

# MERCURY AND RADIONUCLIDES IN SEDIMENTS OF THE KASTELA BAY (CROATIA) : EVALUATION OF THE SEDIMENT POLLUTION HISTORY.

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## Abstract

Mercury and radionuclides (<sup>226</sup>Ra, <sup>238</sup>U and <sup>137</sup>Cs) were measured in sediments of the Kastela bay (Eastern Adriatic Coast), polluted with mercury by the chlor-alkali plant. From depth distributions of <sup>238</sup>U, <sup>226</sup>Ra and Hg it was revealed that sediment represents a mixture of natural sediment (rich in Hg) and ash (poor in Hg and rich in radionuclides) from coal used in the factory power plant. Distribution of <sup>137</sup>Cs showed that sediment up to a depth of 50 cm was younger than 1986, meaning that dumping of the coal ash to the sea took place after this year.

**Keywords:** mercury, radionuclides, Kastela bay, pollution history

## Introduction

Kastela bay is a semi-enclosed bay, situated in the central part of the Eastern Adriatic coast, which is heavily polluted with mercury by 40-years activity (1949-1989) of the chlor-alkali plant. High concentrations of total and methyl mercury were demonstrated in sediment and marine organisms of this area (1). Although the factory is closed already for more than 10 years, mercury buried in sediment still represents an important source of this metal for the whole ecosystem (2). In order to elucidate the fate of mercury deposited in sediment and to evaluate pollution history of the area, sediment cores sampled in front of the chlor-alkali plant were analyzed for mercury and radionuclides content.

## Sampling and methods

Sediment cores were sampled in June 2000, February and October 2001 at a distance of 100 m from the chlor-alkali plant. Cores, 20 to 50 cm long, were sliced onto 2 to 5 cm thick layers. A portion of each sediment slice was dried at room temperature for Hg analysis and another one at 106 °C for radionuclide analysis. After wet digestion of sediment with concentrated HNO<sub>3</sub>, mercury was determined by CVAFS (cold-vapor atomic fluorescence spectrometry). For radionuclides a HPGe detector connected to a 4096 channel analyzer was used. Spectra were recorded for 80000 s and analyzed on PC using GENIE 2000 software.

## Results and discussion

Mercury distribution in sediments sampled in front of the chlor-alkali plant demonstrated anomalous behavior – an absence of correlation with organic carbon (C<sub>org</sub>), a strong positive correlation with inorganic carbon (C<sub>inorg</sub>) and very irregular depth distribution. Results of radionuclides analyses (Table 1) revealed that this sediment was highly contaminated with <sup>226</sup>Ra and <sup>238</sup>U, in comparison with the Adriatic Sea sediments (3), and that a negative correlation existed between Hg and radionuclides. Typical sediment depth profiles of Hg and radionuclides (Fig. 1) illustrated opposite depth distributions of Hg and <sup>226</sup>Ra or <sup>238</sup>U. On the basis of all data obtained from 4 different sediment cores, it was reconstructed that the ash from the

coal used in the factory power plant was dumped to the sea and that analyzed sediments represented a mixture of such artificial material and natural sediment. Obtained negative correlations between Hg, C<sub>inorg</sub> and <sup>226</sup>Ra or <sup>238</sup>U were a consequence of mixing coal ash, which was low in Hg and C<sub>inorg</sub> and high in radionuclides, with natural sediment, which was

high in Hg and C<sub>inorg</sub> and low in natural radionuclides content (Table 1). It was estimated that sediment contained between 15 and 80 % of the coal ash and analyzed sediment cores demonstrated that sediment and ash were mixed in very irregular manner, regarding both spatial and depth distributions.

**Table 1. Average concentrations of some parameters in coal ash, sediments from the Kastela bay and, for comparison, in sediments from the Adriatic Sea (KB - Kastela bay; AS - Adriatic sea).**

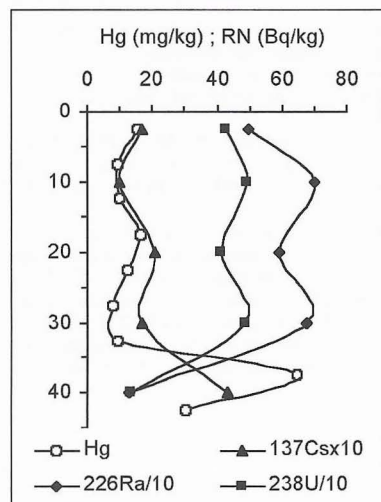
Sample type	Hg (mg/kg)	C <sub>inorg</sub> (g/kg)	C <sub>org</sub> (g/kg)	<sup>226</sup> Ra (Bq/kg)	<sup>238</sup> U (Bq/kg)	<sup>137</sup> Cs (Bq/kg)
Coal ash	1.9 ± 0.2	14 ± 2	38 ± 2	1350 ± 80	832 ± 36	0.9 ± 0.1
KB sediment	28 ± 14	26 ± 12	54 ± 6	460 ± 145	345 ± 110	2.4 ± 1.2
AS sediment	0.1 – 0.4	45 – 90	10 – 20	10 – 30	10 – 40	1 – 15

Data on <sup>137</sup>Cs content (Table 1, Fig. 1) showed that sediment was characterized with relatively large range of <sup>137</sup>Cs activity (0.5 – 5.0 Bq/kg) and that <sup>137</sup>Cs was positively correlated with Hg. Very similar depth profiles of <sup>137</sup>Cs and Hg obtained in analyzed sediment cores (Fig. 1) illustrate this correlation. The obtained positive correlation confirm the a consequence of mixing the coal ash with low <sup>137</sup>Cs content with sediment that contained much higher <sup>137</sup>Cs concentrations (Table 1). Sediment containing low percentage of ash at the bottom of the sediment core (Fig. 1) had high <sup>137</sup>Cs concentration (about 5.0 Bq/kg) which was typical for sediments deposited after the Chernobyl accident. Accordingly, it was concluded that dumping of the coal ash to the sea took place after 1986.

These results did not allowed a more precise dating of the mercury pollution history of the area due to artificial nature of the investigated sediments. For this purpose longer sediment cores at various distance from the factory should be analyzed. However, obtained results explained well recent pollution history of the investigated sediment and for the first time demonstrated that the Kastela bay is heavily polluted not only with mercury, but also with radionuclides.

## References

- 1 - Mikac, N., Picer, M., Stegnar, P. and Tusek-Znidaric, M., 1985. Mercury distribution in polluted marine area, ratio of total mercury, methyl mercury and selenium in sediments, mussels and fish. *Water Res.*, 19: 1387-1392.
- 2 - Kwokal, Z., Franciskovic-Bilinski, S., Bilinski, H. and Branica, M., 2002. A comparison of anthropogenic mercury pollution in Kastela Bay (Croatia) and pristine estuaries in Ore (Sweden) and Krka (Croatia). *Mar. Pollut. Bull.*, 44: 1150-1155.
- 3 - Barisic, D., Vertacnik, A., Lulic, S., Mihelcic, G., Sondi, I., Juracic, M., Prohic, E. and Crmaric, R., 1998. Natural radionuclides in recent marine sediments of the Adriatic Sea. *Rapp. Comm. int. Mer Médit.* 35: 228-229.



**Fig. 1. Depth distributions of Hg and radionuclides in sediment core sampled in February 2001.**