

Importance du macroplankton gélatineux dans le stockage et le transfert de métaux traces en Méditerranée nord-occidentale

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Des organismes du macroplankton gélatineux appartenant aux Thaliacés : *Thalia democratica* et *Salpa fusiformis* et aux Siphonophores : *Agalma elegans*, *Hippopodius hippopus*, *Chelophyes appendiculata* et *Abylopsis tetragona* ont été prélevés à la sortie de la rade de Villefranche-sur-mer en Méditerranée Nord-Occidentale au printemps 1987 à une période où ces organismes étaient particulièrement abondants. Parallèlement des échantillons de matière en suspension ont été collectés dans des pièges à sédiments placés à 200 m de profondeur en zone côtière (Programme Dyfamed en coopération avec l'A.I.E.A. de Monaco). Des analyses de Cd, Cu, Pb et Zn ont été effectuées par absorption atomique (four et flamme) et par polarographie de redissolution anodique sur ces différents échantillons.

Le Tableau 1 donne les concentrations en métaux trouvées dans les Siphonophores :

Tableau 1 : Concentrations exprimées en μg métal / g (poids sec)

Espèce :	Cd	Cu	Pb	Zn
<i>Chelophyes</i> n=13	1.3±0.4	7.7±4.5	1.5±0.7	75±27
<i>Agalma</i> n=7	0.5±0.1	4.4±1.9	2.6±0.5	36±6
<i>Abylopsis</i> n=5	0.6±0.1	3.2±1.7	0.6±0.3	82±23
<i>Hippopodius</i> n=4	1.0±0.7	4.9±2.5	2.4±0.7	180±49

Le Tableau 2 donne les concentrations dans les Thaliacés (*Salpa* et *Thalia*) ainsi que dans les échantillons recueillis dans les pièges à sédiments. Ces concentrations sont exprimées en ng métal/ μg phosphore.

Tableau 2 : Concentrations exprimées en ng métal / μg phosphore

Echantillon	Cd	Cu	Pb	Zn
Galpes	0.1	1.8	0.9	8.7
Matériel pièges	0.66	50	292	163

Les concentrations en Cu et en Zn trouvées dans les pièges sont comparées à celles données par Krishnaswami *et al.* (1985) pour les fèces de mêmes Salpes (9ng Cu/ μg P et 54 ng Zn/ μg P) et montrent que, dans le matériel particulaire, 18% du Cu et 33% du Zn proviendraient des fèces. En estimant une contribution moyenne de 25% de métal apporté par les fèces de Salpes au matériel particulaire, on peut en déduire les concentrations en Cd et en Pb dans les fèces de Salpes qui seraient de l'ordre de 0,16 ng Cd / μg P et de 50 ngPb / μg P. On note des facteurs d'enrichissement (Métal dans fèces/Métal dans Salpes) de 1,6 pour Cd, 5 pour Cu, 55 pour Pb et 6 pour Zn.

En conclusion, les organismes gélatineux n'ont pas de concentrations très élevées en métaux sauf en zinc qui est accumulé particulièrement par les Siphonophores ; ce phénomène avait été déjà observé pour des échantillons prélevés en 1984 (Roméo *et al.*, 1986, 1987). D'autre part, les Salpes contribuent d'une façon notable, par leurs fèces, aux flux des métaux, et en particulier du plomb en Méditerranée.

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On interaction of Copper with surface active material in natural waters

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Copper ions are very important for natural aquatic system as copper is in lower concentrations an essential element necessary to biota (few nanograms) and very toxic at higher concentrations. Because of its wide application in agriculture and industry copper is potentially very hazardous trace element. The distribution and fate of copper ions in natural waters is mainly influenced by the presence of organic matter as well as by the adsorption processes on different surfaces (1,2,3).

Copper ions form very stable organic complexes and because of that organic compounds, especially those which at the same time have surface active properties, influence greatly the behaviour of copper ions in the solution and at the interfaces. The representatives of such substances are proteins, fatty acids and lipids as well as humic substances.

Very useful information about the behaviour and interactions of copper ions with organic matter in the solution and on the different interfaces can be obtain from the electrochemical investigation at the model interface mercury electrode/aqueous solution.

Anodic stripping voltammetry is widely used for trace metal speciation in natural waters because of its sensitivity. During the preelectrolysis time the adsorption of surface active substance can influence the available free electrode surface and the rate constant for reduction of heavy metal ions.

The great majority of surface active substances has the maximum adsorption on the mercury electrode at -0.6 V vs Ag/AgCl, i.e. the potential of the electrocapillary maximum where the surface charge of mercury is zero. Because of that heavy metal ions like Cd^{2+} , Pb^{2+} and Zn^{2+} which have the reduction half-wave potential in the region of the surface active material maximum adsorption, are influenced by surface active substances (4,5). Because copper ions have the half-wave potential of reduction at -0.1 V vs Ag/AgCl reference electrode, which is in the potential region of desorption of majority of surface active substances one could expect a weaker influence upon copper oxido-reduction processes. But copper's great tendency to form organic complexes as well as its environmental significance make copper one of very interesting and important heavy metal ion for such studies. The method is based on the previous formation of the adsorbed layer of the surface active substance on the electrode surface at the potential -0.6 V vs Ag/AgCl together with the simultaneous reduction of copper ions at the same potential, and then the study of the anodic dissolution of copper at the modified surface.

Oxido-reduction processes of copper ions have been studied by differential pulse voltammetry using the hanging mercury drop electrode (HMDE) method in the presence of organic film which was formed in the solutions of different concentrations of selected biogenic surface active substances. The adsorption studies of surface active substances were carried out by capacity-current measurements using a.c. polarography, as described previously (6,7). The determination of the complexing properties of the surface active material were carried out by the complexing capacity measurements with Cu^{2+} ions by DPASV (1,8). It has been estimated that geopolymers and biopolymers like humic substances and proteins, respectively have a very pronounced effect on the anodic wave of copper ions. At lower concentrations of copper ions complexing properties of surface active material are most important and the main interaction will be the complexation. At higher concentrations of copper ions and the surface active substances the predominant reaction will be the inhibition of the oxido/reduction process of copper ions because of the adsorption of the organic matter on the electrode.

It has been also investigated the interaction of copper ions with surface active material in the samples of natural aquatic systems: seawater, fresh water, as well as in phytoplankton culture media, and comparison is made with the behaviour of different model compounds.

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