Development of DGT sampler for monitoring estrogenic activity in water with ERE-CALUX bioassay
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Standard Session Themes:

- New techniques and fundamental knowledge
- Application of DGT to aquatic systems (including sediment)
- Application of DGT to soil systems
- DGT for routine monitoring and regulatory purposes

ORAL Presentations from page 2
POSTER Presentations from page 36
ORAL PRESENTATIONS
A comparison of DET, DGT and convention extraction techniques to determine nutrient profiles in riverine sediments influenced by benthic microalgae

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Theme - Application of DGT to aquatic systems (including sediment)

ABSTRACT
Quantification of nitrogen transformations in sediments under a variety of environments is very challenging, due to the presence of benthic microalgae, light-dark cycles, the very narrow zones for nitrification and denitrification and others. Recently, DGT (diffusive gradient in thin films) techniques for measuring ammonium and nitrate in freshwater have been developed by using ion exchange membranes as binding layers. DGT, DET (diffusive equilibrium in thin films) and conventional extraction methods were applied to monitor nutrient vertical profiles in riverine sediment porewaters under different conditions, and their performance were compared. These three methods provided various information of nutrient vertical profiles in sediment porewaters. DGT results presented the effects of benthic microalgae on ammonium and nitrate profiles during light and dark incubation. In addition, DGT, DET and conventional extraction methods provided similar ammonium vertical profiles in sediment porewaters. Ammonium concentrations measured by DET and conventional extraction method were similar, but DGT measurements were generally lower. Furthermore, the nitrate concentrations measured by these three methods were variable. DGT technique provided more measurable nitrate concentrations than DET technique under low nitrate concentrations in sediment porewaters. The study showed that DGT and DET could be useful tools to understand the nutrient profiles drive or driven by biological processes in heterogeneous sediments.
A year-long study of Fe-P interactions in a monomictic lake using DGT

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Theme - Application of DGT to aquatic systems (including sediment)

ABSTRACT

Phosphorus (P) is considered a limiting nutrient in aquatic systems and its balance with N being a determinant of the composition of phytoplankton communities. In the water column of lakes, the redox boundary plays a very important role in transformation of chemical species and thus controls the bioavailability of redox-cycled elements. Iron (Fe) is of importance for its redox sensitive behavior (1) and under reduced conditions, most Fe is found as dissolved Fe (II) while positive pE values favour the oxidized forms of Fe(2). Freshly precipitated Fe hydroxides along with fibrillar organic substances can be found at sub-micron levels, typically in the size range of 50 nm to 500 nm in fresh waters, and which control the behaviour of many other trace species such as phosphate and potentially arsenic through dynamic colloidal interactions(3). This study is thus focused on the coupled redox cycling of P and Fe and the influence of Fe colloids on the bioavailability of P. The bioavailable pool of these species was determined by using ferrihydrite and chelex DGT probes respectively and by chlorophyll-a measurements in the water column. Our results demonstrate the strong tendency of Fe to form colloids which appear to survive reduction under anaerobic conditions for extended periods. Upon dissolution of Fe colloids, DGT-labile P was found to increase linearly with Fe, supporting the inference that these colloids scavenge and control P bioavailability during oxic and sub-oxic conditions in lakes.

References


Application of DGT technique for labile Hg species determination in urbanized surface freshwater environment (Zenne River, Brussels)

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Theme - Application of DGT to aquatic systems (including sediment)

ABSTRACT

Mercury (Hg) is one of the primary health concerns in urban environments due to past and present anthropogenic emissions. Its environmental cycle is controlled by redox, organic matter and microbial reactions, which may facilitate the formation of bioaccumulative organic Hg species; methylmercury (MeHg), with damaging consequences to human and ecosystem health. Knowing the concentration of the labile (proxy for bioavailable) Hg species is particularly important to understand processes leading to enhanced exposure and bioaccumulation.

For the first time, we have investigated Hg species lability with Diffusive Gradient in Thin films (DGT) technique in surface water and sediment of the Zenne River (Brussels, Belgium). Our results indicate seasonal behaviour of labile Hg and MeHg species in both environmental compartments. The seasonality depends on the proximity to urbanized areas. Higher labile Hg concentrations (8.2 ng/L) in surface water in colder season was due to increased emission/deposition via incineration for transport and household heating. Higher MeHg concentration (2.3 ng/L) was observed in the beginning of warmer season, and was more pronounced away from heavily urbanized area. This suggested that although urban-released Hg is very labile, its conversion to the MeHg is likely more microbially controlled by temperature and nutrient availability and not by precursor availability. It also appears that the is a source of Hg to be dispersed and distributed in Zenne River. Sediment pore waters featured an active labile MeHg profile in the warmer season with a subsurface peak (5 ng/L), but is absent in the colder months. Sediments also appear to be a source of MeHg and THg to the water. Finally, our results indicate also the lack of data and understanding of labile Hg urban biogeochemical cycling, including the sources, spatial distribution and fate of Hg species. It is clear there is an intensive transformation occurring in the Zenne and more further work will reveal its potential for its interaction with and danger it may pose to the biota.
As and Sb lability and bioavailability in soils under terrestrial and water-logged conditions

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Theme - Application of DGT to soil systems

ABSTRACT

As and Sb belong to Group 15 metalloids and exist as oxyanion species with predominant oxidation states of +3 and +5. The biogeochemical behaviour of As has been investigated widely, however, Sb soil chemistry and its uptake by plants are poorly understood and generally assumed to be similar to that of As. While background concentrations of As and Sb in soils are low (<10 mg/kg), contamination arises from activities such as mining, waste disposal, fuel combustion, smelting, and shooting activities. The enrichment of soil arsenic (As) and antimony (Sb) is putting increasing pressure on the environment and human health.

In this study, the lability and bioavailability of As and Sb under agricultural conditions in historically and recently contaminated soils was assessed in a series of bioassays. Soils concentration series was established by mixing an uncontaminated soil with (i) historically As and Sb-contaminated soil or (b) recently spiked soils. The lability of As and Sb in the soils was assessed using various approaches: the diffusive gradients in thin films technique (as CDGT), soil solution analysis, and sequential extraction procedure. Lability was compared to the bioaccumulation of As and Sb by various compartments of the water spinach (test species) grown in these soils in a pot experiment. Seeds were germinated and grown for up to 35 days in contaminated soils in an environmental chamber (under controlled light, temperature, and moisture conditions). Both terrestrial and water-logged soil conditions were used to investigate As and Sb dynamics in both soils and plants tissues.

This study will discuss the relationship between As and Sb lability, bioavailability and speciation. Differences between the behaviour of As and Sb will be highlighted.
Biogeochemical implications of bioturbation in legacy contaminated sediments

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Theme - Application of DGT to aquatic systems (including sediment)

ABSTRACT

The global growth in population and infrastructure has increased the pressure placed on aquatic ecosystems. Aquatic sediments serve as important habitats for a range of organisms that perform numerous ecosystem services. Sediments are the depository for many potentially toxic contaminants in the aquatic environment. It is well documented that benthic organisms can modify sediment biogeochemistry and the distribution of chemical and microbial constituents. However, the complex interactions between sediment chemistry and ecosystem function are not always adequately considered during ecotoxicity assessments. An improved understanding of these complex interactions is expected to enable the development of more effective management and remediation strategies. The low-resolution of current analytical techniques used within sediment quality assessments limit their ability to accurately predict subtle changes to sediment/contaminant biogeochemistry. The high-resolution capabilities of diffusive gradients in thin films (DGT) techniques when coupled with planar optodes can address the limitations of current sediment analytical methods, providing a better understanding of the biogeochemistry of these systems. In this study, we utilise a number of different experimental approaches to investigate the importance of bioturbation when assessing the toxicity of sediments to benthic organisms. High-resolution, two-dimensional measurements of contaminant concentrations (e.g. DGT for metals) and additional physicochemical parameters (e.g. planar optodes for dissolved oxygen) were used to enhance our understanding of the biogeochemistry, and possible changes in stressor exposure, in sediments containing multiple contaminants.
Cadmium bioavailability to plants in New Zealand agricultural soils

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Theme - Application of DGT to soil systems

ABSTRACT

The accumulation of Cd in New Zealand (NZ) agricultural soils has been linked to historic phosphate fertilizer applications. Today, the soil Cd concentrations in NZ vary between soil types, regions and land use histories. The transfer of this soil Cd to edible parts of common crop plants grown on some of these soils presents a potential risk to consumers. In recognition of this, NZ has introduced a Tiered Fertilizer Management system that recommends limits to phosphate fertilizer application based on total soil Cd concentrations. However, the decisive factors that determine soil Cd bioavailability to different plants across NZ remain poorly understood. To better understand these factors, we conducted a soil survey covering key agricultural crops grown in different parts of NZ. We collected over 500 soil samples and 400 corresponding plant (spinach, onion, potato and wheat) samples from over 100 cropping farms around NZ. We measured the elemental concentrations in the soils (total extractable) and plant samples, and used 0.05 M Ca(NO3)2 extractions and diffusive gradients in thin-films (DGT) to estimate the bioavailability of the soil Cd to plants. We used the results to assess the relationships between soil Cd concentrations ([Cd]soil) and numerous soil variables and evaluated the predictive capability of the different experimental bioavailability measurements across various plant species and soil types. [Cd]soil varied between 0.07 - 1.03 mg kg-1 and was positively correlated with soil P, Fe and Zn concentrations. The plant uptake factor (PUF= [Cd]plant/[Cd]soil) was negatively correlated with a range of soil variables, including soil C, N, P, Ca, Fe, Al and Mn. The relative predictive capability of the Ca(NO3)2 extraction and DGT varied between soils and plants. Our results have improved understanding of the factors driving soil Cd bioavailability to important crops in NZ and can be used to improve soil management practices to reduce risks posed by soil Cd.
Commercialisation of Diffusive Gradients in Thin-films (DGT) for Phosphorus Measurement in Australian Soils – The story to date

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Theme - Application of DGT to soil systems

ABSTRACT

The Diffusive Gradients in Thin-films technique was first offered as a commercial soil test to measure phosphorus (P) availability in the Australian Summer of 2013. Since this time, we have had a further four seasons worth of data and market status. In the initial year sales reached over 5000 DGT soil tests shared across three commercial laboratories. The initial interest decreased in the first two years of operation where only 2820 samples were tested in 2015. More recently market interest has increased to a point where we have tested over 5500 soil samples for DGT P in 2017 to date. Main strengths of DGT in Australia is that it doesn’t overestimate P availability on our Calcareous soils where our more traditional soil tests (Colwell P) are unreliable. Recent data has also suggested that DGT provides a more accurate assessment of P availability on acidic soils where P is tied up with soil Aluminium and Iron contents. Continued validation of DGT performance with respect to crop response to applications of P has resulted in the development of a robust model where a classification (low, marginal, high) can be allocated to a DGT P result. In addition to a grower knowing the P status across their paddocks we have also developed a model which will provide a recommended P rate that will maximise crop yields.

While the DGT methodology is more labour intensive compared to traditional soil P extract methods commercial laboratories have managed to perform DGT analysis with similar accuracy. In this proposed presentation data including typical quality control measures, comparison of DGT results between laboratories and DGT soil test results with respect to other tests across Australia will be presented. The commercial process of DGT supply chain to laboratories will also be discussed.
Comparison of spot and passive sampling (DGTs) for the regulatory monitoring of metal concentrations in estuaries: an example in the Oiartzun estuary (Northern Spain)

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Theme - DGT for routine monitoring and regulatory purposes

ABSTRACT

The main driver of this study is to respond to European Directive demands for the assessment of the chemical status of transitional and coastal waters. Passive samplers (PS) are already widely used in investigative monitoring and there is an increasing interest in their use for the environmental assessment of water bodies, within European policies requirements. The main barrier hindering the regulatory acceptance of PS for compliance checking is the lack of appropriate Environmental Quality Standards (EQSs). EQSs for metals are defined in the dissolved fraction, preventing the use of DGT-labile concentrations for the establishment of the chemical status of water bodies. Thus, adaptation of EQSs suitable for DGTs would allow their use for regulatory monitoring.

The aims of the present study were: (1) to investigate the relationship between dissolved metal concentrations from spot sampling with DGT-labile metal concentrations, (2) to evaluate the reliability of both used techniques for the measurement of metal concentrations in estuaries and (3) to provide recommendations for the use of DGTs for the development of environmental guidelines. Hence, one station was selected at the mouth of the Oiartzun estuary, which has been classified as highly impacted. At this station, 12 DGTs were deployed simultaneously and triplicates were retrieved after 3, 6, 9 and 12 days. Concurrently, spot water samples were collected every day, at the same depth than DGTs, at low and high tide during the DGT deployment period. Water samples were filtered on site by syringe filters (Whatman® PES, 0.45 µm) for the posterior analysis of metals, dissolved organic carbon and the quantification of SPM. The metals under study were Cd, Cu, Cr, Fe, Mn, Ni, Pb, and Zn. Hydrographic parameters were measured at each sampling time.

We will describe the relationships between dissolved and labile metal concentrations and the environmental factors influencing such correlation. Based on the obtained information, an approach to define quality objectives for DGT-labile metal concentrations will be discussed.
Complexes and colloids - what does DGT measure?

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Theme - New techniques and fundamental knowledge

ABSTRACT
Understanding what a dynamic device like DGT measures is not a trivial matter. We know it is labile species, but how we define labile depends on the characteristics of the measuring device. For very simple solutions interpretation is straightforward, but in natural waters understanding the extent to which complexes and nanoparticulate forms of the analyte are measured is challenging. Through measurement, modeling and mathematical analysis, appreciation of the role of complexes in DGT measurements has progressively developed, particularly with the work of the Lleida research group. This presentation considers how these theoretical developments are consistent with understanding of existing DGT measurements in natural waters and how they can be used more routinely to aid our future interpretation. We still lack definitive data on the extent to which nanoparticles contribute to the DGT measurement. The circumstantial evidence provided by several studies is assessed and apparent contradictions examined. In some work DGT has been used to provide a definition of what is in true solution: that is the measurement is assumed to exclude nanoparticulate forms. In other studies DGT has been proposed as a tool that can be used to measure nanoparticles. Conflicts such as this illustrate the need for a better general appreciation of the difficult to define solution/nanoparticle boundary and for more fundamental measurements using DGT in media that include nanoparticles of appropriate and well-defined size. It is tempting to question whether, with these interpretational difficulties, we should be using DGT measurements in natural waters? Perhaps with our understanding of 50 years ago the answer might have been no, but now we appreciate that to understand the complexities of chemical (and biological) interactions in natural waters we need tools like DGT. The complexities of interpretation of its measurements merely matches the complexities of natural water chemistry.
Comprehensive study of contamination by means of passive samplers (DGTs, SR and POCIS): an example in a Spanish estuary

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Theme - Application of DGT to aquatic systems (including sediment)

ABSTRACT

According to The Water Framework Directive (WFD) the chemical status of water bodies must be determined by comparing the concentrations of priority substances with Environmental Quality Standards (EQSs). However, spot sampling (usually monthly to quarterly sampling frequency), might not provide representative levels of individual pollutants, especially in highly dynamic systems such as estuaries. Thus, this approach may yield values that cannot be compared meaningfully with the established EQSs.

Since the adoption of the first list of priority substances in 2001, new compounds have been included based on the latest scientific knowledge. Nowadays, 45 compounds are listed, including metals and organic compounds. As highlighted by the publication of a ‘Watch List’ in 2015, indicating the contaminants of emerging concern (CEC), as research advances new contaminants will arise as potential priority substances. However, up to date, there are not ready-to-use conventional techniques to guarantee their measurement at relevant EQS level.

Passive samplers might be a suitable alternative to spot sampling for the monitoring of pollutants in estuaries and coastal areas. The aims of the present study were (i) to obtain a comprehensive overview of contaminants distribution within a highly-impacted estuary in the Basque Country (northern Spain) by means of a set of passive samplers and (ii) to investigate their potentiality to comply with the requirements of European Directives. Hence, three types of passive samplers were deployed at two stations and seasons (September 2016 and March 2017) in the estuary, covering a wide range of priority substances and CEC: Diffusive Gradients in Thin-films (DGTs; for metals), Silicon Rubber (SR; for PAHs, PCBs, organochlorine pesticides, UV filters) and Polar Organic Chemical Integrative Samplers (POCIS; for Pharmaceuticals and Personal Care Products). SR and POCIS were deployed in triplicate for 40 days while DGTs were deployed in triplicate every 13 days to cover the entire sampling period. This study provides a step forward the inclusion of passive samplers within monitoring networks.
Development and use of an automatic sequential passif sampler for the monitoring of dissolved metals in marine environments

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Theme - DGT for routine monitoring and regulatory purposes

ABSTRACT

In order to comply with local authorities mining companies in New Caledonia are required to undertake frequent regulatory monitoring of the environments situated in proximity to their installations. In New Caledonia this often translates to regular field trips to sample seawater in the lagoon to determine dissolved metal concentrations. A high sampling frequency is a critical aspect when environmental fluctuations need to be understood, but becomes costly when a vessel is required to access the sampling site.

A patented automatic passive sampler was developed to provide an economic and powerful solution that provides uninterrupted sampling sequences that are not dependent environmental conditions (windy conditions).

The current automatic sampler is capable of sequentially exposing passive samplers for 12 periods that are fully programmable from seconds, to months and has been designed to house DGT® devices manufactured by DGT-Research. A temperature recorder is integrated into the system to allow for accurate calculation of the passive diffusion coefficients for each exposure period. The sampler used has a maximum submergible depth (with PEEK/PETP housing) of 1000 meters and is equipped with a rotating axis and directional vane that ensures the opening points towards the direction of the current.

The sampler has been designed so that parts can be interchanged to accommodate different sampling possibilities, including the exposure of triplicate DGT devices simultaneously.

Five of the samplers are currently being used to monitor the dissolved metals in seawater around the Vale-NC nickel extraction and refinery marine outfall.
Development and calibration of o-DGT for pesticides, hormones and pharmaceuticals

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Theme - New techniques and fundamental knowledge

ABSTRACT

Pesticides, hormones and pharmaceuticals from agricultural or urban sources of contamination are measured in surface water and may have effects on aquatic organisms, even at low concentration levels. For these reasons, it is necessary to estimate their amount in waters. However, concentration in fresh water may vary with time, depending on environmental factors and anthropic activities: consequently, their sampling is a challenge. These last years, passive samplers have been developed with the advantage to improve the temporal representativeness by measuring “Time Weighted Average (TWA) concentrations”.

For the passive sampling of moderately hydrophilic organic contaminants, Polar Organic Chemical Integrative Sampler (POCIS) is the most used and investigated device to date. However, POCIS has some drawbacks: the receiving phase is generally not suitable for the retention of wide range of contaminants, especially ionisable chemicals, and sampling rates are highly affected by water flow velocity, leading to possible bias for TWA concentration estimates (Fauvelle et al., 2014). An alternative is the Diffusive Gradient in Thin-film technique for organic contaminants (o-DGT) (Chen et al., 2012).

Our objective is to develop the o-DGT for a reliable sampling of a wide range of pesticides, hormones and pharmaceuticals in water. For that purpose, we first chose the best diffusive gel and determined diffusion coefficient for all compounds using the slice stacking method (Belles et al., 2017). The concentration in each gel disk was determined over the time, allowing the calculation of diffusion coefficients according to Fick’s second law. The results obtained with this approach are congruent with literature with values ranging from 2.1 to 5.2×10-6 cm2.s-1.

The second step consisted in membrane selection, generally needed to protect diffusive gel, with a low retention of the compounds. Three types of membrane were tested with different pore sizes using a calibration experiment.

Ongoing works will be dedicated to physico-chemical effect studies, and then the in situ deployment of o-DGT to further estimate TWA concentrations.
Development of the diffusive gradients in thin-films technique (DGT) for measurement of platinum group elements Rh, Pd & Pt in natural waters

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Theme - New techniques and fundamental knowledge

ABSTRACT

Platinum Group Elements (PGEs), especially Platinum (Pt), Palladium (Pd), and Rhodium (Rh), are a group of emerging pollutants, whose environmental fate, transport and toxicity are still poorly understood. The aim of this work was to develop the Diffusive Gradients in Thin Films (DGT) technique for platinum (Pt), palladium (Pd), and rhodium (Rh) using novel resins : Magpie MPX 317, Magpie MP 102, Purolite S914, Purolite S920 and Purolite S985, which are specifically designed for these elements. This implies that the binding of the Pt, Pd and Rh to the resin is strong, irreversible, and almost instantaneous and the amount of accumulated metals is well below the capacity of the resin gel. The method development involved several different steps: 1) selection of an appropriate diffusive gel, 2) evaluation of appropriate resins or binding phase for the PGEs and evaluation of the uptake kinetics, 3) development of an efficient elution method for the PGEs from the resin gel, 4) evaluation of the linear response in function of the deployment time and determination of the diffusion coefficients for the PGEs in the diffusive gel, 5) study the selectivity and possible interferences and 6) evaluation of the capacity of the binding gel.

For all the resins investigated, a linear accumulation in function of time was found and diffusion coefficients could be determined. The resins did however, show differences in blank values and reproducibility and this was element specific. Using optimized procedures, the concentrations of Pt, Pd and Rh could be quantified at pg/L levels in natural waters for a 14 day deployment time.
Evaluating use of DGT for routine and regulatory monitoring purposes in water

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Theme - DGT for routine monitoring and regulatory purposes

ABSTRACT

The DGT (diffusive gradients in thin-films) technique is now over 23 years old and features in over 800 journal articles. It is therefore a quite mature technique, although new measurement types and applications are still being developed. As DGT has its “origins in sediment geochemistry” (Davison, 2016), the technique is well suited to application in sediment and soil systems where conventional measurements are often limited. DGT has found a routine monitoring role in some locations for soils and its usefulness as a line of evidence for sediment quality assessment has been demonstrated. While DGT measurements have been thoroughly characterized and demonstrated in many diverse water quality studies, for several major analytes, acceptance by the routine monitoring community has been patchy. This presentation will evaluate the advantages and limitations of DGT measurements for routine and regulatory water quality monitoring, proposing roles for which DGT is particularly well-suited and focus on future research required to address any concerns.
Extending the use of Diffusive Gradients in Thin Films (DGT) to solutions where competition, saturation and kinetic effects are not negligible

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Theme - New techniques and fundamental knowledge

ABSTRACT
The design and the experimental deployment conditions of DGT devices were established to allow interpretation of a linear accumulation of metal with time using a simple expression based on a steady-state flux under perfect sink conditions [1]. However, the extension of DGT to a wide range of analytes and its use in varied conditions has shown that, in some situations, these conditions are not fulfilled, so that some accumulations with time are non-linear [2]. Here we present fundamentally derived equations which reproduce the time accumulations for three situations: i) kinetic limitations in the binding to the resin, ii) saturation or equilibrium effects or iii) non-negligible competitive effects. We show how the accumulations can be quantified in terms of the required kinetic and thermodynamic parameters, and provide practical guidance for their use to obtain reliable estimates of solution concentrations. Media containing Mg and/or Mn, where all three situations can prevail, are used as examples. Such an approach opens up the possibility of using DGT more widely in challenging systems and allows DGT data to be interpreted more fully.

References:
Fertilizer advices by DGTs - from annual to daily fluxes

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Theme - Application of DGT to soil systems

ABSTRACT
Fertilizer management and forecast systems (FMFS) have a proud history in agricultural research, based on a variety of carefully designed soil extract solution tests to estimate plant available nutrients. Millions of such soil tests are carried out worldwide, and relies on the basic concepts:

SOIL CAPACITY
The concentration of nutrients from a soil extraction tests represents a soil reservoir (pool) with varying time span. Many soil tests deliver capacities of 10 – 20 years crop requirements (fex P and K), overestimating the annual need, but is still the best available technology.

SOIL INTENSITY
The porewater concentration represents the pool immediately available to plant roots, but this reservoir lasts from less than a day (P) to a few days (K, N), and is complicated to determine.

The goal has hitherto been to develop estimates for the annual crop requirement. After hundred years research the prediction power for capacity based fertilizer advices face several shortcomings. Several new approaches have been examined, to achieve parameters in between capacities (annual) and intensities (daily) requirements. DGTs have shown promise as DGT-concentrations explain crop yield responses better than by soils tests. This is explained by that DGT extracts nutrients from the soil porewater by diffusion, which mimics plant root uptake processes when diffusion dominates over convection. This research is still in an early phase, but seems to require time consuming documentation work for broadfield use.

My presentation will point out new directions where DGT can open a completely new approach in fertilizer forecast, planning and management. This comprise the combination of crop modelling, DGT fluxes in porewater, NyeTinkerBarber based rhizosphere uptake modelling of plant roots, root system modelling in 2D, 3D, 4D, new soil parameteres for release properties etc. This is combined with rolling out agricultural robots working 8 days a week, performing daily or weekly fertiliser additions. Just dreams? It is all about fluxes, where DGT may help giving feed to models?
Fieldscale Heterogeneity of Trace-element Phytoavailability in Rice Paddies: Evaluation of a Novel Multiplexed DGT/DET Microgel Array Measurement Coupling with Laser Ablation-ICP-MS Analysis

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Theme - Application of DGT to soil systems

ABSTRACT
Rice feeds billions, but its importance is intensifying as the homogeneity of the global food supplies deepens. Future food security will be reliant on the delivery of improvements to field-scale efficiencies in nutrient management, & protection of our grain supplies from harmful toxic-element contaminants. Recent advances in chemical imaging of rice paddy soils, using DGT methods, have improved our understanding of the heterogeneity in element mobilization within flooded soils, with orders of magnitude differences in solute fluxes occurring within micrometre ranges. However, this variability presents an enormous challenge for field-scale management of paddy-soils. Adapting technologies, originally developed for high-resolution 2D-DGT imaging, we evaluate a novel multiplexed microgel-probe configuration for the measurement of in-situ trace element bioavailability at the field-scale. A total of 38 probes were assembled comprising of 864 microgels, encompassing 5 different sampler methods (Fe-DGT, Zr-DGT, SPR-IDA-DGT, AgI-DGT, & DET). The arrays were deployed in a typical paddy field in South China, with marginally elevated toxic trace element concentrations, & a uniform element distribution in total concentrations both across the field, but also with depth (25cm). Laser ablation-ICP-MS analysis protocols were optimised (sample preparation; ablation scanning; data processing; method limits of detection, resolution & calibrations), yielding a robust measurement method with low RSD's (ca.10%) & high sensitivities. As predicted, heterogeneity in labile metal fluxes throughout the field site were high. However, the extensive number & wide distribution of sampler's deployed enabled field-scale trends & element-element relationships across the paddy & at different depths to be successfully resolved. Not only providing a measure of the spatial bioavailability, to enable targeted area management, the deployment provided an indication of overall average element availability at different depths for the whole paddy, which is crucial for tailoring the field-scale biochemistry for higher yield & better quality crops.
From DGT to o-DGT: Challenges and Opportunities

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Theme - New techniques and fundamental knowledge

ABSTRACT

Passive water sampling has several advantages over active methods: it provides time-weighted average (TWA) data, saves time and costs and can yield highly spatially resolved data. One problem of many passive samplers is that their sampling rates are flow-rate dependent, thereby requiring calibration data and other in-situ information to enable water concentrations to be derived. A novel passive water sampler (called o-DGT) for organic chemicals based on diffusive gradients in thin-films (DGT) has been developed1 and tested2 to overcome some drawbacks of current samplers for organic chemicals. Since then, increasing interests have been paid to this sampler. This includes applications to other chemicals such as bisphenols3, 4, pesticides5 and other organic pollutants6, and assessment of chemical removal efficiencies in wastewater treatment plants (WWTPs)7, the concentrations and fluxes of antibiotics in soils8 and desorption kinetics from the soil particles together with the DIFS model 9-11. The development of this technique for other groups of chemicals is ongoing as well as its applications to assess the fate and behaviour of PPCPs in soils, soil–plant system, etc.

This overview will address that what have achieved in the last years about o-DGT, what challenging we are facing when dealing with organic chemicals and what opportunities we can have for the future research on the increasing (emerging) organic compounds with DGT. Overall, o-DGT is a promising tool for understanding the fate and behaviour of organic contaminants in the environment, and it provides an in situ approach for assessing their mobility and availability (potentially bioavailability).
Identifying research priorities in DGT method development

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Theme - New techniques and fundamental knowledge

ABSTRACT
Since the first publication describing DGT in 1994, over 40 different binding layers have been reported in the scientific literature. While some of these binding layers have enabled the expansion of DGT to new and important analytes (e.g. metal-oxide-based layers for oxyanions), many of them provide no clear performance advantage over the original DGT binding layer (i.e. Chelex-100 in a polyacrylamide hydrogel). Here we review the current state of DGT method development in order to highlight areas requiring further research. The aim is to minimise wasted research effort and instead direct it towards addressing the challenges that will provide the most benefit to the DGT community. These research priorities include, for example: further characterisation of Chelex-100 DGT for trace metal measurements in challenging matrices, such as seawater; minimising the impact of biofilms on long-term DGT deployments; the development of DGT for measuring the platinum group elements; and the continued development of DGT for measuring organic compounds. It is hoped that the identification of these research priorities will encourage the DGT research community to address these important challenges, thereby increasing both the adoption of DGT by environmental regulators and the application of DGT to increasingly complex research questions.
In situ tracing of labile trace metals in open sea using DGTs mounted on a SeaExplorer glider

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Theme - New techniques and fundamental knowledge

ABSTRACT

Photosynthesis by marine phytoplankton requires bioavailable forms of several trace metals that are found in extremely low concentrations in the open ocean. The determination of these micronutrient concentrations is, however, a major challenge. An Autonomous Underwater Vehicle, the SeaExplorer glider, was combined with Diffusive Gradients in Thin Films (DGTs) to assess trace metal complexes of various lability in open sea. The glider was treated with a free metal resin to avoid auto-contamination from the vehicle itself. During a field cruise of 3 weeks in the Mediterranean sea, from Isle du Levant (close to Toulon) to the island of Corsica and back, two types of DGTs on the glider, with and without a diffusive hydrogel layer, accumulated labile forms of Cd, Co, Cu, Fe, Mn, Pb and Zn. Element concentrations (in nM) obtained with a fast DGT sampler (diffusive layer of 0.15 mm), resulting from full labile metal complexes, amounted to Co (0.05), Cd (0.04), Pb (0.05), Fe (0.41), Cu (0.35), Mn (0.8), Ni (2.5) and Zn (5.7). Concentrations of metal complexes (also in nM) that are full and partially labile were obtained by a DGT with a thicker diffusive layer (0.9 mm) and were higher for Mn (1.9) and Cu (0.74). We compared our results with the few literature data on labile trace metals available in surface waters of the Western Mediterranean Sea and some other open sea areas. The combination of DGT and SeaExplorer glider shows to be an important tool in the study of labile trace metal concentrations that can be limiting the plankton productivity in High Nutrient Low Chlorophyll regions (HNLC).
Investigating the mobilisation of trace metals and oxyanions in contaminated marine sediment using a combined DET-DGT technique

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Theme - Application of DGT to aquatic systems (including sediment)

ABSTRACT

Sediments are the main repository and an ongoing source of metal contaminants in aquatic systems through mobilization to porewaters and overlying waters. Iron(II) and sulfide are key solutes for understanding the mobilization or sequestration of trace metals in sediment. To effectively investigate it is necessary to measure iron(II) and sulfide with trace metals at the same physical location and to include porewater measurements. Combined DET-DGT probes with iron(II)-DET diffusive layer and Agl and Chelex-Metsorb (MBL) binding layers are able to measure iron(II), metals (cations and oxyanions) and sulfide concentrations simultaneously. This study involved comparison of DET-DGT porewater iron(II), sulfide and trace metals (Cd, Co, Cu, Mn, Ni, Pb, Zn, Al, As, Mo, Sb, V, W) profiles with those obtained using conventional sampling (core) and separation (centrifugation) method. The DET-DGT probes were deployed in the sediment cores and considerable replication was used to facilitate a statistical comparison. Good correlations were found between the profiles of Fe, Mn, Co and As showing a close link between the geochemical behaviour of these elements. Cu, Zn, Pb and Cd are also influenced by the reductive mobilization of Fe and Mn oxides but are also closely linked to the precipitation of metal sulfides in the deeper layers. More detailed metal mobilization patterns will also be presented.
Is DGT an efficient tool to integrate transient trace metals concentrations during a major hydrological event on the Rhone River?

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Theme - Application of DGT to aquatic systems (including sediment)

ABSTRACT

The Rhone River (France) is equipped with many navigation and electricity production facilities. Annually, ~ 0.5 Mm3 of sediment from the Arve river, a torrential tributary of the Rhone river, is trapped upstream of Verbois and Chancy-Pougny dams. This accumulation over time requires conducting regular dam flushing operations to limit sedimentation and prevent flood risks for Geneva due to bed elevation.

In 2012, suspended particulate matter (SPM) were sampled during the dam flushing operations (8 days) showing that particulate Hg concentrations were not altered but As concentrations slightly increased during this period. However, the dissolved fraction was not monitored during this transient event, whereas sediment stocks remobilization could lead to a potential contaminants release in the dissolved phase.

In this context and during last dam flushing operations (20-31 May 2016), we aimed to assess how DGT (Diffusive Gradient in Thin films) could integrate a quick potential release of metals from the particulate to the dissolved phase. Thus, we deployed 3 types of DGT for measuring time-averaged concentrations for cationic metals and As, before, during and after the event (7, 13 and 13 days respectively) at 3 sampling stations along the river (Pougny, Seyssel, Jons) located respectively at 10, 45 and 160 km downstream the dam. This allowed identifying mitigation phenomenon. We sampled dissolved and particulate phases on the sites every other day to explain integration of trace metals potential release by DGT. The sharp increase of SPM concentrations (0.5 [Jons] to 15 g/L [Pougny and Seyssel]) generated an increase in NH4+ concentrations, indicating a change in redox conditions. These changes in water composition induced the release of contaminants (As, Mn, Co, Ni), which was well integrated by DGT measurements. Comparing DGT measurements with time-weighted average of dissolved concentrations in grabbed samples, we can assess the representativeness of DGT measurements for some metals (As, Mn, Pb) and identify metals not so labile and much complexed with organic matter such as Cu.
Monitoring bioavailability of metals and selenium in river waters associated with coal mine water using DGT: Advantages and Limitations

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Theme - Application of DGT to aquatic systems (including sediment)

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).

This presentation will discuss the outcomes of two case studies using DGT as a tool to monitor/measure bioavailable fractions of metals and selenium in river waters associated with coalmine water. The first study was conducted in central Queensland (Australia), coalmine water release into the river during 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 second study was trialled at Trend-Roman Mine, British Columbia (BC). Waste rock from coal mine activities is exposed to water, and selenium from the rock is leached into the receiving environment. The presence of selenium in surface water has been a serious ecological concern, as selenium bioaccumulation can cause severe impact to fish and other aquatic wildlife. The DGT trial was designed to determine Se in surface water at Trend-mine using the DGT technique to provide bioavailability information, and potentially initiate a review of the bioaccumulation model for Se at Trend-mine compliance sites. The trial employed the DGT technique to assess the labile concentrations that could be accumulated by fish or aquatic organisms living in the river. The results of this trial could provide confidence that the risk of environmental harm resulting from the water discharge is being effectively managed.
Monitoring of metals in Irish rivers using DGT passive samplers

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Theme - Application of DGT to aquatic systems (including sediment)

ABSTRACT

Although the occurrence of metals in surface waters is usually low, toxicologists and epidemiologists advise that there may still be significant and widespread adverse environmental and human health consequences associated with these low levels [1]. When considering metal pollutants in water bodies, lead (Pb), iron (Fe), copper (Cu), cadmium (Cd), zinc (Zn), chromium (Cr), mercury (Hg) and arsenic (As) are of primary concern in relation to environmental damage and human poisoning [2]. Metal toxicity can result in a wide range of severe effects, including organ failure, cancer and nervous damage depending on the metals present in a given water body. The accumulative effect of low level exposure can also have significant negative environmental and human health effects [2].

Currently, a 12 month deployment of DGT passive samplers for metal monitoring across South East Ireland is being carried out. The intention of this work is to provide information on the performance of the DGT samplers and seasonal variation in surface water concentrations for a wide range of metals. Various DGT deployment devices and approaches are being used within the sampling campaign. Every two weeks, DGTs are replaced and grab samples are collected for analysis. Two types of DGT are being deployed for metal monitoring: Chelex DGT and Fe-oxide DGT. The metals of interest are as follows: Al, Fe, Mn, Zn, Cd, Cu, Co, Ni, Pb, As, Sb, Mo, Se and W. The data generated will provide useful performance data for passive samplers, such as DGT, as well as information on sampling frequency that has implications for sampling strategies under the EU Water Framework Directive.


**Phosphorus bioavailability in different types of organic materials as predicted by DGT**

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*Theme - Application of DGT to soil systems*

**ABSTRACT**

**Introduction**

Optimal utilization of phosphorus (P) from various P-rich side streams requires the knowledge of P true bioavailability in order to avoid over-use and thus P leaching. In this study we evaluated P fertilization potential of various P sources by growth experiments with concomitant ability of DGT-method to predict the P bioavailability in these P sources as well.

**Material and methods**

Bioavailable P content in P sources with very variable water-soluble P contents (0 to 90%, including manures, sewage sludges, ashes, mineral P fertilizers) was determined by growing barley (Hordeum vulgare) and ryegrass (Lolium multiflorum) in a P deficient sandy soil for up to two consecutive growing seasons. Total of eight ryegrass and two barley yields were obtained. Bioavailable P content of the different P sources was calculated by comparing the grain and grass yields to yield response curve produced by superphosphate-P. Ability of the DGT-method to predict bioavailable P content was tested after incubating the P sources in a sandy soil for 2 weeks.

**Results**

Bioavailability of P in manures and differently treated sewage sludges varied from a few percent up to more than 100% as compared to superphosphate-P. DGT-method predicted the share of bioavailable P well, especially with ryegrass, with improving accuracy as the growing period advanced, and sometimes opposite to solubility tests based on chemical extractants.

**Conclusion**

Results indicated that DGT-method is a promising and quick method for estimating bioavailable P content in various types of organic P sources. The method also seems to predict better the long term than the instant P fertilization value of the organic P sources.
Plant roots activities at the microscale – Assessing element cycling in 2D

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Theme - Application of DGT to soil systems

ABSTRACT

The investigation of microscale processes in soil and sediment always has been challenging due to their inherent small-scale heterogeneity, especially if low nutrient or contaminant concentrations should be assessed. Much of our knowledge on interactions of roots with their immediate environment has been gained in systems where the spatial heterogeneity could not be addressed explicitly. Multi-parameter imaging using diffusive gradients in thin films and complementary techniques not only allows for mapping elemental distributions around roots, but also facilitates mechanistic interpretation of the cycling, solubilisation and immobilization processes.

Using multi-parameter imaging, we could show that roots of the marine seagrass Cymodocea serrulata are able to mobilize phosphorus and iron from carbonate-rich marine sediment by protolytic dissolution of Ca-phosphates, as well as by reductive dissolution of Fe(III)-oxyhydroxides. While the P mobilization capabilities of roots of terrestrial plants are well known, this is the first study to directly demonstrate that marine seagrasses, which are important ecosystem builders, are also able to actively forage for P and Fe. In a second study on the rhizospheric cycling of As(V) and As(III) in As-hyperaccumulating fern species, we observed strong mobilization of As(V) in the rhizosphere of Pteris vittata together with As(III) release from its roots, while P. quadriaurita showed only As(V) uptake. As(III) release from P. vittata roots might be a mechanism to limit As uptake to physiologically tolerable levels. Increased As(V), co-localised with As(III) release, indicates either As(III) re-oxidation or As(V) solubilisation from the soil matrix. Together with O2 images, our data highlight the importance of redox reactions in the rhizosphere of As-hyperaccumulating ferns in aerobic soil.

These studies demonstrate that chemical imaging campaigns should aim at determining sufficient parameters to allow for a mechanistic interpretation of the generated 2D datasets, and points out the need for further increasing the range of parameters that can be mapped simultaneously.
Potentially toxic elements bioavailability in phytoremediated contaminated soils predicted by diffusive gradient in thin films

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Theme - Application of DGT to soil systems

ABSTRACT
The study of rhizosphere-related processes on mobility, availability and toxicity of potentially toxic elements (PTE) in soils is a major challenge to understand their ecodynamic in the context of phytoremediation or natural attenuation of contaminated soils. As the water soluble PTE can easily be mobilized and may be considered as highly bioavailable, soil pore water (SPW) analysis can be an effective assessment tool. The PTE bioavailability in soils can be also assessed by several groups of extraction solutions (Qasim et al., 2015). However an accurate assessment of bioavailability must consider both possibilities of physico-chemical desorption of PTE as well as the biological receptors they can reach.

Alternatively DGT technique has been developed for measuring PTE in soils and their resupply fluxes from the solid phase and predict their bioavailability (Zhang et al., 1995) and potential remobilization.

The aim of this work was thus to assess the speciation, (phyto)availability and potential remobilization of PTE such as Cu, Cr, Zn, Pb, Cd, As and Sb in phytoremediated contaminated soils and technosols with selected laboratory experiments based on DGT probes, soil pore water (SPW) measurements and dwarf bean primary leaves PTE concentrations.

The normal DGT incorporates Chelex-100 cation exchanger were used to measure Cu, Cr, Zn, Cd and Pb, whilst the ferrihydrite-backed DGT have been used for As and Sb measurements. To assess the PTE phytoavailability, a germination test with dwarf beans as plant indicator was also used.

The amount of PTE extracted with the DGT devices were well correlated with total dissolved PTE concentrations in the SPW. Good correlations were also found between each of dissolved PTE concentrations in the SPW, DGT measured PTE concentration and PTE accumulation in dwarf bean primary leaves.

The two methods used to measure the PTE concentrations result in significant correlations between the PTE pools assessed. The chemical assessment of bioavailability using soil solution and DGT measurements may thus provide the information required to predict PTE bioavailability.
Predicting phosphorus availability from chemically diverse conventional and recycling fertilizers

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Theme - Application of DGT to soil systems

ABSTRACT
Due to the limitation of global phosphorus (P) reserves, recycling fertilizers produced from heterogeneous P-rich biowastes such as sewage sludge, slaughterhouse waste or animal manures will become increasingly relevant. Treatment and processing steps (combustion, pyrolysis, anaerobic digestion, etc.) increase the diversity of such fertilizer products and their chemical / physical properties even further. The limited capacity of standard fertilizer and soil extraction methods to predict P bioavailability from contrasting fertilizers requires the development and / or testing of alternative methods.

Here, we investigated several approaches to characterize P availability from a set of 13 contrasting fertilizers. A 6-week pot trial using rye (Secale cereale L.) in a carbonate-free soil (pH CaCl2 = 6.2) served as P-availability reference. We tested the fertilizers directly using H2O, formic acid, citric acid and neutral ammonium citrate batch extractions, as well as a continuous sink-based P extraction (iron bag method), and we performed Olsen, CAL and diffusive gradients in thin films (DGT) tests on fertilized soil.

Standard fertilizer extraction methods did not correlate well with plant P content ($R^2 < 0.40$), whereas the iron bag method showed promising results ($0.73 < R^2 < 0.85$). Among the tests conducted on fertilized soils, DGT was overall equivalent or slightly better than Olsen, showing $R^2$s of about 0.90 for P content.

Overall, our results suggest that the validity of standard P fertilizer tests need to be reassessed in the context of increasingly diverse recycling fertilizers. Combining infinite sink with equilibrium-based extraction methods directly and after application of the fertilisers to soil provides a promising toolbox for product development and assessment in the context of diversifying source materials, fertilizer applications and markets.
Sediment trace metal mobilization under changing oxygen saturation conditions

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Theme - Application of DGT to aquatic systems (including sediment)

ABSTRACT

Primary production by benthic microphyte communities has been identified as a significant contributor to numerous diagenetic processes at the sediment-water interface (SWI). Oxygen microprofile measurements through these communities under light-exposed conditions have shown supersaturation of oxygen below the SWI and relatively large oxygen penetration depths (OPD), with subsequent decreases in both dissolved oxygen concentrations and OPD under dark conditions. We undertook a series of experiments to investigate the effect of changing the OPD on trace metal mobilisation below the SWI. Our objective was to show how diurnal changes in OPD can affect the mobilisation of redox-sensitive metals (Fe and Mn) in sediments, and associated effects on other trace metals (Pb, Cu, Co and Ni).

We exposed replicate mesocosms of a coastal sediment to different dissolved oxygen (DO) concentrations in the overlying water to achieve systematic variations to the OPD. We used two sets of experimental conditions: (1) DO held constant at 0.26 and 1.00 mM (100 and 350% air saturation) for 24 h, (2) DO concentration oscillating between 0.26 and 1.00 mM over 24, 48 and 72 h to simulate a diurnal cycle (24 h period). We used a combined planar optode-diffusive gradients in thin-films (DGT) sandwich probe to measure simultaneously oxygen concentrations and trace metal mobilization across the SWI in high resolution.

Increasing the DO concentration in the overlying water changed the OPD. DGT measurements showed elevated Fe fluxes below the SWI at both OPDs. When the DO concentration in the water was high we observed elevated Fe fluxes deeper in the sediment, where we also observed a zone of elevated Pb release; these were not seen when the DO concentration was lower. These results suggest that redox cycling of Fe (oxyhydr)oxide solid phases and sulphide may be driving Fe and Pb mobilisation dynamics in this sediment within a small depth range. We observed the highest fluxes of Co, Cu and Ni at the SWI, which could be due to decomposition of deposited organic matter.
Simultaneous in-situ measurement of endocrine disrupting compound concentration and potency.

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Theme - Application of DGT to aquatic systems (including sediment)

ABSTRACT

Endocrine disrupting chemicals (EDCs) are substances known to disturb endocrine homeostasis in animals, the ecological impact of which is becoming of increasing concern in freshwater ecosystems. EDCs have been implicated in human and non-human reproductive disorders (sterility, hermaphroditism, cancer) and metabolic disorders (diabetes, obesity). EDCs may also induce cellular (mitochondrial) stress responses.

Synthetic steroid sex hormones, such as 17α-ethynylestradiol (EE2), have the highest estrogenic potency among EDCs and their carcinogenic action has been proven. Bisphenol A (BPA) is widely found in households and industry. It is found in raw sewage and surface waters because it is continuously released into the environment and is a compound of possible concern because of its endocrine disrupting abilities and its carcinogenic action, so-much-so that existing organic materials guidelines can probably be considered obsolete.

Thus the purpose of this research is to investigate the presence of synthetic hormones and the bisphenolic plastics in municipal water systems and to study their environmental and ecological impact. The ecological impact of EDCs will be assessed using a novel combination of methods which will allow the actual levels of endocrine disruption to be ascertained. This will be based on diffusive gradients in thin films (DGTs) coupled with high-performance liquid chromatography/mass spectrometry analysis (HPLC/MS) and the Yeast Estrogen Screen (YES).

DGT estimates time-integrated concentrations while HPLC/MS ensures a robust, automated and sensitive routine analysis. Most significantly, YES, a biomarker-based assay, will be deployed to quantify the total estrogenic potency of the matrices analysed. The unique dimension of this research is to extend the application of DGTs to hormone sampling and to combine the DGT and YES technique to provide in situ quantification of the estrogenic potency of water bodies through time.
Two-dimensional pH measurement in sediment porewaters using a novel DET method based on an anion exchange resin coupled with a pH indicator mixing in a binding gel

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Theme - New techniques and fundamental knowledge

ABSTRACT
Biogeochemical, sorption and mineral dissolution–precipitation reactions in sedimentary deposits generate strong gradients in pH near the sediment-overlying water interface, that play a key role on the mobility of trace metals. These distributions reflect not only the acid–base balances determined by early diagenetic reactions (e.g. reduction of sulfates) but also transport processes such as solute diffusion, advection or bioturbation (worm’s activity for instance) which govern exchange between sediment and overlying water[1]. Protonic reactions in surficial sediments are generally not well stratified with possibly high micro-heterogeneity. For these reasons, accurate characterization of pH distribution is challenging and simple vertical profiles (1D) of pH using H+ ion selective glass electrode by potentiometry in sediment may be inadequate due to the restriction of a one-dimensional measurement (even at a micrometric scale). Advances in digital imaging technology have, however, now permitted the extension of fiber-optic fluorosensor techniques to two dimensions and the development of so-called planar optodes[2] using fluorescence imaging. Here we describe the development and properties of a novel equilibrium gradients in thin films (DET) technique for 2D-pH measurement based on a strong anion exchange resin for pH indicator mixing immobilization in a binding gel that allows in situ, rapid, high-resolution, two-dimensional measurement of pH in natural sediment and overlying water environment over the pH range 5-9. An example of pH 2D-image obtained in the natural freshwater sediment is also presented, suggesting that the sensor held great promise for field applications in the near future.

References:
Use of in situ metal fluxes from sediments in risk assessment: From DGT to DMGs

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Theme - New techniques and fundamental knowledge

ABSTRACT

The quantification of the risk posed by contaminated sediments is critical for regulators. This process considers the concentrations and forms of the contaminants, and the likelihood that they may cause adverse effects to selected receptors in the environment. Both chemical and biological (ecotoxicological and ecological) methods provide useful lines of evidence for sediment quality assessments, but assigning causality for effects often remains problematic. Sediment properties strongly influence contaminant bioavailability, and accurate measurements of parameters such as pH, particle size, organic carbon and acid-volatile sulfide frequently assists in predicting the toxicity of sediment contaminants. However, many approaches that have been demonstrated in the laboratory are not effective or not practical for use in the field. Overall, adequate methods for assessing contaminant bioavailability remain a weakness for assessments. Building on the concept that toxicity to aquatic organisms occurs when the contaminant exposure results in an excessive rate of uptake (internal flux) by an organism, our recent experiences in using measurements of bioavailable metal ‘fluxes’ to predict toxicity are described. This includes the use of diffusive-gradients-in-thin-films (DGTs) for this purpose and also our aims to adapt diffusive milli-gels (DMGs) for a similar purpose. DMGs are composed of 1-mm spherical polyacrylamide gel beads in which Chelex 100 is incorporated. Their small size enables applications as thin layers at sediment surfaces and potentially within organism burrows, thus providing the ability to probe metal bioavailability on environments that few other techniques can assess. The premise is that metal fluxes to DGT and DMG devices can be used to determine when organisms may be excessively exposed to bioavailable metals.
Using integrative passive sampling devices to obtain more meaningful and cost effective data on metal-associated impacts from stormwater runoff

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Theme - DGT for routine monitoring and regulatory purposes

ABSTRACT
In many cases, stormwater compliance monitoring is labor intensive, expensive, and largely unsuccessful in providing the data needed to support stormwater management goals. To help address these issues, passive sampling devices including Diffusive Gradients in Thin film (DGT) for copper, nickel, lead, and zinc, are being used to monitor stormwater runoff adjacent to U.S. Navy facilities in the Puget Sound, Washington and San Diego Bay, California. In the Puget Sound, a network of monitoring stations was established in Sinclair and Dyes Inlets to assess runoff from industrial areas of Naval Base Kitsap as well as commercial, residential, and rural areas within the watershed. In San Diego Bay, passive samplers were co-located with traditional autosamplers within the stormwater conveyance system at Naval Base San Diego (NBSD) to provide a direct comparison with composite sampling. Preliminary results from multiple DGT deployments in Puget Sound showed that time-dependent variability in stormwater impacts on ambient metal concentrations could be detected on small time scales, as well as over multiple days of rainfall. Based on the results from DGTs deployed over different intervals spanning continuous rainfall events of 3 – 56 days, reproducibility was affected by presence of partially labile complexes, mass loading rate (time to equilibrium) which is proportional to free ion concentration, and variation in resin blank values. Best results were obtained for 3 – 7 day DGT deployments, while co-located sampling showed good agreement with the labile fraction of metal estimated from biotic ligand speciation obtained from traditional sampling. Preliminary results from DGTs exposed in the laboratory to composite samples from NBSD stormwater conveyance systems showed increasing uptake over time (range = 1.5 to 24 h) for copper, cadmium, and nickel, with statistically significant positive correlations (r2>0.980) between time exposed and metal mass accumulated. DGTs deployed directly in the conveyance systems also show promise for continuous monitoring that may be more representative than grab or composite sampling.
POSTER PRESENTATIONS
A comparison and characterization of soil phosphorus sampling strategies and their predictive power for estimating plant P uptake

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Theme – Application of DGT to soil systems

ABSTRACT

The soil phosphorus quantity sampled by diffusive gradients in thin films samplers (DGT) has been repeatedly shown to correlate very well with plant P uptake and crop yield. In many cases, DGT P was better or equally good in predicting plant performance on soil compared to conventional batch extraction techniques. As a result, many researchers use DGT for estimating P bioavailability in soils, and commercial soil testing services based on DGT-measured P have already been established. However, only a limited number of studies have been conducted so far to characterize the interrelation of soil P sampling by DGT with chemical and physical soil characteristics, plant P uptake, and conventional P extraction methods.

In this work, we aim at comparing differential soil P sampling strategies and their underlying P mobilization mechanisms, i.e. H2O extraction (desorption enhancement), NaHCO3 extraction (cation complexation), calcium acetate-lactate extraction (acid dissolution, cation complexation), Mehlich 3 extraction (acid dissolution, cation complexation), electro-ultrafiltration (desorption enhancement) and diffusive gradients in thin films (desorption enhancement). Using a set of 40 soil samples, the influence of soil parameters that are potentially relevant to soil P availability (e.g. pH, carbonate content, oxalate-extractable Fe and Al) on the predictive power of the soil tests for plant P uptake and biomass production will be evaluated. Moreover, specific parameters that potentially influence P sampling by DGT, like soil paste incubation conditions and choice of resin gel will be studied systematically. Soil chemical and physical parameters will be related to P uptake in rye grown on the same soils.
A comprehensive DGT study of sediment contamination in a large freshwater Lake Taihu

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Theme - Application of DGT to aquatic systems (including sediment)

ABSTRACT

Sediment is one of the main pools for a wide range of contaminants which can be released to water under certain conditions, posing a high risk on deteriorating aquatic ecosystems. Zr-oxide based diffusion gradients in thin films (Zr-oxide, ZrO-Chelex, and ZrO-AgI DGTs) have been developed for measurements of a range of labile chemicals in sediments, including phosphorus (P), sulfide, oxyanions and metals. These techniques have significant advantages over traditional methods: in situ and simultaneous measurement, time averaged concentrations and high spatial resolution.

Based on the use of the Zr-oxide based DGTs and other high-resolution techniques (e.g., HR-Peeper), the contamination of sediments was studied in a large freshwater Lake Taihu. The results showed high concentrations of labile phosphorus, arsenic and heavy metals in sediments of contaminated regions and induced high fluxes of these chemicals to the overlying waters. The remobilization and release of these elements in sediments were mainly related to Fe and Mn redox. The effects of dominant biological activities (macroinvertebrate bioturbation, algal bloom, macrophyte growth) on the remobilization and release of pollutants from sediments were studied. The effects of capping agent coverage and dredging on inhibiting the lability and release of pollutants in sediments were further assessed. These studies have laid a basis for development of management strategy for sediment contamination.
A comprehensive view of methylmercury cycling and bioaccumulation in trout in geothermal lakes

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Theme - Application of DGT to aquatic systems (including sediment)

ABSTRACT

New Zealand has a natural mercury source that many other countries do not, namely geothermal mercury emissions. Geothermal areas situated throughout the country contribute mercury to air and water. The majority of these areas are located in the Taupo Volcanic Zone, situated in the Waikato and Eastern Bay of Plenty regions. In addition, the small catchments of some lakes and the presence of geothermal fluids in others produce waters ranging in composition from that of rainfall through to that of salt-rich geothermal water and dilute sulphuric acid (Timperly and Vigor-Brown, 1986). Mercury in lake sediments can diffuse into the water column, be re-suspended, be buried by other sediments, or be methylated. Methylmercury can enter the food chain, or it can be released back to the atmosphere by volatilization (Baya et al., 2015). Bioaccumulation and biomagnification of methylmercury (MeHg) may result in adverse effects on aquatic animals and associated wildlife, but can also cause increased dietary intakes of methylmercury in the human population through consumption of fish (Mergler et al., 2007). Elevated levels of MeHg in aquatic organisms, especially fish, represent both an ecological and human health concern. Diffusive gradients in thin films (DGT) samplers have recently been developed for adsorption of mercury and methylmercury using 3-mercaptopropyl functionalized silica gel (3MFSG) and are employed in this study (Fernández-Gómez et al., 2011). This study assesses the relative roles of geochemistry and ecology in determining MeHg bioaccumulation in trout and the effect of redox reactions on MeHg bioavailability using DGT.
A modified DGT technique for the simultaneous measurement of dissolved inorganic nitrogen and phosphorus in freshwaters

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Theme - Application of DGT to aquatic systems (including sediment)

ABSTRACT
A modified diffusive gradients in thin films (DGT) technique using both mixed and multiple binding layers for the simultaneous measurement of dissolved inorganic nitrogen (nitrate and ammonium) and phosphate in freshwater (INP-DGT) was developed. High uptake and elution efficiencies were determined for a mixed (PrCH/A520E) binding gel for dissolved inorganic nitrogen and an agarose-based Metsorb binding layer for PO4-P. Diffusion coefficients (D) were characterised over a wider range of ionic strengths. D for NO3-N and PO4-P were constant over a range of ionic strengths (between 100 and 800 µS cm⁻¹) while the diffusion coefficient for NH4-N decreased with increasing ionic strength. The measurement of NH4-N, NO3-N and PO4-P using the INP-DGT was independent of pH (3.5 - 8.5) and quantitative over varying ionic strength ranges for a 24 h deployment time. Performance of INP-DGT in two field sites with differing conductivity indicated good performance for NO3-N and PO4-P over deployment period and for NH4-N over a 24 h deployment period with low conductivity. The results of this study have demonstrated that INP-DGT could provide a cost-effective monitoring technique for measuring time-weighted average concentrations of dissolved inorganic nutrients in freshwaters.
A modified gel-based CID method for sub-millimeter scale imaging of labile phosphorus and sulfide in sediments and soils with the diffusive gradients in thin films technique

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**Theme - DGT for routine monitoring and regulatory purposes**

**ABSTRACT**

We developed a modified high-resolution imaging method for labile phosphorus (P) and sulfide (S) in sediments and soils in combination with the diffusive gradients in thin films technique (DGT). This promising method was based on the modified Zr-oxide binding gel (MZrG) and the optimal computer-imaging densitometry (CID). Compared to the original Zr-oxide gel (OZrG), the modified binding gel was made using newly prepared Zr-oxide slurry with a changed composition ratios of the gel solution. Besides the traditional performances that obeyed the principle of DGT theory, the modified gel was further demonstrated to have two improved characters: one was the higher homogeneity of the distribution of Zr-oxide slurry on the binding side, which could simplify the procedure of coloration of P-loaded gel; the other was the integrity of the dried gel without any 2D shrinkage and cracks, which could keep the color on the gels for a long time. Furthermore, to eliminate the color difference among images obtained by various scanners, the color management (ICC) was introduced to calibrate the scanned images of colorized gels. Thus a unified calibrated curve of P or S could be achieved for different scanners. Based on these improvements, the CID method was standardized as the following: colorization; drying; scan; ICC; and calculation. The DGT devices with MZrG and OZrG were applied to image sub-millimeter scale profiles of labile P and S in the same homogeneous sediment and analyzed using the standardized and traditional CID method respectively. From the compared results, it can be determined that not only the validity of the new method stayed the same but also the precision and the efficiency of the new method were quite improved.
A novel colorimetric DET technique for the in situ, two-dimensional high-resolution measurement of sulfide in sediment porewaters

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Theme - New techniques and fundamental knowledge

ABSTRACT

In aquatic environments a portion of the organic matter reaching the sediments is oxidized by anaerobes utilizing sulfate, the most oxidized form of sulfur, as an electron acceptor and releasing sulfide as the reduced product. A new high-resolution, two-dimensional colorimetric diffusive equilibration in thin films (DET) technique is described for measuring porewater distributions of total sulfide in coastal sediments using methylene blue method. Computer imaging densitometry (CID) is used to analyze the retrieved samplers following exposure to mixed diamine reagent (MDR), a colorimetric reagent selective for sulfide. The technique was optimized to allow detection of up to 1000 µmol L⁻¹ sulfide. The CID processing of the scanned color image was also optimized to adjust the sensitivity of the assay as required; by processing the image with different color channel filters. The lower detection limit of the optimized technique was 1.1 µmol L⁻¹ sulfide. The new method was used, in association with the existing iron(II) colorimetric DET technique, to measure porewater co-distributions in a coastal seagrass (Zostera capricorni) meadow in Queensland, Australia. The two-dimensional, high resolution distributions obtained provide a highly representative measurement of the co-distributions of porewater solutes, allowing heterogeneous features and biogeochemical processes to be observed and interpreted.

Keywords: diffusive equilibration in thin films (DET); porewater; sediment biogeochemistry; Computer imaging densitometry (CID); high-resolution; two-dimensional.
A Sensor Combining In Situ Preconcentration and On Site Colorimetric Analysis for Phosphate Detection in Freshwaters

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Theme - New techniques and fundamental knowledge

ABSTRACT

Algal blooms as a result of excess nutrients of phosphorus and nitrogen cause water quality deterioration and hypoxic conditions in waters which lead to the death of animals and plants in large numbers. Affordable sensors to monitor nutrient levels in waters are in need. However, existing techniques such as molybdate blue ultraviolet spectroscopy, anion chromatography or inductively coupled plasma mass spectrometry are costly, labour intensive, time consuming and prone to cross contamination over the course of the sampling procedures. Although there are on-line sensors available on the market in recent years based on direct spectroscopic measurements of molybdate blue/phosphates compounds, they often encounter difficulties in measuring trace concentrations in natural waters.

A novel on-line sensor system combining in situ preconcentration and on-site colorimetric detection is recently developed in our lab. In situ preconcentration process includes a diffusion of phosphates through a dialysis membrane and selective binding of phosphates by a commercial polymer aqueous solution, which greatly lowered detection limits (<5ug L⁻¹). Phosphorus concentrations are estimated alongside the flux through the membrane based on Fick’s Law of diffusion. On-site colorimetric detection is made with small sized light emitting / photo diodes with wireless data transmission.

A linear relationship of measured absorbance vs phosphorus concentrations in water is achieved with the auto-injection/preconcentration system.
Availability of Mg to Diffusive Gradients in Thin Films (DGT) devices. Influence of the ionic strength

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Theme - Application of DGT to aquatic systems (including sediment)

ABSTRACT

Diffusive gradients in thin films (DGT) is a dynamic speciation technique for in situ measurement of the availability of different chemicals, nutrients or pollutants. DGT devices were designed to allow interpretation of a linear accumulation with time using a simple expression based on a steady-state flux under perfect sink conditions [1]. However, in some situations, these conditions are not fulfilled, so that accumulations with time may also be non-linear.

Magnesium has important roles in soils (influencing the compactation, structuration and plant growth) and waters (responsible of hardness and membrane fouling) so that its availability is an issue of environmental concern. Data reported indicate that non-linear DGT accumulations of Mg are obtained at high ionic strengths (I) whereas the accumulations largely increase and become linear with time as the ionic strength decreases [2].

This dependence can be explained from i) the increase of both the equilibrium and association rate constants of the reaction between Mg cations and resin sites, and ii) the growing contribution of the partitioning of Mg cations at the resin-gel interface, as I decreases.

A simulation tool that explicitly includes the electrical migration of the Mg cations due to the electrical interactions with the resin sites is considered. This simulation tool shows that a simple model based on a Donnan partitioning at the resin-gel interface can be used to obtain approximate analytical expressions for the accumulation.

The main effect responsible of the increase of the Mg accumulation as I decreases is the increase of the stability and association rate constants. At salinities below 5mM, the binding of Mg is so fast and strong that the simplest perfect-sink DGT expression can be used to predict the Mg accumulation.

References


2.- Altier, A; Jimenez-Piedrahita, M; Cecilia, J; Rey-Castro, C; Galceran, J; Puy, J; Anal. Chem., 88 (2016) 10245–10251
Better relationship between DGT-Cd and subcellular concentrations of Cd in two earthworms: implications for species-specific sensitivity

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Theme - Application of DGT to soil systems

ABSTRACT

The toxicity and uptake of metals in organisms are determined by metal bioavailability, and the diffusive gradients in thin films (DGT) technique is verified to be effective to assess the bioavailable fraction of metals. For insights into the mechanism of sensitivity difference, we analyzed the subcellular distribution of Cd in two ecologically different earthworm species, Metaphire guillelmi and Eisenia fetida, and their relationship with DGT-Cd in soils.

Five Cd-containing subcellular fractions: granules (D), tissue fragments, cell membranes, and intact cells (E), microsomes (F), heat-denatured protein (G), and heat-stable protein (H) were determined. The saturation model was fitted well (R2 > 0.97 for most cases) to the Cd concentrations in all fractions and DGT-Cd in soils. However when total Cd in soil was used, both the standard error and the derived parameters are, in some cases, unrealistically high. This indicated that DGT-Cd was more appropriate than total Cd for fitting the model. According to fitting results, whole-body Cd binding capacity (Cmax) was much higher in E. fetida than in M. guillelmi, despite the similar Cd binding affinities (logK), indicating that binding capacity is more species-specific than affinity. Though Cd accumulation capacity of E. fetida was greater, it was less sensitive to the metal than M. guillelmi, because fraction H in E. fetida contributed much more to Cd accumulation in the earthworm’s whole body, and Cd in this fraction is biologically inert. Given the higher logK of fraction G and the higher toxicity of Cd to M. guillelmi than to E. fetida, fraction G must be a metal sensitive fraction, which may relate to the toxicity.

Metal toxicity in organisms is strongly determined by the concentration of the metal in target tissues or fractions rather than by the total body burden. Accordingly, the Cd binding characteristics of subcellular fractions obtained by fitting with DGT-Cd can provide valuable information on the metal toxicity and earthworm’s tolerance.
Bioavailability and bioaccumulation of uranium in mining environment: a geochemical and biological approach

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Theme - Application of DGT to aquatic systems (including sediment)

ABSTRACT

Current environmental regulation is becoming more ecosystems-oriented. In this respect, the target for the given standards is the habitat’s faunal biodiversity, meaning that the contaminant’s bioavailability is taken into account. As the bioavailable fraction depends on the chemical speciation, it also varies with the geochemical conditions of the aquatic system (water composition and nature of sediments). For several elements EQS standards have been proposed for different environmental conditions. Sediment Quality Standard (SQS) have been proposed and are being evaluated for a number of elements. However, the bioavailable fraction in sediments is also dependant on geochemical factors and sediment mineralogy. The objectives of the present study are to evaluate the mobility and potential bioavailability of U using both a geochemical approach (total concentrations, sequential extraction techniques, pore water concentrations, Diffusive Gradients in Thin Films (DGT), speciation modelling) and a biological approach (accumulation of trace elements in the larvae of the nonbiting midge Chironomus riparius). Both field studies as well as laboratory experiments using specific mineral phases spiked with uranium are conducted. A field study was performed in the former uranium mining site Bois Noir Limouzat in Loire, France. Sediments and Chironomus riparius were collected in river sediments upstream and downstream of the mining site as well as in iron oxide rich sediments of mine waters prior to treatment. The relationship between sediment characteristics and bioaccumulation of U was investigated.

Laboratory experiments are currently being performed on the bioaccumulation of uranium in Chironomus riparius exposed to specific mineralogical phases (quartz, kaolinite, smectite, ferrihydrite) spiked with uranium. During a ten days’ exposure experiment, the uptake of uranium in the chironomid larvae in function of time is investigated and and DGT devices are deployed simultaneously. The relationship between uptake of U in the chironomid larvae, concentrations in sediment, overlying water, porewater and DGT will be presented.
Comparing dissolved arsenic species measured by DGT with 3MP, ferrihydrite, Metsorb, zinc ferrite and zirconium dioxide binding gels

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Theme - Application of DGT to aquatic systems (including sediment)

ABSTRACT
Bennett and co-workers\(^1\) had written interesting comments on our previous works describing a new diffusive gradients in thin films (DGT) binding gel, which is based on zinc ferrite (ZnFe2O4), for the measurement of total arsenic (As) in natural waters\(^2\). These comments discussed several points of our analytical development and the validation of the ZnFe2O4-based DGT: (i) no comparison with ZrO2 DGT; (ii) the choice of the deployment solutions for testing the DGT performances; and (iii) the impact of redox sensitive species and bicarbonates (generated by the bacterial respiration of particulate organic matter) during DGT deployment in sediment pore waters. To clarify all these questions, an important comparison exercise has been carried out using various experiments (batch experiments, time-series accumulation, DGT deployment in realistic waters) for better understanding the response and limits of each DGT (3MP, ferrihydrite, Metsorb, ZnFe2O4 and ZrO2) in natural waters. The presentation is going both to answer open questions from Bennett and co-workers and to provide new information on the use of existing DGT techniques for measuring arsenic in natural waters.

References:


Determination of the effect of biofilm growth on the surface of the DGT membrane on the calculated concentrations in a tropical lagoonal environment

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Theme - DGT for routine monitoring and regulatory purposes

ABSTRACT

The use of passive samplers and in particular DGT® devices to determine concentrations of dissolved metals in seawater are becoming more common-place for use in regulatory monitoring. However, these devices are subject to undesirable biological growth, or biofouling, on the DGT® devices membrane that may influence the flux of dissolved metal concentrations being transferred through the diffusive gel. The effect of the development of a biofilm on these devices has been a topic of discussion by a number of authors; therefore, the main objective of this study was to determine the effect the biofilm has on the calculated dissolved metal concentrations measured using the technique in tropical areas of intense primary production.

The aim of this study was to observe the growth and estimate the influence of biofilm developments on the surface of the DGT® membrane. Triplicate DGT® devices were simultaneously immersed at four stations for a period of between 1 and 28 days during a warm and cool season in the SW lagoon of New Caledonia subjected to a wide variety of environmental conditions. DGT® devices were submerged regularly along the period of immersion. At the end of the 28 days period all the DGT™ devices were removed and re-immersed simultaneously for a period of 24 hours in seawater spiked with a radiotracer (Ni-63) that made it possible the study of the effect of the biofilm.

Biofilm development in the majority of cases resulted in an overestimation of the calculated Ni-63 concentrations relative to DGT® devices with no biofilm development. This over-estimation varied according to the duration, location and season, and is likely to be caused by an accumulation of metals in the biofilm that are subsequently available for transfer through the diffusive gel. The results obtained meant it was possible to determine, for each specific area, the maximum recommended period of immersion of these devices that varied from 5 to 10 days.
Development and evaluation of a diffusive gradients in thin films (DGT) technique for measuring vanadium, molybdenum and uranium in marine sediment porewaters

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Theme - New techniques and fundamental knowledge

ABSTRACT
Vanadium (V), molybdenum (Mo) and uranium (U) are redox-sensitive trace metals that enrich or deplete in marine sediments to differing degrees, depending on the prevalent redox conditions. As such, these elements can provide an insight into the concentration of dissolved oxygen in the water-column at the time of sediment deposition, which is useful for tracing oxygen concentrations in both the recent and ancient past. However, to accurately interpret these ‘paleoredox’ tracers, their biogeochemistry must be well characterised. Conventional sediment porewater sampling techniques (e.g. squeezing or slicing at the centimetre scale) fail to provide adequate spatial resolution. The use of a high-resolution technique for sediment porewater analysis, such as the diffusive gradients in thin films (DGT) technique, can provide an ideal tool for studying the biogeochemistry of these trace metals in marine sediments, yet such a technique has not yet been validated under the conditions typically encountered in marine sediment pore waters (i.e. high concentrations of ferrous iron and bicarbonate). Here we report the development of a DGT technique, based on a titanium dioxide binding layer, for the measurement of V, Mo, and U in marine sediment porewaters. This method was tested over a range of ferrous iron concentrations (0 – 1 mmol L⁻¹) and bicarbonate concentrations (2 – 20 mmol L⁻¹) representative of those in productive marine sediments. Following this, DGT samplers containing the tested binding layer were deployed into sediment cores collected from the Gold Coast Broadwater, Australia, for 24 hours. Following retrieval they were sectioned at 1 mm intervals, eluted, and analysed by ICP-MS. Concentration profiles obtained from the DGT samplers were compared to those determined by slicing the sediment cores at 1cm intervals, centrifuging, and directly analysing the porewater by ICP-MS. The superior spatial resolution and minimal disturbance of the DGT approach confirmed its utility for investigating the biogeochemistry of V, Mo and U in marine sediment porewaters.
Development of DGT sampler for monitoring estrogenic activity in water with ERE-CALUX bioassay

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Theme - Application of DGT to aquatic systems (including sediment)

ABSTRACT

Monitoring the estrogenic effects of these compounds demands efficient, simple and sensitive techniques. In this study, a combination of a new type of diffusive gradients in thin-film (DGT) technique with an estrogen responsive element-chemically activated luciferase gene expression (ERE-CALUX) bioassay was developed. The performance of this novel method was assessed with 17β-estradiol (E2) as the model steroid hormone, XAD 18 resin gel as binding phase in the DGT method and VM7Luc4E2 cells (formerly BG1Luc4E2) for the ERE-CALUX bioassay. The laboratory tests showed that DGT components and the experimental matrix do not influence the estrogenic activity of ERE-CALUX cells. The effective diffusion coefficient of steroid hormones in agarose diffusive gel was 5.16 ×10⁻⁶ cm² s⁻¹ at 25 °C. The detection limit of this combined DGT/ERE-CALUX method for a 1 day sampling period (0.026 ng L⁻¹ of E2), is significantly lower than that obtained by active sampling combined with GC-MS/MS and LC-MS/MS analysis. This method was independent of pH (5-8), ionic strength (0.001-0.5 M) and dissolved organic matter (DOM) concentrations (0-30 mg L⁻¹). The estrogenic effects of steroid hormones of effluent in Beijing sewage treatment plant determined by DGT for a 6h deployment time were comparable to those measured by an active sampling method, with a relative standard deviation of 20%. This study demonstrates that DGT combined with ERE-CALUX is an effective tool for pre-concentrating steroid estrogens and possibly also in the monitoring of estrogenic activity in wastewaters.
DGT - future directions

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Theme - New techniques and fundamental knowledge

ABSTRACT
DGT technology is growing up, has passed it teens and is now in its early 20thies. DGTs has faced a considerable evolution on sampler design, adsorbent and membrane technology. The future requirements of sampler can now be sorted in at least two major directions:

Inorganic DGT
Mostly consisting of inorganic dissolved ions, complexes or species of elements from Li to U and even some trans-uranes

Organic DGT
The collection of dissolved organic contaminants or dissolved organic compounds in general.

This has required developments and modifications of both the sampler design and composition of the membranes and the adsorbents.

The DGT history will be quickly summarized, but this lecture will mainly focus on the development of the inorganic DGT. This, as I am particularly interested in the development of a sampler suited for agricultural research, as this probably has the largest and most promising application area of DGT technology. I will focus on the perspective for the development of an “all in one DGT sampler”, which collect both anionic and cationic species in the same sampling operation. This should cover most plant nutrients, classical heavy metals and trace elements (non-metals, oxyanions etc) and. This will require a rethinking of adsorbent design, a new “neutral” membrane and some other considerations of the sampler to accomplish this goal. This will be discussed in the lecture.
Ferry-based passive sampling of trace metals in seawater

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Theme - DGT for routine monitoring and regulatory purposes

ABSTRACT
This work reports a tentative measurement of the spatial concentration of dissolved As, Cd, Cu, Cr, Ni, Pb, and V in the Western Mediterranean Sea by using DGT devices. A Ferrybox (Mod. 4H Jena) was installed in 2015 in the passenger ferry Mega Express Three owned by the Corsica-Sardinia Ferries company, which operates between France and Italy (main routes are Toulon-Ajaccio in autumn-winter and Livorno-Olbia in spring-summer). The Ferrybox, which is mainly intended to measure pH, salinity, temperature, and chlorophill “a” in seawater, was equipped with a unit for passive sampling (PS), allowing the exposure of DGT devices and of passive samplers for organics (silicone rubber, POCIS, Chemcatcher). The PS unit for DGTs consist in three PVC-U PN4 tubes 300 mm high and with a diameter of 110 mm. Seawater is pumped by a Teflon pump throughout a hole in the fore of the ship and it flows in the DGT tubes at the speed of about 0.2 m/s. The system is shut down before the ship enters a harbor. This work discusses the results of the first two campaign of measurements. Chelex-100 DGTs were utilized for the measure of Cd, Cu, Cr, Ni and Pb, while V and As were accumulated in Fe-oxyhydroxide DGTs. Average exposure times for DGTs were 48 hours.
In situ using DGT technique to measure labile P around the root of Oryza sativa L. in flooded soils while minimizing P fertilizers applying

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Theme - Application of DGT to soil systems

ABSTRACT

The use of phosphorus (P) fertilizers in excess of crop requirements has led to the accumulation of a largely unavailable pool of soil P and eutrophication. Our previous work indicated that P fertilization during the wheat season only in a rice–wheat crop rotation can sustain rice crop yield due to a sufficient supply of available P. Now the diffusive gradients in thin films technique (DGT) was used as a novel approach to investigating the distributions of labile P and iron (Fe) in close proximity to Asian rice (Oryza sativa L.) roots in situ throughout the rice-growing season at submillimeter to millimeter spatial resolutions. A seven-year field experiment with four P fertilizer treatments was conducted. After seven years, the one- and two-dimensional changes of labile P showed that the wheat season only fertilization treatment had sufficient labile P pools in the flooded soil, similar to those in the rice season only fertilization treatment, despite a lower P concentration in solution. The coincident distributions and significantly positive correlation between labile P and Fe due to a concomitant release from soil solids demonstrated Fe-coupled mobilization of P in flooded soils. Moreover, a significant and strong positive relationship was found between the average measured P concentration and soil Olsen P and total rice P concentration. Here we show for the first time that DGT is a new and direct technique for analyzing labile P in flooded soils and provide further evidence that the application of P fertilizers can be minimized to reduce the risk of surface-water nutrient enrichment and eutrophication without reducing crop yields.
Investigating the influence on seasons on performance of passive samplers and their uptake of antibiotics and down the drain chemicals.

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Theme - DGT for routine monitoring and regulatory purposes

ABSTRACT
Pharmaceutical and down the drain chemicals in water bodies are of increasing concern in today’s society. Although not thought to be of immediate concern to human health, Studies have shown that aquatic life is being harmed significantly. [1] Contaminants include fragrances, lotions, prescription drugs, veterinary medicines and detergents. [2] This study investigates the presence of various down the drain chemicals and pharmaceutical residues. The work will be carried out over an extended period to investigate if changes in temperature, rainfall and seasonal events have an effect on the performance of the samplers and if so how significant it is. It is hoped that the results will provide conclusive evidence of this. Such information can then be used for sampling programmes and compliance with policies such as the water framework directive set out by the E.U.

DGT samplers will be deployed in triplicate for a 12 month period with a biweekly replacement schedule generating 78 samples per site. As the main source of the target chemicals to surface waters is the discharge of treated effluent from sewerage treatment plants all deployment sites are located downstream of discharge points. Grab samples will be collected at the same time creating another 26 samples per site. Three sites will be tested in total all situated in the southern Ireland. In total 104 samples will be generated per site. Freely available weather data will also be correlated to allow for the determination of weather influence on the samplers performance. In addition to this work, Horizon Atlantic HLB-L SPE Disks will be deployed in triplicate using ChemCatcher housings. This will allow for performance comparisons for both samplers. It is hoped the samplers will complement each other and that a wide range of organics will be detected by both samplers. It will help determine the optimum sampler and if one has a higher accuracy/selectivity.

Investigation of synthetic ferrihydrite transformation in soils using two-steps sequential extraction and Diffusive Gradient Thin Film technique (DGT)

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Theme - Application of DGT to soil systems

ABSTRACT
Ferrihydrite is prevalent used as an absorbent for removing the arsenic (As) in waters, soils and sediments due to its big specific surface area (>200m²/g). However, its instability sometimes limits its efficiency of As adsorption. The objective of this research is to investigate the effect of soil properties and water management on the ferrihydrite stability during 180 days by coupling the sequential extraction and DGT. The result of sequential extraction revealed that ferrihydrite transformation occurred within all the treatments of three different soils (SM1, SM2 and SM3). Ferrihydrite in 70%SWHC transformed about two times faster than 30%SWHC. The result of DGT measurement indicated that ferrihydrite dissolution was greater in 70%SWHC compared to 30%SWHC. The peak points for 70%SWHC in each soil appeared later (on 30d, 60d and 15d for SM1, SM2 and SM3) than 30%SWHC (15d, 15d and 7d for SM1, SM2 and SM3). After the peak points, the decreased trend of liable Fe in 70%SWHC was stable until to the end while in 30%SWHC the concentration of liable Fe decreased quickly in following 30-45 days and then became stable. Ferrihydrite dissolution rate under 30%SWHC followed the order SM1>SM2>SM3 while under 70%SWHC followed the order SM2>SM1>SM3 in three soils. Ferrihydrite transformation and dissolution was proved to have a strong relationship with SWHC, variance of pH in three soils and pH increment was bigger in 70%SWHC. However, the real variance between two different SWHC was probably due the effect Fe (II) starts working in 70%SWHC treatments after 30ds as a result of continually anaerobic condition occurred after 30d. The variances of ferrihydrite transformation and dissolution process among three soils was supposed to be different content of soil total organic matters, available Fe and the percentage of clay minerals (particulate size<0.02mm) in three soils. The result of this study indicated it is more likely to present a high risk of ferrihydrite utilization as an adsorbent for arsenic remediation in long time waterlogged or a higher SWHC acid farmland which may significantly decrease its effectiveness.
Labile Hg speciation in coastal, mine-impacted Gulf of Trieste (Northern Adriatic)

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Theme - Application of DGT to aquatic systems (including sediment)

ABSTRACT

Mercury (Hg) is a toxic element, prone to microbial methylation to monomethyl mercury (MeHg) in anoxic marine sediments during sulphate and metal reduction processes. Bioaccumulation of Hg species results in biomagnification in marine food webs, often with detrimental effects to local ecosystems and increased exposure to humans. Gulf of Trieste has been under continuous 500 year-long Hg stress due to Hg mining in Idrija, Slovenia. 1.5 tons of Hg are annually still transported into the Gulf, deposited onto the sediment or distributed further towards Adriatic, while actively involved in biogeochemistries.

To assess the lability, and by extension bioavailability, of Hg species, we applied for the first time Diffusive Gradients in Thin films (DGT) technique in the water column and sediment in the Gulf of Trieste. Our results showed that ratios of MeHg/THg in the water column and sediment porewaters ranged 10-75%, thus much higher than previously observed values. Comparison of our results with previously published labile Hg assessments (filtration and SnCl2 reduction) revealed that labile THg values coincided more for water column and less for sediment porewater. On the contrary, labile MeHg values assessed with these techniques were more similar in porewater than seawater.

In sediment porewater, labile THg and MeHg concentrations varied with depth (1-7 ng/L and 0.3-2.3 ng/L for THg and MeHg, respectively). MeHg concentrations were higher at known depths of sulphate reduction. THg variations were probably due to fractionation between solid and dissolved phase. Compared to water column concentrations (1.13 ng/L and 0.78 ng/L for THg and MeHg, respectively), sediments appear to be a source of labile Hg species to the water column, facilitating complexation and transport with organic matter and/or uptake into the lower food web. Our results show that values of labile Hg species for water column and sediments in Gulf of Trieste do not agree entirely with previous research, highlighting the need for more investigation into Hg bioavailability in this representative Hg-laden environment.
Mixture Effects in Diffusion Gradients in Thin Films (DGT). Ni accumulation in presence of NTA and Etdiam

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Theme - New techniques and fundamental knowledge

ABSTRACT

Natural waters contain mixtures of simple and heterogeneous ligands. The lability degree quantifies the contribution of one or more complexes to the metal flux arriving to a consuming surface. It can be experimentally measured in a single ligand system as a normalized flux [1]. This work focusses on the use of the lability degree measured in a single ligand system to predict the accumulation in mixtures.

A first effort is devoted to analyse the dependence of the lability degree on the composition of the single ligand system. Although a decrease in the lability degree as the ligand concentration increases is expected, this effect is of low relevance in DGT, since dissociation of complexes inside the resin is the dominant way of the complex contribution [2]. For any ligand-to-metal ratio, the lability degree decreases as the ligand concentration decreases, due to the association of the free metal with the increasing ligand concentration found close to the resin domain where most complex dissociation occurs.

The lability degree determined in a single ligand system at a common bulk ligand concentration is suggested as surrogate of the lability degree of this complex in the mixture. The Ni accumulation in a mixture of nitrilotriacetic acid (NTA) and ethylenediamine (Etdiam) ligands can be predicted with an error less than 5 % when the lability degree of the single ligand system is used in the mixture as shown in the poster.

However, simulation indicates that, in a parallel complexation scheme, there is a mutual influence of the lability degrees. This influence will be discussed and quantified. A main result is that due to cancellation (mutually opposite effects of a couple of complexes), in general, the total metal accumulation is not very sensitive to the replacement of the lability degree in the mixture by the lability degree in the single ligand system.

References
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MnOOH membrane as a novel binding phase in DGT for selective monitoring of As(V)

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Theme - DGT for routine monitoring and regulatory purposes

ABSTRACT

A MnOOH membrane consists of MnOOH nanofibers was fabricated. The MnOOH exhibits rapid and high adsorption capacities towards Cu(II) (~105 mg/g) and As(V) (~75 mg/g) in single component solution. Importantly, the MnOOH could be used as direct binding phase in DGT devices for monitoring Cu(II) (~100 ppb) and As(V) (~100 ppb) by deploying the DGT devices in single component solutions and Cu(II) and As(II) binary solution. Field experiments showed that the DGT devices with MnOOH binding membranes have good accumulation selectivity towards As(V) (~20 ppb). It could be demonstrated by the adsorption selectivity of MnOOH fibres towards As(V) in binary solution [Cu(II) and As(V)] with trace concentration. In conclusion, the MnOOH fibre membrane is a novel binding phase for directly used in DGT devices for selective trace monitoring of As(V) in aquatic system.
SH-LDH resin in DGT probes for dissolved mercury monitoring in paddy soil

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Theme - Application of DGT to soil systems

ABSTRACT

The diffusive gradient in thin films technique (DGT) was investigated and used to measure dissolved mercury in paddy soil. We used 3-Mercaptopropyl functionalized LDH (SH-LDH) as new material to make the resin gel, agarose gel was found as the diffusive gel for mercury measurements. The advantage of the SH-LDH material was that it was easy dissolved in acid, and made the extract become transparent, this method was more accurately determine mercury concentration. We verified the adsorption of the resin to mercury, through a series of experiments, the experimental work included: (1) measurement of the DGT uptake and elution efficiencies for Hg (II); (2) effects of pH and ionic strength on uptake of Hg (II); (3) assessment of the adsorption rate for Hg (II) in-between SH-LDH, SH-SBA, and Spheron-Thiol; (4) determination of Hg (II) in paddy soil with Tongren district, Guizhou province, China. The method detection limits (MDL), based on three times the standard deviation of replicate measurements of a blank solution in the DGT sample, and was as follows: $6.09 \pm 0.44$ ng for resin gel blank, respectively, and the instrument detection limits was from 0.1 to 0.2 ng/L for dissolved mercury. The adsorption efficiency of the SH-LDH resin was about 85-90% of the Hg from mercury standard solution in the DGT. So this method was an effective in-situ method for dissolved mercury, and applied in paddy ecosystem to investigate the transportation pathways and biological availability of Hg (II) in pore water.
Smart sampling for phosphate monitoring in water using DGT’s

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Theme - DGT for routine monitoring and regulatory purposes

**ABSTRACT**

This work aims to progress the use of DGT analysis for phosphate monitoring in water, by being able to carry out on-site analysis through the use of colorimetric chemistry on the DGT. Colorimetry employs chemical reactions which produce a colour change that can be attributed to the concentration of an analyte of interest in a given solution.

Looking at specific eluents that can extract phosphate along with the molybdenum blue method a preliminary colour change has been seen to identify the presence of phosphate on the DGT resin gel layer following deployment in a water body. The analysis will focus on keeping the resin gel layer for further lab analysis, while the filter and diffusive layer give a colour change which can be used to positively identify the presence of phosphate. The strength of the colour relates to an approximate concentration as a deciding factor to estimate whether the water is above or below the required or expected limit. This concentration will be approximated on site using a specially developed phone application. It provides a concentration by simply taking a picture of the colour formed beside a colour checker chart. It will make use of current IOT technologies to log sample location, give weather information and access historical data to help identify pollution sources.

For this research, ongoing deployments of DGT devices in rivers in the South East of Ireland are deployed for a period of two weeks; these DGTs are retrieved, and a new set of DGT devices deployed for another period of two weeks. This sampling cycle is taking place over a period of three months. Grab samples are routinely taken. A laboratory calibration is carried out with known amounts of phosphate.

Using this phone app, pre-screening for the presence of phosphate pollutants in specific sampling locations will be achieved, assisting in the identification of pollution sources. Hence, sampling could be concentrated in areas of suspected pollution outputs, potentially saving time and resources.
Stability investigation of AMP binding gel

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Theme - New techniques and fundamental knowledge

ABSTRACT

Radio-cesium is one of the most important artificial radionuclides in the environment. It may be released from anthropogenic activities such as nuclear weapon testing, nuclear facility accidents, and nuclear waste management. Once entering the environment, radio-cesium can be assimilated by organisms due to its chemical analogies to the essential element potassium. For this reason, it is important to understand the cesium behavior in aquatic environments, soils and sediments. Murdock et al.1 have developed a DGT method using an Ammonium MolydoPhosphate (AMP) binding gel for measuring radio-cesium concentration in natural waters.

AMP is commercially available either as only inorganic or organic-inorganic composite ion exchangers. As Murdock and co-workers have not specified the adsorbent used in their study, binding gels have been created from different manufactured ion exchangers. A set of experience in controlled conditions (batch experiments at different pH, time-series accumulation, DGT deployment in realistic waters,...) underlined a partial degradation of the binding gel depending on the chemical conditions and the manufactured AMP. Our results highlight the necessity to check carefully the stability of the binding gels before its use in DGT tools.

Study on the Migration Characteristics and Plant Availability of Phosphate Fertilizer in Cotton Field Based on DGT Technology

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Theme - Application of DGT to soil systems

ABSTRACT
Soil nutrients measured in situ field have an important significance for practicing rational application of fertilizer especially during crop growth period. Using DGT techniques measures phosphorus in farmland soil at this project. The processes which phosphorus sorbent absorbs H2PO4- through diffusive gel simulate that plant roots absorb H2PO4- in soil solution. Field plot experiment was carried out to show migration characteristics in soil profile and plant-availability of phosphate fertilizer at different phosphate fertilizer application time. The results showed: 1) In vertical direction of soil profile, DGT-P of phosphate fertilizer dropped after sowing and in bud stage were significant high than that as basal in 0-2cm, 2-4cm, 4-6cm, 6-8cm, 8-10cm and 10-15cm soil, respectively. The migration depth of phosphate fertilizer dropped was significant high than that as basal in soil profile. 2) In horizontal direction of soil profile, DGT-P of phosphate fertilizer dropped after sowing and at bud stage were significant high than that as basal at dropping point, 5cm, 10cm, 15cm away from the dropping point, respectively. The migration distance of phosphate fertilizer dropped was significant high than that as basal in the horizontal direction of soil profile. 3) In 0-60cm soil, Compared with non-phosphate fertilizer, dry weight of cotton roots of phosphate fertilizer drooped after sowing and in bud stage were increased by 45.0% and 18.86%, and increased by 116.17% and 116.82% in 0-10cm soil, respectively. Compared with non-phosphate fertilizer, yields of phosphate fertilizer drooped after sowing, dropped in bud stage and as basal were increased by 12.03%, 8.59% and 8.09%, biomass were increased by 14.07%, 10.20% and 10.73%, P uptake were increased by 48.83%?42.48% and 41.53%, respectively, phosphorus use efficiency of phosphate fertilizer drooped after sowing, dropped in bud stage and phosphate fertilizer as basal were 30.15?26.23% and 25.65%, respectively. Plant availability of phosphate fertilizer drooped was significant high than that as basal, especially phosphate fertilizer drooped after sowing.
The potential of different types of organic matter for reducing soil Cd bioavailability

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Theme - Application of DGT to soil systems

ABSTRACT

Accumulation of Cd in agricultural soils worldwide has increased the probability of this non-essential trace element entering human food through plant uptake. This presents a health risk to consumers and an economic risk to food-producing countries. Soil amendments manufactured from organic matter (OM) have been shown to reduce the plant uptake of Cd, while providing essential micronutrients (e.g. Zn and Cu). The reasons for this divergent trace element-binding behaviour are not well understood. We hypothesised that different types of OM, and blends of OMs used as commercially available composts, will have different chemical characteristics, and therefore exhibit different abilities to bind Cd and potential for use as soil amendments in Cd contaminated soils.

To test this hypothesis, we collected two types of OM-rich soil (eutrophic and oligotrophic peat), two types of biosolids, coffee grounds and five commercially available composts made from contrasting raw materials: pig manure, waste from mushroom manufacture, seaweed and fish waste, and municipal waste. These OMs were carefully characterised for their chemical properties. Batch Cd sorption experiments showed the different OM’s capacity to bind Cd and we also examined the lability of dissolved metal-OM complexes in calcium nitrate extracts using a diffusive gradients in thin-films (DGT) method adapted for small sample volumes; we also tested the quality of the extracted OM using spectroscopic methods.

Cd sorption capacity was high in all the composts, while biosolids, peats and coffee grounds sorbed Cd poorly. Differences in variable cation binding capacities of the different OMs suggested that specific functional groups were important. The analyses of the extracted solutions showed that the quality of the extracted OM and lability of the different metals’ OM complexes were highly variable between OMs. This work has shown the potential for different composts to be used for reducing the bioavailability of soil Cd and developed further insight into the key mechanisms.
Towards in-situ DGT measurements in cave dripwaters

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Theme - New techniques and fundamental knowledge

ABSTRACT

Cave waters from which speleothems (cave carbonates like stalagmites) are formed, are typically low ionic strength (< 0.1 M), alkaline (pH 7.5-8.5) solutions that are slightly saturated with respect to calcium carbonate. These drip waters typically contain a multitude of trace metals at ppm (e.g. Sr, Ba, Mg) and ppb (e.g. Co, Ni, Cu) levels along with colloidal and dissolved organic matter. The concentrations of these components vary in response to external climatic forcing, along with drip point discharge which can exhibit a range of hydrographic characteristics depending the specific plumbing of the overlying aquifer.

Here we present the results of ongoing attempts to characterise metal-ligand interactions in cave drips with a view to elucidating the role of these species in controlling speleothem trace element geochemistry. In particular, we present the results of a series of experiments involving a channelized-flow sampler in which flow occurs subcutaneously through chelex-100 binding resin. The results of these experiments are discussed in the context of the climate signals potentially encoded by metal-ligand interactions in speleothems.
Validation of the use of DGT® devices coupled with automatic sampling as an alternative to traditional spot sampling techniques: comparison with offline preconcentration

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Theme - DGT for routine monitoring and regulatory purposes

ABSTRACT

DGT® devices provide average concentrations of dissolved metals in water over a given time period and are frequently replacing conventional spot sampling methods that do not incorporate all the concentration changes that occur due to natural variations (e.g. tidal influences). Passive sampling also provides uninterrupted time series related to the environmental conditions that are preferable for regulatory authorities.

However, given that this regulatory monitoring has been carried out often using a specific technique for many years, regulatory bodies often require the assurance that altered sampling strategies will still comply with the initial purpose of the monitoring. Therefore, calibration of these new techniques is required.

To validate the use of the DGT® device as an alternative solution sampling was carried out in the Moselle port of Noumea (New Caledonia). During a 9 day period three automatic DGT® samplers were moored at a depth of 2 meters and each DGT® sampler was programmed to expose each DGT® device for a period of 3 days. During the exposure period spot samples were collected daily and analysed using two preconcentration methods: the first, involving a high fold (250x) off-line preconcentration technique followed by ICP-OES analysis and the second, involving a low fold (10x) off-line preconcentration followed by ICP-MS analysis. The results obtained by the three techniques were in good agreement and provide proof that monitoring with DGT® devices couple with an automatic sampler can provide a suitable alternative to traditional spot sampling techniques.