HIGH FREQUENCY MEASUREMENT OF METALS: STEPS TOWARDS THE ACCEPTANCE OF PASSIVE SAMPLERS FOR REGULATORY MONITORING

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INTRODUCTION

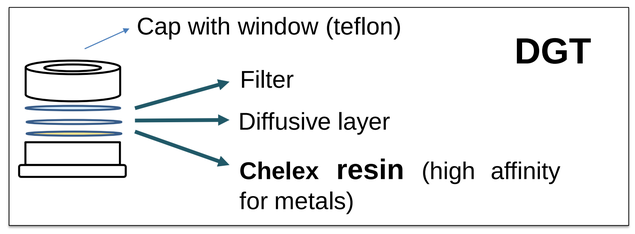
Diffusive Gradient in Thin Films (DGT), and passive samplers (PS), in general, are already widely used in **investigative monitoring** and there is an **increasing interest** in their use for the environmental assessment of water bodies, within European policies requirements. In the regulatory context of the European Water Framework Directive (WFD) (2000/60/EC), the **main barrier for the acceptance of PS is the lack of appropriate Environmental Quality Standards (EQSs).**

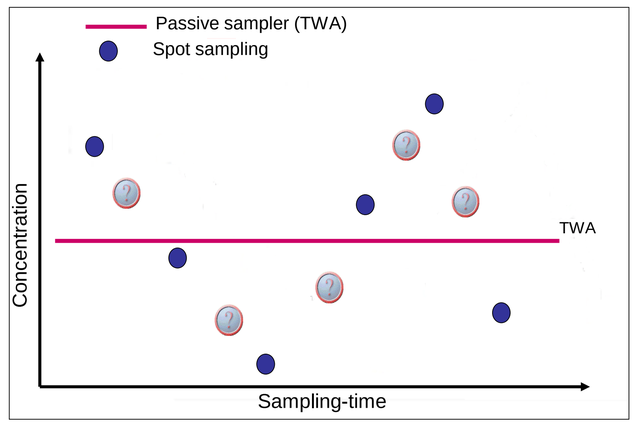
Regulatory EQSs for metals in water are defined in the dissolved fraction, preventing the use of DGT-labile concentrations for the establishment of the chemical status of water bodies. Hence, the study of the relationships between dissolved metal (spot sampling) and DGT-labile metal concentrations is necessary.

OBJECTIVES

(i) Which is the **intra-day variability** of the monitoring of metal concentrations in estuaries by different techniques?

(ii) Which is the **relationship** between dissolved metal concentrations from spot sampling with passive samplers-labile metal concentrations?





Spot sampling

DGT deployment

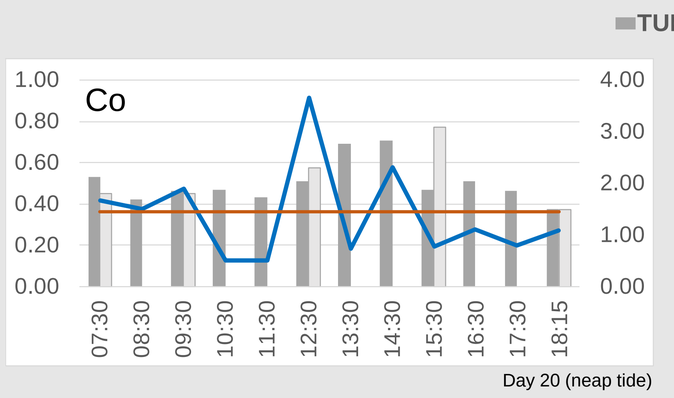
MATERIAL AND METHODS

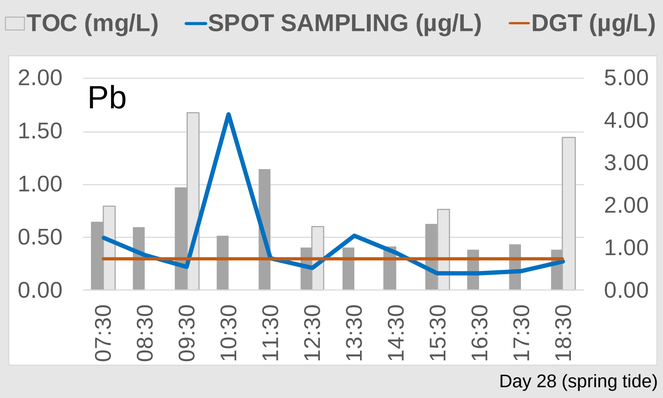
1. **When/Where?** In November 2019, five sampling days (07, 20, 21, 27 and 28 November) were carried out in the Oiartzun estuary (**Basque Country**, Bay of Biscay), an area with high presence of industrial and port activities.

2. **Field works.** DGTs (triplicates) were deployed during 1 tidal cycle and retrieved after 12 hours. During that period, hourly spot water samples were taken by means of Niskin bottles, at the same depth than DGTs.

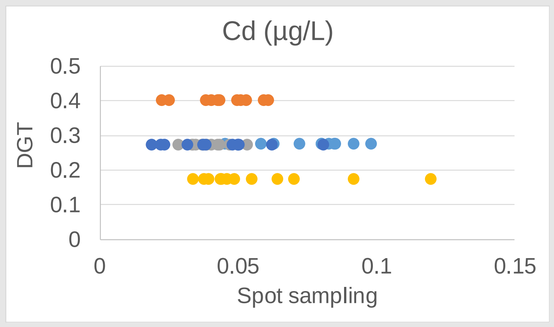
3. **Laboratory works.** Water samples were filtered for the posterior analysis of metals. Dissolved (DOC) and total organic carbon (TOC), suspended particulate matter (SPM) and turbidity (NTU) were also analysed in extra water samples. Priority metals (Cd, Ni, Pb) and other specific metals (Cu, Co, Zn) were analysed in the 2 defined fractions (dissolved water and DGT fraction) by ICP-MS. Hydrographic variables were measured at each sampling time (salinity, temperature, dissolved oxygen and pH).

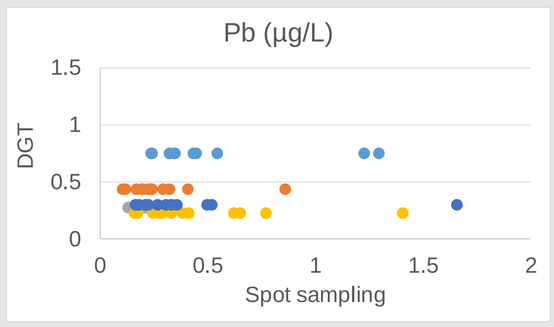
RESULTS AND DISCUSSION

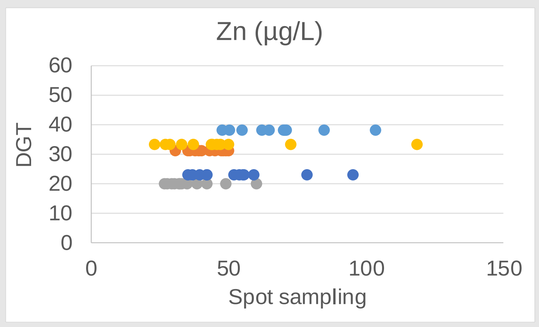




Spot sampling: the intra-day coefficient of variation is higher than >70% for Co (days 27/28), for Ni (days 20/27/28), for Cu (day 20) and for Pb (all sampling days, except 21). This could be related with high intra-day variation of hydrographic conditions and/or turbidity, TOC, etc.







07-Nov 20-Nov 21-Nov 27-Nov 28-Nov

The results show that for this sampling period (12 hours), except for Zn, there is **no relationship** between dissolved metal concentrations from spot sampling with labile metal concentration from DGT.

CONCLUSIONS

I. The **high intra-day coefficient of variation** of dissolved metal concentrations from spot sampling and the **high variability of the ratio** between dissolved metal concentrations and labile metal concentration from DGT should be considered in **estuarine water monitoring design**.

II. With a **short sampling-time of DGT exposure** (12 hours), there is **no relationship** between mean dissolved metal concentrations (spot sampling) with labile metal concentration (DGT), except for Zn. Previous studies (MONITOOL project) showed strong relationship with longer DGT exposure time (3-5 days).

III. In addition to the sampling period, the influence of physical-chemical parameters (salinity, TOC, SPM,…) in the studied relationship must be analysed and taken into account.

ACKNOWLEDGEMENTS

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