SPATIAL DISTRIBUTION OF URANIUM AND RADIIUM IN THE SEDIMENTS, MUSSELS (MYTILUS SP.) AND SEA WATER IN PORT OF ŠIBENIK

ABSTRACT

The purpose of this study is to assess the response of the aquatic environment (sediment, seawater and mussels Mytilus sp.) on uranium and radium activity and concentration following the decrease of phosphate discharges from a technologically improved transhipment terminal, situated at the Croatian Adriatic coast in the port of Šibenik. The highest $^{238}\text{U}$ activities (485±16 Bq kg$^{-1}$ dry weight) and $^{226}\text{Ra}$ activities (662±6 Bq kg$^{-1}$ dry weight) were found in the sediment sample collected from the sampling site closest to the terminal. The maximum concentrations in the sediment samples are above the natural ranges and are clearly indicative of technological influence.

Mussel samples from the port of Šibenik showed levels of $^{238}\text{U}$ activities in the range from 12.1±2.9 to 19.4±7.2 Bq kg$^{-1}$ dry weight and $^{226}\text{Ra}$ activities from 1.9±0.5 to 5.9±1.1 Bq kg$^{-1}$ dry weight, which is somewhat higher than in consume mussels. Only the seawater sample at the sampling site, taken just above the bottom sediment, shows higher uranium concentration (3.1±0.2 μg L$^{-1}$) comparing to the samples taken in upper seawater layers (2.1±0.2 μg L$^{-1}$). Higher concentration in the range of the concentration level of uranium in natural seawater.

Since the transhipment terminal in the port of Šibenik was modernised in the eighties, the discharge of the phosphate ore into the seawater was drastically reduced and, consequently, uranium concentration levels in the seawater decreased. The enhanced uranium and radium activity levels are found only in the sediment near operational docks, and in the mussels which live on this docks.

KEYWORDS

uranium, radium, sediment, seawater, mussels Mytilus sp., Krka river Estuary, phosphate

1. INTRODUCTION

Uranium ($^{238}\text{U}$) and radium ($^{226}\text{Ra}$) are universal environmental elements present in radioactive decay series $^{238}\text{U}$ to $^{206}\text{Pb}$. Most crustal rocks contain a few parts per million of uranium, with an average of 2.8 ppm. Due to weathering and subsequent transport, these rocks were carried away by the rivers, which are the major source of dissolved uranium to the oceans (Goldberg et al. 1971).

The Krka River flows through the coastal karstic region of Croatia and from there into the Adriatic Sea. The Estuary was formed during the Holocene transgression in the total length of 22 km. It is a typical stratified Estuary with fresh-brackish surface layer moving seawards and bottom seawater layer as counter-current moving upward. A clastic material input in the Krka River Estuary is small (Juračić and Prohić, 1991). The main input of the terrigenous material in the Krka River Estuary originates from a very small Guduča River inflowing into the Prokljan Lake downstream the Krka River. The Krka River contains larger quantities of fresh-water (an average of 55 m$^3$/s) than the Guduča River (average< 1 m$^3$/s). However, a number of waterfalls along the Krka River, upstream the town of Skradin, significantly reduce the suspended material transport (Juračić and Prohić, 1991; Cukrov et al., 2004). The largest settlement in the region of the Krka River Estuary is the town of Šibenik. Šibenik is the main Croatian port for the phosphate ore import. The phosphate ore transhipped in the Šibenik port introduces radioactive material in the Krka River Estuary. The phosphate materials used for the production of phosphates fer-
tilizers contain elevated quantity of radioactive material, mainly the disintegration products of the $^{238}\text{U}$ series (Barisic et al., 1992). Shipments of the phosphate ores in the Šibenik port started in the sixties of the last century (http://www.lukasibenik.hr/). The frequency of traffic was highest in 1988 (740,000 tons), with a break from 1992 to 1995. In the year 2003 the phosphate ore traffic was about 300,000 tons. During the eighties of the last century, a modern terminal for transfer of scattered cargo with a capacity of 2 million tons per year was constructed. After having constructed the scattered cargo terminal, specialized in raw phosphates and artificial fertilizer handling, the material input into the sea became negligible.

In this work, the uranium concentrations in sediment, seawater and mussels *Mytilus sp.* of the Krka River Estuary have been analysed and compared with the existing literature data. Spatial distribution of uranium and radium in the recent sediments are studied, too. The paper also discusses the influence of the improved transhipment terminal for scattered cargo (mainly phosphate ore) in the port of Šibenik, on uranium and radium concentration changes in the Estuary compartments.

### 2. EXPERIMENT

#### 2.1. Sampling sites and methods

Sediment and mussel samples were collected during 2003 and 2004, while seawater samples were collected in October 2004. Seawater samples were taken at one (SP1), and sediment samples at six (SP1-SP6) sites (Figure 1). The bottom sediment samples were collected by scuba diving using hand-driven plexiglas corers.

![Figure 1 - Map of sampling area](image)

Mussels (*Mytilus sp.*) were sampled at 4-6 m depth by scuba diving at three locations (SP1, SP5 & SP6). Each time 2-4 kg of wet weight were sampled and 90% of mussels were 3 to 5 cm long. Seawater samples at vertical profile were taken at the sampling sites SP1 (3, 5, 7 and 9.5 m). Samples were directly collected in the pre-cleaned SIMAX Kavalier borosilicate glass reagent bottles (Sázava, Czech Republic) with a total volume of 0.5 l, by scuba diving.

#### 2.2. Equipment and experimental procedure

Prior to gamma-spectrometry measurements, sediment samples were thawed at room temperature and dried at 106°C during 24 hours, counted in special vessels, sealed and stored for at least 4 weeks in order to allow its radiochemical equilibrium between gaseous $^{222}\text{Rn}$ and its $^{214}\text{Bi}$ progeny. Samples were counted on HPGe detector with a Canberra 8192 channel analyser (Meriden, USA). The system was calibrated using the standards supplied by Amersham International (Buckinghamshire, UK), IAEA-306 and IAEA-314.

Prior to gamma-spectrometry measurements, soft tissue of mussels was separated, drained and dried at 106°C until constant mass. Dry samples were counted in special vessels, sealed and stored for at least 4 weeks in order to allow radiochemical equilibrium.

Seawater sample measurements by voltammetric techniques were performed using the ECO Chemie µAUTOLAB multimode potentiostat controlled by GPES 4.5, General Purpose Electrochemical System software package through a personal computer with data acquisition routine (Utrecht, The Netherlands). Samples were measured with a three-electrode system Metrohm 663 VA STAND (Herissau, Switzerland). The area of the mercury drop was $0.52±0.05 \text{ mm}^2$.

### 3. RESULTS AND DISCUSSION

#### 3.1. Sediment and mussel samples

Activities of the radionuclide $^{238}\text{U}$ measured in the sediment at sampling sites SP1 to SP6 are presented in Figure 2 and the activities of the radionuclide $^{226}\text{Ra}$ in Figure 3. $^{238}\text{U}$ activities in sediment near operational dock (SP1, 2) were approximately ten to thirty times higher than in the unpolluted (9-17 Bq kg$^{-1}$) Adriatic coastal sediment (Barisic et al., 1996). However, the activities of $^{238}\text{U}$ at the SP3 site which is located less than 1 km from the operational dock (Figure 1), were only 3-4 times higher than unpolluted Adriatic sediment. $^{238}\text{U}$ activities upstream (SP4, SP6) and down-
226Ra activities in the sediments were six to eight times higher than in Table 1. 238U activities were in the range from 12.1±2.9 to 19.4±7.1 Bq kg⁻¹ dry weight at site SP1. These activities were six to eight times higher than in consume mussels (2-3 Bq kg⁻¹ dry weight) 5 km upstream at site SP6 and three times higher than in mussels downstream at site SP5 (Table 1). Activities of 226Ra do not show the same distribution because remobilisation of 226Ra from sediment is very low (Aguado et al., 2004). Concentrations of radium in the sediment are almost the same from sedimentation time. On the contrary, about 30% of uranium was dissolved from sedimentation time.

Table 1 - Activities of 226Ra & 238U in tissue of mussels (Mytilus sp.)

<table>
<thead>
<tr>
<th>site</th>
<th>date</th>
<th>226Ra/Bq kg⁻¹ dry weight</th>
<th>238U/Bq kg⁻¹ dry weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>SP1</td>
<td>April 2003</td>
<td>5.9 ± 1.1</td>
<td>13.4 ± 4.8</td>
</tr>
<tr>
<td></td>
<td>October 2003</td>
<td>2.6 ± 0.7</td>
<td>13.5 ± 3.9</td>
</tr>
<tr>
<td></td>
<td>April 2004</td>
<td>6.5 ± 1.6</td>
<td>19.4 ± 7.2</td>
</tr>
<tr>
<td></td>
<td>October 2004</td>
<td>1.9 ± 0.5</td>
<td>12.1 ± 2.9</td>
</tr>
<tr>
<td>SP5</td>
<td>April 2003</td>
<td>3.8 ± 0.5</td>
<td>5.3 ± 2.4</td>
</tr>
<tr>
<td></td>
<td>October 2003</td>
<td>2.4 ± 0.7</td>
<td>5.1 ± 3.2</td>
</tr>
<tr>
<td></td>
<td>April 2004</td>
<td>3.1 ± 1.0</td>
<td>4.6 ± 4.3</td>
</tr>
<tr>
<td></td>
<td>April 2003</td>
<td>2.3 ± 0.6</td>
<td>2.7 ± 2.6</td>
</tr>
<tr>
<td></td>
<td>October 2003</td>
<td>1.1 ± 0.7</td>
<td>&lt; 2.2</td>
</tr>
<tr>
<td>SP6</td>
<td>April 2004</td>
<td>4.4 ± 1.4</td>
<td>&lt; 2.8</td>
</tr>
<tr>
<td></td>
<td>October 2004</td>
<td>4.4 ± 1.4</td>
<td>&lt; 2.8</td>
</tr>
</tbody>
</table>

238U activities in the sediments were consistently higher than in the mussels (Figure 2, 3; Table 1). This is expected taking into account that biota has only limited lifespan in which it takes up radionuclides, whilst sediment contamination is comparatively permanent (i.e. only likely to be diminished by slow processes such as dilution and dispersion). Sediments also showed much higher 226Ra and 238U values variation than mussels and seawater samples. This variation of activities can be related to the grain-size, but mostly to diminishing of the phosphate ore input because these variations are greater at the sites near the operational dock.

3.2. Seawater samples

The Uranium in seawater predominates in the dissolved, anionic form, and does not react with organic material, or with negatively charged, suspended par-
ticulate matter sized from 0.45 μm up (Djogić and Branica, 1991; Djogić et al., 1986). Additionally, uranium in marine environment is concentrated in colloids of the 1.6 to 2.2 nm size (Singhal et al., 2004). Hence, acidification of non-filtered seawater samples immediately after sampling at pH<2.5 assures total uranium concentration analysis.

Total uranium concentrations in seawater samples lie between 2.1 and 3.1 μg L⁻¹ in SP1 sampling site (Figure 4). The highest concentration (3.1±0.2 μg L⁻¹) of uranium was observed in the sample taken 0.5 m above the bottom sediment at 9.5 m (36%). Lower uranium concentrations (about 2.1 μg L⁻¹) were observed in three upper seawater layers (depths 3, 5 and 7 m) and there is no statistically significant difference among them. However, the difference is statistically significant between the deepest (9.5 m) and the upper samples (Figure 2). Upper samples are also seawater (33-36%) and uranium concentrations are in the range of the coastal marine samples, from 1.3 to 3 μg L⁻¹ (Veeh, 1967). The highest uranium concentration found in the sample taken near the bottom (3.1±0.2 μg L⁻¹) is the result of the equilibrium between the sediment and the seawater bulk, as well as due to the presence of the higher quantity of the suspended material in the bottom water layer. However, this concentration (3.1 μg L⁻¹) is still within the natural uranium level in seawater (Goldberg et al., 1971).

Uranium concentrations in seawater samples from sampling site SP1 (Figure 4) were almost three times lower than reported previously: 6.7±1.2 μg L⁻¹ (Mlakar and Branica, 1989, 1994), 5.7±1.0 μg L⁻¹ and 6.2±1.0 μg L⁻¹ (Djogić et al., 2001). Moreover, seawater uranium concentrations are lower than in southern Baltic surface waters (from 3.7±0.1 to 6.1±0.1 μg L⁻¹) and in the range of Baltic bottom waters (from 1.8±0.1 to 3.8±0.1 μg L⁻¹) (Skwarzec et al., 2002).

Accordingly, the operational dock modernization in the eighties of the last century was probably the main reason for the significant uranium concentration decrease in seawater column.

4. CONCLUSIONS

The response of the aquatic environment (sediment, seawater and mussels Mytilus sp.) on uranium concentration following the decrease of the phosphate ore discharges from the improved transhipment terminal in the port of Šibenik was assessed. Until its technological modernization in the eighties of the last century, it was responsible for the phosphate ore spilling into the sea. The phosphate ore spilling was recognized as the cause of enhanced uranium and radium activities in the sediment and biota. Spatial distribution of ²²⁶Ra and ²³⁸U shows that most of the phosphate ore which entered the estuarine environment stays near the operational docks.

The highest uranium and radium activities are found in deeper sediment layers near the operational dock. These values are significant above the natural ranges and are the indicator of technological influence. Mussels sampled below the operational dock showed levels of uranium activities several times higher than in the consume mussels a few kilometres upstream and downstream, while activities of radium are uniform. Uranium concentration levels in seawater samples showed characteristic values for unpolluted environment. The increased uranium concentration in the seawater sample taken near the bottom (3.1±0.2 μg L⁻¹) is probably the result of the dissolving of uranium from the sediment.

The enhanced uranium activity levels found in the deeper layers of the sediment are directly connected with the greater input of the phosphate ore into the Estuary during the seventies and the eighties of the last century. Slightly enhanced uranium levels in mussels near the operational docks are present due to the diminished, but constant input of phosphate particles from the docks into the estuarine environment even today and from the dissolving of uranium from sediment.

The contaminated sediment could also present a future source of toxicants for seawater and marine organisms. Therefore, it is very important to continue work on understanding of the transfer and distribution of toxicants in the Krka River Estuary.

ACKNOWLEDGEMENT

The financial support of the Ministry of science, education and sports of the Republic of Croatia (through the Grant No. 0098121), is gratefully acknowledged.
fosfatne rude u morski okolisi, a time su se smanjile i prekrcaj rasutih tereta Sibenske luke, znacajno se smanjio unos jednosti izmjerene u uzorcima sedimenta nalaze se iznad postaji dvjestotinjak metara od operativne obale. Najvece radija nadene su samo u sedimentima u neposrednoj blizini KIJUCNE RUECI tuarij rijeke operativne obale, te u centracije urana u morskoj vodi.

PROSTORNA RASPODUELA URANA I RADIA U SEDIMENTU, ŠKOLJKAŠU (MYTILUS SP.) I VODI LUKE SIBENIK

Mjerjenjem aktivnosti urana (238U) i radija (226Ra) u sedimentu i školjkašu (Mytilus sp.) te mjerjenjem ukupne koncentracije urana u morskoj vodi istrajenje utjecaj moderniziranog sustava za prekrcaj rasutog tereta. Najvece aktivnosti suhij od onih u konzumnim radioactivity of waters.

E-mail: mlakar@irb.hr

Bijenicka 54, 10000 Zagreb, Republika Hrvatska

SAŽETAK

N. Cukrov et al.: Spatial Distribution of Uranium and Radium in the Sediments, Musels (Mytilus sp.) and Sea Water in Port of Šibenik

Mr. sc. NEVEN CUKROV
E-mail: ncuksr@irb.hr
Dr. sc. VLADO CUCULIĆ
E-mail: cuculic@irb.hr
Dr. sc. DELKO BARIŠIĆ
E-mail: dbarisic@irb.hr
Dr. sc. MARINA MLAKAR
E-mail: mlakar@irb.hr

Institut Ruder Bošković
Zavod za istraživanje mora i okoliša
Bijenička 54, 10000 Zagreb, Republika Hrvatska

E-mail: ncukrov@irb.hr

REFERENCES


