

# DETERMINATION OF VARIOUS SPECIES OF COPPER, ZINC AND CADMIUM IN THE GULF OF ELEFSIS, GREECE, USING DGT IN COMBINATION WITH DPASV

Karavoltzos S. and M. Scoullou\*

University of Athens, Chemistry Department, Div. III, Inorganic and Environmental Chemistry and Technology, Athens, Greece  
skarav@cc.uoa.gr

## Abstract

In this work we examined the speciation of dissolved Cu, Zn and Cd in seawater in the Gulf of Elefsis, Greece. We used two powerful techniques for determining the speciation of heavy metals in complex systems such as coastal seawater: the DGT (Diffusive Gradients in Thin films) assemblies and the DPASV (Differential Pulse Anodic Stripping Voltametry). With the use of DGTs we determine the labile dissolved fraction of heavy metals fixed on a chelex-100 resin 'in situ', while with DPASV we measured the kinetically labile fraction of metals which includes mostly inorganic species of these metals. From the difference of these determinations we may conclude that in the Gulf of Elefsis, the predominant fractions of labile dissolved Cu, Zn and Cd are complexed with organic ligands. In particular, more than 92% of DGT labile Cu, 79% of DGT labile Zn and 50% of DGT labile Cd were found to be DPASV inert.

*Keywords: metals, speciation*

## Introduction

The determination of the various chemical species of trace metals in natural waters has been recognised as of particular importance for the understanding of their geochemical and biological behaviour, toxicity etc [1]. In this work the chemical speciation of dissolved copper, zinc and cadmium was studied throughout the Gulf of Elefsis, a geomorphologically very interesting and intensely industrialized embayment in the vicinity of Athens metropolitan area which has been a site thoroughly examined by our laboratory in the last 25 years [2, 3]. The speciation measurements were carried out by combining two powerful techniques: the DPASV (Differential Pulse Anodic Stripping Voltametry) and DGT (Diffusive Gradients in Thin films) which is a relatively new 'in situ' speciation measurement technique for dissolved trace metals which involves the use of polyacrylamide diffusive gels [4, 5].

## Methodology

This research was carried out during the second half of 2000. Sea water samples were collected with GO-FLO polypropylene sampling bottles while at the same time a number of DGT assemblies were immersed at approximately 30 cm below the surface, for three consecutive days, at selected coastal sites identified as 'hot spots' through the MED-POL/UNEP monitoring programme at the Gulf of Elefsis (Figure 1). The water samples were filtered immediately after sampling through 0.45 µm Millipore membrane filters. Measurements of kinetically labile metal fractions were performed by using DPASV. The deposition potential applied for Cu was -0.45 V (Ag/AgCl) and for Cd and Zn -0.80 V and -1.2 V, respectively [6]. Metal concentrations were determined by using the 'standard addition' technique.

Recovery of the metals from each DGT assembly was obtained by using 1 ml nitric acid (supra pure). The concentrations of all metals (copper, zinc and cadmium) were measured in a flameless atomic absorption spectrophotometer (VARIAN SpectrAA 640 Z) equipped with a Zeeman background correction. The treatment of all samples was carried out inside a positive pressure chamber and all apparatus used were plastic very carefully cleaned.

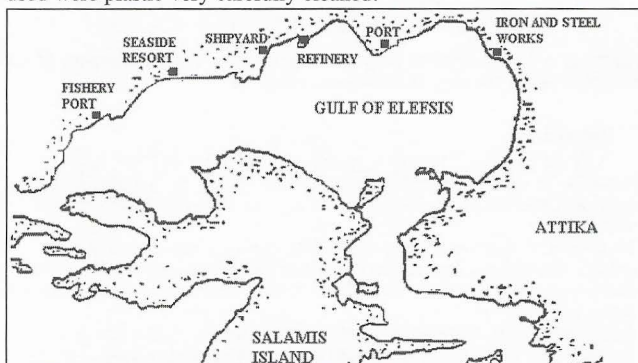


Figure 1 : Sampling stations at the Gulf of Elefsis

## Results and discussion

It is clear that in the specific period and coastal stations studied, more than 92% of DGT labile Cu, 79% of DGT labile Zn and 50% of DGT labile Cd were DPASV inert corresponding mainly to metal complexed with organic ligands (Table 2).

Table 1 : Mean values of physical and chemical parameters at selected sampling stations

	Temperature (°C)	Salinity (psu)	pH	DOC <sup>1</sup> (mg/l)
Iron and steel works	20	38.5	7.77	1.22
Port	20	38.7	7.85	1.12
Refinery	20	38.6	7.58	1.07
Shipyard	20	36.9	7.65	2.17
Seaside resort	20	36.7	8.06	1.10

<sup>1</sup> Dissolved organic carbon

Table 2 DGT and DPASV labile species of Cu, Zn and Cd at coastal sampling stations in the Gulf of Elefsis (in µg/l)

	C <sub>DGT-Cu</sub>	Cu <sup>1</sup>	C <sub>DGT-Zn</sub>	Zn <sup>1</sup>	C <sub>DGT-Cd</sub>	Cd <sup>1</sup>
Iron and steel works	0.63	N.D.2	15.4	1.64	0.028	N.D.3
Port	7.20	N.D.	26.3	0.45	0.029	N.D.
Refinery	0.70	N.D.	11.9	2.49	0.010	N.D.
Shipyard	1.41	N.D.	20.8	2.40	0.022	N.D.
Seaside resort	0.66	N.D.	25.0	0.03	0.021	N.D.

<sup>1</sup> DPASV labile Cu

<sup>2</sup> Not detected, <0.05 µg/l

<sup>3</sup> Not detected, <0.005 µg/l

It is noteworthy that in coastal areas identified as 'hot spots' such as refineries, shipyards and iron and steel works the DPASV labile zinc fraction which corresponds largely to ions and ion pairs and therefore is easily bioavailable, is considerably higher than in other sites which do not receive direct input from land based pollution sources (Table 2).

In conclusion it is clear that the combined application in seawater of both techniques, DGT and DPASV, could help in determining in a relatively simple way the prevailing forms, species of trace metals in marine waters.

## References

1. Tercier M-L, Buffle J., 1993. In situ voltammetric measurements in natural waters: future prospects and challenges. *Electroanalysis*, 5:187-200.
2. Scoullou M., 1983. Trace metals in a landlocked intermittently anoxic basin. In: Wong, C., Boyle, E., Bruland, K., Burton, J., Goldberg, E. (Eds.), *Trace Metals in Seawater*. Plenum Press, New York, pp. 351-366.
3. Scoullou M., Oldfield F., 1986. Trace metal and magnetic studies of sediments in Greek estuaries and enclosed gulfs. *Marine Chemistry*, 18: 249-268.
4. Davison W., Zhang H., 1994. In situ speciation measurements of trace components in natural waters using thin-film gels. *Nature*, 367:546-548.
5. Zhang H., Davison W., 1995. Performance characteristics of diffusion gradients in thin films for the in situ measurement of trace metals in aqueous solution. *Anal. Chem.*, 67:3391-3400.
6. Plavsic M., Krznaric D., Branica M., 1982. Determination of the apparent copper complexing capacity of seawater by anodic stripping voltammetry. *Mar. Chem.*, 11:17-31.