STUDY OF THE SPATIAL AND HISTORICAL DISTRIBUTION OF SEDIMENT INORGANIC AND ORGANIC CONTAMINATION IN THE TOULON BAY (FRANCE)

E. Tessier [1]*, C. Garnier [1], G. Durrieu [1], D. François [2], V. Lenoble [1], G. Tua [2], J. U. Mullot [2], D. Cossa [3], M. Arnaud [4] and S. Mounier [1]

[1] Laboratoire PROTEE, Université du Sud Toulon Var, BP20132 83957 La Garde, France - tessier@univ-tln.fr

[2] LASEM, Base Navale de Toulon, BP 61, 83800 Toulon, France

[3] IFREMER, Département Biogéochimie et Ecotoxicologie, B.P.330 Zone Portuaire de Brégaillon, 83507 La Seyne/mer cedex, France

[4] IRSN, Laboratoire d'Etudes Radioécologiques du milieu Continental et Marin, Base Ifremer, BP 330, 83507 La Seyne/mer cedex, France

Abstract

The Toulon bay (France), situated in the north-western part of the Mediterranean sea, was the object of an intensive investigation of its sediment contamination, in the framework of a multi-partners collaborative project. Surface and deep sediment sampling campaigns were performed, covering the whole Bay with spatial and deep resolutions allowing a very fine cartography. The obtained results attest its strong contamination, particularly in the small part of the Bay, were the water residence time is the longest with historic nautical activities and their associated pollutions (ex. antifouling paint release). For some pollutants, the measured values are in the order of the highest values recorded by the scientific community in the world. Study of deep sediment cores will allow investigating the history of these contamination episodes.

Keywords: Analytical Methods, Chemical Speciation, Metals, Sediments, Coastal Systems

Experimental

The Toulon bay is a semi-closed Mediterranean area, separated in two non-equal parts by a sea wall, submitted to various anthropogenic inputs, in particular to nautical activities (marina, industry, Navy). Because of this separation and the absence of regular freshwater inputs, associated to low tide, circulation of water in the small part of the bay is weak, leading to low water regeneration and so a possibly high contaminant accumulation in sediments. To map the surface contamination of this specific environment, sediments were sampled in the whole bay and chemically analysed for physico-chemical parameters, and metals, organic pollutants and radioactive elements. The first sampling strategy was dedicated to surface sediment, by specifically sampling the water/sediment interface, followed by a second sampling campaign aiming at defining the history of the sediment contamination. Surface sediment sampling campaigns were performed in November 2008, February and June 2009, with the help of French Navy boat and material, allowing the sampling of surface sediment cores (1m, in duplicate), preserving the water/sediment interface integrity. 50 points were sampled (Fig.1), covering the entire bay. Remaining water in the upper part of sediment cores was filtered and analysed to determine dissolved organic carbon (DOC) and dissolved metal (DPASV) concentrations of the water column. For each point, both sampled cores were sliced (0-5 and 5-10cm), pooled, frozen, freeze-dried, and sieved (2 mm). The obtained sediments were analysed to determine the following parameters: water content, granulometry (laser), organic and inorganic carbon contents (TOC-meter), metal/metalloid (acidic extraction under micro-wave, GFAAS) and mercury (combustion, AAS) levels.

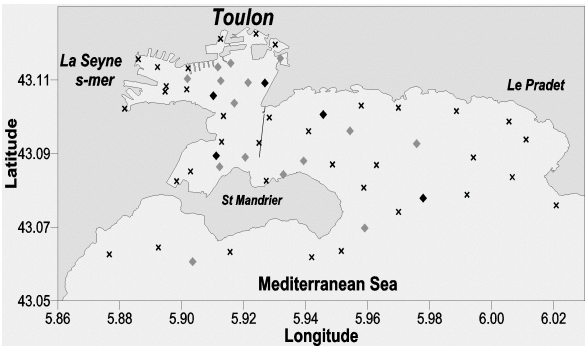

Fig. 1. Location of the sampling points (cross: 1-m interface cores only; diamond: 1-m interface and 5-m Küllenberg cores, gray and black symbols: low/medium and high resolution respectively)

A fourth sampling campaign was performed in October/November 2009, using the BeauTemps BeauPré oceanographic boat from the French Navy, allowing the sampling of deep sediments by the way of a 5m-Küllenberg corer. 20 points were sampled (Fig.1). The obtained cores were sliced depending on the defined resolution: each 10, 20 or 50 cm respectively for the High, Medium or Low Resolution points. Additionally, at the HR points, 4 interface cores were also sampled. The first 2 were used for sedimentation dating (sliced each 2 cm) and pH/Eh measurements. The 2 other were treated as follow: slicing each 2 cm (under nitrogen conditions), pooling, interstitial water extraction by centrifugation, sediment freezing, freeze-dried, and sieving (2 mm). The obtained sediments were analysed as samples originating from the surface sediment sampling campaigns. On interstitial waters, the following analyses were performed: DOC, 3-D spectroscopic fluorescence, total dissolved metal concentration (DPASV) and metal speciation (pseudo-polarography).

Results and discussion

DOC values of water column are quite homogeneous (0.9-1.2 mgC L^{-1}) in the entire bay, contrary to total dissolved metal concentrations which showed marked contamination in the small bay, particularly for Cu near the different harbours due to antifouling paint release (concentrations as high as 85 nM in the Toulon harbour). So, it can be suspected that the dissolved organic ligands will not be in sufficient concentration to maintain the free metal concentrations below the toxicity limit in the water column (ex. 10^{-11} M for Cu^{2+} [1]). Eh sediment depth profiles attests that sediments are under anoxic state from the first cm. Metallic contamination of surface sediments shows dramatically high levels, above the N2 level (French legislation on marine and estuarine sediment dredging [2], N2 levels for As, Cd, Cr, Cu, Hg, Ni, Pb and Zn respectively: 50, 2.4, 180, 90, 0.8, 74, 200 and 552 µg/g dw) by some order of magnitude, especially for the most enclosed parts of the small bay, where the water residence time are longer associated to strong nautical activities. It has to be pointed out that some specific points in the second part of the bay, directly open to the Mediterranean Sea, are also markedly polluted, signature of past anthropogenic activities and/or water circulation. Measurements on the Küllenberg cores will give information on the history of these different contaminations. Associated to measurements on interstitial water, such information will allow a better understanding of the contaminant behaviour at the water/sediment interface, influenced by diagenetic processes, which could partly control the contaminant remobilisation at the interface. This study will be completed by remobilisation experiments aiming at defining the possible contaminant remobilisation in natural events (ex. storm) or anthropogenic ones (ex. dredging) [3].

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