, synthetic anion exchange resins and (oxy)hydroxide minerals. . Long equilibration times (>72h) were observed and might have been partly caused by the ampholytic properties of the (oxy)hydroxide surfaces. Cation chelating resins such as SPR-IDA showed no interferences due to their different solute binding mechanism and showed shorter equilibration times (90 min). For gel characterisation, we tested the DGT properties for gel capacity, resin gel homogeneity, blank levels, LOD and LOQ and the POS properties for emission spectra of DCIFODA, performance and RGB calibration, equilibration time and ionic strength dependency.

We conclude that combining POS for pH and DGT has great potential for rhizosphere research.

REFERENCES

1. Kreuzeder, A.; Santner, J.; Prohaska, T.; Wenzel, W. W., Gel for simultaneous chemical imaging of anionic and cationic solutes using diffusive gradients in thin films. Anal Chem 2013, 85, (24), 12028-36.
2. Larsen, M.; Borisov, S. M.; Grunwald, B.; Klimant, I.; Glud, R. N., A simple and inexpensive high resolution color ratiometric planar optode imaging approach: application to oxygen and pH sensing. Limnol Oceanogr-Meth 2011, 9, (SEP), 348-360.

KEY WORDS

co-localized chemical imaging, pH, solutes, gel development, planar optodes, LA-ICP-MS

Use and assessment of passive samplers by the French water national and regional authorities to improve the WFD implementation

Pierre-François Staub [a]

[a]Onema, 5 square Nadar, 94300 Vincennes, France.
Pierre-francois.staub@onema.fr

ABSTRACT

The Water framework directive (WFD, 2000/60/EC) does regulate the monitoring of tens of chemicals in waters by members states and river basin authorities, as well as the assessment of the water bodies status by comparisons of the chemical annual average concentrations with environmental quality standards (EQS). The decision to undertake expensive corrective measures to ensure good chemical status relies upon the reliability of the above status assessment, which itself largedly depends on the representativity of the sampling. Grab sampling once a month is the typical way to address the chemical monitoring under WFD, but this might give ground to large uncertatinty with respect to both temporal and concentration representativities of the derived average values. Moreover, more recent daughter directives of WFD promote the monitoring of bioaccumulative chemicals in aquatic biota, which poses many issues in terms of accessing organisms, in a comparable way, at all surveillance sites.

With regards to these issues, integrative passive samplers theoretically offers better sampling representativity, and could also be used for preliminary assessment of water quality prior to undertake biota sampling. On the other hand, passive sampling still exhibits weaknesses, especially with respect to the reliability of the data interpretation of the sampled chemical quantity.

During the recent years various developpements and studies have been stimulated in France by national and river basin authorities, and conducted by research institutes, in order to assess the performances and practical aspects of passive sampling, adressing metals (using DGT) or organic compounds contaminations (hydrophobic or hydrophilic compounds considered separately) of either surface or ground waters. This lecture will attempt to provide a general scope of these activities, ranging from R&D up to the production of strategic recommendations for policy makers and scientists, emphasizing also some necessary and instructive activities such as the coordination of collaborative tool performance assessment events, on the ground studies (at both local and national scales), or the delivery of technical guidances and recipes for passive sampler users.

KEY WORDS

WFD, chemical monitoring, Passive sampling, Integrative sampling, DGT, POCIS, SBSE, SPMD,

Assessment of the Production of Diffusive Gradient Thin Films (DGT) and Associated Quality Control Protocols in a University Laboratory Setting

Julia Caprio[a*], Danny Reible[b]

[a]*Geosyntec Consultants, Knoxville Tennessee, USA*
[b]*Civil and Environmental Engineering, Texas Tech University, Lubbock, Texas, USA*
**Jklenscaprio@geosyntec.com*

ABSTRACT

Assessing environmental conditions through the use of passive sampling devices such as diffusive gradient thin film (DGT) is becoming more widely recognized as a viable sample collection tool. This is especially true for measuring analytes such as Mercury (Hg) and methylmercury (MeHg) which are of substantial concern in sediment environments for pore water measurements. DGTs are most commonly produced in non-commercial settings such as university laboratories where rigorous quality control practices may not be routinely employed. Since there is currently no regulatory guidance that indicates how DGTs should be produced or utilized for sampling in environmental settings, standardization of DGTs is not required or monitored. Additionally the transient work force inherent to university laboratories can provide challenges to achieving consistent quality if standard operating procedures (SOPs) are not developed and maintained during research and investigative ,activities. Therefore it is incombant on the laboratory to make a concerted effort to establish a strong quality assurance culture.

Data used for site characterization, human and environmental risk based studies, and remedial design must be defensible, transparent, and of known quality. The first line of defense for achieving data that meet these requirements is to collect samples in an appropriate manner using collection devices that are shown to be free of the contaminants of concern prior to sample collection and after sample collection and analysis. Other parameters, such as extraction efficiencies, also need to be confirmed and documented. This is accomplished by incorporating quality control procedures into DGT production, sampling protocols and sample analytical methodologies.

This presentation will describe the results of a quality audit of a university laboratory involved in producing DGTs for sampling and then subsequent extraction and analysis for mercury and methyl mercury. The audit involved review of SOPs developed by the laboratory, the laboratory quality manual, and documentation performed by the laboratory staff that trace quality control measurements and results.

KEY WORDS

Quality Control, Mercury, Methyl Mercury, Pore water

"Large scale" application of the passive sampling techniques: Evaluation of DGT technique as a monitoring tool for the assessment of the chemical status of water bodies

Gonzalez J-L.[a*], Foan L.[b], Montero N.[c,d,e], Belzunce-Segarra M-J.[c]

[a] *Ifremer Unité "Biogéochimie et Ecotoxicologie" CS 20330 Zone Portuaire de Brégaillon, 83507 La Seyne/mer Cede, France.. Tel: 33 (4) 94 30 48 56 ; Fax: 33(4) 94 30 44 17*
[b] *CEA, LETI, Département des micro-technologies pour la Biologie et la Santé. 17 rue des Martyrs, 38054, Grenoble Cedex 9, France.*
[c] *Marine Research Division, AZTI-FOUNDATION, Muelle de la Herrera, Recinto Portuario s/n, 20110 Pasaia, Spain.*
[d] *National Research Centre for Environmental Toxicology, ENTOX/University of Queensland, 39 Kessels Road, Coopers Plains, Queensland 4108, Australia*
[e] *IKERBASQUE, Basque Foundation for Science, María Díaz de Haro 3, 48013 Bilbao, Spain*
* *Jean.Louis.Gonzalez@ifremer.fr*

ABSTRACT

In the aquatic environment, most chemical contaminants occur at trace levels, especially in the "dissolved fraction". The use of passive samplers enables the extraction and concentration of many compounds in situ, reducing some of the difficulties and costs related to the analysis of contaminants at trace levels (sampling, treatment of the sample before analysis, possible contamination during the various stages). These techniques also ensure low disturbance of the speciation of sampled contaminants (no water sampling, filtration or storage steps). Another considerable advantage is that these techniques can be easily implemented by non-specialist (but previously sensitized and trained) staff.

For many contaminants, the use of the passive sampling techniques can already contribute to the development strategies implemented in the Water Framework Directive. The aim is to provide a reliable, fast and low cost assessment of contamination of water bodies. These techniques can be used for continental waters (ground and surface) and marine waters. The implementation of the WFD and the many control programs related to the directive will result in a significant increase in time and money spent on operations of sampling and analysis of these different water masses.

Since 2008, various projects supported by French government agencies were dedicated to test the potential use of different techniques (DGT, POCIS, SBSE) for the assessment of chemical contamination of water bodies by trace metals, hydrophilic and hydrophobic organic compounds under the WFD.

Chemical status of coastal and transitional water bodies has been assessed at a "large scale" by passive sampling techniques developed by the Ifremer. With passive sampling techniques (DGT, POCIS, SBSE), concentrations of many pollutants (trace metals, pesticides, PAHs, PCB, alkylphenols and pharmaceutical compounds) have been measured in their "dissolved" forms. The studies showed the operational assets of these systems, as low quantification limits required by the WFD are reached and ensure measurement of metals and organic pollutants at trace levels, which are generally difficult to quantify with classical methods (particularly in marine waters).

The key objective of these study is to test in "large scale", in different "field conditions" the operational capability of these systems in terms of cost reduction, reliability and speed results acquisition, but also in terms of ease of implementation (by non-specialist personnel).

This presentation will focus on the results obtained by the DGT technique (trace metals), limitations and advantages of this passive sampling technique and its application in the context of the WFD.

KEY WORDS

Contaminants concentration, trace metal, coastal water, WFD, DGT.

Monitoring bioavailability of metals and metalloids in river water receiving mine water discharge using DGT

Trang Huynh[a*], Sue Vink[b]

[a] Centre for Mined Land Rehabilitation, Sustainable Minerals Institute, The University of Queensland, Brisbane, QLD, 4072 AUSTRALIA
[b] Centre for Water in the Minerals Industry, Sustainable Minerals Institute, The University of Queensland, Brisbane, QLD, 4072 AUSTRALIA
*trang.huynh@uq.edu.au

ABSTRACT

The ecological risk associated with heavy metals in water is currently assessed using the total and dissolved concentrations (ANZECC, 2000). In fact, the biological response of organisms to metals in water is proportional to the free-ion activity of the metals rather than to their total or dissolved concentrations (Templeton *et al.*, 2000). Determining the bioavailable fractions of metals in water is recognised as a necessary step for assessing their effect on biota and for assessment of water quality by researchers and regulators (Batley *et al.*, 2004). The Diffusive Gradients in Thin film (DGT) technique has been reported as a surrogate for mussel bioaccumulation (Cu, Cd, Pb and Zn) (Webb and Keough, 2000) and rainbow trout (Cu) (Luider *et al.*, 2004). Copper toxicity on *Daphnia magna* could be predicted from DGT measurements (Tusseau-Vuillemin *et al.*, 2004).

Coalmine water release into the river during recent wet seasons has raised concerns about the impact of metals on the aquatic biota. The water quality monitoring data showed that occasionally total and dissolved metals (e.g. Cr, Cu, Ni and Zn) exceeded the ANZECC (2000) guidelines. The bioavailable fractions of these metals measured by the DGT technique varied. In the case of Cu, as an example, the bioavailable concentrations measured by the DGT technique were significantly lower, 13% and 23% respectively, than the measured total Cu and dissolved Cu concentrations. The bioavailability of other metals including Cd, Ni and Zn ranged from 60% to 80% of the dissolved concentrations. This is likely due to their differences in elemental characteristics and the physicochemical properties of the water column and the complexation of Cu strongly affects the bioavailability of Cu (Renner, 1997).

The outcomes of this project provide the benefits in allowing researchers and regulators to more accurately assess the ecological risk associated metals in water.

KEY WORDS

metals, bioavailability, water quality

Mobile passive sampling with DGTs for the measurement of trace metals in seawater

Marco Schintu[a*], Barbara Marras[a], Alessandro Marrucci[a], Daniela S. Pace[b] , Silvia Giuliani[c]

[a] Università di Cagliari, Cagliari (Italy);
[b] Oceanomare Delphis, Rimini (Italy);
[c] ISPRA, Istituto Superiore per la Protezione e la Ricerca Ambientale, Livorno (Italy)
** schintu@unica.it*

ABSTRACT

In July 2014 the once luxury vessel Costa Concordia arrived at the northern Italian city of Genoa after a four-day, 320-kilometre journey from the Tuscan island of Giglio where it shipwrecked. The transfer was carried out at an average speed of about two knots per hour. With the aim of evaluating the mean concentration of organic and inorganic contaminants in bioavailable form released from the wreck during the voyage, a total of 27 DGT devices (9 DGTs with Chelex resin for Cd, Cr, Cu, Ni and Pb, 9 DGTs with Spheron-Thiol resin for Hg, 9 DGTs with Fe-oxyde resin for V) were attached with ropes at the aft ship. The DGTs were kept at the seawater surface by buoys. The wreck also dragged 3 canisters each of them containing 3 SPMD and 3 POCIS for the measurement of apolar and polar organic contaminants. All the samplers were retrieved before the wreck entered the harbor of Genoa, in order to avoid contamination. The background was achieved by attaching the same passive samplers to a sailboat that preceded the wreck. The experiment for the first time provided information on the average concentration of trace metals in a wide area of the Western Mediterranean. Besides, this work discusses the possibility of using DGT for spatial measures of contaminants in seawater, even through the use of instrumentation installed on board of commercial ferries, such as the Ferrybox.

KEY WORDS

DGTs, seawater, mobile passive sampling, Costa Concordia

DGTs, a complementary tool towards more efficient biomonitoring practices

Jonathan Richir[a,b,c,*], Gilles Lepoint[b], Annick Donnay[a,b], Pierre Lejeune[a], Krishna Das[b], Sylvie Gobert[b]

[a] STARESO SAS, Pointe Revellata, BP 33, F-20260 Calvi, France
[b] Laboratory of Oceanology, MARE Centre, University of LIEGE, B6C, 4000 LIEGE, Sart Tilman, Belgium
[c] Numerical Ecology of Aquatic Systems, University of Mons, Pentagone 3D08, 6, Avenue du Champ de Mars, 7000 Mons, Belgium
* jonathan.richir@alumni.ulg.ac.be

ABSTRACT

Among the diversity of contaminants, trace elements (TEs) remain of concern because of their persistence, their ability to accumulate in biota and their toxicity. The direct measurement of their dissolved concentrations only gives punctual and fluctuating information, and often remains below detection limits of analytical methods. The more appropriate use of sentinel organisms, or bioindicators, to monitor TEs has thus often been preferred in environmental surveys. The introduction of the diffusive gradients in thin films (DGTs) technique has however participated to progressively change this binary view - bioindicator vs water - of the coastal monitoring of TEs, and DGTs rapidly became a relevant complementary tool to bioindicators, has illustrated below.

In the framework of the STARECAPMED project, the ecology and the ecotoxicology of TEs were studied in the seagrass *Posidonia oceanica* (L.) Delile and the mussel *Mytilus galloprovincialis* Lamarck, 1819. DGTs (free- and pore-water probes) were deployed before sampling of organisms. TEs were also analyzed in suspended matter (dissolved and suspended-particulate TE speciation). Studies were performed in the Calvi Bay (Corsica, France), northwestern Mediterranean. TE concentrations in organisms and suspended matter or in DGT resins were measured by DRC-ICP-MS after HNO3/H2O2 mineralization or after a 24h elution in HNO3 1M, respectively.

(1) TE bioaccumulation was first seasonally studied in *P. oceanica* over 3 years. Dissolved TE concentrations monitored with DGTs were low to very low. TE bioaccumulation dynamics in *P. oceanica* could thus be linked to the natural physiological cycle of the plant, in clean environmental conditions. (2) To complement that field survey, isolated seagrasses were *in situ* contaminated with TEs at environmental relevant concentrations. Through the use of DGTs, TE uptake kinetics were modelled for seagrasses exposed to know bioavailable concentrations of contaminants, as were loss kinetics during the following depuration phase. The TE sequestration ability of a healthy *P. oceanica* meadow facing sudden trace metal contamination events could also be quantified. (3) The deployment of pore-water DGT probes in bare-sand or seagrass colonized sediments further showed that, through its stabilizing function of the seabed, *P. oceanica* maintained higher TE levels in the pore-water. *P. oceanica* meadows thus offer a significant "depuration-filtering" ecological service along highly anthropized Mediterranean coasts. *M. galloprovincialis* are widely used in large spatial scale coastal monitoring surveys. (4) The deployment of caged mussels together with DGTs showed that the little contaminated water body of the Calvi Bay was relatively homogenous. It also allowed to calculate TE bioaccumulation towards mussels in reference conditions, and to compare it to native mussel populations. (5) Finally, during a 5 months mussel caging survey, mussels and suspended matter were collected weekly to monthly, such as were deployed DGTs. The physiological status of mussels, the speciation of TEs between their dissolved and suspended-particulate phases, and their relative influence on TE bioaccumulation dynamics in mussels were investigated. In conclusion, these case studies properly demonstrate how DGT probes can be used as a relevant and complementary tool to bioindicators. Their concomitant use should therefore be privileged in monitoring surveys.

KEY WORDS

DGT, monitoring, bioindicator, trace element speciation

An in-depth assessment into simultaneous monitoring of dissolved reactive phosphorus (DRP) and low-molecular-weight organic phosphorus (LMWOP) in aquatic environments using diffusive gradients in thin films (DGT)

Christian Wilhelm Mohr[a*], Rolf David Vogt[a], Oddvar Røyset[b], Tom Andersen[c] and Neha Amit Parekh[a]

[a] *Department of Chemistry, University of Oslo, Norway*
[b] *Norwegian Institute for Water Research (NIVA), Oslo, Norway*
[c] *Department of Bioscience, University of Oslo, Norway*
** c.w.mohr@kjemi.uio.no*

ABSTRACT

Long-term laborious and thus costly monitoring of phosphorus (P) fractions is required in order to provide reasonable estimates of the levels of bioavailable phosphorus for eutrophication studies. A practical solution to this problem is the application of passive samplers, known as Diffusive Gradient in Thin films (DGTs), providing time-average concentrations. DGT, with the phosphate adsorbent Fe-oxide based binding gel, is capable of collecting both orthophosphate and low molecular weight organic phosphorus (LMWOP) compounds, such as adenosine monophosphate (AMP) and myo-inositol hexakisphosphate (IP6). The diffusion coefficient (D) is a key parameter relating the amount of analyte determined from the DGT to a time averaged ambient concentration. D at 20 °C for AMP and IP6 were experimentally determined to be 2.9×10^{-6} cm^{2}s^{-1} and 1.0×10^{-6} cm^{2}s^{-1} respectively. Estimations by conceptual models of LMWOP uptake by DGTs indicated that this fraction constituted more than 75% of the dissolved organic phosphorus (DOP) accumulated. Since there is no one *D* for LMWOP, a *D* range was estimated through assessment of *D* models. The models tested for estimating *D* for a variety of common LMWOP molecules proved to be still too uncertain for practical use. The experimentally determined *D* for AMP and IP6 were therefore used as upper and lower *D*, respectively, in order to estimate minimum and maximum ambient concentrations of LMWOP. Validation of the DGT data was performed by comparing concentrations of P fractions determined in natural water samples with concentration of P fractions determined using DGT. Stream water draining three catchments with different land-use (forest, mixed and agriculture) showed clear differences in relative and absolute concentrations of dissolved reactive phosphorus (DRP) and dissolved organic P (DOP). There was no significant difference between water sample and DGT DRP ($p > 0.05$). Moreover, the upper and lower limit *D* for LMWOP proved reasonable as water sample determined DOP was found to lie in-between the limits of DGT LMWOP concentrations, indicating that on average DOP consists mainly of LMWOP. “Best fit” *D* was determined for each stream in order to practically use the DGTs for estimating time average DOP. Applying DGT in a eutrophic lake provided insight into P cycling in the water column.

KEY WORDS

Phosphorus, Low-Molecular-Weight Organic Phosphorus, eutrophication, diffusive membrane restriction, diffusion modelling

Field evaluation of o-DGT for in situ measurement of pharmaceutical and personal care ingredients in wastewaters

Wei Chen[a*], Yanyin Li[a], Olive R Price[b], Chang’er Chen[a], Hong Li[a], Hao Zhang[a], Andy J. Sweetman[a] and Kevin C. Jones[a]

[a] *Lancaster Environment Centre, Lancaster University, Lancaster, LA1 4YQ, UK*
[b] *Safety and Environmental Assurance Centre, Unilever, Sharnbrook, MK44 1LQ, UK*
* *w.chen5@lancaster.ac.uk, Craig040051@gmail.com*

ABSTRACT

To evaluate the applicability of o-DGT under field conditions for the measurement of ingredients of pharmaceuticals and personal care products, HLB-o-DGT devices were deployed *in situ* at a wastewater treatment plant (WWTP) in the UK for 2 weeks and compared with active sampling approaches (both grab-samples and auto-samplers).

All 11 target chemicals, except IPRP[1], were detected in the influent, for both active and passive sampling; while only 9 of 11 chemicals (except IPRP and PRP) were found in the effluent. For most of the detected chemicals, the mass accumulated into the o-DGT increased linearly with deployment time for 14 days in both the effluent and influent and confirmed the o-DGT is capable for field water sampling application and can provide quantitative measurements of pharmaceuticals and personal care products.

The 14-day time-weighted average (TWA) concentrations of detected chemicals measured by o-DGT were calculated and compared with the average concentration of active samples. It was noticed that, o-DGT TWA-concentrations were generally different from the results of active samples. One possible reason could be that o-DGT accumulated only the dissolved labile fraction of compounds, but grab/auto samples also contained some particulate fraction although filtered (0.7 µm) which led to higher concentrations. The lack of representative grab/auto samples could be another reason for the differences between the two sampling methods, while o-DGT accumulated target compounds throughout the period, measuring a TWA-concentration.

REFERENCE

1. Wei Chen, *et al.* A Passive Sampler for in situ Measurement of Pharmaceutical and Personal Care Ingredients in Waters. 23rd Annual Meeting of SETAC Europe, Glasgow, UK. May 12-16, 2013

KEY WORDS

o-DGT, Pharmaceutical and personal care products, Wastewater

Assessment of seasonal inorganic arsenic speciation in surface waters of a small vineyard watershed by passive sampling

Aymeric Dabrin[a*], Marie Chappedelaine[a], Aurélie Larrose[a], Lysiane Dherret[a], Linda Ayouni-Derouiche[b], Frédérique Barbier-Besueille[b], Marina Coquery[a]

[a] *Irstea, UR MALY, 5 rue de la Doua-CS70077, F-69626 Villeurbanne cedex, France*
[b] *ISA, UMR 5280, 5 rue de la Doua-CS70077, F-69626 Villeurbanne cedex, France*
** aymeric.dabrin@irstea.fr*

ABSTRACT

Surface waters of the Ardières and Morcille Rivers (South-East of France) are polluted by arsenic (As), with total dissolved As concentrations reaching up to 40 µg/L. These high concentrations are resulting from natural high geochemical background and from utilization of enriched-As pesticides until 2001. High frequency monitoring of surface waters during 3 years showed a strong seasonal variability of total dissolved concentrations of As, with low concentrations in winter (high flow, 2-3 µg/L) and high concentrations in summer (low flow, 20-40 µg/L). These findings suggest that there is a more pronounced contribution of low-oxygenated water originating from groundwater to the river during summer than during winter period. Under this assumption, we suggest that dissolved concentrations of reduced As (As III) in the river are probably also higher in summer than in winter. Since the reduced form of As (As III) is known to be more toxic for aquatic organisms than the oxidized form of As (As V), there is a need to assess the temporal variability of inorganic As speciation in these surface waters. Yet, a practical difficulty stands from the fact that inorganic forms of As are highly unstable, especially when pH and/or redox potential vary.

Passive sampling technique such as Diffusive Gradient in Thin films (DGT) presents several advantages to better assess *in-situ* As speciation. Indeed, by directly trapping in-situ As III and As V, permits to avoid contamination problems, especially by reducing likely modification of speciation during water sampling and storage. Thus, we worked with commercially available DGT with a resin constituted by ferrihydrite (DGT-FH). Firstly, we determined diffusive coefficients of As III and As V by realizing laboratory kinetic experiments. Then, we tested several extractants (HNO_3 0.8M, HNO_3 1M, HCl 4M with acid acetic 10% and hydroxylamine 0.4M) to maximize the resin extraction step and its reproducibly for the two As species, by minimizing transformation of As III into As V. We also optimized the HPLC-ICP-MS analytical method, including limit of quantification (0.5 µg/L).

Finally we deployed triplicates of DGT-FH during 1 week, in summer and in winter, in the Ardières and Morcille Rivers to assess inorganic As speciation. Kinetic experiments allowed determining diffusive coefficients for As III ($6.52\ 10^{-6}$ cm² s^{-1}) and As V ($4.76\ 10^{-6}$ cm² s^{-1}), which are in the same range as those found in literature. In-situ deployments showed that DGT-FH was well adapted to trap As III and As V during the summer campaign. Results highlighted that in low flow conditions, As III concentrations in surface waters were ~1 µg/L, accounting for 5 to 10 % of total dissolved As concentrations. Results of the winter campaign are in progress and will also be presented. This study provides the first attempt to develop an integrative method allowing to trap inorganic species of As in-situ by DGT-FH, then extract and analyze the As speciation by HPLC-ICP-MS at low environmental concentrations. Moreover, this approach allowed to better characterizing temporal variability of aquatic organisms exposed to As species in surface water.

KEYWORDS

Inorganic arsenic, seasonal variability, speciation

The application of DGT technique for the estimation of the bioavailable fraction of uranium in mining impacted environments

Jagoda Drozdzak[a]*, Martine Leermakers[a], Yue Gao[a], Vannapha Phrommavanh[b], Michael Descostes[b]

[a] Environmental Chemistry and Geochemistry (AMGC), Vrije Universiteit Brussels (VUB), Pleinlaan 2, 1050 Brussels, Belgium
[b] AREVA Mines - DEXP/DRD, Tour AREVA, 1 Place Jean Millier, 92084 Paris La Défense, France
** jdrozdza@vub.ac.be*

ABSTRACT

Uranium is a *primordial, naturally-occurring radionuclide, however its natural abundance in terrestrial and aquatic ecosystems might be elevated by several anthropogenic activities*. Considering its tendency to migrate in natural waters, U poses potential risk to aquatic biota and therefore threatens human beings along the food chain, what becomes a subject of an interest of many researchers from different fields (i.e. biology, toxicology, environmental chemistry). Although the radiological impact of uranium is determined by the total concentration, the aquatic chemistry, chemical toxicity and bioavailability (*i.e.* the ability to bind or traverse the cell surface of an organism) are determined by chemical speciation. In this context, the Diffusive Gradients in Thin Films (DGT) technique is a potential monitoring tool for the bioavailable fraction, as it provides *in situ* measurement of the time-averaged concentrations of labile metal species in solution.

This study provides for the first time an insight on the feasibility of the DGT technique for the estimation of U labile fraction in mining impacted environments. Those environments are characterized by pH variations, high ionic strength and high concentrations of competing and interfering ions. Thus, the binding phase used must have a high and selective binding capacity towards U and display a good performance under the environmental and mining conditions.

The DGT technique for the determination of uranium species was evaluated in the laboratory tests with different resins used as a binding phase, that were investigated under the conditions encountered in mining environments. A new resin- Diphonix® (Eichrom Technologies) was investigated and compared with previously used resins for uranium, Chelex®-100 and Metsorb™. The DGT gel preparation and the elution procedures were optimized for Diphonix® resin, resulting in very low MDL and good elution efficiency. All resins demonstrated a very good performance across a wide pH (3 9) and ionic strength (0.001 0.7 M $NaNO_3$) range. Diphonix® resin gel exhibited greater U capacity, than Chelex®-100 and Metsorb™ resin gel discs. Possible interferences with Ca^{2+} (up to 12.5 mM), PO_4^{3-} (up to 0.05 mM), SO_4^{2-} (up to 2.1 mM) and HCO_3^- (up to 8.2 mM) on U-DGT uptake were investigated as well. Diffusion coefficients of uranium at different pH were determined using both, a diffusion cell and U uptake on DGT devices, demonstrating the necessity of the implementation of the effective diffusion coefficients into U-DGT calculations.

This study has shown the importance of a comprehensive laboratory evaluation of a new application of DGT technique prior the field investigation. Furthermore, the use of Diphonix® resin leads to significant advance in the development of DGT technique for U speciation and its applicability for the estimation of labile U fraction in mining impacted environments.

KEY WORDS

Uranium species, DGT, Uranium diffusion coefficients, Chelex®-100, Metsorb™, Diphonix®

Environmental impact assessment of a metal alloy production plant on the water quality of a tributary of the largest Brazilian river (São Francisco River)

Fonseca, Rita*, Araújo, António, Martins, Luísa, Dias, Nuno, Gomes, Catarina, Matos, João

Department of Geosciences, School of Sciences and Technology and Institute of Earth Sciences, University of Évora, Portugal
**rfonseca@uevora.pt*

ABSTRACT

Over more than 50 years, the activity of one of the world's largest metal alloy producers, located in the margins of São Francisco River (SF), Brazil, have produced tailings that have been accumulated in the surrounding area. The lack of an environmental concern lead to a heavy metal contamination, much above the critical levels, which accumulate in the soils of the drainage area and in the sediments and water column of the nearby waterways.

To reverse the negative impact of this contamination and to prevent its extension to the largest Brazilian river, under the request and payment of the company, it has been conducted an extensive study to characterize the area affected by the industrial activity, with particular emphasis on the geochemistry of the soils, sediments and water column. This work aims to discuss the heavy metal contamination level of the water of a small waterway, tributary of SF, which receive all the drainage coming from the affected area. Beside the knowledge of its extent, this study also sought to discuss its linkage with the levels and chemical forms in which metals occur in the sediments accumulated in the bottom and alluvial plains.

The analysis of the waterway was performed in the rainy and dried season. Two different studies had been done: (1) water sampling; (2) placing DGT (Chelex and Fe-oxide Gel) at various depths in water for 5 days. At the time of the sampling and of the placement/collection of DGT, it was recorded the time and measured physical-chemical parameters (temperature, pH, conductivity , redox potential). Water samples (acidified) and DGT, were chilled since the time of collection until the analysis in laboratory. The resin of the DGT was placed in acid solutions to give the passage of ions into the aqueous phase (1) 1M HNO_3 solution, 24H for Chelex DGT and (2) 0,25M H_2SO_4 solution, followed by shaking for 2H, for Fe-Oxide DGT. The solutions and the filtered water samples were analyzed for metallic elements (As, Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn) by ICP-OES in axial view mode, coupled with an ultrasonic nebulizer.

The analysis of physic-chemical parameters showed higher values of Eh and conductivity and a pH reduction in the dried period. Among the analyzed elements, Cd, Cu, Mn and Zn are in failure in respect of the limit allowed for fresh waters, in particular Zn which has contents about a hundred times higher. These values are in agreement with the high concentrations found in sediments and the chemical forms in which metals preferably occur, soluble phase in pore water and as exchangeable cations, demonstrating the high mobility of these elements and their environmental hazard. For the effectiveness of the environmental remediation of this area and for the improvement of the water quality, it's urgent to prevent the migration of toxic elements to São Francisco River. To do this, it's necessary to cease all contamination sources and to establish a soil and alluvium recovery strategy, which lead to the chemical immobilization of these metals.

Development of DGT for the analysis of anticancer drugs in water samples

Helena Franquet-Griell[a*], Chang-Er Chen[b], Silvia Lacorte[a], Hao Zhang[b], Kevin Jones[b]

[a] *Department of Environmental Chemistry IDAEA-CSIC. C/Jordi Girona 18, 08034, Barcelona*
[b] *Lancaster Environment Centre, Lancaster University, Lancaster, LA1 4YQ, United Kingdom*
* *hfgqam@cid.csic.es*

ABSTRACT

The incidence of cancer has increased considerably in the last years. Cancer is treated with cytostatic drugs which can be excreted unchanged or modified as metabolites and be discharged into the sewer system. Besides, elimination of these drugs in waste water treatment plants (WWTPs) is often incomplete and they can finally reach surface waters. The level of these compounds in the environment can be highly variable and depends on many factors: their consumption patterns, the excretion fraction and the effectiveness of the processes used for wastewater treatment. For this reason passive sampling provides a great advantage for the monitoring of these compounds, providing time-integrated data. In particular, diffusive gradients in thin films (DGT) provide *in situ* measurements without field calibration. This sampler has been widely applied for inorganic species [1], and recently extended to some organic chemicals such as antibiotics, bisphenols [2-3]. The application of DGT technique for cytostatic drugs would be of great interest.

The aim of this work was testing the o-DGT (DGT for organics) for six anticancer drugs, selected among the most persistent cytostatics in the environment. Agarose diffusive gel was used and two different binding resins (XAD18 and HLB) and different filters (PES and GHP) were tested. Diffusion coefficients for the six compounds were measured using a diffusion cell. The mass accumulated by o-DGT samplers increased with time and decreased with diffusion layer thickness, following the principle of DGT theory. The DGT measurements in concentration were independent of pH (5-8) and ionic strength (0.001-0.5M). Both XAD18 and HLB showed high capacity and quick adsorption kinetics. The different tests performed showed that both resins are suitable as binding layer in o-DGT.

REFERENCES

1 Villanueva, J.D., *et al.*, *Trends of labile trace metals in tropical urban water under highly contrasted weather conditions*. Environmental Science and Pollution Research, 2015.

2 Chen, C.E., *et al.*, *JEM, 2012* and ES&T 2013..

3 Zheng, J.L., *et al.*, *Activated charcoal based diffusive gradients in thin films for in situ monitoring of bisphenols in waters*. Analytical Chemistry, 2015. 87(1): p. 801-807.

KEY WORDS

o-DGT, anticancer drugs, water,

Determination of total arsenic using a novel Zn-ferrite doped resin for DGT techniques

Josselin Gorny[a], Ludovic Lesven[a], Gabriel Billon[a], David Dumoulin[a], Catherine Noiriel[b], Caroline Pirovano[c] and Benoît Madé[d]

[a] Laboratory LASIR; UMR CNRS 8516 – University Lille 1, Sciences and technologies, Villeneuve d'Ascq, France
[b] Laboratory Géosciences Environnement Toulouse, Observatoire Midi-Pyrénées, UMR 5563 – University Paul Sabatier, CNRS, IRD, Toulouse, France
[c] Laboratory UCCS; UMR 8012 CNRS – University Lille 1, Villeneuve d'Ascq, France
[d] French National Radioactive Waste Management Agency (Andra), Research and Development Division (DRD), Châtenay-Malabry, France

ABSTRACT

A new home-made Zn-ferrite ($ZnFe_2O_4$) resin is fully tested using DGT (Diffusive Gradient in Thin films) probes to measure total As [including inorganic As(III) and As(V), as well as $MMAA^V$ (MonoMethyl Arsenic Acid) and $DMAA^V$ (DiMethyl Arsenic Acid)] in natural waters. Several series of triplicate tests have been carried out to validate the use of the Zn-ferrite resin in the most of aquatic compartments, in order to test: (i) pH effects on the accumulation efficiency of inorganic As species, (ii) reproducibility of the results, (iii) accumulation efficiency of As species, (iv) ionic strength effects and possible competitive anions, and (v) elution efficiency of As species after accumulation in the resin. This new binding resin has been compared with two classical resins (ferrihydrite and Metsorb® HMRP 50) using the same experimental conditions. In conclusion, the most adapted resin for measurement of total As in water column and sediments will be defined.

KEY WORDS

arsenic, DGT, analytical development, Zn-ferrite

Diffusion coefficients of cations and oxyanions in different polyacrylamide hydrogels used by the DGT technique

Amir Houshang Shiva*, Peter R. Teasdale, William W. Bennett, David T. Welsh

Environmental Futures Research Institute, School of Environment, Griffith University, Gold Coast campus, QLD 4222, Australia
** amir.shiva@griffithuni.edu.au*

ABSTRACT

A systematic comparison of the diffusion coefficients of cations (Al, Cd, Co, Cu, Mn, Ni, Pb, Zn) and oxyanions (As, Mo, Sb, V, W) in open (ODL) and restricted (RDL) diffusive layers, used by the DGT technique, was undertaken. Diffusion coefficients were measured using both the DGT time-series (D_{DGT}) method at pH 4.01 and 7.04 (8.30 for Al), and the diffusion cell (D_{cell}) method at pH 4.00. The recent mixed binding layer (MBL, containing both Chelex and Metsorb) was used for the DGT time-series measurement of diffusion coefficients. Reasonable agreement was observed between D_{cell} and D_{DGT} measurements for both ODL and RDL except for V and W. The ratios of D_{cell}/D_{DGT} for V of 0.44 and 0.39, and for W of 0.66 and 0.63 with ODL and RDL respectively, were much lower with the D_{cell} measurements due to the formation of a high proportion of polyoxometalate species at the higher concentrations required. The ratios of diffusion coefficients between the RDL and ODL in both methods were in the range of 0.66–0.78 for all elements, confirming that the diffusional pathway through the RDL was more tortuous. The D_{DGT} values for oxyanions in both hydrogels were retarded more relative to diffusion coefficients of free metal ions in water (D_W) than for cations. This is likely due to partial hydrolysis of acrylamide functional groups to acrylic acid which would be negatively charged, enhancing diffusion of cations and retarding diffusion of oxyanions. At pH 7.04 cations had a slightly higher D_{DGT} and oxyanions had a slightly lower D_{DGT} than at pH 4.01 in both ODL and RDL. This is consistent with the effect described above as acrylic acid functional groups (pK_a) are fully deprotonated at pH 7.04 and only slightly deprotonated at pH 4.01. The D_{DGT} values for Al changed substantially between pH 4.01 and 8.30 due to the very different species present at each pH and are also consistent with the above observation. Besides the diffusion coefficient measurements, the performance of Chelex-Metsorb as a new DGT binding layer for Al uptake was also evaluated for the first time. Good linearity (R^2 = 0.9991 for ODL and R^2 = 0.9973 for RDL at pH 8.30; R^2 = 0.9938 for ODL and R^2 = 0.9974 for RDL at pH 4.01) was observed for accumulated Al over the 32 h experiment, indicating the suitability of this mixed binding layer for DGT measurements of Al.

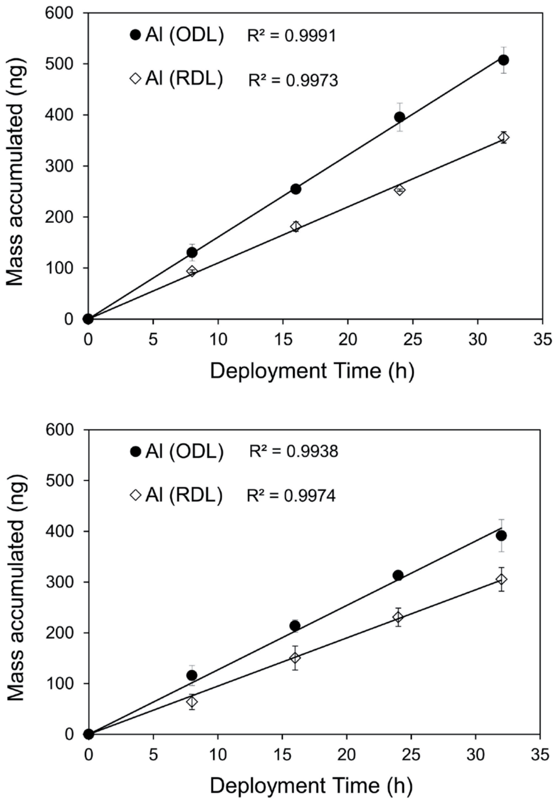

Figure 1: Time-series accumulation of Al by DGT-MBL using open (ODL) and restricted (RDL) diffusive layers at pH 8.30 (a) and pH 4.01 (b).

KEY WORDS

Diffusion coefficient; diffusive gradients in a thin film; open diffusive gel; restricted diffusive gel; diffusion cell; Al

New DGT techniques to determine nitrate and ammonium in low salinity freshwaters

Jianyin Huang*, William W. Bennett, Peter R. Teasdale, David T. Welsh

Environmental Future Research Institute, School of Environment, Griffith University, Gold Coast campus, QLD 4222, Australia
** Jianyin.huang@griffithuni.edu.au*

ABSTRACT

New DGT techniques have been developed for NO_3-N and for NH_4-N using Purolite A520E anion exchange resin and Microlite PrCH cation exchange resin, respectively, as binding materials. NO_3-N was quantitatively accumulated (>98%) on Purolite A520E over a range of concentrations and was eluted optimally (82.7%) with 2 mol L^{-1} NaCl. NH_4-N was quantitatively accumulated (92.5%) on Purolite A520E over a range of concentrations and was eluted optimally (87.2%) with 2 mol L^{-1} NaCl. The finding of 2 mol L^{-1} NaCl as the best eluent for both anionic NO_3- and cationic NH4+ was rather surprising, but was established by comparison with several other eluents. This result also indicates limitations for deploying these two DGT techniques in saline waters. Linear mass uptake was observed for both NO_3-N ($R^2 \geq 0.9970$) and NH_4-N ($R^2 \geq 0.9960$) over 24 h deployments (Figure 1). NO_3-N and NH_4-N uptake was quantitative in varying pH (3.5-8.5) and ionic strength (0.0001-0.008 mol L^{-1} NaCl for NO_3-N and 0.003-0.012 mol L^{-1} NaCl for NH_4-N) conditions. The capacity of A520E and PrCH bind phase was over 1204 ± 43 µg for NO3-N and about 2990 ± 194 µg for NH_4-N. Cl^- interfered most with NO_3-N measurement while Ca^{2+} interfered most with NH4-N measurement. Mass-uptake experiments over 5 days in a synthetic freshwater indicated that these binding capacities may limit the deployment time in some natural waters – deployment times of about 2-3 days may be suitable though. The results of field studies will be described in another presentation.

KEY WORDS

validation of new techniques, nitrate, Purolite A520E anion exchange resin, ammonium, Microlite PrCH cation exchange resin

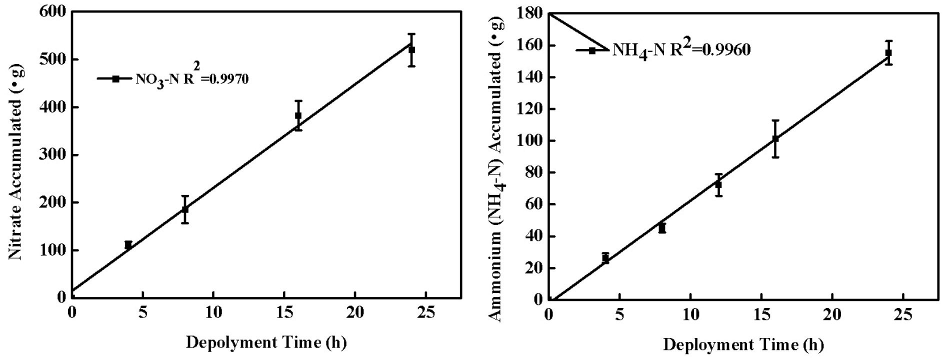

Figure 1 Mass of NO_3-N and NH_4-N accumulated by A520E DGT and PrCH-DGT over 24 h.

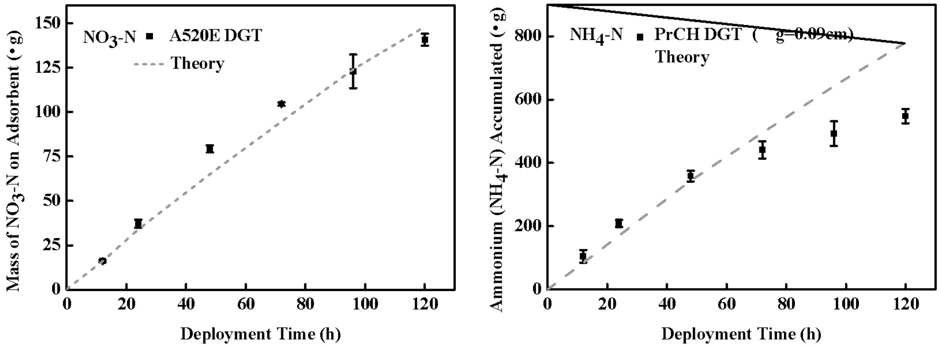

Figure 2 Mass of NO_3-N and NH_4-Naccumulated by A520E DGT and PrCH-DGT over 5 days in

Development of DGT for measuring pesticides in waters and soils

Yanying Li*, Chang'er Chen, Kevin Jones and Hao Zhang

Lancaster Environment Centre, Lancaster University, Lancaster, LA1 4YQ, UK
** y.li44@lancaster.ac.uk*

ABSTRACT

Pesticides significantly contribute to the provision of world food. However, their adverse effects on biodiversity, environment, food quality and human health have been of great concern. It is essential to monitor the pesticides concentrations to ensure the quality of waters and soils. The diffusive gradients in thin films (DGT) technique can measure quantitative in-situ labile (available) concentrations of chemicals in water, soil and sediments. Application of the technique to pesticides is of great importance to monitoring and to advancing our understanding of environmental processes of pesticides.

This study describes the laboratory tests of DGT for 9 selected pesticides with two types of resin (HLB and XAD 18) as binding layer materials. The diffusion coefficients of these 9 pesticides were measured in an independent diffusion cell and the effect of temperature can be predicted from the Stokes–Einstein equation. Resin gel HLB showed higher capacity than resin gel XAD18 for the 9 pesticides but with slower uptake kinetic. Both of the resin gels were tested for the effects of typical environmental factors on the DGT measurements. The concentration measured by DGT was independent of pH in the range of 4.7-8.2 and ionic strength from 0.01 to 0.25M, slightly affected by ionic strength of 0.5M. The mass accumulated by DGT devices was proportional to the deployment time and inversely proportional to the thickness of diffusive layer, following the DGT theoretical prediction . The performance tests of DGT *in situ* in field conditions (rivers and lakes) are undergoing by comparing with an automatic sampler and grab sampling.

KEY WORDS

DGT, pesticides, *in situ*, water, soil, monitoring

Development of new methods, based on passive samples and ICP, for analytical control of uranium radionuclides in water

Julio Llorca Pórcel*, Sergio Tejada Alarcón, Alicia Romo Moreno, Isabel de Blas, Ricardo Pedraza Berenguer

Labaqua, S. A.
**julio.llorca@labaqua.com*

ABSTRACT

Water and adjacent compartments (such as soils and sediments) are highly vulnerable to radionuclide contamination. Both natural and anthropogenic radioactive sources continuously contribute to the radionuclide occurrence in water. As the potential of contamination exist, several competent organizations have regulated the radionuclide concentration in drinking water. Within the EU, the new European Directive (ED2013/51/EURATOM) has increased the requirements in terms of number of analysis of radioactivity parameters. If the volume of distributed water is above 100000 m^3/day, a minimum of 10 analysis/year will be legally required. State members have 2 years to implement this recent regulation. In addition, Spain presents numerous sites with natural radioactivity (total alpha activity above the reference level of 0.1 (mSv/year). Hence, there is an urgent need to improve the existing analytical methodology to control the radioactivity of drinking water distributed. A novel, rapid and automated methodology focusing on the reduction of time analysis, sample size and analyst exposition to radionuclides is needed. In addition, this method should also improve the radionuclide isolation and pre-concentration prior to detection. Finally, the method sensitivity (limit of detection and quantification) should be able to quantify in the vicinity of the regulation limits.

The strategy to analyze radionuclide consists of the following stages: i) collection of the sample, ii) sample pre-treatment, iii) separation and pre-concentration of radioactive isotopes and iv) final analytical determination.

Passive samplers are a useful technique applicable to the monitoring of dissolve phase radionuclides in the aquatic environment, and have several advantages over conventional sampling methods including – simplicity, provision of time-weighted average concentrations, and automatic in-situ pre-concentration of analytes. DGT device has been identified as one type of passive sampler that can effectively measure dissolved concentrations of uranium. The DGT sampler is comprised of a gel assembly that is enclosed in a piston-like plastic casing. The plastic casing consists of separate base and cap components which when pressed together exclude water from within device except through a 20 mm diameter exposure window in the cap. The gel assembly consists of a high affinity cation exchange binding resin (Chelex-100) embedded in a polyacrlyamide hydrogel which is separated from the bulk solution by a polyacrlyamide diffusive gel of standard uniform pore size and thickness, and a cellulose nitrate 0.45µm membrane filter (to exclude particulate matter).

After the sample is collected, a separation step starts which involves 3 different parts: i) sample preparation, conditioning and preparing the sampler to an efficient extraction. ii) chemical separation (SPE sample extraction, preparation of cartridges, sample and elution step) and iii) electrodeposition, placing radionuclides on a surface where it is possible to measure the radioactivity by alpha spectrometry.

Finally the ICP-MS technique is the analytical tool used to quantify the concentrations of the different isotopes of uranium.

KEY WORDS

DGT, passive sampler, uranium radionuclide

Pollutant behaviour using DGTs under ocean acidification conditions

M. Camino Martín-Torre[a*], Ana R. Borrero-Santiago[b**], Murat V. Ardelan[c], M. Inmaculada Riba[b], T. Ángel DelValls[b], Javier R. Viguri[a]

[a] Department of Chemistry and Process & Resources Engineering, ETSIIT, University of Cantabria, Avda. de los Castros s/n, 39005 Santander, Cantabria, Spain
[b] Department Marine Science Faculty. University of Cádiz. Polígono Río S. Pedro s/n, 11510 Puerto Real, Cádiz, Spain
[c] Department of Chemistry. Norwegian University of Science and Technology 7491 Trondheim, Norway
** mariadelcamino.martin@unican.es*
*** ana.borrero@uca.es*

ABSTRACT

Ocean acidification, due to natural or anthropogenic causes, provokes a pH reduction of the marine system and may cause metal mobilisation. These two effects could affect biologically essential processes. Therefore, the assessment of metal behaviour under different ocean acidification conditions is essential to plan an appropriate risk management strategy.

In this work, Diffusive Gradients in Thin Films (DGT) are used to analyse Al, Cd, Cr, Cu, Pb, Sn and Zn metals and the oxyanion As in seawater due to their toxic effects to animal and human health.

Filtered and unfiltered seawater from the Trondheimfjord (Norway) was acidified to obtain pH values of 7 and 7.5 in order to compare the mobilisation of these pollutants at different levels of acidification with the natural pH (around 7.7), as well as to evaluate the influence of the filtration treatment in the pollutant mobility assessment.

As expected, element concentrations increase over time for all the elements under study. It would be expected that at more acidic conditions, higher mobility would be observed; however, it does not happen for most of the studied pollutants. In general, concentrations when unfiltered seawater is used are higher than when the seawater is filtered. In some metals, such as Cu, Pb and Zn, it does not happen possibly due to their complexation with the organic matter being these complexes removed when seawater is filtered. The consumption of the bioavailable fraction of these elements by organisms present in unfiltered seawater can contribute to the obtained concentration reduction.

Obtained results would be useful for a better understanding of metal mobilisation depending on the treatment of the seawater when using DGTs and also to better understand the behaviour of different metals under acidification conditions.

KEYWORDS

ocean acidification; trace element; mobilisation

Optimization of an agarose-based diffusive gel for in-situ measurements of methyl mercury in natural waters by diffusive gradients in a thin-films (DGT) technique

Heng Yao*, Xinbin Feng

State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang, 550002, China
** yaoheng28@gmail.com*

ABSTRACT

Methylated mercury compounds (MeHg) are ubiquitous neurotoxins that exist in natural waters typically at ultra-trace level (<1.0 ng L-1). In contrast to traditional methods, the relatively newly developed diffusive gradients in the thin-films (DGT) technique have been demonstrated capable of *in situ* measuring trace metals in aqueous matrices. The DGT technique employs a membrane, a diffusive gel and a binding gel. For Hg determination, however, prevalently used polyacrylamide diffusive gel has proven unsuitable, due to the affinity of mercuric compounds to the polymer's amine groups. By implementing an agarose-based diffusive gel, we aimed in this study to optimize the DGT method for measuring MeHg concentration in natural waters. The experimental work included: 1) performance test of agarose-based gels of various preparation formulae; 2) determination of the MeHg diffusivity in various gel formula matrices; 3) assessment of the adsorption rate for MeHg in-between polyacrylamide and agarose gels; 4) measurement of the DGT uptake and elution efficiencies for MeHg. The results are in support of that such modified DGT device can be used for biogeochemical exploration of MeHg in aqueous systems. The developed metho dwill be applied in paddy ecosystem to investigate the transportation pathways of MeHg between paddy pore water and rice plants.

KEY WORDS

Methylmercury; agorose gel; DGT; paddy soil

Using DGT to study the stratification of underground waters

Segolene Maghe-Chauvin*, Nicolas Sauzay

MINELIS, Toulouse, France
**segolene.chauvin@minelis.com*

ABSTRACT

Underground waters could have a stratification that cannot be observed with sampling performed by a pump. A measurement of physical and chemical parameters (pH, conductivity, dissolved oxygen, temperature) has been made in two piezometers on an industrial polluted site, a former metallurgic site. When differences were seen in these parameters depending on depth, DGT were used to make a stratigraphy for a better understanding of the repartition of the three main metals of the site (lead, zinc and cadmium) in underground waters. The results show that there is a low dispersion of triplicata of DGT for cadmium and zinc but a more important one for low lead concentrations. The stratification of cadmium and zinc is very clear with high levels in the last meter depth. Moreover, the magnitude of DGT results is coherent with punctual water sampling.

The present study reveals that the DGT with Chelex resin are a useful tool to study the repartition of different metals in underground water. It could help to have better information to take decisions for sampling or pumping polluted waters.

KEY WORDS

passive samplers, DGT, diagraphy, stratification, underground water, zinc, cadmium, lead, piezometer.

Advances in the use of Diffusive Gradients in Thin-films (DGTs) for the measurement of Hg within the Water Framework Directive: laboratory and field experiments

N.Montero[a,b,c], J-L. Gonzalez[d], M.J. Belzunce-Segarra[a*], F. Marco-Miralles[d]

[a] *Marine Research Division, AZTI-FOUNDATION, Muelle de la Herrera, Recinto Portuario s/n, 20110 Pasaia, Spain. *jbelzunce@azti.es*
[b] *National Research Centre for Environmental Toxicology, ENTOX/University of Queensland, 39 Kessels Road, Coopers Plains, Queensland 4108, Australia.*
[c] *IKERBASQUE, Basque Foundation for Science, María Díaz de Haro 3, 48013 Bilbao, Spain.*
[d] *Ifremer Unité "Biogéochimie et Ecotoxicologie" CS 20330 Zone Portuaire de Brégaillon, 83507 La Seyne/mer Cede, France.*

ABSTRACT

Mercury (Hg) is a widely distributed persistent pollutant. In natural waters, the main Hg species present in the dissolved state are elemental Hg (Hgº), inorganic mercury (Hg^{2+} and its complexes) and organic Hg (monomethylmercury and dimethylmercury). However, methylmercury is the most ecotoxicologically relevant species due to its liposolubility and biomagnification along the food web (e.g. Boening 2000; Chen *et al.* 2008). The potential environmental hazard of mercury is regulated under different guidelines (e.g. OSPAR 2004; European Commission 2012; USEPA 2012). It is also considered as a priority hazardous substance under the Water Framework Directive (WFD; Directive 2000/60/EC, 2013/39/EU) and its concentration must be monitored to establish the chemical status of water bodies. However, its complex speciation and its presence at trace concentration imply a complicated treatment and analysis of the samples. These shortcomings could be overcome by using Diffusive Gradients and Thin Films (DGTs) devices which have been successfully applied for the measurement of several trace metals (Cd, Cu, Zn, Pb, Ni, Cr, Co, etc.) in different environments.

In this study, the performance of DGTs for the measurement of Hg was investigated, testing different combinations of membranes, types of elution and analytical techniques in a laboratory tank study, to select the most operationally feasible combination for the measurement of Hg. Additionally, in order to test the performance of the selected combination under field conditions, the selected DGTs were deployed at two sites (the Toulon bay in France and the Oiartzun estuary in Spain) affected by different pressures.

No quantifiable results were obtained after the elution of the resins by thiourea, while the results obtained after the aqua regia elution were lower than those obtained by direct combustion of the resin (CV-AAS, Cold Vapor Atomic Adsorption Spectrometry). The polyacrylamide (P) did not present an inherent capacity for the accumulation of Hg. However, the use of agarose (A) diffusive membranes in combination with Chelex-100 (C) and Spheron-thiol (S) binding resins enables the performance of speciation analysis. Besides, the use of AS DGTs in the field allowed the measurement of Hg at very low concentrations (2-4 ng L^{-1}) and the detection of potential Hg sources. Thus, the use of AS and AC DGTs and the measurement of the accumulated Hg by CV-AAS are recommended for the measurement of Hg in highly dynamic systems and at ecotoxicologically relevant low concentrations. This study provides a step forward in the operational use of DGTs for the measurement of Hg within the WFD requirements.

REFERENCES

Boening, D.W. (2000) Ecological effects, transport, and fate of mercury: a general review. Chemosphere 40(12), 1335-1351.

Chen, C.Y., Amirbahman, A., Fisher, N., Harding, G., Lamborg, C., Nacci, D., Taylor, D. (2008) Methylmercury in Marine Ecosystems: Spatial Patterns and Processes of Production, Bioaccumulation, and Biomagnification. EcoHealth 5(4), 399-408.

European Commission (2012) Regulation (EU) No 847/2012 of the European Parliament and of the Council of 19 September 2012 amending Annex XVII to regulation (EC) No 1907/2006 of the European Parliament and of the Council on the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH) as regards mercury. Official Journal of the European Union L253, pp 1-4.

OSPAR (2004) OSPAR/ICES Workshop on the evaluation and update of background reference concentrations (B/RCs) and ecotoxicological assessment criteria (EACs) and how these assessment tools should be used in assessing contaminants in water, sediment and biota. Workshop on BRC-EAC 9-13 February 2004, Final report, pp 1-167.

USEPA (2012) National emission standards for hazardous air pollutants from coal- and oil-fired electric utility steam generating units and standards of performance for fossil-fuel-fired electric utility, industrial-commercial-institutional, and small industrial-commercial-institutional steam generating units; final rule. Fed Reg 77(32):9304–9513 (2012);

Development of DGT for the determination of organotin compounds in sediment pore-water

Russell Cole[a*], Gary R. Fones[a], Graham A. Mills[b], Thi Bolam[c] and Ruth Parker[c]

[a] *School of Earth and Environmental Sciences, University of Portsmouth, Portsmouth, PO1 3QL*
[b] *School of Pharmacy and Biomedical Sciences, University of Portsmouth, Portsmouth, PO1 2DT*
[c] *Centre for Environment, Fisheries and Aquaculture Science, Lowestoft Laboratory, Pakefield Road, Lowestoft, Suffolk, UK, NR33 0HT*
** russell.cole@port.ac.uk*

ABSTRACT

Organotin compounds derived principally from anti-foulant paints are ubiquitous within coastal sediments, especially in areas with high boating activity. Due to high toxicity (observed effects at < 1 ng Sn L^{-1})[1] and long-term persistence of tributyltin (TBT), low environmental quality standards (EQS) within the EU Water Framework Directive are mandated (0.2 ng L^{-1} annual average and 1.5 ng L^{-1} maximum allowable aqueous concentrations). Measuring TBT at these concentrations presents an analytical challenge. Due to their physico-chemical properties (e.g. log K_{ow} = 4.10 for TBTOH), sediments are the major sink for organotin compounds in the aquatic environment. However, there is currently limited knowledge on the fluxes of labile, potentially bioavailable organotin species, at the sediment-water interface and in sub-surface sediment pore-waters. DGT has been identified as a technique that could provide information on the behaviour of TBT, triphenyltin (TPhT) and their degradation products within coastal sediments and at disposal sites used for dredged material.

We investigated a number of non-polar chromatographic materials as potential receiving phases for DGT. Both silica-bound octyl (C_8) and octadecyl (C_{18}) solid-phase sorbents are used to extract organotins from water and a C_{18} Empore™ disk has been used with the Chemcatcher® passive sampler to sequester organotins from sea water[2]. In our work, 5 µm Silicycle sorbents and 40 µm Bondesil® C_{18}, C_8 and C_{18}/C_8 mixed phases were tested as potential DGT binding gel sorbents.

Optimum sorbent homogeneity was observed using C_8 40 µm particles at a 1 % loading, using a methanol conditioned 40 % acrylamide/bis-acrylamide gel. The performance of this DGT binding gel for monitoring tri-, di- and mono-butyltin and phenyltin compounds was evaluated against that of commercially available C_{18} and C_8 Empore™ disks. A similar performance was shown for both the disks and binding gel phases. The uptake rate of TBT with the C_8 DGT-binding gels was found to be faster in comparison to C_{18}- binding gels and was easier to cast into DGT sediment probes. Elution efficiencies for organotin species were in the range 72–112 % for C_{18} and 78–91 % for the C_8 DGT binding gel; being influenced by changes in organotin speciation under variable pH conditions. Extraction was undertaken using 13 M methanolic acid (1:3 v/v methanol: acetic acid) with sodium tetraethylborate ($NaBEt_4$) derivatisation with the concentrations of organotins determined by large volume injection GC/MS. Preliminary data obtained from field trials using these devices will be presented.

REFERENCES

1. Graceli, J. B.; Sena, G. C.; Lopes, P. F. I.; Zamprogno, G. C.; da Costa, M. B.; Godoi, A. F. L.; dos Santos, D. M.; de Marchi, M. R. R.; dos Santos Fernandez, M. A., Organotins: A review of their reproductive toxicity, biochemistry, and environmental fate. *Reproductive Toxicology* **2013**, *36*, 40-52.
2. Aguilar-Martinez, R.; Palacios-Corvillo, M.; Greenwood, R.; Mills, G.; Vrana, B.; Gomez-Gomez, M., Calibration and use of the Chemcatcher$^{(R)}$ passive sampler for monitoring organotin compounds in water. *Analytica Chimica Acta* **2008**, *618* (2), 157-167.

Pockets of sub toxic concentrations of DGT-labile As in river sediments layers in Laos and Guatemala determined by DGT-probes

Åsgeir Rossebø Almås[a]*, Gudny Okkenhaug[b]

[a] Norwegian University of Life Sciences, Department of Environmental Sciences, Post Box 5003, 1432 Ås, Norway.
[b] Norwegian Geotechnical Institute, Sognsveien 72, 0806 Oslo, Norway
* asgeir.almas@nmbu.no

ABSTRACT

Arsenic in nature form oxyanions in the oxidations states III and V. The geochemistry of As is mostly controlled by pH and redox conditions, and hence directly related to the speciation og iron (Fe). The history of ground water extracted from sediments in Bangladesh and uptake of As in rice grown in paddy rice fields, have demonstrated the importance of As-Fe interactions. In both stations, the water logging is stabile and provides only limited amounts of oxygen, although it is known that the rice plants lead O_2 down to the root zone. That process initiate the Fe precipitation at root surfaces and flowingly the As accumulation.

The pitfalls of ground water extraction in Bangladesh, was partly connected to the unexpected mobilisation of dissolved As from modestly As contaminated sediments due to the special geochemistry at those depths. The combinations of strongly reducing conditions and pH at the alkaline range, promoted As solubility. Here, we report evidences identifying pockets of reducing conditions in river sediments after installing DGT probes in sediments near two active mining sites: One in the vicinity of a gold mine in North-West Guatemala and the other near a cupper mine in North-West Laos. The interesting findings were discovered in the sediments investigated at the control sites. The total concentrations of As in these sites were low, from top down to 15 cm depths. At both sites a peak of a substantial increase of DGT-labile As was discovered. The first one in Laos. Unfortunately, the chelex loaded DGT probe got damaged during the installation, but in Guatemala also the chelex-loaded DGT was intact. Extraction of this probe showed parallel increase of Fe in the same depth as the As peak occurred. This is taken as evidence that pockets of reducing conditions occur also in environments supposedly in excess of O_2 due to free running water just above. The Fe- lability was not related to depth and lack of oxygen by depth. There was no relationship with depth. The was a peak, and this was located in one fairly isolated layer. The same was the situations with the As labilities in Laos and Guatemala: The peak concentrations were sharp and narrow. Hence, we firstly believe that the sediment layer might have contained a layer of organic material (not determined), and secondly that this layer have exchanged limited amounts of O_2 for reducing conditions to develop. Such results are difficult to reproduce in field as they might occur randomly, but the coinciding Fe-peak strongly suggest the development of small pockets of reducing conditions, also in shallow river sediments.

KEY WORDS

Arsenic, reducing conditions, river sediments, DGT probes

Comparison of methods for measurement of porewater iron(II) and sulfide: *in situ* colorimetric DET and DGT vs. *ex situ* centrifugation of homogenised sediment core sections followed by colorimetric analysis of the pore waters

Nadeeka Rathnayake Kankanamge, Peter Teasdale*, David Welsh and William Bennett

Environmental Futures Research Institute, Griffith University, Gold Coast campus, Queensland, Australia,
** p.teasdale@griffith.edu.au*

ABSTRACT

Coastal sediments are complex environments that play an important role in the cycling of carbon and other elements. Organic carbon is decomposed by bacterial respiration, which consumes electron acceptors in order of the energy yield of the corresponding respiration type, producing three major biogeochemical zones – oxic, sub-oxic and anoxic. The sub-oxic zone is characterized by iron(III)-reduction to produce soluble iron(II), while the anoxic zone is dominated by sulphate-reduction producing sulphide. In productive coastal sediments, the distance between the oxic and anoxic layers may be as little as a few millimeters. These sediments may also experience intense bioturbation processes, due to benthic fauna and the presence of plant habitats (seagrass and mangroves), which make the sediment highly heterogeneous. In such sediment the distributions of products of different respiration types can form a complex 'mosaics' resulting in iron(II) and sulphide being present at the same depth horizons on scales sampled by common methods. Many porewater sampling and analysis methods simply cannot distinguish changes over such small distances. Therefore, in sediment with complex, three-dimensional, time-dependent heterogeneity, it can be extremely difficult to examine the fine-scale (mm to sub-mm) chemical distributions of important chemical species using typical sampling and measurement methods. Typical porewater sampling techniques require the removal and processing of sediment cores. Porewater profiles are obtained by slicing the collected cores at 1 cm resolution, homogenizing the material and centrifugation of the section to extract pore waters, which are then analysed. This mixes the porewater solutes, which is likely to result in chemical reactions (e.g. formation of FeS) that change the solute concentrations considerably, making the final porewater concentrations measured inaccurate and non-representative. The diffusive equilibration in thin films (DET) and the diffusive gradients in thin films (DGT) techniques allow the *in situ* determination of elemental solute concentration profiles in sediment pore waters and also provide two-dimensional distributions at higher spatial resolution than is possible employing conventional techniques. This allows measurement of mm-scale features, facilitating the investigation of small scale biogeochemical processes and heterogeneity within the sediment. Furthermore, the *in situ* nature of the DGT and DET techniques limits inaccuracies caused by removal and processing of sediment pore waters. This study has obtained measurements of sediment porewater Fe(II) and sulphide co-distributions using conventional core sampling technique and new colorimetric passive sampler techniques. These two approaches were used at several study sites to facilitate a statistical comparison. This study suggests that the colorimetric Fe(II)-DET and sulphide-DGT measurements are both more accurate and more representative than the conventional analysis of porewaters separated by centrifugation, even with the precautions taken against oxidation. This comparison will be an important validation step that will lead to the new techniques being accepted.

KEYWORDS

heterogeneous sediment; DET and DGT co-distributions; high-resolution, two-dimensional measurements; conventional porewater processing and analysis; iron(II) and sulphide

Assessment of pahs mobility in marine sediments using new Organic Diffusive Probe (ODP)

M.L.Ruello[a*] , E.Prokofyeva[a,b] , A.Bondarenko[b]

[a] *Department of Materials, Environmental Science and Urban Planning (SIMAU), Università Politecnica delle Marche, Via Brecce Bianche, Ancona, 60131, Italy;*
[b] *Department of Chemistry, Lipetsk State Technical University, Moskovskaya St., 30, Lipetsk, 398055, Russia.*
**Tel.:+39 071 2204726; Email: m.l.ruello@univpm.it*

ABSTRACT

This work is devoted to describing the activities performed to test a method for measuring the mobility of organic pollutants in the solid phase of soils or sediments within the context of environmental pollution risk assessment. The method is based on a new probe for the passive sampling of organic pollutant.

In the research the Chemcatcher and the theory of Diffusive Gradient in Thin film (DGT) were combined. This research adopted and modified configuration of the Chemcatcher probe with the principles of DGT to evaluate the new passive sampler as probe for predicting the bioavailability of Polycyclic Aromatic Hydrocarbons (PAHs) in marine sediments. In the new configuration the sampler can work with the principles of measurement of the DGT technique.

The passive sampling device consists of a C18 Empore disc as binding material. The C18 disc is overlaid with a glass microfiber membrane as inert diffusive water layer. The standard PAHs solution EPA 610 was used as inoculum for the batch tests. The research examined the kinetic of desorption of phenanthrene in marine sediments for a range of times (1d to 35d). The effect of thickness of the diffusion layer on measurements of time-integrated concentrations CDGT and sampling rate R were studied experimentally and using a dynamic model (DIFS, DGT induced fluxes in soils). The mass of individual PAH accumulated in the adsorbing phase (C18) of the passive sampling devices was well correlated with the time. Moreover, trends in time of R observed in this work for phenanthrene are similar to observed ones in the study of metal exchange interpreted from DGT measured fluxes. The sampling probe with C18 is a promising tool for analyzing PAHs with low molecular weights.

Collectively these results show the possibility of applying such adopted configuration of the passive probe (diffusive water layer and C18 Empore disk) to measure the labile fraction of PAHs in marine sediments. The information obtained with the new configuration of the passive probe is very useful to predict the fate of the pollutants in the environment.

KEY WORDS

Passive sampling, Chemcatcher, DGT technique, water diffusive layer, PAHs, POPs

In situ characterization of arsenic mobility in sediments of an eutrophic lake with DGT

Qin Sun*, Shiming Ding, Paul N. Williams, Chaosheng Zhang

Key Laboratory of Integrated Regulation and Resource Development on Shallow Lakes, Ministry of Education, College of Environment, Hohai University.
** sunqinnj@hhu.edu.cn*

ABSTRACT

The release of arsenic (As) from sediments may exert a prominent impact on its behavior in water of eutrophic lakes, making it necessary to monitor and assess its mobility in sediments. In this study, the mobility of As in the sediments of a eutrophic Lake Taihu was investigated in the field through in-situ measurements of labile As using a Zr-oxide diffusive gradients in thin films (Zr-oxide DGT) technique. The distribution of DGT-labile As, interpreted as DGT flux (F_{DGT}), exhibited three different patterns in the contaminated, macrophyte-covered and other regions, respectively. All the patterns exhibited generally an increasing followed by decreasing phases in F_{DGT} values with sediment depth, reflecting increasing and decreasing mobility of As in the upper and deeper sediment layers respectively. The mobility of As in the sediments could be characterized by the average F_{DGT} in the top 10 mm surface sediments in a range of 0.06-1.27 pg cm^{-2} s^{-1}. The maximal FDGT at the end of the increasing phase (F_{DGT-M}) varied in a range of 0.18-2.44 pg cm^{-2} s^{-1}, and the diffusion length from the depth showing the F_{DGT-M} to the sediment-water interface (ΔL) varied in a range of 28-66 mm. The F_{DGT-M} and the average F_{DGT} in the top surface sediments were found to be positively correlated with the concentrations of total As in the overlying water, while the mobilization of labile As from the deep sediments to the top surface sediments and overlying water became evident when $F_{DGT-M} > 1.5$ pg cm^{-2} s^{-1} or $\Delta L < 43$ mm. It was suggested that the increasing mobility of As in the upper sediments was controlled by the reduction of As(V) and the reductive dissolution of Fe(III) (hydr)oxides, while the decreasing mobility in the deep sediments was attributed to immobilization of As by secondary Fe(II)-bearing minerals.

KEY WORDS

Arsenic, sediment, mobility, Zr-oxide DGT, eutrophication

Electrostatic and kinetic effects on DGT metal accumulations. Systems at low ionic strength

Alexandra Altier[a], Josep Galceran, Sara Cruz-González, Calin A. David, Carlos Rey-Castro, Martin Jiménez-Piedrahita, Jaume Puy.

[a]*Department of Chemistry, Universitat de Lleida, Spain.*

ABSTRACT

DGT measurements at low ionic strength have arisen controversy(*1*). Recently, a systematic approach to understand the interplay of the relevant phenomena at low ionic strength has been undertaken. It has been shown that the standard Eigen model cannot account for Ni accumulation in DGT devices deployed in systems where the dominant species is NiNTA (*2*). Instead, a ligand-assisted mechanism in the resin domain has been suggested. According to this mechanism, dissociation of NiNTA is facilitated by the formation of a chemical bond between Ni and the resin site. This is an exchange mechanism between two charged species, the NiNTA complex and the resin site. Since kinetic constants between negatively charged reactants decrease as the ionic strength of the sample decreases, this mechanism can explain: i) the reduction of the mass accumulation experimentally observed and ii) the increase in the back accumulation percentage when DGT devices with a stack of two resin discs are used.

Another electrostatic effect, due to the negatively charged resin sites, is the Donnan partitioning of the charged species across the resin-diffusive gel interface. This partitioning tends to reduce the metal accumulation for negatively charged partially labile complexes, and, conversely, it tends to increase the metal accumulation when positively charged complexes are the dominant species. Experimental data corresponding to Ni, Cu, Co, Cd or Zn with NTA or ethylenediamine will be presented. The opposite charge of the NTA and ethylenediamine complexes leads to an opposite behaviour of these complexes (in the metal accumulation in DGT devices) as the ionic strength of the sample decreases. Experimental data will be discussed and quantitatively modelled by taking into account the above explained physical phenomena. Numerical simulations and analytical expressions(*3*) shed light on the behaviour of the system.

REFERENCES

1. Alfaro-De la Torre, MC; Beaulieu, P. Y.; Tessier, A. *In situ* measurement of trace metals in lakewater using the dialysis and DGT techniques. *Anal.Chim.Acta* **2000,** *418*, 53-68.
2. Puy, J.; Galceran, J.; Cruz-Gonzalez, S.; David, C. A.; Uribe, R.; Lin, C.; Zhang, H.; Davison, W. Metal accumulation in DGT: Impact of ionic strength and kinetics of dissociation of complexes in the resin domain. *Anal.Chem.* **2014,** *86*, 7740-7748.
3. Galceran, J.,Puy, J. Interpretation of diffusion gradients in thin films (DGT) measurements: a systematic approach. *Environ.Chem.* **2015,** *12*, 112-122.

KEY WORDS

Bioavailablity, DGT, Kinetic effects, low ionic strength, Donnan

Influence of the inhomogeneous distribution of the binding resin beads on DGT measurements

Martín Jiménez-Piedrahita[a], Alexandra Altier[a], Joan Cecilia[b], Carlos Rey-Castro[a], Josep Galceran[a] and Jaume Puy[a]*

[a]*Departament de Química*
[b]*Departament de Matemàtica, Universitat de Lleida and AGROTECNIO, Rovira Roure 191, 25198, Lleida, Spain*
** Phone number 34 973 702529. Email: jpuy@quimica.udl.cat*

ABSTRACT

Recent publications have shown that in presence of partially labile complexes, most of the metal accumulation in the DGT device comes from dissociation of the complex in the resin disc [1, 2]. The distribution of the resin beads might, then, play an important role in the metal accumulation. For simplicity, it is usually assumed that there is a homogeneous distribution of the binding sites in the resin [3]. However, this assumption is not fully accurate, since, during the preparation of the resin, the binding beads settle to one side of the resin. The influence of this inhomogeneity on metal accumulation is here assessed using numerical simulation of DGT devices with resin beads in only one half of the resin disc. Results indicate that the mild loss of mass accumulation only reaches 13% for inhomogeneous devices in the presence of complexes with stability constant K around10^5 M^{-1} dominating the metal speciation. The loss increases as K increases, but always remains lower than the volume fraction of resin disc without binding sites. The impact of the inhomogeneous distribution of binding resin beads is negligible for very labile or inert complexes.

Additionally, DGT devices with a stack of two resin discs can be used to estimate kinetic dissociation constants of complexes [3-5]. The influence of the inhomogeneity on the recovered kinetic constant is also analyzed. It has been found that the recovered kinetic dissociation constant, $k_{d,\text{recovered}}$, and the true value, k_d, are practically proportional: $k_d \approx f^{-1} k_{d,\text{recovered}}$, being f the fraction of volume of the resin disc with resin beads. This relationship is quite independent of the value of K and k_d.

REFERENCES

1. Galceran, J. and Puy, J., Interpretation of diffusion gradients in thin films (DGT) measurements: a systematic approach, Environmental Chemistry, 12 (2015) 112-122
2. N. J. Lehto, W. Davison, H. Zhang, W. Tych, An evaluation of DGT performance using a dynamic numerical model, Environ. Sci. Technol., 40 (2006) 6368-6376.
3. M. R. Shafaei-Arvajeh, N. Lehto, O. A. Garmo, H. Zhang, Kinetic Studies of Ni Organic Complexes Using Diffusive Gradients in Thin Films (DGT) with Double Binding Layers and a Dynamic Numerical Model, Environ. Sci. Technol., 47 (2013) 463-470.
4. J. Puy, J. Galceran, S. Cruz-Gonzalez, C. A. David, R. Uribe, C. Lin, H. Zhang, W. Davison, Metal accumulation in DGT: Impact of ionic strength and kinetics of dissociation of complexes in the resin domain, Anal. Chem., 86 (2014) 7740-7748.
5. J. L. Levy, H. Zhang, W. Davison, J. Puy, J. Galceran, Assessment of trace metal binding kinetics in the resin phase of diffusive gradients in thin films, Anal. Chim. Acta, 717 (2012) 143-150.

KEY WORDS

DGT, resin disc, metals, kinetics, lability, diffusion, inhomogeneity.

Assessing the ageing effect on availability of ^{79}Se, ^{99}Tc and U isotopes

Alex Chapman*, Jackie Pates, Hao Zhang

Lancaster Environment Centre, Lancaster University, Lancaster, LA1 4YQ, United Kingdom
** a.chapman@lancaster.ac.uk*

ABSTRACT

^{79}Se, ^{99}Tc and ^{238}U are major by-products of the nuclear industry and have been identified as being of particular importance in long-term safety assessments of nuclear waste disposal. Understanding their availability for plant uptake in soils is crucial in ascertaining the potential transfer of these radionuclides from the soil and their subsequent incorporation into the biosphere through plant uptake. This scenario would arise should they become mobilised within the soil environment following disposal of nuclear waste in deep geological repositories.

The objective is to investigate whether short-term DGT measurements of radionuclide availability throughout a three-year soil incubation period can be used to predict long-term availability on the order of several decades, and potentially even on a timescale relevant to nuclear waste disposal. 16 soils from the UK and 4 from the Chernobyl Exclusion Zone (CEZ) spanning a range of physico-chemical properties were spiked with Se, Tc and U and incubated at ~10°C. DGT deployments are made at progressively-increasing time intervals to assess the ageing effect for these elements. Further deployments in 'aged' soils from lysimeter studies and highly-contaminated areas of the CEZ will add to this dataset and also allow for the testing of models parameterised from the laboratory incubation study. Plant uptake experiments will be carried out to validate the relationship between DGT-available and plant-available Se, Tc and U, and therefore test the suitability of the technique as a measure of bioavailability.

Initial results from the first 143 days of the incubation study demonstrate a clear decline in availability of Se, Tc and U in most of the soils as would be expected due to its progressive incorporation into less exchangeable soil fractions. The ageing trend for Se and U however fluctuates in a number of soils following an initial decline in availability over the first ~40 days. It is possible that changes in the redox-potential may be responsible, but the concentration of solubilised Fe and Mn at the corresponding time points does not appear to markedly increase. The effect of the soil wetting and drying cycle associated with DGT deployments on the availability of Se and U should be elucidated in order to aid interpretation of the data, in addition to assessing the solid phase distribution of the elements following wetting.

KEY WORDS

ageing, selenium, technetium, uranium, soil

Small-scale P availability at intact soil macropore surfaces using DGT

Nadia Glæsner[a,b*], Simon Mundus[a], Horst Gerke[b], Martin Leue[b], Jakob Magid[a]

[a] *University of Copenhagen, Denmark;*
[b] *Leibniz-Centre for Agricultural Landscape Research, Germany;*
**nagl@plen.ku.dk*

ABSTRACT

Soil is a heterogeneous system with properties and processes occurring specifically at local scales. However, studies examining the heterogeneous nature of soil are few and represent a large gap within soil science research.

This study aims at examining intact surfaces of soil macropores, namely earthworm burrows. Organic matter composition was analysed at mm scale along earthworm burrows using Diffuse Reflectance Infrared Fourier Transform (DRIFT) in top- and subsoils from a long-term field experiment on waste application. Results showed that organic matter composition differed largely along the macropore surfaces as well as in the soils with different type of waste application. E.g. ratios of CH:C=O was larger in soils treated with household compost compared to soils treated with sewage sludge and untreated soils indicating less wettability of the soil treated with household compost.

The aim is to compare the findings of organic matter composition with employing DGT gels directly at the macropore surfaces and create chemical imaging of the macropore surfaces with a laser ablation coupled to an ICP-MS of the DGT gels. Using ZrO-µChelex gels allow analysing for P as well as metals.

KEY WORDS

Macropores, nutrient availability, organic matter composition, intact soil

Use of DGT for the evaluation of metal plant availability in sewage sludge amended soils

Manuela Hidalgo[a*], Maria Sedó[a], Francesc Camps[b], Mònica Iglesias[a], Eva Marguí[a]

[a] *University of Girona. Department of Chemistry. Campus Montilivi, s/n. 17071 Girona. Spain,*
[b] *Mas Badia Field Station–IRTA. Crta. de la Tallada, s/n. 17134 La Tallada, Girona. Spain*
** manuela.hidalgo@udg.edu*

ABSTRACT

Wastewater treatment plants produce increasingly large amounts of sewage sludge worldwide. The treatment and disposal of the ultimate product of the sludge (biosolids), includes incineration, landfill and agricultural application as soil conditioners or fertilizers. Although agricultural use seems to be the natural fate of sludge given their high levels of nutrients and organic matter, there are severe concerns about the presence of contaminants such as metals. When sludge is repeatedly applied to the land metals will tend to accumulate in the cultivated layer of topsoil to concentrations which might affect, for example, crop growth and quality, soil fertility and the food chain.

In this context, metal plant availability was studied in an agricultural soil repeatedly amended with sludge for sixteen years. Field experiments were carried out at the agricultural experimental station of Mas Badia-IRTA (Girona, NE Spain). Experimental plots were arranged to account for different scenarios: control soil (no fertilizer), chemical fertilization of the soil, biosolids amended soil (dose applied pre-sown) and combined fertilization (biosolids and chemical fertilization). Two different sets of plots were used to crop barley (winter season) and maize (summer season) and metal concentrations in different parts of the plants were determined. Moreover, several extraction tests and the Diffusive Gradients in thin Films (DGT) technique were applied to assess soil metal mobility/bioavailability.

The results obtained indicate a correlation between the concentrations of cadmium, chromium, nickel and zinc from DGT measurements and concentrations in barley grain. Using DGT technique, clear differences have been observed for Cu and Zn bioavailability in the studied soil samples (control, chemical fertilization and fertilization with biosolids). The same trend has been found when using extraction test such as DTPA. In addition, relatively higher concentrations were found in the plots treated with biosolids. No correlation was obtained between the total metal concentrations in soils and those obtained using DGT devices, except for Zn.

KEY WORDS

metal bioavailability, barley, sewage sludge amended soil, DGT, leaching tests

Assessment of P plant-availability in cotton soils using the diffusive gradient in thin films (DGT) technique

Qingjun Li*, Yan Zhang, Jinxin Wang, harlhax.ybat

Institute of Soil Fertilizer and Agricultural Water-saving, Xinjiang Academy of Agricultural Sciences,
Urumqi, 830091 P.R. China.
**gyqc@163.com*

ABSTRACT

Phosphorus deficiency has become a limiting fact for getting high crop yield in cotton soil in Xinjiang, China. The critical values that are used to evaluate plant-available phosphorus have not adapted to agricultural production. So the measuring methods that can represent objectively soil phosphorus supply ability and plant-available phosphorus are needed imminently. Using DGT techniques measure phosphorus in soil solution at this project. The processes which phosphorus sorbent absorb H_2PO_4- through diffusive gel simulate that plant roots absorb phosphorus in soil solution. So these processes can show soil phosphorus supply ability and plant-available phosphorus. A suite of 34 surface soils (0-20cm) was collected from Xinjiang cotton fields. Selected basic physical and chemical characteristics of the soils were analysed. Total phosphorus, available phosphorus(Olsen-P) and DGT-P of these soils were measured also. The correlation between DGT-P of soils and Olsen-P of soils is highly significant (R^2=0.8807**, n=34), but the correlations between DGT-P and total phosphorus was not significant. A pot experiment study and the field plot test were undertaken in the 34 test soils, the pot experiment designed without P and added P, respectively, while the field plot test designed without P , added low rate P, added medium rate P and added high rate P,respectively. Potted cotton shoots were harvested after 50 days and cotton fields were harvested at maturity, respectively, then dry matter and seed cotton yield were determined. Regression analysis of relative cotton dry matter production and seed cotton yield responses demonstrated that the DGT method predicted plant response to applied P more accurately than Olsen-P. The correlation between DGT-P of soils and potted cotton dry matter was highly significant(R^2=0.7165**,n=32), and the correlation between Olsen-P of soils and potted cotton dry matter was significant(R^2=0.3862*, n=32). When applied low P, the measured concentration in soils at the DGT surface, DGT-P, explained 62% of the variation in response for aboveground biomass and 67% for seed cotton yield, compared to 36% for aboveground biomass and 35% for seed cotton yield using the Olsen P method. When applied medium P, the DGT-P explained 70% of the variation in response for aboveground biomass and 72% for seed cotton yield, compared to 38% for aboveground biomass and 39% for seed cotton yield using the Olsen P method. When applied high P, the DGT-P explained 44% of the variation in response for aboveground biomass and 29% for seed cotton yield, compared to 24% for aboveground biomass and 12% for seed cotton yield using the Olsen P method. These observations suggest that the DGT technique can assess plant available P in soils with significantly greater accuracy than traditional soil P testing methods, but the DGT technique has limitations that assess plant available P in high-phosphorus soils. The critical value was obtained about P availability in Xinjiang cotton soil, the critical P threshold, expressed as DGT-P, was 56.1 µg L^{-1} for potted cotton dry matter and 54.5 µg L^{-1} for seed cotton yield.

KEY WORDS

DGT; Phosphorus; Plant-available phosphorus

Measuring available concentrations of ZnO NPs in soils using Nano-DGT

Hamid M. Pouran[a*], Steve Lofts[b], Steve McGrath[c] and Hao Zhang[a**]

[a] Lancaster Environment Center, Lancaster University, Lancaster, LA1 4YQ, UK
[b]CEH, Lancaster Environment Center, Lancaster University, Lancaster, LA1 4AP, UK
[c] Rothamsted Research, Harpenden AL5 2JQ, UK
** hamidpouran@gmail.com*
*** h.zhang@lancaster.ac.uk*

ABSTRACT

Zinc oxide nanoparticles, ZnO NPs, are used in a range of commercially available products including sun tan lotions and semiconductors. Increasing number of ZnO NPs incorporated products will likely raise concentration of this nanomaterial in the environment. Available information suggests that ZnO NPs can easily enter soil and water resources. ZnO NPs have adverse effects on different components of the environment in particular because of their toxicological impacts. Zinc oxide nanoparticles are one of the most toxic nanomaterials and could inhibit the root growth of plants and embryonic development of some of marine species.

To better understand fate and behaviour of these nanoparticles in the environment and their potential pathways, determining in-situ concentration of these nanomaterials is essential. We have recently used Nano-DGT in combination with standard DGT devices to determine available concentrations of zinc oxide nanoparticle and its ionic species in soil samples spiked with a range of concentrations from 100 mg/kg to 2200 mg/kg of ZnO NPs and Zn^{2+}. The samples were aged approximately for 80 Days after spiking. For each soil sample a Nano-DGT and a standard DGT device were deployed for approximately 20 hours (in triplicates).

The results showed that for the samples spiked with ZnO NPs, available concentrations of zinc species measured by DGT devices were notably higher than Nano-DGT devices. Nevertheless considerably high concentrations of available zinc were also measured by Nano-DGTs, which could partly be attributed to dissolution of ZnO NPs and released Zn^{2+} because of the soil pH (5.5). In the soil samples spiked with ionic zinc the available concentrations measured by Nano-DGT and DGT devices were approximately 1.5X higher for the spiked samples with 100, 225, 500 and 1100 mg/kg ZnO NP. This ratio was more than twice for the soil samples spiked with 2200 mg/kg ionic zinc.

KEY WORDS

Nanomaterials, Metal Ions, Nano DGT, Soil,

Measuring Available Concentrations of Nanomaterials in Contaminated Soils

Hamid M. Pouran[a*], Steve Lofts[b], Steve McGrath[c] and Hao Zhang[a**]

[a] Lancaster Environment Center, Lancaster University, Lancaster, LA1 4YQ, UK
[b]CEH, Lancaster Environment Center, Lancaster University, Lancaster, LA1 4AP, UK
[c] Rothamsted Research, Harpenden AL5 2JQ, UK
** hamidpouran@gmail.com*
*** h.zhang@lancaster.ac.uk*

ABSTRACT

Nanoscience is facing a turning point, after years of research it has entered commercialization stage and a number of nanotechnology products are expected to enter the market. Apart from environmental impacts of emerging products there are a number of nanomaterials that are already widely used in different industries namely, ZnO, Ag and TiO_2 nanoparticles. These nanomaterials could enter into the environment through different paths including the production stage, waste management and recycling or accidents.

It is known that these nanomaterial have adverse environmental impacts. However, a major challenge that still exists is to better understand their fate and behaviour in the environment, which is not possible without access to proper and reliable sampling techniques.

Here we present application of a modified DGT device known as Nano-DGT, which in combination with standard DGT devices could provide a reliable approach to measure available concentrations of zinc oxide, silver and titanium dioxide nanoparticles in the environment.

In this research, as part of TINE (Transatlantic Initiative for Nanotechnology and the Environment) collaborations, soil samples were spiked with different concentrations of ZnO, Ag and TiO_2 nanoparticles and their respective ionic forms were studied. For each soil sample a Nano-DGT, with 1000 MWCO (molecular weight cut off) dialysis membrane in the front of the diffusive gel layer, and a standard DGT device (DGT Total) were deployed in triplicates. The deployment times were approximately 18 hours.

As it has been difficult to obtain accurate diffusion coefficients of those nanomaterials due to their variable nature, average mass accumulated (M) by DGT was used as a reliable measure to reveal differences between available metals in their nanoparticle and ionic forms. Among three different metals used in these studies, ZnO NP and ionic zinc seem to be the most available ones. Average concentrations of accumulated metal (M) are significantly lower for TiO_2 NP and its ionic form followed by Ag NP and Ag+. This could be attributed to retention of these metallic spices by active surfaces in the soils samples (e.g. organic matter), which make them less available for DGT measurements. Interestingly the samples, even those that were spiked by ionic metals only, showed considerably higher accumulated metals for the DGT devices compared to Nano-DGT. This indicates notable fraction of freely available ions formed high molecular weight complexes in the soil.

KEY WORDS

Nanomaterials, Metal Ions, Nano DGT, Soil,

The rate of P uptake in Fe-oxide loaded DGT´s exposed to long term field trial soils treated with different P-fertilizer rates

Åsgeir Rossebø Almås[a], Hilmar Sævarsson[b], Tore Krogstad[a]

[a] *Norwegian University of Life Sciences, Department of Environmental Sciences, Post Box 5003, 1432 Ås, Norway. asgeir.almas@nmbu.no*
[b] *Lindum AS, Lerpeveien 155, N-3036 Drammen, Norway, hilmar.thor.saevarsson@lindum.no*

ABSTRACT

Phosphorus is a non-renewable recourse, which currently is applied to growing crops through farmyard manure or commercial fertilizers. The P, in contrast to N, has to be mined from mineral sources. The fact that P is a nonrenewable recourse, an essential element for all life, which binds strongly in mineral soil, necessitates is precise application to field soils. Over the years, P has been applied in excess to ensure sufficient supply to farm crops. But erosion of such soils has resulted in eutrophication of low land waters. This is well know, and the challenge in future seems to be to provide sustainable supply of P to feed an increasing world population, without compromising the quality of low land aquatic systems.

During the growth season, plants take up P from soil solution, but the uptake is limited due to strong retention in soils. Several extraction methods have been applied, and in Norway the Ammonium Lactate (AL) extraction method have been established as the method used for advising purposes. However, the use of AL by the preparation of soil slurries conceals the kinetic of P release with time. We have used DGT to investigate the P-kinetic release to soil solution in soils withdrawn from long term field trials. In these trials P have been applied in different amount since 1956... The DGT were exposed to these soils at increasing time from hours to 3 days. In addition, the same soils were extracted using the AL-method. The initial results are interesting, as they show the applicability of DGT for such purposes: The uptake of P in the DGT was not linear with time; it curved and flattened out, and this was consistent from all soils taken from the different P-treatment sites. This is not connected to saturation of the Fe-oxide gel, but due to the partitioning of "biaoavailable" P in these soils. The AL-extractions naturally failed to reflect this phenomenon, and further test of the data will show how the AL extracted P is related to the DGT available P.

We expect that the partitioning of quickly and slowly available P change during growth season, and new trials are executed to test this hypothesis. This may have important applications, as the supply of P to plants can be conducted more precisely during the active part of vegetative growth. Our results indicate that applying DGT´s for such purposes, the amount of quickly and slowly available P can be determined before field season starts. We also believe that the geochemical premises determining the active P store in soil, will be more easily determined by the use of DGT, and hence aid in a better practice in P management and its biogeochemistry.

KEY WORDS

Soil P, Soil, uptake rate, quickly available, slowly available

Measuring plant available phosphorus using diffusive gradients in thin films and X-Ray fluorescence spectrometry

Rothwell SA*, Surridge BWJ, Quinton JN, Dodd IC, Zhang H.

Lancaster Environment Centre, Lancaster University, UK
** s.rothwell1@lancaster.ac.uk*

ABSTRACT

Global concerns of phosphorus (P) deficiency limiting crop yields, and finite supplies of mineral P reserves, suggest a need to maximise P use efficiency in agriculture. To accurately predict the availability of soil P to crops, and subsequent P fertiliser recommendations, soil P tests must determine only the P that will be accessed and utilised by a crop. However, there is growing doubt regarding the ability of current extraction techniques (water, bicarbonate, resin) to accurately determine plant-available P across a range of soils. Indeed, the most widely-used test (Olsen P) across all soil types was only designed for alkaline soils and therefore it is inappropriate as a national standard soil test. Thus, there is an urgent need to develop a standard approach to measuring P availability applicable across a range of soil types. Diffusive Gradients in Thin Films (DGT) may be a more accurate technique for measuring the P available to plants than P measured using current extraction techniques because the measurement responds to both soil solution P and the P rapidly resupplied from the solid phase. However, elution by acid extraction of P retained within the resin gel of a DGT device, followed by analysis via a colorimetric method or inductively coupled plasma-based techniques, typically results in a delay of several days between DGT deployment and reporting of P concentrations. Our research seeks to develop a novel combination of two existing techniques, DGT with portable x-ray fluorescence spectrometry (pXRF) to achieve rapid, non-destructive analysis of P within a DGT device, thus significantly reducing the length of time between DGT deployment and the final determination of plant-available P in agricultural soils. We aim to develop DGT-pXRF as a robust routine analytical procedure suitable for analysis of plant available P in a wide range of agricultural soil types.

KEY WORDS

Phosphorus, DGT, XRF, Bioavailability

Comparison of phosphorus availability in soils with different methods

Kari Ylivainio*, Eila Turtola

Natural Resources Institute Finland, FI-31600 Jokioinen, Finland
** kari.ylivainio@luke.fi*

ABSTRACT

Phosphorus (P) is a finite natural resource and irreplaceable in plant production and, paradoxically, a major cause of eutrophication due to over-fertilization. To guide reasonable fertilization, recommendations for P fertilization are based on extraction of soil with various chemical extractants (soil test P; STP), however, so far no universal STP methods exists, but a large number of different methods. Recently method based on P diffusion (Diffusive Gradient in Thin-films, DGT), mimicking P uptake of roots has shown potential for such a method.

In this study we selected P deficient post-glacial clay and sandy soils and incubated them for two weeks with P sources of variable solubility (superphosphate, manures, sewage sludges), after which different STP methods were used to evaluate P solubility in the soils. The methods included both chemical extractions (Mehlich-3 (M3), Olsen P (O-P), acid ammonium acetate, pH 4.65 (Paaac)) and DGT.

M3 (11 mg l^{-1} from both soil), O-P (14 and 8 mg l^{-1} for sandy and clay soil) and Paaac (1 mg l^{-1} for both soils) extracted about the same amount of P from both soils, whereas DGT-method showed higher solubility for P in clay soils (3.3 and 11.7 µg P l^{-1} in sandy and clay soils) in the control treatment (no P addition). Similarly, all the P sources also increased STP values to the same range independent of soil type, whereas DGT values were higher in clay than in sandy soils. DGT thus predicted P availability to be affected by the soil type and the solubility of the used P source, which may have implications for recommendations of efficient P use.

KEY WORDS

acid ammonium acetate, DGT, Mehlich-3, Olsen P, P availability, STP

Effect of Exogenous Phosphate on the Lability and Phytoavailability of Arsenic in Soil

Jinjin Wang[ab], Xibai Zeng[a*], Hao Zhang[b*], Lingyu Bai[a], Shiming Su[a]

[a] Institute of Agricultural Environment and Sustainable Development, Chinese Academy of Agriculture Sciences/Key Laboratory of Agro-Environment, Ministry of Agriculture, Beijing, 100081, China
[b] Lancaster Environment Center, Lancaster University, LA1 4YQ, UK
** Corresponding authors: zengxibai@caas.sn (X. B. Zeng); h.zhang@lancaster.ac.uk (H. Zhang)*
Tel: +86 (0)10 82106009   Email: j.wang1988@outlook.com; j.wang1988@foxmail.com

ABSTRACT

Arsenic (As) poses a serious problem for the safe production of food crops and may pose risks to humans. Manipulating the mobilization of As in soils using chemical means is an universal approach in remediation of As-contaminated soils, including phytoremediation and chemical washing. Phosphate (P) have been commonly used due to the chemical similarity of phosphate and arsenate, which may lead to a ubiquitous competition in the sorption on both soil particles and plant roots. However, interactions of P and As in soil-plant system with different types of soil are still not clear. The objective of this study was to discuss the effect of exogenous P (200 mg·kg-1 soil) on the lability and phytoavailability of As in a dataset of As-amended soil samples (n = 11), and to attempt to explorer the relationship between labile P/As molar ratio and As phytoavailability. The diffusive gradients in thin films (DGT) technique was introduced in this study. Lettuce were grown on the As-amended soils following 90 days' stabilization of soil labile As concentration. Exogenous P (NH4H2PO4) was applied 7, 14, and 21 days after seeding to achieve a total amount of 200 mg P·kg-1 soil. The results indicated that P application generally facilitated plant growth except one grown on P-sufficient soil. Soil labile As concentration increased in all the soils after P application due to a competition effect. Plant As concentration increased in red soils collected from Hunan Province, while decreases were observed in the other soils. This variation was related to soil activated Al content from the stepwise multiple regression analysis. An overall trend of decrease was obtained in As phytoavailability along with the increase of DGT-measured soil labile P/As molar ratio, which provided a quantitative relationship between them. The functional equation between P/As and As phytoavailability provided a critical value of 1.7, which could be used as a guidance for rational P fertilization, thus avoiding overfertilization.

KEY WORDS

DGT, P/As molar ratio, As phytoavailability

Benefit of using DGT in complement of conventional survey for aluminum monitoring in drinking water catchments

Delphine Devillers, Rémy Buzier*, Alexia Auvity, Patrice Fondanèche, Emmanuelle Ducloux, Karine Cleries, Thierry Hak, François Bordas, Adeline Charriau, Sophie Lissalde, Gilles Guibaud

Research Group on Water, Soil and Environment (GRESE - EA 4330), University of Limoges, 123 Avenue Albert Thomas, 87060 Limoges Cedex, France
** remy.buzier@unilim.fr*

ABSTRACT

Aluminum, one of the major soil constituent, is easily mobilized under acidic conditions. Given that Al is highly suspected of being involved in Alzheimer disease, the resulting enrichment of waters could compromise their use for drinking purpose (regulatory limit of 200 µg.L^{-1}). The eastern part of the Limousin region in France is located on granitic/metamorphic bedrock and displays an important forestry activity and a lot of acidic wetlands. These main characteristics create very acidic conditions (soil solutions pH <5.5) and consequently Al concentrations of hundreds µg.L^{-1} in waters are frequently recorded. For this reason, a one year survey of Al in 6 sensitive drinking water catchments has been established. This conventional survey is based on the weekly determination of dissolved Al in spot samples. Given that the DGT technique grants access to time-weighted average concentrations and discriminates less reactive forms (i.e strongly bound), the benefit of using such tool in complement of conventional survey has been evaluated.

Part of this work aimed at providing insights about Al availability and is devoted to labile Al measurement. Given the acidic nature of the studied site, chelex based DGT are used to ensure the most reliable results. The studied solutions being poorly mineralized (conductivity of 30-40 µS.cm^{-1}), the diffusion coefficient of Al is measured in a diffusion cell with synthetic solutions mimicking the studied waters composition. Laboratory DGT deployments were performed on spot samples. Preliminary results indicate that labile Al account for about 40-60% of dissolved Al. However, Al concentrations were found to decrease during batch deployment. It highlights that for this element, prone to induce flocculation, *ex situ* studies can be biased.

The second part of the work was devoted to *in situ* application of DGT. Given that acrylamide monomer is highly toxic, it is advisable to not deploy DGT based on polyacrylamide gels in drinking water catchment. For this reason, DGT based on agarose gels were investigated. Preliminary results showed that Al recovery after elution was not fulfilled. A methodology for measuring labile Al with agarose based DGT must therefore be developed. Until then, *in situ* application is performed after a by-pass of part of the drinking water flow in order to deploy polyacrylamide based DGT.

KEY WORDS

Aluminum, Drinking water, *in situ* deployment, agarose based DGT

DGT as a tool for monitoring metal concentrations in rivers – strengths and limitations

Øyvind A. Garmo, Ian J. Allan, Kari Austnes, Hans Fredrik Veiteberg Braaten, Marianne Olsen.

Norwegian Institute for Water Research,
oga@niva.no

ABSTRACT

The importance of trace metal speciation is recognised in EU's Water framework directive (WFD) where thresholds for priority metals in surface water are defined as "dissolved concentration" (Cd, Hg) or "bioavailable concentration" (Ni, Pb). The DGT technique can potentially be used to provide a measure of both, but is still not widely used in monitoring programmes. Possible reasons for this can be confusion concerning the interpretation of the measurements (what is this "DGT-labile metal concentration") and lack of control during DGT deployments. In this study DGT was used as a supplement to conventional monthly bottle sampling in the monitoring of six rivers. The trial was part of a program designed to monitor riverine and direct discharges to Norwegian coastal waters. DGTs were deployed by lay persons and returned to the laboratory via mail. There were four deployments lasting 2-4 weeks in each river. The results show that in four of six rivers dissolved concentrations, estimated using DGT and speciation modelling, of Pb and Ni were only a small fraction (<25 %) of total concentrations measured in bottle samples. For Cd, Zn and Cu both approaches tended to give similar results (i.e. no systematic difference). Deployment of triplicate DGTs indicated that precision was acceptable. Inorganic mercury could not be quantified because of high blank levels. Promising results were obtained for methylated Hg in laboratory tests. Advantages, disadvantages and some practical challenges with the use of DGT for river monitoring are briefly discussed.

KEY WORDS

Rivers, Monitoring, Trace metals, Methyl mercury

Application of DGT as a monitoring tool in impacted urban rivers and estuaries: case study of the Zenne river and Scheldt Estuary, Belgium and the Netherlands

Martine Leermakers*, J. Drozdzak, E. AbdulBurAlfakhory, Y. Gao, N. Brion, M. Elskens

Department of Analytical, Environmental and Geochemistry, Vrije Universiteit Brussel, Pleinlaan 2, 1050 Brussels, Belgium
**mleermak@vub.ac.be*

ABSTRACT

The European Water Directive (WFD 2000), imposing a "good ecological status" of surface waters by 2015 was translated in a national Water Management Plan (WBP). Large investments made by the Brussels Capital region for the construction and maintenance of sewage collectors and water treatment plants (WWTP), have had positive effects on the water quality of the Zenne River in terms of the restoration of the oxygen levels and reduction of nutrient loads. Although the construction of the WWTPs and the pollution abatement strategies have led to a general decrease in the total metal load, the metal dynamics andinfluence of the changing water quality parameters on the biogeochemistry of metals and metalloids and on the mobility of sediment bound pollutants is poorly understood. Results of the GESZ project (Towards a Good Ecological Status of the Zenne River) have demonstrated that large variations can be observed in dissolved and particulate metal concentrations during rain events (up to 250 times higher). These short term variations observed by high frequency sampling during rain events are much larger than the long term variations monitored by low frequency (usually monthly sampling) and may have an important influence on the ecological status of the river. Passive sampling devices such as diffusive gradients in thin films (DGT) accumulate chemicals continuously from water and can provide time weighted average concentrations of pollutants over the exposure period. Hence, they offer a number of advantages over conventional monitoring techniques such as spot or grab sampling. In addition, as the compounds measured by DGT must diffuse through a hydrogel and bind on a resin gel, the DGT technique has speciation capacities

Sediments may be an important source of pollutants to the overlying water, especially in shallow rivers, such as the Zenne. The DGT technique can also be applied in sediments, providing high resolution porewater profiles. These profiles can be used to calculate benthic diffusive fluxes and evaluate the importance of sediments as a source or sink of pollutants.

Monitoring trace metal concentrations in dynamic estuarine waters is not straightforward. Estuarine mixing, point sources and sediment remobilisation, especially in the zone of maximum turbidity may significantly influence dissolved metal concentrations. Here, the DGT technique can be used to provide time-integrated response to changes in trace metal concentrations.

In the tidal section of the Zenne river, for several elements large variations in dissolved element concentrations were observed in function of the tide. Time averaged DGT values were in agreement with the average values of the samples taken each hour over a tidal cycle. The sediment DGT porewater results showed that the sediments probably have an importance contribution in the dissolved concentrations for several elements in this zone.

DGT optimization and validation was performed by testing different resins (Chelex, Metsorb, Diphonix, experimental resins of Dow and Magpie Polymers) under laboratory conditions and field conditions for trace metals, As and PGMs. Possible interferences were evaluated.

The DGT probes with various resins were deployed along the salinity gradient in the Scheldt estuary different several tidal cycles. The differences observed indicate the importance of competition for the binding sites and the necessity to apply selective resins for correct interpretations of the results.

The results show that DGT can effectively be applied as a simple monitoring tool to monitor both water and sediment quality.

KEY WORDS

metals, arsenic, PGMs, water, sediment, DGT

Passive sampling as a catchment-screening tool for emerging chemicals: An overview of an Irish study

Fiona Regan[a], Lisa Jones[a], Brendan McHugh[b], Jenny Ronan[a,b]

[a] *Marine and Environmental Sensing Technology Hub, Dublin City University, Glasnevin, Dublin 9, Ireland*
[b] *Marine Institute, Rinville, Co. Galway, Ireland*

ABSTRACT

The challenges of monitoring our waters for compliance with WFD and the expansion of the list of organic chemicals that are to be added for monitoring, provides impetus for investigation of alternative monitoring approaches such as passive sampling. The impact of this study may lie in the establishment of a capability to utilise passive sampling in the monitoring programme in Ireland for WFD. This project pilots the use of passive sampling technology (PDMS and POCIS) combined with biota monitoring to assess the presence of priority substances in Irish surface waters. The project focuses in particular on new pollutants earmarked as candidates for the Annex X priority substances list under the EU Water Framework Directive (2000/60/EC) e.g. E2 and EE2, pharmaceuticals, pesticides, PFOS etc. This considers the implications for compliance with current and proposed EQS and investigates the potential for incorporating passive sampling and biota testing in future compliance, investigative and trend monitoring. Results of water, biota and passive sampling will be presented together for samples collected in two catchments studied. The POCIS is designed to sample water-soluble (polar or hydrophilic) organic chemicals from aqueous environments. The POCIS samples chemicals from the dissolved phase, and mimics the respiratory exposure of aquatic organisms. The POCIS provides a reproducible means for monitoring contaminant levels. Coupling POCIS with water samples taken in-situ will provide further data on WFD priority substance concentration in Irish waters. Several sites along the River Liffey, Dublin, were sampled for pharmaceutical as well as other organic pollutants. A POCIS device was deployed at each location and water samples were collected at T-0 and T-4weeks. There are a number of potential point sources of pollution to this catchment with 3 wastewater treatment plants in the area. A second catchment was studied to investigate levels of 17β estradiol (E2) and 17α ethynylestradiol (EE2) at selected locations along the River Lee, Cork, Ireland in 2013 and 2014 allowing for specific point sources and pressures for these compounds along the water body to be identified thus providing focal points for any proposed more targeted monitoring.

The POCIS sampler was deployed at each of five sites along the River Lee and water samples were collected at T-0 and T-4 weeks. Passive sampling devices allowed for lower limits of detection of target analytes when compared to traditional grab sampling techniques. Deploying passive sampling devices at intervals along this catchment highlighted approximate locations in which estrogens are entering the system with this small scale study suggesting that concentrations of E2 and EE2 may increase through the catchment before entering the Celtic Sea. From this work it is clear that passive sampling can play an important role in screening and trend monitoring of waters for emerging contaminants and can be a useful supporting technique in a toolbox for monitoring within the WFD and the Marine Strategy Framework Directive (MSFD).

KEY WORDS

Passive sampling, catchment approach, risk, trend monitoring, emerging contaminants.

Trace metal speciation? An essential aspect of biomonitoring to avoid wrong conclusions

Jonathan Richir[a,b,c*], Gilles Lepoint[b], Annick Donnay[a,b], Pierre Lejeune[a], Jean-Louis Gonzalez[d], Marc Bouchoucha[d], Jean-François Chiffoleau[d], Bruno Andral[d], Sylvie Gobert[b]

[a] *STARESO SAS, Pointe Revellata, BP 33, F-20260 Calvi, France*
[b] *Laboratory of Oceanology, MARE Centre, University of LIEGE, B6C, 4000 LIEGE, Sart Tilman, Belgium*
[c] *Numerical Ecology of Aquatic Systems, University of Mons, Pentagone 3D08, 6, Avenue du Champ de Mars, 7000 Mons, Belgium*
[d] *IFREMER, Laboratoire Environnement Ressource Provence Azur Corse, BP 330-83507 La Seyne sur Mer Cedex, France*
** jonathan.richir@alumni.ulg.ac.be*

ABSTRACT

The Mediterranean mussel *Mytilus galloprovincialis* is widely used as a bioindicator species in active monitoring surveys. As a filter feeder artificially maintained in the water column, it bioaccumulates trace metals from the surrounding water in their dissolved and particulate forms. However, most monitoring surveys don't take into account that speciation aspect when studying trace metal accumulation kinetics in mussels. In the framework of the STARECAPMED project, we monitored trace metal concentrations in the flesh of mussels together with their "most bioavailable" dissolved and particulate fractions in the water column for almost 5 months (February-June 2011).

Mussels were purchased from 2 little contaminated French shellfish farms (*SARL Etang de Diane* and *ferme marine des Aresquiers*), placed in several pouches to allow regular sampling, and immerged near the Oceanographic Research Station STARESO in the Calvi bay, northwestern Corsica. Mussels and water samples for suspended matter filtration were collected every week to two weeks, as were deployed DGTs. Seawater samples were filtered through 47 mm hydrophilic PTFE membrane filters with a 1.0 µm pore size until clogging. In the laboratory, mussel flesh and filters were digested in Teflon vessels with acids (HNO_3/H_2O_2) in a closed microwave digestion lab station. DGT resins were eluted for 24h in 1.0 M HNO_3. Trace metal concentrations (Cr, Mn, Co, Ni, Cu, Zn, Ag, Cd, Pb) were measured by DRC-ICP-MS. Analytical accuracy was checked by analyzing CRMs.

All the studied metals except Pb were present in the water column to over 80% in their dissolved form. The contribution of the dissolved pathway was thus likely to be predominant in the oligotrophic Calvi bay. Dissolved trace metals showed little temporal variability of their levels, likely resulting from the integration over time of their levels in the DGT probes and the lack of seasonality of this fraction. In contrast, Zn showed great variability of its particulate fraction during the survey. Such temporal variability was also observed for Cr, more abundant in its particulate form at the end of the survey, and for Mn and Pb that conversely tended to decrease. The dynamic of trace metals in the mussel flesh is regulated by the environmental bioavailability of dissolved and particulate metals, the ecophysiological status of mussels and the trophic conditions of the water body. In the oligotrophic Calvi bay, showing background contamination levels by metals, the trophic conditions played a major role once out of the spring plankton bloom. It led to the increase of metal concentrations measured in the flesh of mussels undergoing starvation. However, some metals such as Cu and Co displayed only little temporal variations of their concentrations, these essential micronutrients being well regulated.

The combined study of trace metal bioavailability and mussel ecophysiology in defined environmental conditions allows discriminating against biotic and abiotic factors regulating contaminant uptake in mussels, thus avoiding wrong conclusions about the observed dynamics of the studied contaminants. Mussels are a good proxy of coastal water quality, but their proper use notably requires adjustment of raw contaminant concentrations with trophic status of monitored sites.

KEY WORDS

Trace metal, speciation, biomonitoring, Mytilus galloprovincialis, Calvi bay

Two years monitoring of trace metals in seawater with DGTs in the area of the Costa Concordia disaster (Isola del Giglio, Italy)

Schintu M., Marrucci A, Marras B., Atzori M., Cocco E.

Dipartimento di Sanità Pubblica, Medicina Clinica e Molecolare – Università degli Studi di Cagliari,
Via GT Porcell 4 09124 Cagliari (Italy)

ABSTRACT

This work presents the results of two years monitoring of trace metals in seawater with diffusive gradients in thin films (DGTs) in the area of the sinking of the Costa Concordia cruise ship, which was wrecked off the coast of Isola del Giglio (Italy) on January 2012. The aim was to monitor bioavailable metals released by the wreck and/or produced by the yard during the operations of refloating and removal (Parbuckling project). Sampling was carried out at three sites from May 2012 to September 2014, one month after the wreck removal. Two sites were fixed in the vicinity of wreck, at the bow and at the aft of the ship; the third one was located in an unexposed beach of the island. Nine sampling campaigns were carried out. In each station a canister containing semipermeable membrane devices (SPMDs) and polar organic chemical integrative samplers (POCIS) was deployed. At each canister, fixed at a buoy by scuba divers at about 10 m depth, were also attached 9 devices. DGTs were purchased by DGT Research ltd. Devices with three different resins have been used: Chelex-100 for cadmium, chromium, copper, nickel, and lead; Fe-oxide for vanadium; spheron-thiol for mercury.

Deployment time for all samplers ranged from 5 to 7 weeks. Trace metals accumulated by DGTs were analyzed, after elution, by GFAAS. Mercury was determined with a Direct Mercury Analyzer. The results show higher concentrations of trace metals in the station at the bow of the ship. A significant correlation between polycyclic aromatic hydrocarbons (PAHs) measured with SPMDs and vanadium was pointed out, indicating a contamination by oil, maybe as a result of the yard activities.

KEY WORDS

DGT, Trace metals, Seawater, Costa Concordia

Development of a rapid screening technique for contaminants in environmental monitoring and regulation

Shuang Wu* and Hao Zhang

Lancaster Environment Centre, Lancaster University, Lancaster, LA1 4YQ, UK
** s.wu7@lancaster.ac.uk*

ABSTRACT

Rapid screening technique is important and efficient for routine monitoring of chemical pollutants, risk assessment and decision making in dealing with contaminants in waters and soils. In this work we are developing simple screening methods based on well-developed technique of DGT. Combining the digital colorimetric analysis using a flat-bed scanner for quantifying Cu, Co, Ni in water following the DGT uptake of metals to Chelex resin gel without involving further reactive reagents. Analysis of exposed binding discs by CID provided the linear range of Cu, Ni and Co is 1.50~165 (µg cm^{-2}), 2.70~153 (µg cm^{-2}) and 1.60~ 160 (µg cm^{-2}) respectively. In addition, Cu, Ni and Co can be detected by visual inspection when the mass accumulated reach 50µg, 100µg and100µg.

This study has formulated a guideline list for using DGT as a rapid screening technique to determine if the concentration of metals have exceeded Maximum Contaminant Level based on regulation standard set by different countries. At the end of the deployment, any color observed will indicate the concentrations of trace metals have exceeded the Maximum Contaminant Level based on each regulation or standard. The results at different temperature of deployment were discussed in two modalities, visual and scanning.

The technique has also been developed for screening labile phosphate in water and soils . It was based on the coloration on the surface of Zr-oxide binding gel using the conventional molybdenum blue method following the DGT uptake of P to the gel. The pretreatment period has been decreased and the conditions of color development have been modified to meet the criteria of being rapid screening technique.

New development on accimulating Cr (IV) using a highly selective and high capacity binding phase followed by colorimetric measurement will also be presented.

KEY WORDS

screening, *in situ*, metals, phosphorus, monitoring, regulation

An *in situ* intercomparison exercise on "home-made" DGT for the monitoring of trace metals and mercury in surface freshwaters

A. Magnier[a], L. Lesven[b], Y. Gao[c], A. Dabrin[a], M. Coquery[a]

[1] *Irstea, UR MALY, 5 rue de la Doua-CS70077, F-69626 Villeurbanne cedex, France*
[2] *LASIR laboratory (UMR 8516), Equipe Physico-Chemistry of Environment, University of Lille 1 Sciences and Technologies, F-59655 Villeneuve d'Ascq, France*
[3] *Department of Analytical and Environmental Chemistry (ANCH), Vrije Universiteit Brussel (VUB), Brussels, Belgium*

ABSTRACT

Most monitoring programs for surface waters within a legislative framework such as the Water Framework Directive (WFD) rely on conventional techniques, like spot or automated sampling to determine concentrations of a target substance. These sampling methods are generally time-consuming, they poorly represent temporal variability and could induce samples contamination, loss of analyte or speciation modifications. The Diffusive Gradient in Thin films (DGT) technique is an alternative sampling method to assess a time-weighted average (TWA) metal concentration in surface waters. DGT based on a polyacrylamide diffusive gel and a Chelex resin has been widely used to measure TWA concentration for cationic metals such as cadmium (Cd), nickel (Ni), lead (Pb), zinc (Zn) and copper (Cu). Recently, the gel and/or the resin were modified to propose a similar tool allowing trapping mercury (Hg) species and arsenic (As).

These different DGTs are now commercially available. In addition, several laboratories are developing home-made DGTs. As each laboratory prepares its home-made gel and/or resin in different working conditions by using different reagents (i.e. purity and/or supplier), and also uses different methods to determine diffusive coefficients, the comparability of in-situ results obtained with these tools should be verified.

Hence, the objective of our study was to compare commercial and "home-made" DGT performances for cationic metals (i.e., Cd, Pb, Ni, Cu, Zn, Co) and total mercury. In this aim, we organized an *in situ* intercomparison exercise with 3 laboratories that was carried out in July 2014 in the Deûle River (northern France) for two weeks. Results are addressed in terms of (i) blank values, (ii) accumulated metals mass and (ii) TWA concentrations. The design of the intercomparison exercise allowed overcoming analytical bias. First results highlight the effect of different working conditions on blank values and their impact for the determination of TWA concentrations. Additionally, data showed the importance of systematically characterizing diffusion coefficients for each type of home-made DGT in order to compare concentrations determined by DGT tool.

KEY WORDS

Chelex-DGT, 3-MP-DGT, mercury, metals, intercomparison exercise

Numerical evaluation of lateral diffusion inside DGT samplers

Jakob Santner[a,b*], Andreas Kreuzeder[a,c], Andrea Schnepf[d] and Walter W. Wenzel[a]

[a] *Institute of Soil Research, University of Natural Resources and Life Sciences, Vienna, Konrad-Lorenz-Strasse 24, 3430 Tulln, AT,*
[b] *Division of Agronomy, University of Natural Resources and Life Sciences, Vienna, Konrad-Lorenz-Strasse 24, 3430 Tulln, AT,*
[c] *Land Salzburg, Abteilung 5 - Natur- und Umweltschutz, Gewerbe, Michael-Pacher-Straße 36, 5020 Salzburg, Austria,*
[d] *Forschungszentrum Jülich IBG-3, Wilhelm-Johnen-Straße, Jülich, DE*
** jakob.santner@boku.ac.at*

ABSTRACT

The standard model used for converting the solute mass taken up by a DGT sampler, the DGT equation, is based on one-dimensional solute diffusion. This model was adopted for evaluating DGT results as it was assumed that the diffusive boundary layer (DBL) forming just outside the sampler, but also lateral solute diffusion inside the sampler, have negligible effect on solute uptake. Later, it was recognized that the DBL can significantly decrease solute uptake, while lateral diffusion increases the mass uptake. In the standard sampler geometry these effects tend to balance each other, so that the DGT-measured concentration is often close to the directly measured solution concentration. The experimental determination of increased solute uptake due to lateral diffusion lead to the conclusion that lateral diffusion does not depend on geometric parameters of the sampler. Therefore, a constant relative flux increase factor of ~ 1.2 was adopted to account for lateral diffusion. In this study we aimed to investigate lateral diffusion inside DGT samplers using numerical simulation in a 2D-axisymetric geometry.

Our results indicate that the relative flux increase due to lateral diffusion depends on the diffusion layer thickness, as well as on the physical sampling window surface area. The lateral diffusion flux increase factor, k_{LD}, can be conveniently determined using simple equations for standard solution- and soil-type DGT samplers. Moreover we show, that the effect of lateral diffusion inside to sampler is propagated to the DBL, where it causes a slightly stronger decrease in the sampler's mass uptake than deemed previously. When applied to estimations of the bulk solution concentration, c_b, and the diffusive boundary layer thickness, δ, using samplers with different diffusion layer thickness, k_{LD} as correction for the lateral diffusion flux increase yields better results than the effective sampling area, A_{eff}. This study may hence contribute to more accurate determinations of c_b and δ in solute monitoring applications in waters.

KEY WORDS

Lateral diffusion, correction, diffusive boundary layer

Measurement of mercury and methylmercury in sediment porewater using DGT technique

Sam De Craemer*, Yue Gao, Willy Baeyens

[1] *Analytical, Environmental and Geochemistry (AMAGC), Vrije Universiteit Brussel (VUB), Belgium*
sam.de.craemer@vub.ac.be

ABSTRACT

Given the dynamics of mercury and methyl mercury and their relationship with reactive organic matter there is a clear need to enable their measurements in porewaters to be made at high spatial resolution. Provided that in the porewater of natural sediment the majority of all Hg species are present as inorganic Hg, a real challenge now is to develop a procedure that allows a good recovery of MeHg. Previous research suggests a correlation between the mercury methylation rate and the sulphate reduction rate (Merritt and Amirbahman, 2009). The simultaneous measurement of dissolved sulphide and mercury species can supply more detailed information.

The DGT technique is a suitable technique to measure low level of solute in aquatic systems due to its precentration ability. The sampling technique of DGT was validated in the laboratory for mercury speciation using PSA total Hg Analyser and HS-GC-AFS (Perkin Elmer). Agarose gel was used as diffusive gel in the sampler and 3-mecaptoproply functionalized silica resin gel was used as resin gel in DGT samplers. The instrument for inorganic mercury analysis is PSA mercury analyser (PSA 10.035 Millennium Merlin AA instrument) and the instrument for MeHg analysis is a Perkin Elmer Turbo Matrix 40 Trap headspace sampler coupled to a Perkin Elmer Clarus 500 gas chromatograph through a heated fused silica transfer line. Headspace, chromatographic and detection parameter were optimized with the trap mode and a good linear calibration curve was obtained with the concentration range of 1-10 ng L-1. A couple of DGT probes consisting agarose gel, AgI resin gel, 3-mecaptopropyl functionalized resin gel were deployed in a sediment core, which was collected from Zenne River. The DGT probes were deployed for 24 hours in dark and the AgI gels were peeled off from the probe after the deployment. The colour change of AgI from pale yellow to black, due to the formation of silver sulphide at various locations, was scanned by a flat-bed scanner (HP 3100). ImageJ software allows measurement of average optical density for a chosen area. The optical density for AgI gel deployed in sulphide standard solutions was plotted as greyscale density versus the amount of sulphide determined per unit area of AgI gel (nmol cm-2). One of 3- mecaptopropyl functionalized resin gel sheet was cut into 5mm slices and extracted with 5% thiourea for inorganic Hg analysis using PSA Hg analyser and another gel slices were extracted for MeHg using the extraction protocol from Gao et al., (2010 hair) and analysed by HS-GC-AFS instrument.

The MeHg peak close to the sediment-water interface might be related to the sulphide peak, since sulphate reducing bacteria produce both sulphides and MeHg. Furthermore, MeHg production is usually optimal near the transition from oxic to anoxic conditions, which is normally close to the sediment/water interface (Fitzgerald, 2007). For this reason a correlation between the MeHg and the sulphide profile is possible. However, further interpretation can obtained when seasonal sampling in the same location will be carried out in recent future.

KEY WORDS

Mercury, methylmercury, sediment porewater, DGT

ORGANIZED BY:

azti tecnalia Transforming Science into Business

Environment Centre Lancaster University

SUPPORTED BY:

ura ur agentzia agencia vasca del agua

DGT®

EUSKADI BASQUE COUNTRY