Ricerca e applicazione di metodologie ecotossicologiche in ambienti marini e salmastri
Viareggio 25-26 novembre 2008

Heavy metals in sediments and in *Mytilus galloprovincialis* near an off shore gas platform in the Central Adriatic sea

A. M. De Biasi[1], L. Pacciardi [1], G. Fabi[2], E. Tavolini[3], M. Puletti[3]

[1]Centro Interuniversitario di Biologia Marina ed Ecologia Applicata – V.le N. Sauro 4, 57128 Livorno, Italia
[2] IRPEM-CNR - Largo Fiera della Pesca, 60125 Ancona, Italia
[3] ENI S.p.A. Divisione Exploration & Production, UGITSAOP Via del Marchesato, 13 48023 - Marina di Ravenna (RA)

Objective – To investigate over a 3-year period the temporal trends of some heavy metal (Hg, Cd, Pb, Cu, Cr e Zn), both in the sediments near an offshore gas platform in the Central Adriatic sea, and in *Mytilus galloprovincialis* Lam.,1819 settled on the submerged part of the platform in the Central Adriatic sea.

This approach should allow to estimate the temporal evolution of metal concentrations in sediments and the bioavailability of these contaminants in the water column through their assimilation in filter feeding organisms**.**

Sampling and Analytical procedures - Six cruises were performed (the first about 10 months after the drilling activities ceased, i.e. April 2000) from 2000 to 2002 every September and April of each year.
Sediments: collected by box corer in 5 stations located a maximum distance of 30 m from BNW.
Organisms: scrapped from the jacket in two different sites near and far from the galvanic anodes, then separated in three size classes 3-4 cm, 4-5 cm, >5 cm and their tissues collected and dried at 60° for 8 hours. Unfortunately some size classes were not always present on the jackets preventing us from sample them (see Tab. 1).

Heavy metal analysis: 0.5 g of fresh sediment were digested in Teflon vessels with a mixture of concentrated HNO3, HCl and HF (suprapur). Hydrofluoric acid was neutralized by a saturated solution of boric acid. The analyses were performed by graphite furnace absorption spectrometry (Cd and Pb), atomic emission spectrometry (ICP AES) (Cu, Cr, Zn) and cold vapour atomic absorption spectrometry after reduction by stannous chloride (Hg).

Data Analyses - The Trellis graphs were used to investigate the temporal trends of each contaminant in the sediments surrounding the structure.
The results regarding the organisms were included in a matrix and subjected to the Principal Component Analysis (PCA) using Brodgard software package (© Highland Statistics Ltd).

Results – <u>*M. galloprovincialis*</u>: PCA ordination plot (Fig. 1): yellow points (regarding samples collected in April) are located along the positive right part of the first axis whereas the empty ones (regarding samples collected in September) are located in the opposite left side of the plot ⟹ seasonal gradient explained by the higher concentrations of all the selected metals.
Beyond the season variability, Zn, Pb, Cu, Cr showed a clear increasing trend from September 2000 to September 2002, whereas Cd and Hg exhibited weak fluctuations over time (Fig. 2).

<u>Sediments</u>: The highest concentrations were detected during the first survey and they generally decreased in the following surveys (Fig. 3).

Study area – Gas platform Barbara NW (BNW) located approximately 55 km off Ancona on a muddy sand seabed at 68 m depth.
BNW frame installed in January-February 1999, drilling operations started immediately after and finished in June 2002. Production began at the end of this month.

Tab. 1 Sample sites and size classes (I=3-4 cm, II=4-5 cm, III>5 cm) of *M. galloprovincialis* collected during the study period. A=April, S=September.

	2000		2001		2002	
Site	A	S	A	S	A	S
Far Anodes	I, II	II,III	I,II,III	I,II,III	I,II,III	II,III
Near Anodes	-	II,III	III	II,III	II,III	I,II,III

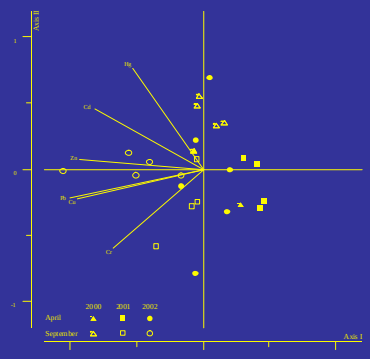

Fig. 1 Bidimensional ordination plot obtained by Principal Component Analysis applied to metal concentration determined in the soft tissues of *Mytilus galloprovincialis* over the 3-year study period. Total variance 72.1% (55.5%, 16.5%, I and II axis respectively).

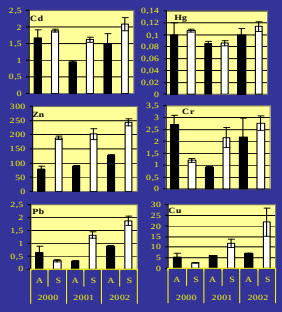

Fig. 2 Concentrations (mg/kg) of Cd, Hg, Zn, Cr, Pb and Cu in *M. galloprovincialis* after averaging size classes and sites. A=April, S=September.

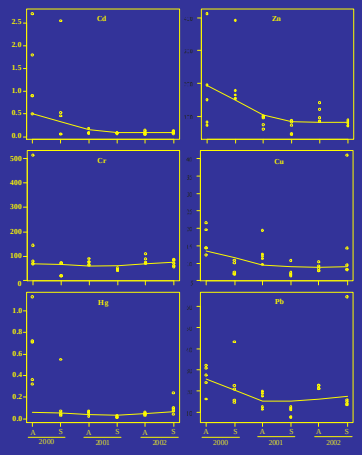

Fig. 3 Trellis graphs regarding the heavy metal content determined in the sediments. Concentrations in mg/kg. A=April, S=September.

Discussion – *M. galloprovincialis*: Cd, Zn showed marked seasonal fluctuations that reflect the natural fluctuations of both environmental and biological factors. However, natural temporal variability do not explain the clear increasing values detected for Pb, Zn, Cr and Cu. This is probably a sign of impact.
In addition all the selected metals, but Pb, are comparatively higher than those reported in mussels from the Portonovo Bay (Fattorini *et al*., 2008), a commonly accepted suitable control being not subjected to pollution or marked anthropogenic pressure.
Sediments: apparently contrasting results. A decreasing trend of metal concentrations were observed from the first survey onward, trend that corroborates the hypothesis according which the platform impact is more related to the installation phase and drilling operations rather than to the production phase.
The fate of contaminants present in drilling muds depends on different local constraints. It is bound that the seabed surrounding the well is primarily perturbed by drilling activities that represent a pulse disturbance. In fact when they cease the source contamination ceases in turn.

Mytilus vs sediments: Our data suggested that sediments are good descriptors of this initial pulse impact, whereas organisms are not. As concerning *M. galloprovincialis* the metal contents increased over time suggesting that they are gradually bioaccumulated.
The sacrificial anodes and the paints used in the submerged parts of the structure are the most probable source of metals directly released into the water and hence available for *Mytilus*.
In addition this kind of contamination, opposite to drilling operations, works over all the production phase acting as a chronic impact.

Conclusions – Temporal pattern of metal contents determined in sediments can not be directly compared to that observed in bivalve tissues because the first responds to a local, pulse contamination, the latter to a slow, chronic release of contaminants.
Hence both these approaches should be included in a correct monitoring program for a better interpretation of the impact related to off-shore gas platforms.

Fattorini D., Notti A., Di Mento R., Cicero A.M., Gabellini M., Russo A., Regoli F. (2008) - Seasonal, spatial and inter-annual variations of trace metals in mussels from the Adriatic sea: a regional gradient for arsenic and implications for monitoring the impact of off-shore activities. *Chemosphere*, 72 (10): 1524-33.