PLUTONIUM AND POLONIUM CONCENTRATION LEVELS IN MUSSELS FROM THE SPANISH COAST

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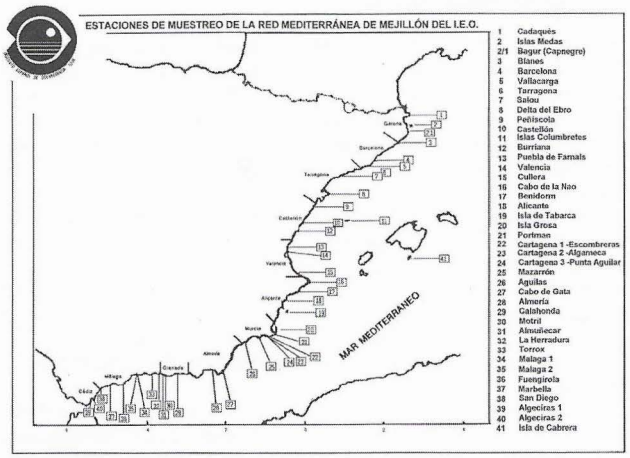
Within the frame of the Mediterranean Mussel Watch Program some wild mussels Mytilus galloprovincialis samples were collected by the Instituto Español de Oceanografía, IEO in the late spring of 2002 in several locations of the Spanish Mediterranean coast. At CIEMAT laboratories these samples were pretreated and analyzed to measure the $^{239+240}$Pu, 210Po and ^{137}Cs content. Polonium values ranged from 48±2 to 60±2 Bq/kg. Plutonium concentrations were around 10 mBq/kg. Cesium concentrations were below the detection limit. Concentration activities obtained in samples taken from mussels farms located in Galicia (northwestern Spain) are also presented.

Keywords: mussels, Spanish Mediterranean coast, plutonium, polonium

The large capacity of mussels to accumulate pollutants has favoured their use as bioindicators of the contamination of the surrounding ecosystem, avoiding the analysis of other matrices which require more sophisticated and expensive techniques (water/sediments). Mussels are considered appropriate bioindicators due to their sedentary, filter-feeding habit, common abundance and ease of collection. Since 1991, biomonitoring of the Iberian Mediterranean coast has been performed by the Group "Studies on Marine Contamination" from the IEO located in Murcia. This Group examines the quality of surface coastal waters in 40 different stations, analysing heavy metals (mercury, cadmium, lead, zinc and copper) and organic compounds like PCBs, DDTs, HCB, etc. [1,2].

In 2002, CIEMAT got involved in the Mediterranean Mussel Watch Program, sponsored by CIESM, with the aim of determining the radionuclides content in *Mytilus galloprovincialis* from selected Mediterranean locations, namely Delta del Ebro (fishing region/marine farms), Cullera (medium populated area, 10000-100000 inhabitants) and Algeciras-Guadarranque (heavily populated zone, >100000 people/ industrilized area) [Fig. 1].



Mussel samples (about 200 units per station) were kindly taken by IEO between mid-May and mid-June 2002. Following collection, samples were cleaned with seawater, appropriately packaged and fast-mailed to CIEMAT laboratories, where they were measured, weighed (fresh weight), freeze-dried and weighed again (dry weight).

Polonium was analysed in 5 grams aliquots digested with concentrated HNO_3 and H_2O_2 . The internal tracer ^{209}Po was added to the solution so obtained, then it was evaporated to near dryness. The residue was dissolved with concentrated HCl and evaporated again. The residue was treated with concentrated HCl; hydroxylamine hydrochoride, bismuth and sodium citrate were also added. The samples were then filtered through a paper filter and the residue was rinsed with distilled water until reaching the appropriate volume for the autodeposition of polonium following Flynn´s method. Quantification was done by alpha-spectrometry.

For cesium measurements, the mussels flesh was ashed at 450ºC for 12 hours. Gamma determinations were performed with a hyperpure N-type germanium detector.

Plutonium analyses were carried out in stations Delta del Ebro and Algeciras in about 6 grams subsamples following calcination at 450ºC. Galicia sample was ashed at 550ºC; sample size was 2 grams. Briefly, the ashes were digested with hot HNO_3 8N (3x) and then filtered through a 0.45 µm glass fiber filter. Following the attacks, ^{242}Pu was added as an internal tracer to calculate chemical recoveries. Plutonium was purified using two ionic resins, namely AG 1x8 (20-50 mesh) to eliminate with HCl 10N most of the natural radionuclides such as thorium and uranium and AG 1x8 (50-100 mesh) to remove Th and U traces. Plutonium was eluted from the column with NH_4I/HCl, then electroplated following Talvitie´s method onto stainless steel discs. At last, it was quantified by alpha-spectrometry using PIPS detectors.

The results obtained are displayed in Table 1. As it can be observed, in the Mediterranean stations polonium values vary from 48±2 to 60±2 Bq/kg. The two studied stations present similar average values. Plutonium values were identical in both stations, namely 10±2.4 and 11±3.1 mBq/kg. Cesium values were below the detection limit, since the amounts of sample available for gamma measurements were not big enough.

STATION	DELTA DEL EBRO	CULLERA**	ALGECIRAS	GALICIA
Temperature (ºC)	17.5	----	16.8	----
Salinity (‰)	37.1	----	37.2	----
Average size mm ± SD	43±5	----	37±6	81±8
Condition Index*	13.7	----	9.4	20.8
Weight ratios	Ww/Dw=6.6 Dw/Aw=4.4	----	Ww/Dw=6.9 Dw/Aw=4.2	Ww/Dw=7.1 Dw/Aw=5.6
$^{239+240}$Pu mBq/kg±1s D.w.	11±3.1	----	10±2.4	58.9±9.2
^{210}Po Bq/kg±1s D.w. mean	49.40±1.81 59.97±2.37 53.04±2.12 **54.14±1.2**	----	57.71±2.24 48.40±2.00 ---- **53.1±1.5**	48.7±1.8 53.5±2.0 40.4±1.5 **47.5±1.0**
^{137}Cs Bq/kg±1s	<0.21	----	<0.99	---

*CI=(Mussel flesh wet weight/mussel shell wet weight)x100
Ww: Wet weight; Dw: Dry weight (freeze-dried); Aw: Ashed weight
**sample lost due to technical problems within Ciemat electrical system

Mussel samples from Galicia present Po values similar to those obtained in the Mediterranean stations. However, Pu results are close to 6 times higher.

References

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