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Uranium in sediments, mussels (*Mytilus* sp.) and seawater of the Krka river estuary

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Abstract

The response of an aquatic environment to the decrease of phosphate discharges from a technologically improved transhipment terminal, situated at the Croatian Adriatic coast in the port of Šibenik, has been assessed based on uranium activity and concentration in sediment, seawater and mussels *Mytilus* sp. The highest ^{238}U activities (485 ± 16 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 clearly indicate the harbour activities' influence. The ^{238}U/^{226}Ra activity ratios in sediment samples demonstrate the decreasing trend of phosphate ore input. Mussel samples showed levels of ^{238}U activities in the range from 12.1 ± 2.9 to 19.4 ± 7.2 Bq kg^{-1} dry weight, thus being slightly higher than in normally consumed mussels. Only the seawater, taken just above the bottom sediment at the sampling site closest to the terminal, shows a slightly higher uranium concentration (3.1 ± 0.2 μg L^{-1}) when compared to the samples taken in upper seawater layers (2.1 ± 0.2 μg L^{-1}) but is in the range of the concentration level of uranium in natural seawater. Since the transhipment terminal in the port of Šibenik was modernised in 1988, discharge of phosphate ore into the seawater was drastically reduced and, consequently,

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uranium concentration levels in seawater have decreased. However, enhanced uranium activity levels are still found in deeper sediment layer samples and in mussel.

Keywords: Uranium; ^{238}U; ^{226}Ra; Activity ratio; Sediment; Seawater; Mussels *Mytilus* sp.; Krka river estuary; Gamma-spectrometry; Linear scan voltammetry

1. Introduction

Uranium is an environmentally universal element present in two radioactive decay series, i.e. ^{235}U and ^{238}U. Most crystal rocks contain a few parts per million of uranium, with an average of 2.8 ppm. Phosphate, igneous rock and granite rocks generally contain a higher amount of uranium, while lower concentrations are found in sedimentary rocks such as limestone. Due to weathering and subsequent transport, these rocks were carried away by rivers, which are the major source of dissolved uranium to the oceans (Goldberg et al., 1971).

The Krka river is situated in the coastal karstic region of Croatia and flows from there into the Adriatic Sea. The estuary was formed during the Holocene transgression. Located between the Skradinski Buk waterfalls (calc-tufa barrier) through the Prokljan Lake to the St. Ante Channel, the estuary has a 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 upwards. A clastic material input in the Krka river estuary is small (Juračić and Prohić, 1991). Main input of the terrigenous material in the Krka river estuary originates from a very small Guduča river flowing into the Prokljan Lake downstream the Krka river. The Krka river has a higher turnover rate 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 of the town of Skradin, significantly reduce suspended material transport (Cukrov et al., 2004).

Šibenik is the main Croatian port for the phosphate ore import introducing radioactive material into the Krka river estuary. Phosphate materials used for the production of phosphate fertilizers contain elevated radioactivity resulting mainly from the disintegration products of the ^{238}U series (Barišić et al., 1992). Shipments of the phosphate ores in the Šibenik port started about in 1966 (Port of Šibenik, 2001). Most frequent traffic was in 1988 (740 000 tons), with a break from 1992 to 1995. In 2003 phosphates traffic was about 300 000 tons. In 1988 a modern transhipment terminal for bulk cargo in the port of Šibenik was constructed in a way that the phosphate material input into the sea became negligible.

The naturally occurring uranium (4+) in rocks and minerals is released to fresh water and seawater (6+) during chemical weathering (under oxidizing conditions) and tends to be more mobile as uranyl ion (UO_2^{2+}). Predominant uranium (VI) species form a soluble uranyl-tricarbonato complex $UO_2(CO_3)_3^{4-}$ in seawater (Djogić et al., 1986) and uranyl-dicarbonato-hydrogenperoxo complex $UO_2(CO_3)_2(HO_2)^{3-}$ in the marine photic zone (Djogić and Branica, 1991). The average concentration of