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## SPATIAL DISTRIBUTION OF URANIUM AND RADIUM 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 transshipment terminal, situated at the Croatian Adriatic coast in the port of Šibenik. The highest  $^{238}\text{U}$  activities ( $485 \pm 16 \text{ Bq kg}^{-1}$  dry weight) and  $^{226}\text{Ra}$  activities ( $662 \pm 6 \text{ Bq kg}^{-1}$  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  $12.1 \pm 2.9$  to  $19.4 \pm 7.2 \text{ Bq kg}^{-1}$  dry weight and  $^{226}\text{Ra}$  activities from  $1.9 \pm 0.5$  to  $5.9 \pm 1.1 \text{ Bq kg}^{-1}$  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 ( $3.1 \pm 0.2 \mu\text{g L}^{-1}$ ) comparing to the samples taken in upper seawater layers ( $2.1 \pm 0.2 \mu\text{g L}^{-1}$ ). Higher concentration is in the range of the concentration level of uranium in natural seawater.

Since the transshipment 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  $55 \text{ m}^3/\text{s}$ ) than the Guduča River (average  $< 1 \text{ m}^3/\text{s}$ ). 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 (Barišić 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 transshipment 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.

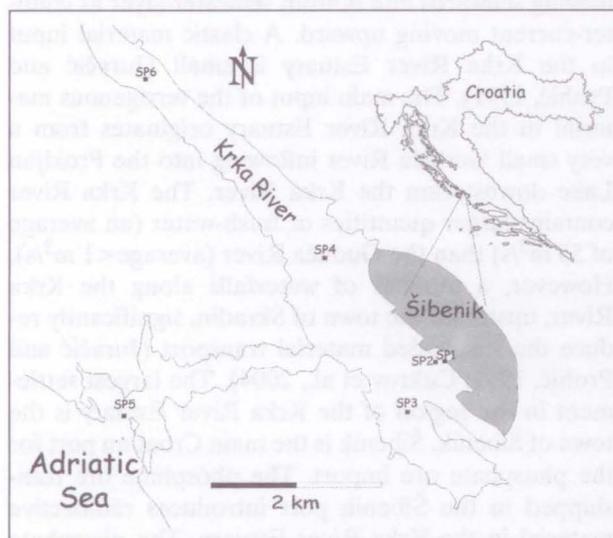


Figure 1 - Map of sampling area

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 Sklářny 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  $106^{\circ}\text{C}$  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  $106^{\circ}\text{C}$  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  $\mu\text{AUTOLAB}$  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  $0.52 \pm 0.05 \text{ mm}^2$ .

## 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 ( $9\text{--}17 \text{ Bq kg}^{-1}$ ) Adriatic coastal sediment (Barišić 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-

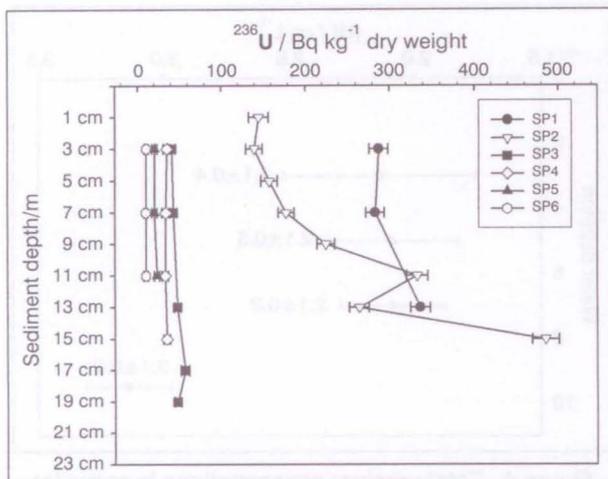


Figure 2 - Activities of  $^{238}\text{U}$  in the sediment

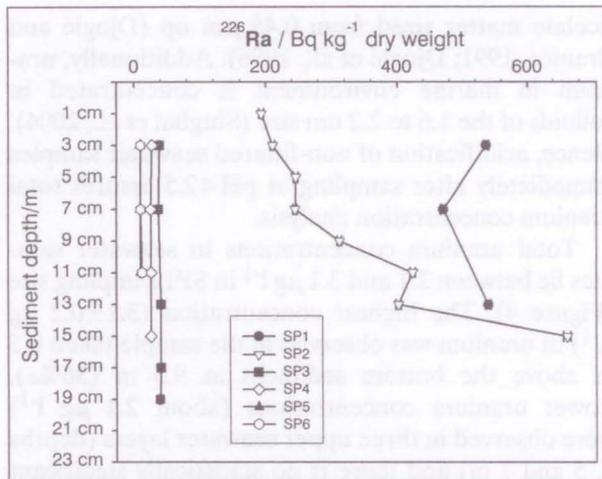


Figure 3 - Activities of  $^{226}\text{Ra}$  in the sediment

stream (SP5) are almost at the natural level. Spatial distributions of  $^{226}\text{Ra}$  activities in sediments are very similar to distribution of  $^{238}\text{U}$  activities.

In SP2 samples,  $^{238}\text{U}$  activity of  $485 \pm 16$  at deeper and  $145 \pm 10 \text{ Bq kg}^{-1}$  at surface sediment layer, probably indicate that radionuclides activity in sediment column reflects the decrease of the phosphate ore input into estuarine environment (Figure 2).  $^{238}\text{U}$  activity at this site was up to 30% lower compared to  $^{226}\text{Ra}$  activity (Figures 2, 3). The ratio  $^{238}\text{U}/^{226}\text{Ra}$  was about 0.7. Normally, the ratio is about 1 (Gonzales-Lobajo et al., 2001), but 30% of uranium were dissolved in water from sedimentation time. In SP1 sediment sample diminution of  $^{226}\text{Ra}$  and  $^{238}\text{U}$  activities is not so clear because of the repeating deepening beside the operational dock.

$^{238}\text{U}$  levels in the sediments in the Šibenik port decreased considerably following the reduction in the discharges since the eighties of the last century. However, today almost 20 years later, they still appear to be very high in comparison with the levels in the Adriatic coastal sediments (Barišić et al., 1996).

Sediments are not only a reservoir for contaminants, but also a source of toxicants for marine organisms (Long et al., 1996; Fichet et al., 1998).

The activities of the  $^{226}\text{Ra}$  and  $^{238}\text{U}$  radionuclides measured in the mussels (*Mytilus sp.*) are presented in Table 1.  $^{238}\text{U}$  activities were in the range from  $12.1 \pm 2.9$  to  $19.4 \pm 7.1 \text{ Bq kg}^{-1}$  dry weight at site SP1. These activities were six to eight times higher than in consume mussels ( $2\text{--}3 \text{ Bq kg}^{-1}$  dry weight) 5 km upstream at site SP6 and three times higher than in mussels downstream at site SP5 (Table 1). Activities of  $^{226}\text{Ra}$  do not show the same distribution because remobilisation of  $^{226}\text{Ra}$  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  $^{226}\text{Ra}$  &  $^{238}\text{U}$  in tissue of mussels (*Mytilus sp.*)

site	date	$^{226}\text{Ra}/\text{Bq kg}^{-1}$ dry weight	$^{238}\text{U}/\text{Bq kg}^{-1}$ dry weight
SP1	April 2003	$5.9 \pm 1.1$	$13.4 \pm 4.8$
	October 2003	$2.6 \pm 0.7$	$13.5 \pm 3.9$
	April 2004	$6.5 \pm 1.6$	$19.4 \pm 7.2$
	October 2004	$1.9 \pm 0.5$	$12.1 \pm 2.9$
SP5	April 2003	$3.8 \pm 0.5$	$5.3 \pm 2.4$
	October 2003	$2.4 \pm 0.7$	$5.1 \pm 3.2$
	April 2004	$3.1 \pm 1.0$	$4.6 \pm 4.3$
SP6	April 2003	$2.3 \pm 0.6$	$2.7 \pm 2.6$
	October 2003	$1.1 \pm 0.7$	$< 2.2$
	April 2004	$4.4 \pm 1.4$	$< 2.8$
	October 2004	$4.4 \pm 1.4$	$< 2.8$

$^{238}\text{U}$  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  $^{226}\text{Ra}$  and  $^{238}\text{U}$  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 (Figures 1, 3).

### 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  $0.45 \mu\text{m}$  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  $\text{pH} < 2.5$  assures total uranium concentration analysis.

Total uranium concentrations in seawater samples lie between 2.1 and  $3.1 \mu\text{g l}^{-1}$  in SP1 sampling site (Figure 4). The highest concentration ( $3.1 \pm 0.2 \mu\text{g l}^{-1}$ ) of uranium was observed in the sample taken 0.5 m above the bottom sediment at 9.5 m (36‰). Lower uranium concentrations (about  $2.1 \mu\text{g l}^{-1}$ ) 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  $3 \mu\text{g l}^{-1}$  (Veeh, 1967). The highest uranium concentration found in the sample taken near the bottom ( $3.1 \pm 0.2 \mu\text{g l}^{-1}$ ) 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 ( $3.1 \mu\text{g l}^{-1}$ ) 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:  $6.7 \pm 1.2 \mu\text{g l}^{-1}$  (Mlakar and Branica, 1989, 1994),  $5.7 \pm 1.0 \mu\text{g l}^{-1}$  and  $6.2 \pm 1.0 \mu\text{g l}^{-1}$  (Djogić et al., 2001). Moreover, seawater uranium concentrations are lower than in southern Baltic surface waters (from  $3.7 \pm 0.1$  to  $6.1 \pm 0.1 \mu\text{g l}^{-1}$ ) and in the range of Baltic bottom waters (from  $1.8 \pm 0.1$  to  $3.8 \pm 0.1 \mu\text{g l}^{-1}$ ) (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 transshipment 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 distribu-

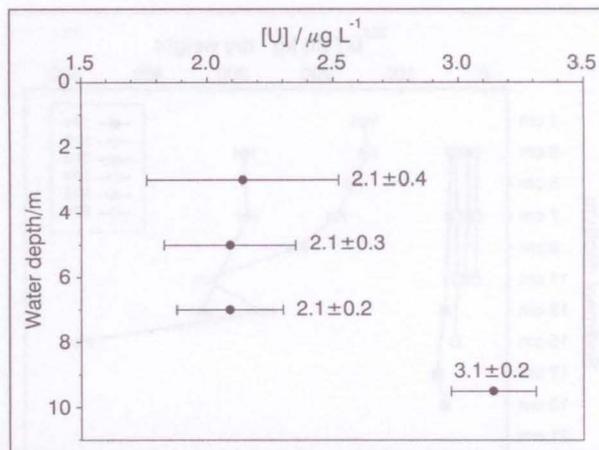


Figure 4 - Total uranium concentrations in seawater with 95% confidence intervals

tion of  $^{226}\text{Ra}$  and  $^{238}\text{U}$  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 ( $3.1 \pm 0.2 \mu\text{g l}^{-1}$ ) 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.

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## SAŽETAK

### PROSTORNA RASPODIJELA URANA I RADIJA U SEDIMENTU, ŠKOLJKAŠU (*MYTILUS SP.*) I VODI LUKE ŠIBENIK

Mjerenjem aktivnosti urana ( $^{238}\text{U}$ ) i radija ( $^{226}\text{Ra}$ ) u sedimentu i školjkašu (*Mytilus sp.*) te mjerenjem ukupne koncentracije urana u morskoj vodi istražen je utjecaj moderniziranog sustava za prekrcaj easutog tereta. Najveće aktivnosti  $^{238}\text{U}$  ( $485 \pm 16 \text{ Bq kg}^{-1}$  suhe mase) i  $^{226}\text{Ra}$  ( $662 \pm 6 \text{ Bq kg}^{-1}$  suhe mase) izmjerene su u dubljim dijelovima sedimenta uzorkovanog na postaji dvjestotinjak metara od operativne obale. Najveće vrijednosti izmjerene u uzorcima sedimenta nalaze se iznad prirodno prisutnih te ukazuju na utjecaj lučkih djelatnosti. U uzorcima školjkaša u luci izmjerene su aktivnosti urana od  $12,1 \pm 2,9$  do  $19,4 \pm 7,2 \text{ Bq kg}^{-1}$  suhe mase te aktivnosti radija od  $1,9 \pm 0,5$  do  $5,9 \pm 1,1 \text{ Bq kg}^{-1}$  suhe mase. Te aktivnosti su nešto veće od onih u konzumnim školjkašima iz obližnjih uzgajališta.

Koncentracije ukupnog urana u morskoj vodi su na razini izmjerenih u čistoj morskoj vodi ( $2,1 \pm 0,2 \mu\text{g L}^{-1}$ ). Samo je u uzorku morske vode uzetom na mjestu najbližem terminalu, neposredno iznad dna, izmjerena povišena koncentracija ukupnog urana ( $3,1 \pm 0,2 \mu\text{g L}^{-1}$ ).

Nakon što je osamdesetih godina moderniziran sustav za prekrcaj rasutih tereta šibenske luke, značajno se smanjio unos fosfatne rude u morski okoliš, a time su se smanjile i koncentracije urana u morskoj vodi. Povećane aktivnosti urana i radija nadene su samo u sedimentima u neposrednoj blizini operativne obale, te u školjkašima koji rastu na toj samoj obali.

## KLJUČNE RIJEČI

uran, radij, sediment, morska voda, školjkaš *Mytilus sp.*, Estuarij rijeke Krke, fosfati

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