Application of Passive Samplers for Labile Metal Fraction Evaluation in Estuarine Waters: an Example from the Bay of Biscay (North-Eastern Spain)

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Abstract

This study was carried out in 13 estuaries of the Bay of Biscay. In situ deployment of DGT devices was done in the inner and outer part of the estuaries covering a wide salinity gradient. The devices were deployed during about ten days and accumulated metals concentration was determined in the laboratory. The results obtained have been compared with the historical data series of filterable-metal concentrations in these estuaries. The results highlight the advantages and disadvantages of in situ specific and routine monitoring techniques.

Key words: Bay of Biscay, estuary, heavy metals, labile metal, Diffusive Gradients in Thin-Films, monitoring techniques

Introduction

Traditional monitoring programmes in waters normally rely on the determination of dissolved/particulate concentrations of contaminants. However, novel technologies that permit the measurement of contaminants labile fraction (free ions and easily dissociable species) are achieving importance as a more realistic approach to the biological impact on the systems (Garofalo et al., 2004; Sherwood et al., 2009). Furthermore, the publication of the European Water Framework Directive (WFD; 2000/60/EC) that requires the achievement of the good ecological status in marine waters by 2015, has promoted the development of efficient methodologies to fill the gap between chemical analysis and adverse biological effects.

Passive samplers represent a well assessed technology for the determination of freely dissolved concentrations of contaminants (Davison and Zhang, 1994). This in situ technique avoids samples contamination due to sampling and treatment before analysis. Moreover, metallic compounds are preconcentrated reducing some of the difficulties and costs related to the analysis of trace metals. The metal species measured represents the fraction most potentially bioavailable to the biota, having a more ecotoxicological relevance. In this study, Diffusive Gradients in Thin Films (DGTs) have been used to determine the labile concentration of Cd, Cu, Ni, Pb and Zn in water bodies of different salinities (13 estuaries; Bay of Biscay).

Materials and methods

DGT relies on the transport of solutes across a well-defined gradient in concentration, typically established within a layer of hydrogel and outer filter membrane. After diffusing through the outer layers, metals are irreversibly chelated at the backside resin (Chelex-100 immersed in polyacrylamide).

In the present study, DGTs were deployed in triplicates in 13 estuaries of the Bay of Biscay (Figure 1), in the inner and outer part of the estuaries, covering a wide salinity gradient. DGTs were immersed in the water column at 2 m depth and collected after about 10 days of deployment. Physical parameters were recorded (pH,DO,salinity and T^{a}) and immersion time was registered to the nearest minute. When retrieved, DGT surface was cleaned in situ with MQ water, to discard any particle adhered to the surface, and each device was stored in an individual

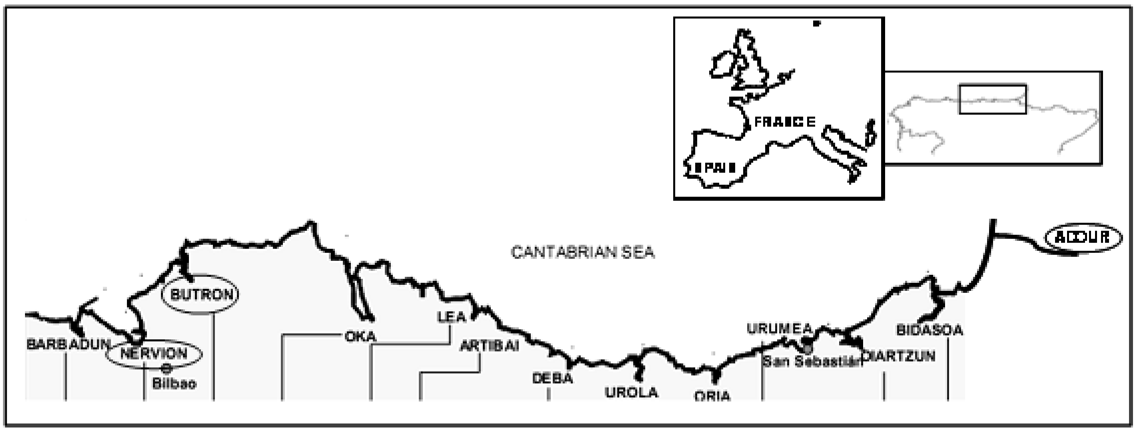

Figure 1. Geographical location of the estuaries along the Basque-French coast. Modified from Belzunce et al. (2004)

clean plastic bag. DGT probes were carried to the lab and preserved at 4ºC until chemical analysis.

The theory behind calculation of DGT-labile metal concentrations in the water column has been described elsewhere (Davison and Zhang, 1994). Briefly, the average concentration of DGT-labile metal over the period of deployment is calculated from equation (1). Once metal concentration in the eluate is determined (Ce), the mass of metal accumulated in the Chelex-100 resin (M) is calculated (1). Then, the average labile metal concentration in water (Cb) can be backward calculated (2).

(1) $M = C_e (V_g + V_{HNO3})/f_e$

Where Ce is the metal concentration measured in the eluate, V_g and V_{HNO3} are the volumes of the gel and the nitric acid, respectively and f_e is the elution factor (i.e. ratio of metal that is eluted from the resin).

(2) $C_b = (M\Delta g/DtA)$

Where, M is the mass of metal accumulated in the resin, Δg is the diffusive layer thickness, D is the diffusion coefficient of the metal, t is the immersion time of the DGT probe and A is the exposure area.

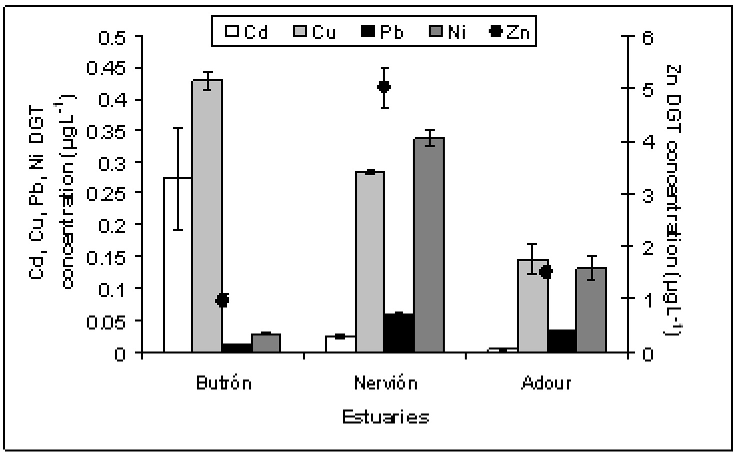

Figure 2. Results of metal labile concentration (Cd,Cu,Pb,Ni and Zn)measured by DGTs in seawater (μgL-1) in three estuaries along the Basque-French coast.

Results and discussion

The results of dissolved labile metal concentrations (Cd, Cu, Pb, Ni and Zn) measured by DGTs in three estuaries of the Basque-French coast have been collected in Figure 2. Based on DGT results, water trace metals concentration decreased in the order Zn>Cu~Ni>Cd~Pb.

The comparison of the results obtained by DGTs with the historical data series of filterable-metal concentrations in these estuaries highlights some shortcomings of the latter. On one hand, estuaries are highly dynamic systems characterized by fast changes of water metal concentrations, being difficult to be interpreted only based in temporally discrete sampling. However, DGTs accumulate constantly in situ, representing the time-averaged concentration of trace metals during the deployment time. On the other hand, saline matrix effects are overcame (nitric acid extraction) and the metals are concentrated, increasing the sensitivity of analyses.

Therefore, DGTs seem to be a promising tool for the measurement of trace metal labile concentration in highly variable systems. However, more studies are recommended in different environmental conditions in order to validate their use within European guidelines.

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