The Application of a VIP (Voltammetric In-situ Profiling) System in Estuaries for the Quantification and Speciation of Cu, Pb, and Cd Trace Metals

Introduction

Recent literature has reported the use of a submersible, compact, fully automated, in-situ VIP (voltammetric in-situ profiling) system\(^1\). The VIP system was developed by the University of Geneva, in collaboration with Idronaut, Milan. The VIP system allows the quantification of truly dissolved trace metals in aquatic systems, through rapid, continuous, automated profiling of trace metals (Cd[II], Cu[II], Pb[II]) in both sea and fresh water. The applications of the VIP system to dynamic estuarine waters are currently being explored. The VIP system has been deployed in the Tamar and Fal estuaries, UK, in order to obtain valuable information on trace metal speciation which would allow a better understanding of the geochemistry within aquatic systems. This poster presents laboratory characterisation and estuarine deployment of the VIP system.

Volatammetric Scan

Sample is pumped through the cell and trace metals are reduced and pre-concentrated or deposited in the Hg film. After deposition, a current is applied to the electrode to change the concentration of the metal in the sample. The deposition is repeated periodically, resulting in a cyclic deposition and stripping of the metal in the sample (Figure 3).

Analytical Figures of Merit

A calibration curve is produced for each metal against a 100 nM working standard. The precision of the instrument is determined by calculating the correlation coefficient (R\(^2\)) of the linear range (n=3), containing 20 nM of each of Cu, Cd, and Pb, followed by blanks (n=3) measured at these settings. An instrument memory effect was observed for all metals. In addition there was an underestimation of the first measurement due to inefficient flushing of the system with fresh sample. The underestimation of the first measurement due to insufficient gel equilibration period these problems were eliminated (Figure 4).

Effect of Estuarine Variables

An estuarine environment is highly dynamic and physico-chemical variables within it lead to changes in the speciation of trace metals. This section shows the results of adding and subtracting different variables to observe its effects on the VIP system.

1. Salinity

The conductivity of estuarine water in the salinity range 0.5 to 35% shows a linear relationship to NaNO\(_3\) concentrations. NaNO\(_3\) was used as an analogue for estuarine waters.

2. Dissolved Oxygen

Calibrations using oxygen saturated and de-oxygenated standard were carried out at pH 2 and there was found to be no effect on the sensitivity of the instrument (Figures 10-12).

In-situ Deployments

A tidal cycle was undertaken in the Tamar estuary (a macro-tidal estuary) on 2002/01/01 and results for Cu, Pb and Cd are shown in (Figure 14). The concentration of the VIP labile Cu is much lower than the total labile (0.45 µM, polycarbonate filter). The VIP measures only truly dissolved Cu ions. The total labile concentration includes metal ions bound to macromolecular ligands and to colloids. The largest difference between the two measurements was observed at lowest salinity (highest riverine input) suggesting that a large proportion of Cu is strongly bound in low salinity waters, compared to seawater. Maximum concentrations for both VIP labile and total filterable Cu were observed at lowest salinity (ebb tide).

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