

# PHYTOPLANKTON INFLUENCE ON THE CHROMIUM SPECIATION IN SEAWATER

M. Mlakar<sup>1\*</sup>, Y. Auger<sup>2</sup>, M. Branica<sup>1</sup>

<sup>1</sup> Laboratory of Physical Chemistry of Traces, Rudjer Boskovic Institute, Bijenicka 54, 10000 Zagreb, Croatia  
<sup>2</sup> Laboratory for Analytical and Marine Chemistry, University of Sciences and Technology of Lille, UPRES A CNRS 8013, 59655 Villeneuve d'Ascq, France

## Abstract

Processes controlling dissolved chromium species distribution in seawater were studied. Various organic matter distributions, in-situ reduction and absorption/desorption by algae cells, particulate organic matter, contribute to the spatial speciation of dissolved chromium.

**Keywords:** chromium speciation, organic matter, phytoplankton.

## Introduction

In seawater chromium exists as Cr(VI) and Cr(III) [1-3]. Cr(VI) is present as  $\text{CrO}_4^{2-}$  which adsorbs on proton-specific mineral surfaces, limited in the presence of competing anions such as sulfate [4]. It has high bioavailability regarding aquatic organisms. Cr(III) forms strong, kinetically inert complexes [5] and it is very stable in a hydrolyzed form [6,7]. Its toxicity and bioavailability, controlled by a solubility and formation of strong complexes with organic and hydroxo-complexes, is low. Oxidation states are influenced by: oxic and anoxic conditions [1], photochemical [8]/geochemical processes [9], and biological activities (phytoplankton bloom) [10].

## Materials and methods

Sampling was done in the region of Irish sea and Celtic Sea, including surface, subsurface - 5 m and bottom waters - 5 m above. Voltammograms were recorded with Autolab polarograph (Ecochemie, Netherlands). The system was supported by the GPES4.3 electroanalytical program. Metrohm model 663 hanging mercury drop electrode (HMDE) was used as a working (0.4 mm<sup>2</sup>), Ag/AgCl as a reference and glassy carbon as a counter electrode, and teflon cell.

Axenic and specific strain of phytoplankton *Rhodella violacea* culture was grown in thermostated flasks (16°C) and illuminated by the 150  $\mu\text{E}/\text{m}^2\text{s}$  light in artificial seawater.

## Results and discussion

Main goal of this study was to investigate Cr(VI)/(III) distribution in correlation with organic matter in seawater [2,8-10]. Samples were taken in the region of Celtic and Irish Sea, with different characteristics concerning temperature, stratification and homogeneity of water column, respectively. In the Celtic Sea thermocline is formed between 20 and 40 m, while Irish Sea is homogeneous. Celtic Sea samples were taken at the surface, over and under the thermocline (20 and 45 m), and on the bottom (120 m). Dissolved Cr(VI) concentration is constant down to 20 m, in the region of thermocline increases until 40 m and remains unchanged until the bottom. The behavior of dissolved Cr(III) is opposite. These results were correlated with the appearance of the particulate organic matter. In the Celtic Sea concentration of particulate organic carbon (POC) is much higher on the surface than on the bottom. POC decrease was pronounced in the region below the thermocline. POC fractions indicate: surface waters contain an important algal but lesser content of bacterial fraction, separated by the thermocline. In the non-stratified water column of Irish Sea POC change with depth uniformly. Bacterial contribution is pronounced on the bottom, suggesting mineralization processes of the phytoplankton organic matter. Taking into account the POC origin and abundance, dissolved chromium distribution could be described: phytoplankton cells absorb Cr(VI) in the form of the chromate anion due to its resemblance to the nutrient sulfate anion. In cells reduces and after destruction is released into the sea as Cr(III). Among other processes, Cr(III) adsorbs on the phytoplankton detritus and in that way is partially eliminated from the seawater column. In the homogeneous water column same process is more pronounced in a zone of the nutrient regeneration, near sediments.

In order to verify these presumptions experiments in the laboratory with a phytoplankton batch culture of *Rhodella violacea* (chosen as one of most stable algae cultures in laboratory conditions), were done. The algae growth occurs in three phases:

1. until 9<sup>th</sup> day: the culture grows slowly and number of cells duplicate in chosen periods;
2. significant growth, from 9<sup>th</sup> to 23<sup>rd</sup> day, the phytoplankton bloom;
3. cell number decreases rapidly, different from the stationary phase normally achieved in the traditional medium for the culture development.

In each sample of the phytoplankton culture 20 nM of Cr(VI) was added. Dissolved Cr(VI) concentration diminished from 4<sup>th</sup> to 23<sup>rd</sup> day, assuming uptake by phytoplankton (Fig. 1). Cr(III) concentration increased with cell number decrease. It was presumed that Cr(VI) is reduced in the cells to Cr(III) and released as cells were destructed.

However, phytoplankton cannot completely drive the fate of chromium in dissolved phase. Positive correlations between particulate chromium and organic carbon from bacterial and uncharacterized origins appear, what suggests an "association" between chromium and organic particles built-up from senescent or degraded phytoplanktonic cells. Examination of organic carbon fractions showed more precisely that this correlation was almost exclusively due to the fresh algal component representing the larger part of the POC. It suggests that chromium behaviour could be influenced by phytoplankton activity. This activity produces organic exudates which are well known as chelating agents [11], i.e. phytoplanktonic exudates. Algal cells that were in a good physiological condition could remove chromium (VI) from seawater column (negative correlation), and after its incorporation/transformation, could release chromium (III) (positive correlation).

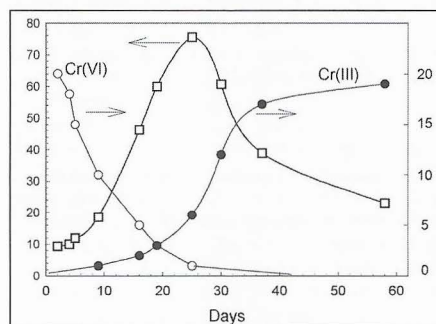


Fig. 1. Dissolved [Cr(VI)] and [Cr(III)] in dependence of time of contact with the batch culture of *Rhodella violacea*.

## References

- 1 - Ahern, F., Eckert, J.M., Payne, C. & Williams, K.L., 1985. Speciation of Chromium in Seawater, *Anal. Chim. Acta*, 175: 147-151. And lit. cited therein.
- 2 - Jeandel, C., 1987. Cycles biogéochimiques océaniques du chrome et du vanadium. Ph.D. Thesis, University of Paris, 264 p.
- 3 - Boussemart, M., van den Berg, C.M.G. & Gaddaf, M. (1992). The determination of the chromium species in seawater using catalytic cathodic stripping voltammetry. *Anal. Chim. Acta*, 262: 103-115.
- 4 - Zachara, J.M., Girvin, D.C., Schmidt, R.L. & Resch, C.T., 1987. Chromate adsorption on amorphous iron hydroxide in the presence of major groundwater ions. *Environ. Sci. Technol.*, 21: 589-594.
- 5 - Pearson, R.G., 1966. Acids and Bases, *Science*, 151: 172-177.
- 6 - Rai, D., Sass, B.M. & Moore, D.A., 1987. Chromium hydrolysis constants and solubility of chromium hydroxide. *Inorg. Chem.*, 26: 345-349.
- 7 - Murray, J.W., Spell, B. & Paul, B., 1983. *The contrasting geochemistry of manganese and chromium in eastern Pacific Ocean*. Pp. 643-669. In: C.S. Wong et al. (ed.), *Trace Metals in Seawater*, Plenum Press.
- 8 - Kleber, R.J. & George, R.H., 1992. Indirect Photoreduction of Aqueous Chromium(VI). *Environm. Sci. Technol.*, 26: 307-312.
- 9 - Abu-Saba, K.E. & Flegal, A.R., 1995. Chromium in San Francisco Bay: superposition of geochemical processes causes complex spatial distribution of redox species. *Mar. Chem.*, 49: 189-199.
- 10 - Eckert, J.M., Stewart, J.J., Waite, T.D., Szymezek, R. & Williams, K.L., 1990. Reduction of chromium (VI) at sub- $\mu\text{g}/\text{l}$  levels by fulvic acids. *Anal. Chim. Acta*, 236: 357-362.
- 11 - Sunda, W.G. and Huntsman, S.A., 1995. Iron uptake and growth limitation in oceanic and coastal phytoplankton. *Marine Chemistry* 50: 189-206.