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VALIDATION OF THE USE OF DGT® DEVICES COUPLED WITH AUTOMATIC SAMPLING AS AN ALTERNATIVE TO TRADITIONAL SPOT SAMPLING TECHNIQUES: COMPARISON WITH OFF-LINE PRECONCENTRATION

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Introduction

Monitoring of the marine environment has been carried out for many years using specific analytical techniques that are reliable, but dependent on the sampling strategy (spot sampling). This constraint generates significant logistical costs and therefore does not allow the high frequency sample collection.

A new, easier sampling strategy emerged with the development of DGT technology. However, as the methodology is different, it was necessary to compare the analytical performances in order to demonstrate the efficiency and the advantages offered by this new technique of determining dissolved metal concentrations. In particular, regulatory bodies require the assurance that any modification in the sampling and analytical strategies will still comply with, on the one hand, the initial purpose of the monitoring and, on the other hand, allow comparison with historical data sets.

To validate the use of the DGT® devices, three automatic samplers (THOE®, AEL/TECHNICAP) were exposed as an alternative solution to spot sampling. During a 9-day period the samplers were moored in the harbour of Noumea (New-Caledonia) at a depth of 2 meters and each DGT® was exposed for 3 days. During this 9-day 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 (SeaFast®) followed by ICP-MS analysis.

Methodology

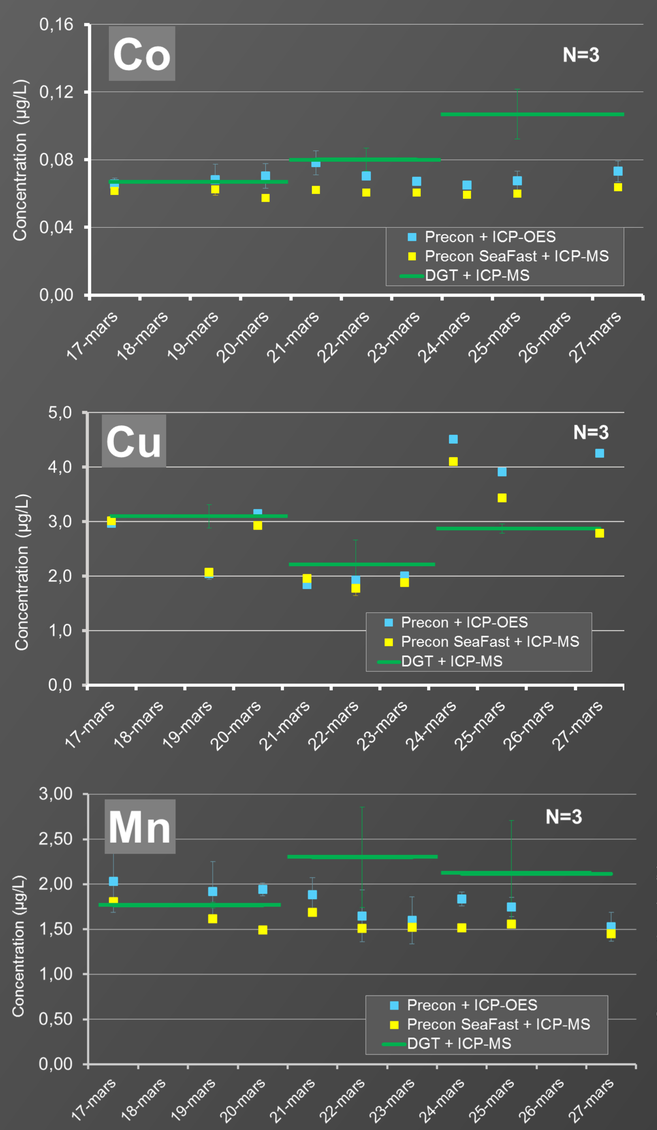
The 3 methods for the analysis of dissolved metals

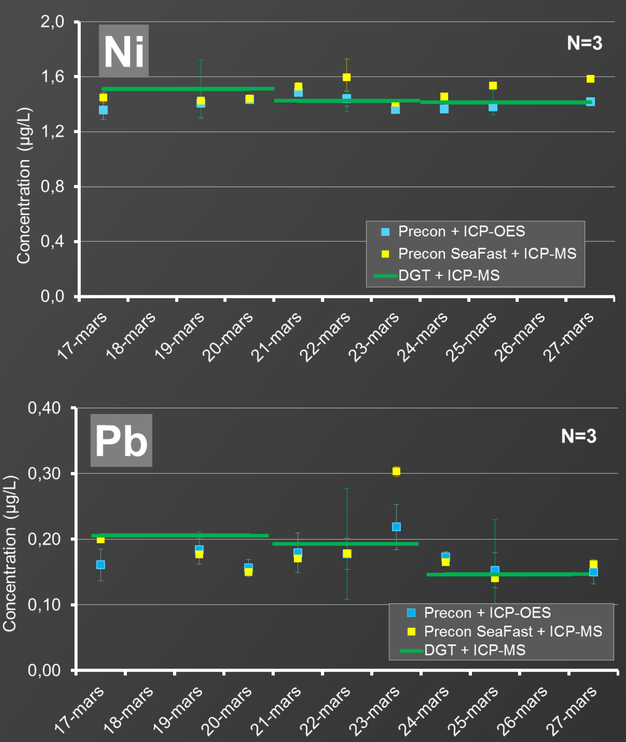
Technique		
Passive sampling with DGT devices coupled with automatic sampling and ICP-MS analysis	Spot sampling followed by off-line matrix removal and preconcentration with ICP-OES analysis (Moreton, *et al*, 2009)	Spot sampling followed by off-line matrix removal and preconcentration using the ESI SeaFAST® system and ICP-MS analysis
Simultaneous sampling protocol		
Triplicate DGT devices sequentially exposed for three days each	9 spot samples collected in triplicate over a 9 day period	9 spot samples collected in triplicate over a 9 day period
Sample treatment		
Chelex® binding layer (Styrene divinylbenzene copolymer containing paired iminodiacetate ions) Immersion in 4 ml of 1M HNO_3 solution for 24 hours	250 x preconcentration using Dionex® OnGuard II M 1cc iminodiacetate chelating cartridges and elution with 2M HNO_3 solution	10 x preconcentration using SeaFAST® iminodiacetate column (IDA) and elution with 1M HNO_3 solution
Analytical instrumentation		
Perkin Elmer NexION® 350 ICP-MS	Varian® 730 ICP-OES	Perkin Elmer NexION® 350 ICP-MS

Results

Overall, the results show that:

- The concentrations measured after off-line pre-concentration of sea water and analysis by ICP-MS and ICP-OES are very similar. The average difference between these two techniques is around 7%;
- Both the off-line pre-concentration techniques show that Ni, in particular, but also Co and Mn concentrations are very stable, meanwhile Pb concentrations, and especially Cu, seem to vary over time;
- The concentrations measured by the 3 techniques are very similar for Ni and Pb, with mean deviations of 5% and 14%, respectively. For Mn concentrations, the deviation between the off-line pre-concentration techniques and DGT technique reached a maximum of 32%, whereas for Co and Cu the maximum differences were higher at 40% and 50%, respectively. For these latter two dissolved metals, this discrepancy was observed during the last 3 days.





Conclusions

In the Noumea harbour, dissolved metal concentrations obtained by exposing DGT devices (3 days) and through spot sampling with a pre-concentration step are overall comparable. The similarities are particularly high for Ni and acceptable for Mn et Pb. Point discrepancies for Co and Cu are observed without explanations at this stage.

Indeed, despite similarities in the chemical principle of binding divalent metals (identical iminodiacetate functional groups), a direct comparison of the concentrations is not always obvious. Discrepancies can be generated when concentration levels vary quickly over time and in this case tidal influences in the harbour are likely to be responsible for the differences observed.

While differences exist, they are relatively low and acceptable. This work demonstrates to local authorities that replacing existing monitoring techniques with those using DGT devices is justifiable.

Since this study, five automatic sampling device have been successfully deployed to monitor dissolved metal concentrations of the marine environment around an industrial effluent outfall (diffuser 1km length).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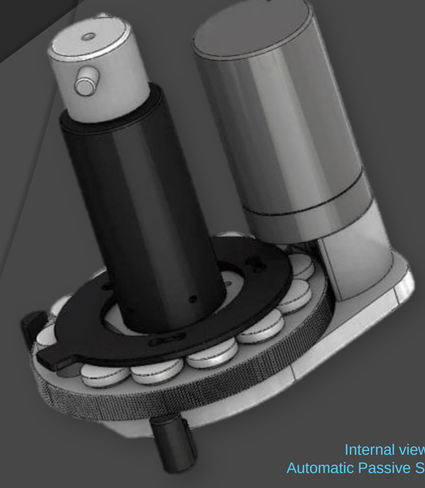
Perspectives

Further tests are planned to ensure compatibility of the DGT devices for use in the monitoring of the lagoon of New Caledonia.

Moreover, tests are planned using DGT devices with different binding layers. In particular, DGT devices that can be used to determine CrVI in water.


Internal view of the Automatic Passive Sampler

Cited references

Moreton B, Fernandez JM, Dolbecq M (2009). Development of a field preconcentration/elution unit for routine determination of dissolved metal concentrations by ICP-OES in marine waters: Application for monitoring of the New Caledonia lagoon. Geostandards and Geoanalytical Research 33 (2) : 205-218.

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