Cs-137 geochronology, epithermal neutron activation analysis, and principal component analysis of heavy metals pollution of the Black Sea anoxic continental shelf sediments

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Anthropogenic Cs-137 Gamma-ray Spectroscopy assay (GrSA) performed at the National Institute of Research and Development for Physics and Nuclear Engineering – Bucharest (Romania) in correlation with Epithermal Neutrons Activation Analysis (ENAA) performed at the Joint Institute of Nuclear Researches – Dubna (Russia) were used to investigate a 50 cm core containing unconsolidated sediments collected at a depth of 600 m off Romanian town of Constantza, located in the anoxic zone of the Black Sea Continental Shelf. A digital radiography showed the presence of about 265 distinct laminae, 1 to 3 mm thick, a fact attesting a stationary sedimentary process, completely free of bioturbation.

After being radiographed, the core was sliced into 45 segments whose thickness gradually increased from 0.5 to 5 cm, such that the minimum thickness corresponded to the upper part of the core. From each segment two aliquots of about 0.5 g and 50 g were extracted for subsequent ENAA and Cs-137 GrSA.

The Cs-137 vertical profile evidenced two maxima, one of them was very sharp and localized at a depth of 1 cm and the other very broad, almost undistinguished at about 8 cm depth, the first one being attributed to 1986 Chernobyl accident. Based on these date, we have estimated a sedimentation ratio of about 0.5 mm/year, value taken as reference for further assessment of recent pollution history.

By means of ENAA we have determined the vertical content of five presumed pollutants, e.i. Zn, As, Br, Sn and Sb and of Sc, as natural, nonpolluting element. In the first case, all five elements presented a more or less similar vertical profile consisting of an almost exponential decrease for the first 10 cm below sediment surface followed by a plateau until the core base, i.e. 50 cm below surface, dependency better described by the equation:

$$c(z) = c_0 \left[1+k \exp \left(-\frac{z}{Z}\right)\right]$$  \hspace{1cm} (1)

where: where $c(z)$ represents the concentration vertical profile; $z$ represents depth (in absolute value); $c_0$ represents the plateau concentrations; $k$ represents the surface to plateau relative increment of concentration; $Z$ represents concentration decrement: the depth at which the concentration becomes 1+k times greater than plateau one.

Final results have shown with clarity that in the case of Zn, As, Br, Sn and Sb, the concentrations near sediment surface were 1.6 to 4.1 times greater then the plateau ones while Sc vertical profile, excepting some small fluctuations observed between 18 to 25 cm below surface, shown to be almost constant. Moreover, the concentration decrements $Z$ of Zn, Br, Sn and Sb were almost coincident within one standard deviation while in the case of As, this coincidence appears within two standard deviation, these facts pleading for a comparable time evolution in the past 100 years. On the other hand, in the case of Sn and As, the maximum concentrations were
reached 1 cm below the sediment surface, roughly corresponding to 1990 year, while the concentrations of all other three elements monotonously increases up to sediment surface.

Further Principal Components Analysis of the data concerning the vertical distribution of all six elements illustrates the presence of two distinct clusters, one consisting of Zn, As, Br, Sn and Sb and the other only of Sn, attesting both differences and similarities in the vertical distribution of considered elements.

By comparing the experimental concentrations of all five elements with Romania Regulations concerning heavy metal pollution, we remarked that, by respect to these Regulations the only Zn, As, Br and Sb slightly exceeded normal accepted limits while the minimum alert concentrations were exceeded only in few cases by of As and Br, but no elements concentrations reached the intervention threshold.

In our opinion, these results reflect the dynamics of the industrial activity in the riparian to Danube River European countries: a steady increase beginning with the last half of the XIX-th century followed by a slightly decline after the fall of Communism.