

# Spatial Distribution of $^{40}\text{K}$ and $^{232}\text{Th}$ in Recent Sediments of the Krka River Estuary\*

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Spatial radionuclides distribution was studied in recent estuarine sediments in the Krka River Estuary. Sediment samples were analyzed for  $^{40}\text{K}$  and  $^{232}\text{Th}$  by gamma-spectrometry. Activities of  $^{40}\text{K}$  were found in the range of 18–457 Bq kg<sup>-1</sup> and activities of  $^{232}\text{Th}$  in range of 1.9–29.4 Bq kg<sup>-1</sup>. Distribution of  $^{232}\text{Th}$  activities follows that of  $^{40}\text{K}$ , with correlation coefficients higher than 0.97 in all analyzed samples from the Krka River estuary. Spatial distribution of natural radionuclides ( $^{40}\text{K}$  and  $^{232}\text{Th}$ ) in recent estuarine and marine sedimentation area can be a useful tool for recognizing the possible input of terrigenous material, as well as for fast locating of the area where such material is predominantly settled.

## INTRODUCTION

River Krka is located in the central part of the north-east coast of the Adriatic Sea and drains mostly carbonate terrains of karst regions of Croatia. Its estuary was formed during the Holocene transgression. Stretching from the Skradinski Buk waterfalls (calc-tufa barrier, height 46 m) through the Prokljan Lake to the St. Ante Channel, the estuary has a total length of 22 km. The hydrogeologic drainage area of the Krka River is approximately 2427 km<sup>2</sup>. The estuary bottom gradually deepens from 2 m, below the waterfalls, to 42 m in front of Fort Sv. Nikola. It is a typical example of a stratified estuary with a fresh-brackish surface layer moving seawards and a bottom seawater layer, as counter-current, moving upward. Clastic material input in the Krka River estuary is small.<sup>2</sup> The main input of terrigenous material in the Krka River estuary originates from the very small Guduča River inflow-

ing into the Prokljan Lake downstream the Krka River. The Krka River carries larger quantities of fresh-water (on average 55 m<sup>3</sup>/s) than the Guduča River (on average less than 1 m<sup>3</sup>/s). However, a number of calc tufa barriers along the Krka River, upstream of the town of Skradin, significantly reduce suspended material transport.<sup>1,2,3</sup> The largest settlement in the Krka estuary region is Šibenik, located in the lower part of the estuary. Sedimentation rate in the estuary was found to be very low, less than 0.5 mm in the Prokljan Lake.<sup>1</sup>

Contents of naturally occurring radionuclides in different types of the recent Adriatic Sea sediments have not been systematically studied. However, some data on the activities of radionuclides in sediment were published elsewhere.<sup>3,4,5</sup> This work gives a contribution to the knowledge of spatial radionuclide distribution in the Krka River Estuary.

\* Dedicated to the memory of the late Professor Marko Branica.

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## EXPERIMENTAL

### Sampling Sites and Procedures

Sediment samples were collected during 2003 and 2004 by a scuba diver using hand-driven Plexiglas corers ( $\phi = 175$  mm). Starting points of the investigation area were the Skradinski Buk waterfalls (KE-1) and Fort Sv. Nikola (KE-17) was the end point. Additionally, sampling was performed at two locations: the first in the Adriatic Sea near the island of Zlarin (Z-1) and the second in the Prokljan Lake (KE-18) near the small Guduča River mouth (Figure 1).

Sampling positions were located by GPS, model Garmin GPSMap 72 (Kansas City, USA) with accuracy of  $\pm 5$  m. At most locations, the first 15 cm of the bottom sediment were sampled, but at some locations (KE-1, KE-2, KE-4, NPK-1 and Z-1) only the first 5 cm were taken. After sampling, sediment colons were separated in 3 parts (0–5 cm, 5–10 cm, 10–15 cm) and frozen at  $-18$  °C until analysis.

### Equipment and Experimental Procedure

Prior to gamma-spectrometry measurements, sediment samples were thawed at room temperature and dried at  $106$  °C for 24 hours until constant weight. Dried samples were placed into counting vessels of known geometry, sealed and stored for at least 4 weeks to allow ingrowth of gaseous  $^{222}\text{Rn}$  (3.8 day half-life) and its short-lived decay products to equilibrate with long-lived  $^{226}\text{Ra}$  precursor in the sample. At the end of the ingrowth period, the samples were counted on a multichannel gamma spectrometer (HPGe detector joined to a 8192 channel analyzer Canberra, Meriden, USA). The

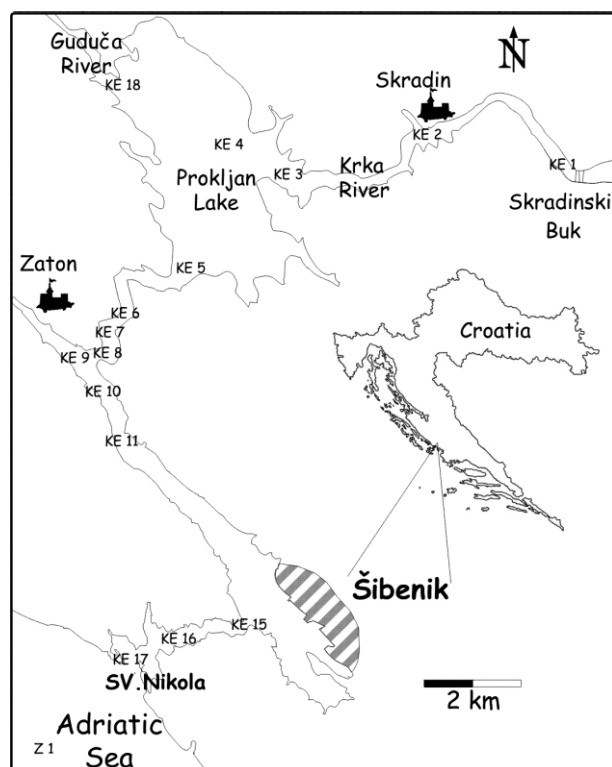


Figure 1. Map of the sampling area.

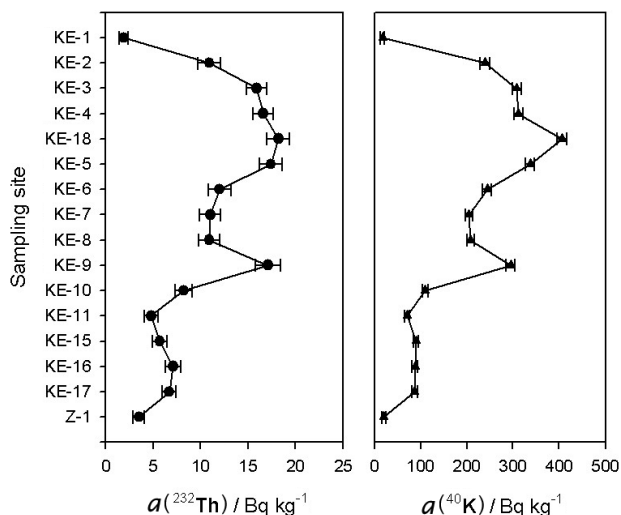


Figure 2. Plots of spatial distribution of  $^{40}\text{K}$  and  $^{232}\text{Th}$  activities expressed in  $\text{Bq/kg}$  dry weight.

system was calibrated using standards supplied by Amersham International (Buckinghamshire, UK) and International Atomic Energy Agency reference materials (marine and stream sediments IAEA-306, IAEA-313 and IAEA-314). Counting time was 80,000 seconds and the recorded spectra were analyzed on a PC using the Canberra GENIE 2K software. Activities of  $^{40}\text{K}$  were calculated from the 1460.75 keV-peak while  $^{228}\text{Ra}$  activities were determined from the 911.1 keV-peak of its  $^{228}\text{Ac}$  progeny. Because of the relatively short half-life of  $^{228}\text{Ra}$  ( $t_{1/2} = 5.75$  years) and thorium conservative behavior, numerous authors equalize measured  $^{228}\text{Ra}$  activities with  $^{232}\text{Th}$  activities in natural samples,<sup>6,7,8</sup> even in cases of possible radium migration in extreme conditions.<sup>9</sup> The  $309.3 \text{ Bq kg}^{-1}$  of  $^{40}\text{K}$  activity corresponds to 1 % total potassium while  $4.06 \text{ Bq kg}^{-1}$  of the  $^{232}\text{Th}$  activities corresponds to a concentration of 1 mg/kg of thorium in the ground.<sup>10</sup>

## RESULTS

Sediments with the highest  $^{40}\text{K}$  activity ( $457.1 \pm 10.4 \text{ Bq kg}^{-1}$ ) were found in the Prokljan Lake in front of the small Guduča River mouth (KE-18) in the sediment layer between 10 and 15 cm depth, while the lowest activities ( $18.0 \pm 4.4 \text{ Bq kg}^{-1}$ ) were found close to the Skradinski Buk waterfalls (KE-1) and ( $20.5 \pm 4.3 \text{ Bq kg}^{-1}$ ) near the island of Zlarin (Z-1) in the sediment layer between the surface and 5 cm depth (Figure 2).

At the same locations (KE-1 and Z-1), the highest ( $29.4 \pm 1.4 \text{ Bq kg}^{-1}$ ) and the lowest ( $1.9 \pm 0.5$  and  $3.5 \pm 0.6 \text{ Bq kg}^{-1}$ )  $^{232}\text{Th}$  activities were also recorded (Figure 2).

In all sediment layers (0–5 cm, 5–10 cm and 10–15 cm), an increasing trend of  $^{40}\text{K}$  and  $^{232}\text{Th}$  activities was found, rising from the open sea to the Prokljan Lake entrance (KE-5). Only one exception was found at sampling site KE-9, close to the Zaton village (Figure 1). From the

KE-5 sampling site (Figure 1), the opposite trend of  $^{40}\text{K}$  and  $^{232}\text{Th}$  activities in sediments was recorded towards the Skradinski Buk waterfalls (KE-4, KE-3, KE-2 and KE-1), and a continuous increase towards the Guduča River mouth (KE-18) where sediments contain the highest  $^{40}\text{K}$  and  $^{232}\text{Th}$  activities (Figure 2).

At sampling sites KE-7, KE-8, KE-9, KE-10 and KE-18, concentrations of  $^{232}\text{Th}$  and  $^{40}\text{K}$  slightly increased from the sediment surface to deeper layers (Figure 2). Such behavior is most significant in samples of layers between 0–5 cm and 5–10 cm.

In all the sampled sediment layers (0–5 cm, 5–10 cm and 10–15 cm) the correlation coefficient of the spatial distribution of  $^{40}\text{K}$  activities with those of  $^{232}\text{Th}$ , was higher than 0.97, indicating very good correlation between  $^{40}\text{K}$  and  $^{232}\text{Th}$  concentrations (Figure 2). Correlation was calculated using the »CORREL« function in Microsoft Excel 2003 between all  $^{40}\text{K}$  and all  $^{232}\text{Th}$  data.

## DISCUSSION

The present work was aimed at stimulating research on natural radionuclides in recent stream, estuarine and marine sedimentation areas as a possible sediment source indicator in recent sediment accumulation.

The Krka River estuary functions as a big pump – fresh water flows on the surface towards the open sea establishing an opposite deep flow of salt water upstream in the estuary. Such circulation makes marine carbonate sedimentation influence the sediment composition even many kilometers inward the estuary.

Low activities of  $^{40}\text{K}$  ( $20.5 \pm 4.3 \text{ Bq kg}^{-1}$ ) and of  $^{232}\text{Th}$  ( $3.5 \pm 0.6 \text{ Bq kg}^{-1}$ ) at Z-1 probably correspond to the characteristic values<sup>4,5</sup> of the sand and silts spread along the Croatian coast representing the marine carbonate sedimentation. At KE-10 and KE-11 sampling points, the marine carbonate sedimentation influence still dominates. On the other hand, low activities of  $^{40}\text{K}$  ( $18.0 \pm 4.4 \text{ Bq kg}^{-1}$ ) and  $^{232}\text{Th}$  ( $1.9 \pm 0.5 \text{ Bq kg}^{-1}$ ) at KE-1 most likely correspond to tufa 11 with  $^{40}\text{K}$  activity of  $12 \text{ Bq kg}^{-1}$  and  $^{232}\text{Th}$  of  $2.5 \text{ Bq kg}^{-1}$  originating from the Krka River input.

Increased activities of  $^{40}\text{K}$  and  $^{232}\text{Th}$  are found in profiles from the Skradinski Buk waterfalls towards Prokljan Lake, reflecting the relative decreasing contribution of tufa material. However, the highest activities were found at the KE-18 sampling point, predominantly under the Guduča River material transportation influence. The Guduča River drainage area consists mainly of the Eocene flysch material, so high concentrations of potassium and moderate concentrations of thorium in sediments are expected. Hence, the spatial distribution of  $^{40}\text{K}$  and  $^{232}\text{Th}$  activities in Prokljan Lake recent sediments additionally confirms that the main input of terrigenous material to the Krka River estuary originates from the small Guduča

River, flowing into the Prokljan Lake downstream the Krka River. It seems that most of the terrigenous material is quickly sedimented in the Prokljan Lake in the vicinity of the Guduča River mouth (Figure 1).

At the KE-5 sampling point, recent sediment contains a higher portion of terrigenous material, also eroded from the Eocene flysch terrains. It seems that even at this point the influence of the Guduča River input significantly prevails over the Krka River input and/or marine carbonate sedimentation. Here, fresh water mostly transports material from the inland canyon configuration (Figure 1) and interrupts the water pump that could otherwise transport recent marine carbonate sediment into that area upstream the estuary. At the KE-9 sampling point, similar local influence of terrigenous material (eroded from Eocene flysch terrains lying west of the Zaton village) was observed as well. However, carbonate marine sedimentation, with minor terrigenous influence, generally prevails in the downstream direction.

In deeper sediment layers (5–10 cm, 10–15 cm), the distribution of  $^{40}\text{K}$  and  $^{232}\text{Th}$  activities was somewhat different than in the surface layer. This probably indicates a different sedimentation regime in the recent past.

## CONCLUSIONS

The distribution of  $^{232}\text{Th}$  activities follows that of  $^{40}\text{K}$ , and their correlation coefficient is higher than 0.97 in all the analyzed samples from the Krka River estuary. On the basis of the prevailing origin of accumulated material, four main sedimentation areas are recognized: (i) from the open sea to the KE-10 sampling point where carbonate marine sedimentation prevails; (ii) from the KE-10 to the KE-6 sampling point where settled material is a mixture of two main origins: marine carbonates and terrigenous flysch material transported by the Guduča River; (iii) upstream of KE-3 where most of the settled material is carried by the Krka River, and (iv) the Prokljan Lake (including the bay of Zaton situated to the west of KE-9) where recent sediment consists mainly of terrigenous flysch material transported by the Guduča River (and occasional local creek in the case of the Zaton bay). It seems that the spatial distribution of natural radionuclides in recent sedimentation areas is under significant influence of terrigenous material input, and could be a useful tool for recognizing the possible sources of material as well as for better locating of the areas where that material is predominantly deposited.

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## SAŽETAK

### Prostorna raspodjela $^{40}\text{K}$ i $^{232}\text{Th}$ u recentnim sedimentima estuarija rijeke Krke

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U radu je proučavana prostorna raspodjela radionuklida u recentnim sedimentima estuarija rijeke Krke. Uzorci sedimenta analizirani su tijekom protekle dvije godine i aktivnost  $^{40}\text{K}$  i  $^{232}\text{Th}$  određena je gamaspektrometrijski. Izmjerene aktivnosti za  $^{40}\text{K}$  bile su između 18–457 Bq kg<sup>-1</sup>, a za  $^{232}\text{Th}$  između 1.9–29.4 Bq kg<sup>-1</sup>. Raspodjela aktivnosti  $^{232}\text{Th}$  prati raspodjelu aktivnosti  $^{40}\text{K}$ , i njihov korelacijski faktor viši je od 0,97 u svim analiziranim uzorcima. Prostorna raspodjela prirodnih radionuklida ( $^{40}\text{K}$  i  $^{232}\text{Th}$ ) u recentnim estuarijskim i morskim sedimentima pod značajnim je utjecajem unosa terigenog materijala i može biti koristan ključ za prepoznavanje mogućeg izvora materijala kao i boljeg određivanja mjesta najvećeg taloženja tog materijala.