

NEW TOOLS FOR MONITORING THE CHEMICAL STATUS IN TRANSITIONAL AND COASTAL WATERS UNDER THE WATER FRAMEWORK DIRECTIVE

AUTHORS

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INTRODUCTION

The protection of waters in Europe is regulated by the Water Framework Directive (WFD), mandatory for all European Union members. Detecting and monitoring the level of contaminants in seawater and inland waterways is a key element of this Directive [1]. In many cases, they are very difficult to determine by traditional techniques (spot sampling), particularly in transitional and coastal waters, and so there is an urgent need to find accurate, reliable, easy and cost-efficient alternatives.

Passive sampling devices (PSDs), such as DGT (Diffusive Gradients in Thin films), have many advantages compared to conventional monitoring methods, since this methodology can provide time weighted average concentrations integrated over a period of time [2]. In addition, the labile concentrations determined by PSDs are recognised as a better proxy to the potential bioavailable fraction than total/dissolved concentrations measured by conventional analytical techniques, providing a better scientific basis for risk assessment.

OBJECTIVE

The aim of the MONITOOL project [3] is to provide a robust database of dissolved and labile metal concentrations in transitional and coastal waters in order to adapt existing metal Environmental Quality Standards (EQS) for passive sampling devices (DGT-type), thus allowing their use to evaluate the chemical status of waters under the WFD and improving the quality of the overall assessment in dynamic marine and estuary waters.

METHOD

Field campaigns and analysis

- Two successful campaigns (wet and dry conditions) for DGT sampling were conducted.
- Common protocols were produced and followed [4,5] to ensure the comparability and reproducibility of data among Partners' regardless of the region.
- Over 500 water samples were collected and analysed by ICP-MS and voltammetry.
- Approx. 250 DGT were deployed, retrieved and analysed by ICP-MS.
- Water physico-chemical parameters recorded.

RESULTS

Database management and correlation studies

Based on these dataset of results, the log-log linear relationships between the dissolved/labile metal concentrations measured in DGTs and in discrete water samples have been investigated [6].

- The observed relationships were:

Metal	R ²
Cd	0.80
Mn	0.73
Cu	0.62
Ni	0.56
Pb	0.56
Zn	0.44
Co	0.41

STRONG MEDIUM WEAK

- DGT sampling/spot sampling ratios were shown to be independent of broad scale environmental variables, such as pH, temperature, salinity, dissolved oxygen, dissolved organic carbon and suspended particulate matter; as well as of sampling season: winter or summer.

- After a thorough statistical process based on the relationships between labile DGT-sampling metals and spot sampling dissolved metals, it was possible to propose EQS_{DGT} for Cd, Ni and Pb.

Substance	EQS _{Annual Average} (µg L ⁻¹)	EQS _{Proposal 1} (µg L ⁻¹)	EQS _{Proposal 2} (µg L ⁻¹)
Cd	0.2	0.20	0.18
Ni	8.6	4.60	3.08
Pb	1.3	0.23	0.12

Proposal 1: Linear model regression

Proposal 2: Linear model regression minus low Prediction Interval (PI 95%)

- The possibility of predicting the metal concentration in the dissolved fraction from the DGT results and comparing these predicted concentrations to the existing EQSs has also been studied.

CONCLUSIONS

- This is the first broad geographical scale study on priority metals by spot measurements and passive samplers in different marine regions, covering a variety of environmental conditions across the Atlantic and Mediterranean regions [7].
- DGTs may improve the quality of the overall assessment in dynamic marine waters to comply with the WFD.
- Allowing a better assessment of the sampling sites (in terms of spatial comparison) and their evolution over time (trend).

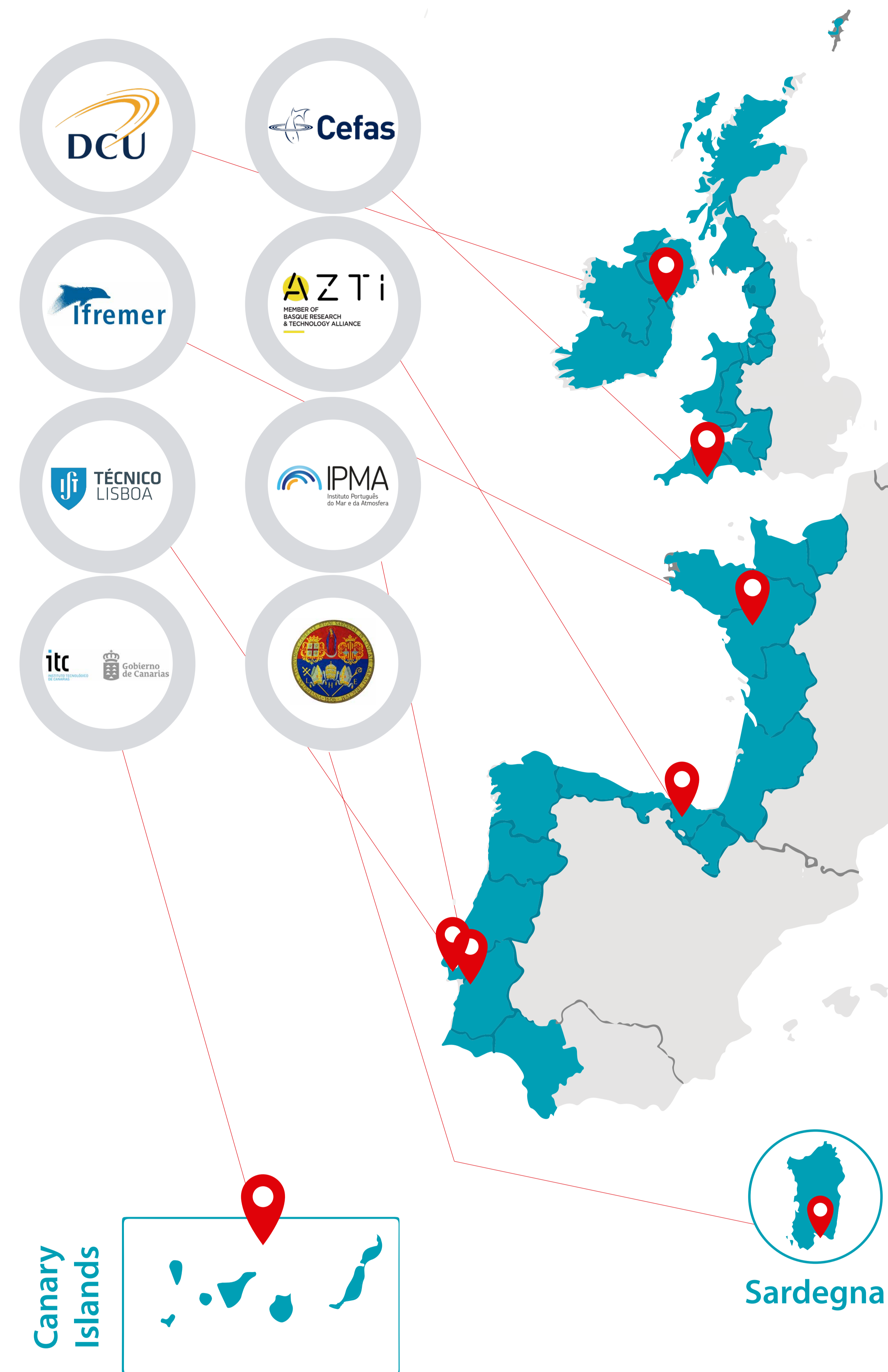


Figure 1. Sampling campaign at Gran Canaria (Source: ITC)



Figure 2. DGT assemblage after the exposure (Source: ITC)

NEXT STEPS

During the granted 18-month project-extension (January 2022-June 2023), MONITOOL will be extended searching for higher metal concentrations in order to validate and improve these results.

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