Trace Elements in *Mytilus galloprovincialis* LMK from Sozopol and Nessebar Areas, Bulgaria

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INTRODUCTION

During the period 1988-1989 the study [1] was continued to determine some trace elements in Mytilus galloprovincialis Lmk from Sozopol and Nessebar (Bulgarian Black Sea coast). Samples cultivated (suspended culture) and rock mussels were taken seasonally and analysed for Cu, Zn, Pb and Cd concentrations. In October 1988 quantitative determinations of four samples were made for other 9 metals.

MATERIALS AND METHODS

The preliminary preparation of the samples was carried out in accordance with the methodology recommended by FAO [2]. Approximately 2g of mussel meat, homogenized and dried at 105°C was weighed with an analytical balance, placed into a quartz glass and 15 ml concentrated solution of HNO_3 was added attentively. In 24 h the mixture was vaporized on a sand bath up to the volume of 5-6 ml and then 5 ml of $HClO_4$ was added to the solution and again vaporized up to the same volume. The solution obtained was placed into a 50 ml beaker and bidistillated water was added up to the mark. The samples were analysed by a AAS "Perkin Elmer 2380" in graphite furnace HGA - 400 applying the method of a standard addition and 0.5% $(NH_4)_2HPO_4$ as a matrix modifier in Pb determination.

The same technique following an extraction of the analysed elements with APDC and MIBK was used to determine other 9 metal components in 4 mussel samples (October 1988).

RESULTS AND DISCUSSION

In Table 1 means of trace metal concentrations in 13 samples cultivated and rock mussels, are given.

The concentration variations of those elements in cultivated and rock mussels from Sozopol and Nessebar areas were comparable with the reproducibility of the analytical method. The relative standard deviation, Sr (n=5) for the concentrations presented does not exceed 10%.

Table I. Means of trace elements concentrations in Mytilus galloprovincialis Lmk from Sozopol and Nessebar mussel farms, 1988 -1989 *)

Period	Average concentrations (mg/kg dry weight) Cu	Zn	Pb	Cd
1988 / X	18.0	93.6	12.3	1.9
1989 / II	9.7	102.1	11.0	1.7
IV	9.9 (12.8)	91.7 (138.3)	6.3 (7.9)	1.3 (2.0)
X	16.3 (18.1)	99.0 (125.4)	8.6 (8.7)	1.4 (1.4)
XI	8.1	83.2	-	-

*) In parentheses concentrations of trace elements in rock mussels

The following concentrations (mg/kg dry weigh) were found for the trace elements in October samples (1988); 27.2 ± 5.3 for Bi, 7.0 ± 0.7 for Ni, 13.7 ± 2.2 for Mn, 2.8 ± 0.4 for Co, 338.4 ± 32.9 for Fe, 18.2 ± 3.5 for Ba, 15.0 ± 2.8 for Cr, 30.2 ± 5.8 for Mo and 48.3 ± 9.4 for V.

In comparison with the concentrations previously determined, the new analyses showed increased values for Cu, Zn, Pb and Cd in mussels attributed likely to increased total pollution of the Black Sea area during the period of study. The comparative results for cultivated and rock mussels (regarding a definite mussel farm & season) indicate higher concentrations for rock mussels. The increased values for trace elements in cultivated mussels (spring generations 1988)in October 1988 and February 1989 is attributed mostly to higher concentrations of those components in the sea water along the coast in 1988. It should be noted that the concntrations of the analysed elements are higher in the samples, collected in October 1988 and 1989.

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Spectral Characterization of the Romanian Bottom Black Sea Sediments Contaminated by 137 Cs

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ABSTRACT. Bottom sediments sampled on the Romanian Black Sea coast, by X-R diffraction, EPR (Electronic Paramagnetic Resonance) and IR (Infra-Red) spectra were investigated in view to explain the higher accumulation of ^{137}Cs in front of Portitza site Razelm lagoon.

INTRODUCTION. The aim of this research is to carry out the investigation on the mineralogical nature of the silty clay sediments sampled on the bottom of the Black Sea Romanian coast, aerobe oxydo-reduction zone.This in view to explain the higher accumulation of ^{137}Cs 30 y important by its accumulation in the biota, especially at Portitza Razelm lagoon,very rich in fishing activities.The chemical composition with the grain size as well as with the retention and exchange of man made radionuclides between crystalline lattice and the soluble form of the radionuclide in water,in previous paper has been discussed (1-2).

MATERIAL AND METHODS. Marine sediment samples were collected at 45°08'N 29°57'E to 44°08'N, 28°57'E coordinates, offshore 13.2 to 17.3 marine Miles at Portitza. Other characteristics at Portitza: liquid discharge of Danube river, Q=6830 m^3/s, on the bottom sea water temperature t = 6.5°C, water salinity S=18.23‰, flow current V=8 cm/s, direction α = 100°. The grain size of the silty clay was 70 +80 µm. The dried sediments at 105°C were submitted to the following investigations: X-ray diffraction carried out by a TUR M-72 installation with the CuKα radiation, EPR (Electronic Paramagnetic Resonance) by means of a EPR Spectrometer ART-5 IFIN-Bucharest type with X-band frequency and IR (Infra-Red) spectra registered in the band of 200-4000 cm^{-1}, making use of a PERKIN-ELMER apparatus type, the samples being packed in KBr.

RESULTS AND DISCUSSION.

- In TABLE 1 are included the results concerning the mineralogical composition of the bottom sediments sampled during June 1989, established by X-ray diffraction. It is to be outlined only at Portitza site in the silty clay are to be found the highest content of *illite*, but lower content in calcite, favorable to accomodate in the crystalline lattice the Cesium ions. On the other hand, by INAA analysys only in this region 8 ppm of stable Cs was found (3). It is known the radionuclide follows the pathway of its stable counterpart.

TABLE 1. Identified minerals by X-Ray diffraction in bottom sediments of the Romanian Black Sea coast, 1989

Sample	ß-Quartz	Calcite	Illite	Kaolinite	Feldspath
Sulina	+ + +	+ +	+	-	-
St.Gheorghe	+ +	+ +	+	+	+ +
Portitza	+ + +	+	+ +	+	-
Constantza	+ + +	+ +	+	+	-

- From IR spectra the following conclusions can be drawn: the calcite ($\tilde{\nu}_3$ = 1460 cm^{-1} and $\tilde{\nu}_2$ = 710 cm^{-1}) in the sample is decreasing as follows: Constantza > Sf.Gheorghe > Sulina > Portitza. Lower content in calcite at Portitza explains higher concentration of Cs and ^{137}Cs. The illite was identified ($\tilde{\nu}_{Si-O-Si}$, Si-O-Al at $\tilde{\nu}$ = 1020-1100 cm^{-1} and δ = 420-520 cm^{-1}, while Kaolinite at $\tilde{\nu}$ = 3600 cm^{-1}. The illite is present at every sampling station also more concentrated at Portitza.By IR spectra it was not be observed the characteristic vibrations of any organic pollutants in the samples.

- EPR spectra shown the Fe^{3+} and Mn^{2+} ions. The highest content of Fe^{3+} about 4% (3) is related to illite presence. The presence of Cr^{3+} is also discussed. In all sediment samples except those of Constantza, the EPR characteristic signal was put in evidence the organic matter named *Kerogen* disseminated in sedimentary facies rocs, generator of petroleum (4). The highest signal of Kerogen was at Portitza sampling site.

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