Passive sampling techniques for monitoring metals in transitional and coastal waters in the Atlantic region

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***Abstract*—In highly dynamic systems, such as transitional and coastal waters, establishing their chemical status is challenging. MONITOOL is an exciting European project consisting of 16 Partners covering the Atlantic region from the Canary Islands to the Scottish Highlands and Islands, which aims to address this complex analytical challenge, responding to European Directive demands for the assessment of the chemical status of transitional and coastal waters. Diffusive Gradient in Thin Films (DGT), and passive samplers (PS), in general, 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 (EQS). 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. The first sampling campaigns were performed during winter 2017/2018 in 4 selected sites (transitional and coastal sites) in each consortium region (8 regions). All partners followed the same protocol for sampling and analysis to minimize the operational variability. Priority metals (Cd, Ni, Pb) and other specific metals (Al, Ag, Cu, Cr, Co, Fe, Mn, Zn) were analysed in waters and in the DGT resins. Statistical analysis is being applied to study relationships between metal concentrations in DGT and in grab water samples. Suitable EQS for DGTs will be calculated on basis the statistical relations obtained previously. This will permit a better implementation of the Water Framework Directive in variable systems like transitional and coastal waters. The work presented here shows initial DGT results from the Irish sampling sites for selected target metals.**

Keywords: DGT, metal, coastal, estuarine, Water Framework Directive.

1. Introduction

The MONITOOL Project is based upon Directive 2013/39/EU with regards to priority metals in the field of water policy, including cadmium, nickel, and lead. Existing Environmental Quality Standards (EQS) for these methods only include biota sampling, and therefore development of new in situ solution sampling methodologies are a priority. The MONITOOL Project aims to define suitable EQS to allow for the use of Diffusive Gradient in Thin film (DGT) passive sampling devices for the monitoring of these priority metals in a regulatory context. DGT devices are composed of an ion-exchange resin, separated from solution by a diffusive ion-permeable gel layer. Their design allows for the continuous accumulation of metals *in situ*, and subsequent quantitation via methods such as ICP-MS. While many of the chemical aspects of the devices have been well studied, effects of environmental physicochemical parameters on the functionality of the devices have not been examined in detail. The MONITOOL Project aims to define suitable EQS to allow for the use DGT devices [2] for the monitoring of these priority metals in a regulatory context. DGT design allows for the continuous accumulation of metals in situ, and subsequent quantitation via methods such as ICP-MS. While many of the chemical aspects of the devices have been well studied [3] effects of environmental physicochemical parameters on the functionality of the devices has not been examined in detail. Five-day deployments of DGT devices, alongside grab sampling and physicochemical parameter measurement, will be conducted in both wet and dry seasons in coastal and transitional waters of the North Atlantic coast.

In MONITOOL, a five-day deployment of DGT devices, alongside grab sampling and physicochemical parameter measurement, is conducted in both wet and dry seasons in coastal and transitional waters of the North Atlantic coast, including locations in Ireland such as Cobh and the Alexandra Basin. The data collected from these sampling campaigns will inform potential future EQS adaptations which will be developed as part of the MONITOOL Project. The MONITOOL Project minimises variation between laboratories by sending all samples for analysis for designated purposes to a chosen laboratory. Triplicate and blank DGT devices are sent to IFREMER where the resin layer is isolated and the metals are extracted via immersion in nitric acid. Diluted aliquots of this solution are then taken after 24 h and analysed by ICP-MS and the measured metal concentrations can be measured through application of well-defined mathematical models.

Grab water samples are analysed separately for their metal concentrations. SeaFAST ICP-MS filtration, pre-concentration and analysis procedures are performed by CEFAS and IPMA. Field-filtered acidified seawater samples are sent to IST where voltammetry is performed.

DGTs from each field campaign are sent to DCU for biofouling analysis. Other parameters of the grab samples, such as solid particulate matter and dissolved organic carbon are analysed individually by each laboratory.

Through the tandem analysis of the DGT passive sampling devices and grab samples, the MONITOOL Project aims to define Environmental Quality Standards for the use of DGTs in Water Framework Directive compliance monitoring in the EU. Through interlaboratory exercises, the Project also aims to develop a network of laboratories in the Atlantic area proficient in analysis of these devices to support WFD monitoring. This paper outlines initial results of Irish sampling and DGT deployment at the start of the project.

2. Materials and Methods

Passive sampling devices

The DGT device is self-contained in a hard plastic casing. A Chelex-100 resin layer, used to bind the priority metals, is separated from solution by a diffusive layer of polyacrylamide gel (Figure 1). Molecular diffusion through the diffusive layer limits transport of mass, and a concentration gradient is developed, approaching zero at the resin layer interface. Multiple DGTs were deployed together (Figure 2) to avoid issues relating to damage and to provide controls.

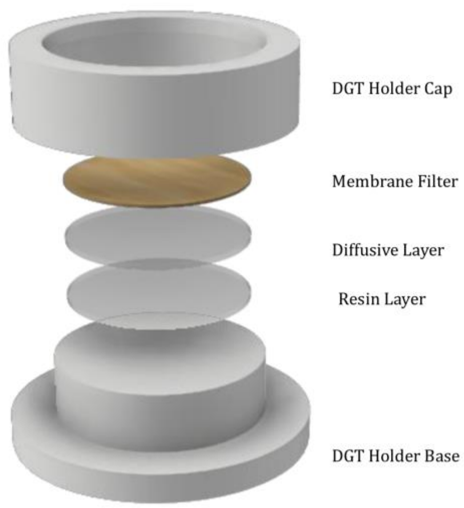

Figure 1: A schematic showing the layered structure of the DGT device.

Figure 2 DGT devices mounted in plexiglass frame for deployment in Dublin and Cork.

Sampling and deployment

DGT devices were deployed at coastal and transitional waterways in Ireland, at areas of potential metal pollution for five-day periods during both wet and dry seasons. Grab samples were also taken regularly alongside deployments.

Sampling sites in Ireland included Cobh in Co. Cork, and the Alexandra Basin in Dublin Port (Figure 3). Both areas have potential sources of metal pollution– the Haulbowline Island steelworks dump at Cobh, and the loading of lead and zinc onto ships for export at Alexandra Basin. Both areas are undergoing major redevelopment projects, and are potential locations of interest for repeated sampling following the MONITOOL Project.

Figure 3: Map of Ireland showing water sampling and DGT deployment sites. To the East is the Alexander Basin and Dublin Bay sites, and the South is the Cobh site.

3. Results and discussion

The chemical status of water bodies is currently assessed by collecting grab samples of water and comparing dissolved metal concentrations (i.e., 0.45-µm filtered) with established Environmental Quality Standards (EQS) in water for metals such as Cd, Ni and Pb. However, this sampling approach is not effective in systems such as transitional and coastal waters due to their dynamic nature. This work is a step toward understanding the link between the WFD, dissolved fraction, 0.45-µm filtered water and labile metal ions. This is currently a barrier to regulatory acceptance of passive samplers for compliance monitoring. This paper provides some initial data of the Irish water samples analysed by partners using ICP-MS and voltammetry as well as the deployed DGT samplers. The analytes of choice are Cd, Ph and Ni. The initial results indicate the potential for passive sampling to provide average concentrations over the time period (5 d) while voltammetry measuremenst aim to provide information on the labile water fraction.

Metal determination results

The data provided in Figures 4-7 show water sample analysis and DGT metal concentrations. The DGT concentration is an average metal concentration over the 5 days. ICP-MS is used for DGT metal uptake measurements. Both voltammetry and ICP-MS is used for water samples to determine the labile (voltammetry) and total (ICP) metal in the samples. Samples are taken at Day 1, 3 and 5 to establish actual concentrations that can compare with the DGT values. Ideally the DGT values should indicate if a spike occurred in metal concentration (labile fraction) during the measurement period. In this case the DGT D 5 where higher than a grab sample can indicate a spike in metal input has occurred during the period of deployment. From the initial results obtained for nickel concentrations it can be seen that 5 d average DGT values are close to those total metal concentrations measured by ICP-MS. Very high voltammetry values are yet to be validated. Nickel concentrations at the Dublin Port location (Figure 4) are generally higher than in the outer bay (Figure 5), with DGT measurement providing a good average value over the 5 days.

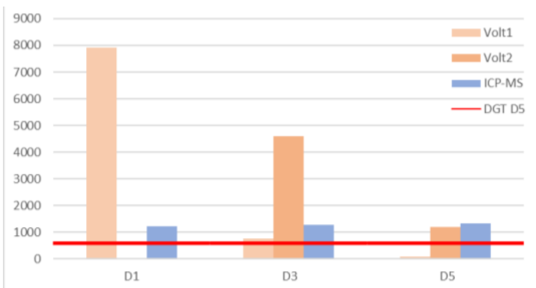

Figure 4: Nickel results comparing DGT D 5 with Voltammetry and ICP-MS grab sample results for the Dublin Alexander Basin site (D 1-D5 = Day 1 – Day 5). X-Axis = time in days; Y-axis = concentration in ng/L.

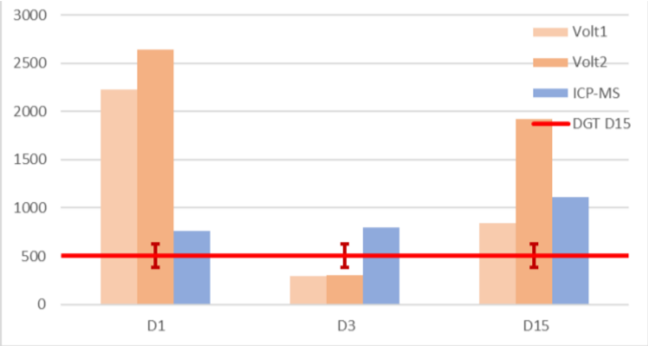

Figure 5: Nickel results comparing DGT D 5 with Voltammetry and ICP-MS grab sample results for the Dublin Bay buoy site. X-Axis = time in days; Y-axis = concentration in ng/L.

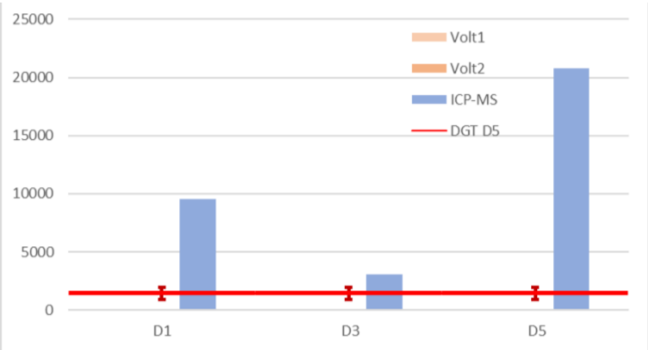

Figure 6: Lead results comparing DGT D 5 with ICP-MS grab sample results. Dublin Alexander Basin site. Voltammetry data not available. X-Axis = time in days; Y-axis = concentration in ng/L.

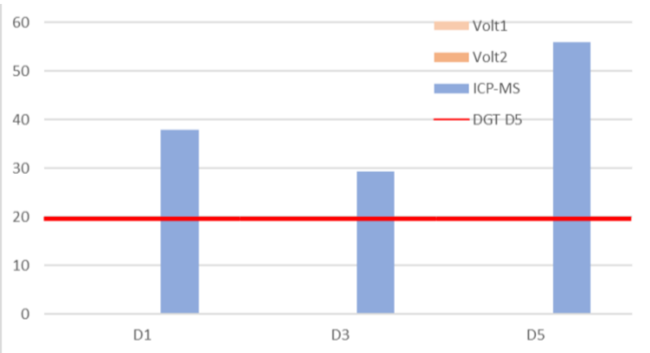

Figure 7: Cadmium results comparing DGT D 5 with Voltammetry and ICP-MS grab sample results. Alexander Basin Dublin. Voltammetry data not available. X-Axis = time in days; Y-axis = concentration in ng/L.

Figures 6 and 7 show lead and cadmium results respectively from ICP-MS determinations and DGT passive sampling results. In the case of lead, the DGT values are lower thank the ICP-MS values and do not pick up an elevated value on day 5, however, cadmium average DGT values are promising. The further studies of each partner location in the Atlantic region will involve sample analysis as shown above and quality control using adequate blank measurements. This is clearly required in relation to the electrochemical measurements because initial measurements indicate elevated values of labile fractions of metal species. The results indicate that DGT passive sampling has potential for monitoring for some metals however, lead is yet to be confirmed in this regard.

Assessment of biofouling

Biofouling can impact the performance of the passive sampling membrane. Initial studies carried out on the first deployments of DGTs have shown some biofouling occurrence.

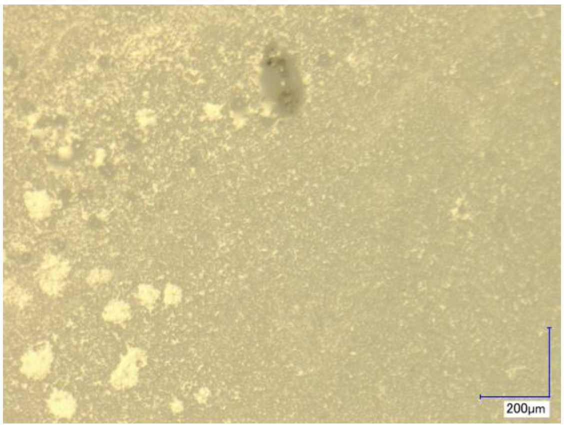

Figure 8: Light microscopy image of biofilm formation on retrieved DGT device from Alexander basin after 5 d.

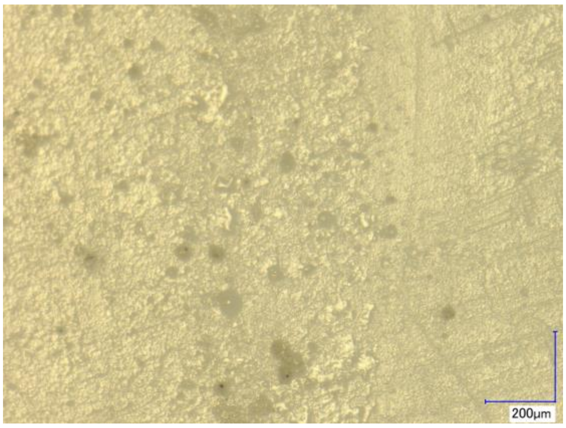

Figure 9: Light microscopy image of biofilm formation on retrieved DGT device from Ballynacorra Transitional Site at Cobh, Co. Cork after 5 d.

Further studies in Monitool will investigate biofilm formation in warmer waters and determine if this growth on the passive sampler has an impact on the uptake of metals over the 5-d deployment period. Figures 8 and 9 show light microscopy images of two DGTs retrieved after 5 d deployments. Figure 8 shows a very light covering of early stage biofilm and figure

9 shows some evidence of geofouling , where sediment has attached to the material surface. Because the deployments occurred during winter resultant fouling was at its lowest on the Irish samplers.

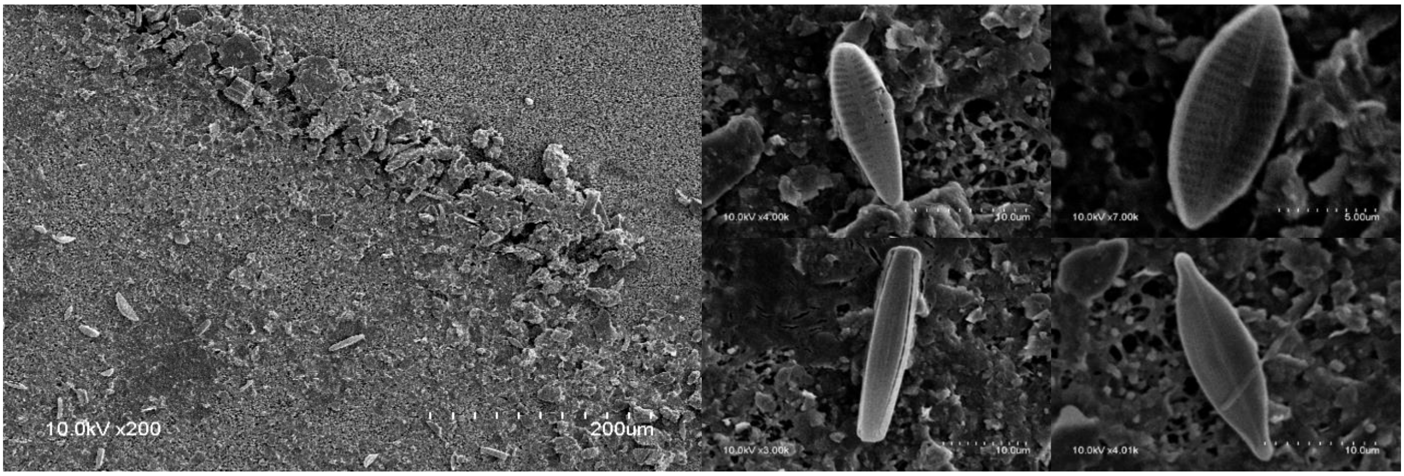

Figure 10 SEM Image showing biofilm formation on outer DGT membrane (left) and right some key early fouling organisms (diatoms).

Conclusions

In this work, the aim is to analyse different metal fractions to enable greater understanding of the relationships between concentrations of total dissolved metals and those of the labile metals retained by DGT.

This paper shows initial results of DGT sampling for Cd, Pb and Ni in Irish waters as part of a collaborative Interreg project, Monitool. The chemically labile and dissolved metal concentrations in water samples collected at Dublin and Cork sites were determined by voltammetry and ICP-MS, respectively. The labile metal represented in DGT was determined by ICP-MS. Initial investigations have shown DGT results to relate well to average ICP-MS data from water samples for nickel and cadmium while lead results do not meet this same conclusion. These initial studies identified the need for careful blank measurements with the electrochemical method, anodic stripping voltammetry. Observations from this work provide valuable insights to developing methods further for DGT use and adaptation to water monitoring. Further studies are needed to understand the relationship between the DGT fraction and labile fraction measured in the water. Initial studies of biolfilm formation on deployed samplers show the occurrence of biofilm even after a 5 d deployment in winter. This would suggest that great fouling will be observed in a warmer sampling period and therefore studies on the impact of that biofilm on metal uptake is desired.

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Conflicts of Interest: The authors declare no conflict of interest.

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