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Activity concentrations and distribution of radionuclides in surface and core sediments of the Neretva Channel (Adriatic Sea, Croatia)

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ABSTRACT

The activity concentrations and the distribution of manmade ^{137}Cs and naturally occurring radionuclides ^{40}K, ^{238}U and ^{232}Th in surface and core sediments of the semi-enclosed, river-dominated marine environment of the Neretva Channel were investigated in relation to the sedimentological characteristics and the total organic carbon (TOC) content. The activity concentrations of radionuclides were determined by gamma spectrometry. Distinct interrelationships between sediment properties and the spatial distribution of radionuclides were observed. The highest accumulation of ^{137}Cs occurs close to the river mouth, in the region of intensive deposition of organic matter of terrestrial origin. This discovery implies that the river-borne organic material and its deposition processes should be considered as the most important factor controlling distribution of ^{137}Cs in this transitional terrestrial-marine environment. Sediment accumulation rates, estimated from the distribution of ^{137}Cs in core sediments, were approximately 6 mm y^{-1} in front of the Neretva River mouth and 4 mm y^{-1} in the channel area. The spatial distribution of natural ^{40}K and ^{232}Th radionuclides indicates their distinct association with fine-grained sediments. The interrelationship of ^{238}U with fine-grained particles was somewhat weaker but still present. The results obtained indicate that the accumulation pattern of natural radionuclides in the Neretva Channel sediments is mainly governed by the deposition of fine-grained material. This study scrutinizes the baseline level for the occurring radionuclides and should be used for monitoring and assessing the radionuclide pollution record in the investigated transitional terrestrial-marine environment of the Adriatic.

Keywords: radiomiclides, sedimentation rate, total organic carbon, fine-grained sediments, Neretva Channel

1. INTRODUCTION

Environmental radioactivity has become a subject of scientific interest in recent decades, not only due to possible risks to human health, but also because radionuclides have been recognized as tracers of many complex biogeochemical processes (PORCELLI & BASKARAN, 2011). Sediment erosion and accumulation rates or transport of elements to the oceans are only a few examples of processes where radionuclide monitoring has been applied.

The mobility of radionuclides in aquatic environments is governed by their geochemical characteristics, such as solubility, complexation ability and affinity for adsorption onto mineral surfaces (CHABAUX et al., 2003). Natural radionuclides, such as ^{238}U, ^{232}Th and ^{40}K, are released into the environment through erosion and chemical weathering of the radionuclide-bearing rocks, and are subsequently transported through surface and ground water systems (VIGIER et al., 2001). The fate of radionuclides in transitional terrestrial-marine and marine environments is mostly influenced by their interaction with clay minerals, organic matter and colloidal iron and manganese oxides and hydroxides (ANDERSSON et al., 2001; McKEE, 2008). River-dominated coastal areas of the Adriatic region are characterized by complex physico-chemical interactions and transformations of dissolved and particulate organic and inorganic compounds (SONDI et al., 1994; SONDI et al., 1995; SONDI et al., 2008). In such environments, the transport and deposition of radionuclides is governed by dispersal processes affecting fine-grained sediments, direct precipitation of oxides and oxyhydroxides and coagulation of inorganic and organic colloidal materials (ANDERSSON et al., 1998; LIGERO et al., 2001).

There are several anthropogenic sources of radionuclides whose contribution to overall environmental radioactivity cannot be neglected. Major sources of radioactive contamination include the nuclear weapons program, nuclear power plants, uranium mining and milling, commercial fuel processing and nuclear accidents (HU et al., 2010). The anthropogenic release of radionuclides into the environment includes both natural and manmade isotopes, such as ^{137}Cs. Once introduced into the environment, these radionuclides are affected by the same processes as other components of the natural systems. However, due to their known source, they often provide a recognisable imprint in the environment which facilitates the identification of processes and changes occurring in natural ecosystems.

In that context, the natural radionuclide ^{40}K and manmade ^{137}Cs were used as tracers of sediment transport and sedimentation dynamics in a river-dominated karstic estuary in the north-eastern Adriatic (SONDI et al., 1995). It was shown that the highest activity concentrations of these radionuclides occur at the river mouth in accordance with the prevalent sedimentation of clayey particles associated with terrestrial organic matter. PETRINEC et al. (2012A) investigated the activity concentrations of manmade ^{137}Cs and natural radionuclides ^{40}K, ^{226}Ra, ^{228}Ra and ^{238}U in seawater and sediments at several locations along the eastern Adriatic coast – from Piran Bay to the Otranto Strait. They discovered significant correlations between the activity concentrations of ^{40}K, ^{228}Ra and ^{238}U and sedimentological characteristics, suggesting that variability in radionuclide activity concentrations can be explained by differences in the mineral composition of the sediments. Distribution of ^{137}Cs activity concentration in core sediments was used to estimate sediment accumulation rates at several locations in the middle and south Adriatic Sea. A sedimentation rate of ~ 1.8 mm y^{-1} was reported for deposits from the South Adriatic Pit, while Albanian offshore shelf sediments had a much higher accumulation rate of ~ 4 mm y^{-1} (PETRINEC et al., 2012B). Sediment accumulation rates of approximately 1 to 5 mm y^{-1} were also reported at different locations in the Krka River estuary (CUKROV et al., 2007). In addition, CUKROV et al. (2009) illustrated that diverse natural sources of sediments can only partially explain the variations in activity concentrations of ^{238}U and ^{226}Ra, and that significant anthropogenic input of radionuclides can be observed in the area close to the town of Šibenik.

This paper reports on a study of the activity concentrations of ^{137}Cs, ^{40}K, ^{238}U and ^{232}Th radionuclides in the sediments of the Neretva Channel. In particular, it reports on the accumulation patterns of these radionuclides in surface and subsurface sediments and the sediment accumulation rates based on vertical distributions of the ^{137}Cs activity concentration. Finally, it addresses the geochemical behaviour of the investigated radionuclides through their association with organic and inorganic compounds in a semi-enclosed and river-dominated coastal environment of the Adriatic region.

2. STUDY AREA

The Neretva Channel is an isolated, narrow part of the Adriatic Sea, semi-enclosed by the Pelješac peninsula on the southern side. The surrounding area is mainly karstic terrain, consisting of Jurassic and Cretaceous limestones and dolomites with some occurrences of Triassic limestones, Eocene limestones and flysch (Fig. 1). The channel itself is a microtidal, low-wave energy environment characterised by river-dominated sedimentation processes (JURINA et al., 2010).

The Neretva River enters the channel on its northern side; it is the largest river on the Croatian part of the eastern Adriatic coast, and the only one forming a deltaic system. The river is approximately 255 km long with a catchment area of about 13000 km^2. In the upland part of the river basin, the river drains a heterogeneous terrain characterised by several geological units: Triassic and Miocene clastic sedimentary rocks, Triassic volcanic rocks and volcano-sedimentary series, a Mesozoic carbonate succession, and Cretaceous flysch (MOJIĆEVIĆ & LAUŠEVIĆ, 1973a; MOJIĆEVIĆ & LAUŠEVIĆ, 1973b; SOFILJ & ŽIVANOVIĆ, 1980; MOJIĆEVIĆ & TOMIĆ, 1982). Most of the sediment load carried by the river originates from the flysch and clastic deposits exposed at the surface in this area. The estimated annual sediment discharge in 2000 was 13.58 x 10^6 tons (EUROSION, 2004). The lowland part of the Neretva River is only 36 km long and flows through Quaternary alluvial deposits. Average annual water discharge is 332 m^{3}s^{-1} with peaks in December and April (ORLIĆ et al., 2006).

3. METHODS

3.1. Sampling and sampling preparation

The field surveys in the Neretva Channel were conducted in October 2009 and June 2010. Three undisturbed sediment

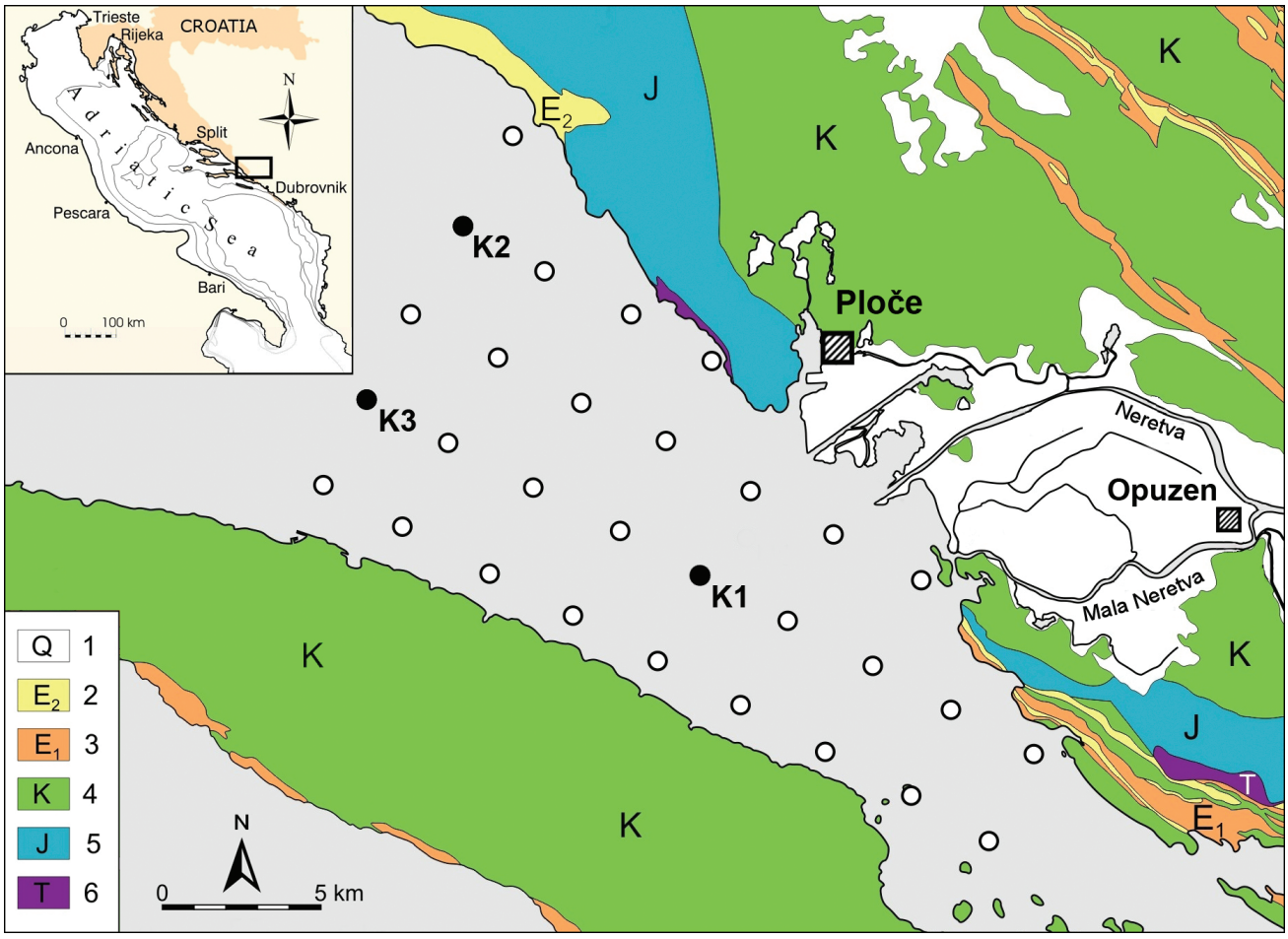

Figure 1: Geological map of the Neretva Channel showing the study area and sampling stations. Legend: 1– Quaternary alluvial deposits; 2 – Eocene flysch; 3 – Eocene limestones; 4 – Cretaceous limestones and dolomites; 5 – Jurassic limestones and dolomites 6 – Triassic limestones.

cores up to 35 cm long were retrieved at stations K1–K3 (Fig. 1). At an additional 28 stations (marked as dotted grid in Fig. 1) only the uppermost 5 cm of core sediments (surface sediments) were collected. All sediment samples were retrieved using a gravity corer (Uwitec, Austria), were frozen immediately after sampling and kept at –20°C. Prior to analysis, frozen sediment cores from stations K1–K3 were cut into 5 cm segments, after which the sediments were freeze dried (FreeZone 2.5, Labconco, USA) and homogenized.

3.2. Analyses

Sediment samples were granulometrically characterized by the laser diffraction particle size analyzer (LS 13 320, Beckman Coulter, USA). One gram of dry sample was suspended in 50 ml of redistilled water and placed in an ultrasound bath for 3 minutes. Approximately 5 to 10 ml of the suspension obtained was placed in a dispersion unit cell and analysed. No surfactants were used. Particle size was calculated on a volume basis using the Mie theory. Samples were measured in triplicate and the average particle size distribution spectra were taken as results. The clay-silt-sand ratios of the sediments were determined according to the modified WENTHWORTH scale (1922) with the clay-silt boundary at 2 μm.

The total organic carbon (TOC) content of the sediments was determined by combustion of acid insoluble matter in a Leco IR–212 carbon analyser (USA), after treatment with hot 1:1 diluted 36.5% HCl.

Gamma-spectrometry measurements were conducted using a low-background hyperpure germanium (HPGe) "Canberra" semiconductor detector system coupled to an 8196-channel analyzer (Meriden, USA). Prior to measurement, sediment samples were oven dried at 105° to constant weight. The expanded uncertainty of measurements are stated as the standard uncertainty of measurement multiplied by the coverage factor k = 2, which for a normal distribution corresponds to a coverage probability of 95%.

3.3. Calculation

Pearson correlation coefficients were calculated using Statistica for Windows Ver. 7.0 (StatSoft Inc., USA). Contour maps were constructed using SURFER 8 (Golden Software, USA) with kriging as an interpolation method.

4. RESULTS AND DISCUSSION

4.1. Granulometric and mineralogical characteristics of sediments

Considering the ratio of different grain size fractions (SHEPARD, 1954), surface sediments from the Neretva Channel were classified as clayey silts (Fig. 2). The significant amount of sand fraction (64 %) was only observed in the sample collected in the vicinity of the small islet located in the southern part of the investigated area (Fig. 1). There were no significant changes in granulometric characteristics in the core sediment samples. The spatial distribution of the fine-grained particles, i.e. mud (< 63 μm), in the surface sediments is presented in Figure 3. It is important to note that the predominant accumulation of fine-grained particles occurs in north-western part of the investigated area, toward the exit from the Neretva Channel. Such an accumulation pattern is in accordance with the observed water circulation, where a hypopycnal river plume formed at the mouth distributing fine-grained particles over the channel area and toward the open sea. The mineral composition of all the investigated surface sediments was similar. Samples were mainly composed of calcite, quartz, feldspars, dolomite and a significant amount of clay minerals, particularly illite (JURINA et al., 2010).

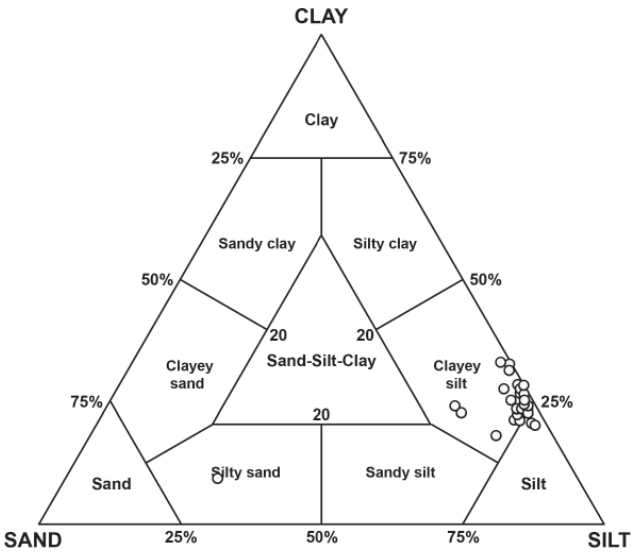

Figure 2: Ternary diagram for the classification of sediments (SHEPARD, 1954) with samples from the study area denoted on the basis of the obtained sand/silt/clay ratios.

4.2. Distribution of radionuclides in surface sediments

The results of the present study provide a good example of the distribution of radionuclides in a semi-enclosed fluvio-marine environment of the Adriatic region. The two dominant processes identified as the most important factors governing the deposition of radionuclides in surface sediments of the Neretva Channel, were the sedimentation of fine-grained material and deposition of the river-borne terrestrial organic matter.

The distribution of ^{137}Cs in surface sediments of the Neretva Channel is shown in Figure 3. The activity concentrations varied from 3.7 ± 1.1 to 13.7 ± 2.1 Bq kg^{-1}. The highest values were found close to the river mouth and decreased seaward. A similar distribution pattern was observed for TOC, with values ranging from 0.29 to 0.98 % and the highest values being determined in the area close to the Neretva River inlet (Fig. 3). This suggests a close association of ^{137}Cs with sedimentary organic matter. The obvious unknown is the mechanism governing the depositional pattern of the TOC and how this process influences the distribution of ^{137}Cs in the surface sediments of the Neretva Channel. We may speculate that the coagulation and deposition of terrestrial dissolved and particulate organic matter in the freshwater-seawater mixing zone results in scavenging of this radionuclide from the water column and its fixation in the seabed sediments. The importance of organic matter for ^{137}Cs accumulation in marine sediments was previously reported by RUBIO et al. (2003) and LIGERO et al. (2001). Correlation between the ^{137}Cs activity concentrations and the TOC content ($r = 0.45$, $p < 0.05$) in the Neretva Channel sediments is in agreement with those observations. River-borne organic material is mainly composed of humic and fulvic acids which are shown to coagulate even at low salinities (SONDI et al., 1996; SONDI et al., 1997; SONDI et al., 1998). Consequently, pronounced deposition of terrestrial organic matter occurs in mixing zones, close to the river mouth, as observed in the Neretva Channel sediments. The TOC content decreases seaward indicating the reduced fluvial influence and probably more pronounced accumulation of marine organic matter in the sediments. The activity concentrations of ^{137}Cs in the surface sediments of the Neretva Channel were found to be higher than those in sediments from the southern Adriatic region (0.8 – 3.8 Bq kg^{-1}, PETRINEC et al., 2012A). This can be attributed to the considerable load of ^{137}Cs in the Neretva River discharge processes. Previous measurements of the ^{137}Cs activity concentrations in the Raša River estuary also revealed a high accumulation at the river mouth, indicating that fluvial discharge should be considered as the main source of ^{137}Cs in the coastal environment of the Adriatic region (SONDI et al., 1995).

The lowest measured activity concentrations of ^{40}K and ^{232}Th were 350.3 ± 44.1 Bq kg^{-1} and 19.8 ± 5.0 Bq kg^{-1}, respectively. The spatial distribution of these two radionuclides displayed a similar accumulation trend. In addition, a strong positive correlation ($r = 0.76$, $p < 0.001$) occurs between these two radionuclides, indicating their close association. High activity concentrations, up to 647.6 ± 74.6 Bq kg^{-1} for ^{40}K and 34.2 ± 6.3 Bq kg^{-1} for ^{232}Th, were observed in surface sediments containing a high percentage of fine-grained particles (Fig. 3). The correlation coefficients between ^{40}K and ^{232}Th activity concentrations and mud content in surface sediments of the Neretva Channel are 0.41 ($p < 0.05$) and 0.48 ($p < 0.01$), respectively, suggesting the important role of fine-grained particles in the transport and deposition of

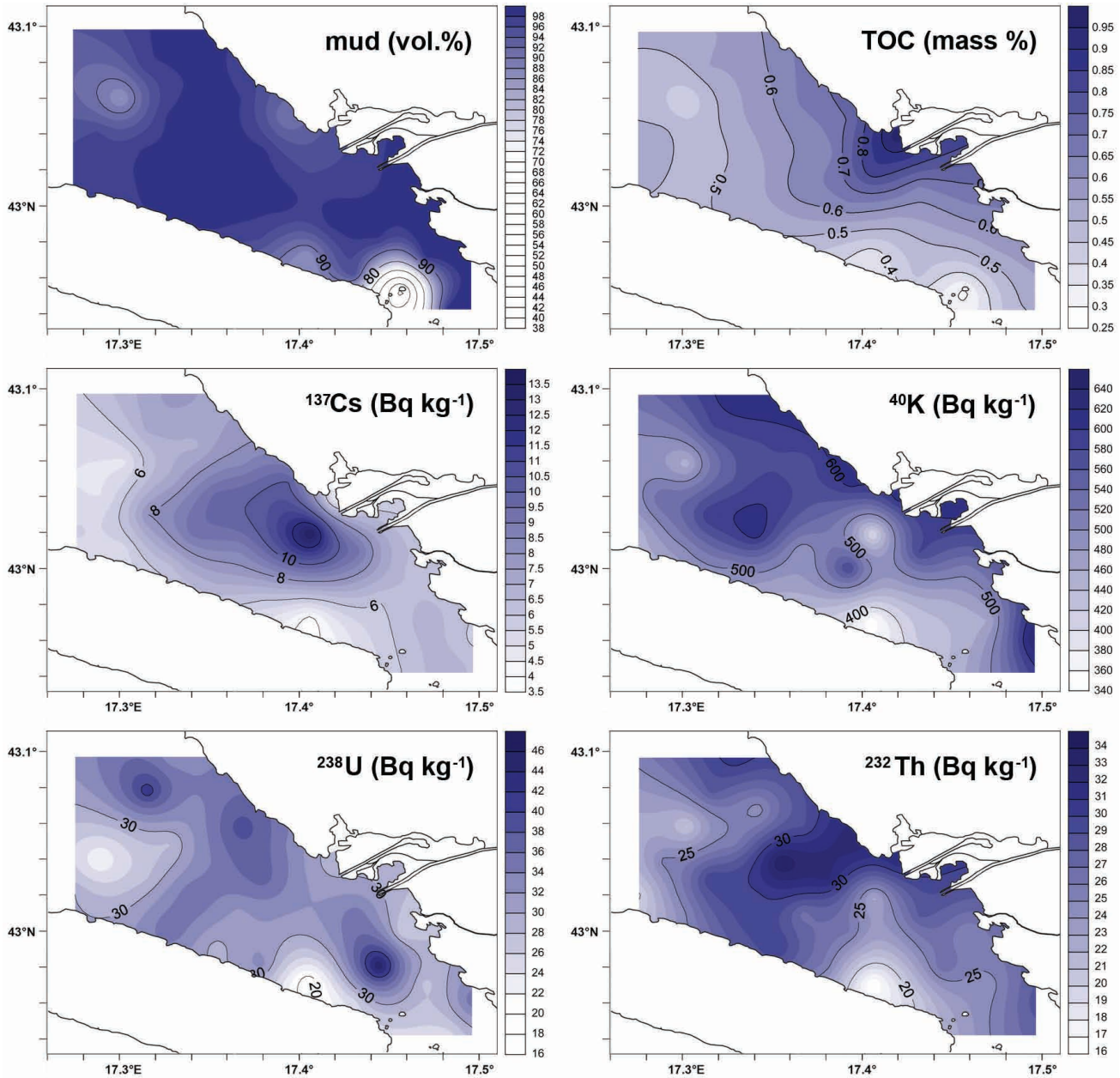

Figure 3. Distributions of mud and TOC content and ^{137}Cs, ^{40}K, ^{238}U and ^{232}Th activity concentrations in the surface sediments of the Neretva Channel.

^{232}Th and ^{40}K in the sediments of the Neretva Channel. Regarding the ^{40}K behaviour, this radionuclide is very soluble and easily incorporated into the clay mineral crystal lattice, particularly in the interlayer sites of an illite-type structure. Thorium isotopes are considered insoluble in cation form (Th^{4+}) but can be mobilised through complexation with organic and inorganic ligands (LANGMUIR & HERMAN, 1980). After entering the surface waters, Th is easily adsorbed onto mineral surfaces, particularly Fe oxyhydroxides (ANDERSSON et al., 1995). Accordingly, the close association of ^{232}Th and ^{40}K in the surface sediments of the Neretva Channel could be a consequence of their mutual inorganic carriers. The transport of both radionuclides is governed by their binding to the clay mineral surfaces and/or co-precipitated Fe oxide and oxyhydroxide coatings. Therefore, the accumulation of these radionuclides in the Neretva Channel area is governed by fine-grained sediment deposition processes.

The activity concentrations of ^{238}U in surface sediments from the Neretva Channel varied from 17.5 ± 9.8 to 46.1 ± 14.2 Bq kg^{-1}. Association of this radionuclide with sedimentary organic matter in the Neretva Channel sediments was not observed, although many studies report organic phases as being important carriers of ^{238}U in river and brackish waters (ANDERSSON et al., 1998). Correlation between ^{238}U and ^{232}Th activity concentrations ($r = 0.51$, $p < 0.01$) suggests that the distribution of these radionuclides in the Neretva Channel sediments is at least partially governed by the same processes. Indeed, an increase of ^{238}U activity concentrations was observed in the area characterized by the accu-

mulation of fine-grained particles, although there was no significant correlation between ^{238}U and the mud content of sediments. The somewhat different distribution of ^{238}U in the Neretva Channel surface sediments could be explained by desorption of this radionuclide from its organic and inorganic carriers. In the coastal mixing zones, fluvial sedimentary material enters an environment of increased alkalinity. This enhances the formation of uranyl carbonate complexes and results in remobilization of uranium (LANGMUIR, 1997). The high activity concentration of ^{238}U (490 Bq m^{-3}) discovered in the seawater in Ploče harbour (PETRINEC et al., 2012A) is in agreement with the proposed desorption behaviour of uranyl species.

The mean activity concentration of ^{40}K (526 Bq kg^{-1}) in the surface sediments of the Neretva Channel is significantly higher than the world average value of 370 Bq kg^{-1} (UNSCEAR, 1988). The high content of fine-grained particles in the Neretva Channel sediments, the abundance of clay minerals, particularly illite, can partially explain the elevated activity concentrations of ^{40}K. However, the Neretva River delta plain, which is adjacent to the study area, is an important agricultural region. Considering that ^{40}K activity concentrations as high as 6500 Bq kg^{-1} have been reported in phosphate fertilizers (KHATER & AL-SEWAIDAN, 2008), their extensive use in the delta plain may be a significant source of ^{40}K radionuclide in the Neretva Channel sediments.

The specific activities of natural radionuclides ^{238}U and ^{232}Th in surface sediments of the investigated area did not vary significantly. In comparison, the study in the nearby Krka River estuary reported activity concentrations from 14.1 ± 2.5 to 485 ± 16 Bq kg^{-1} for ^{238}U (CUKROV et al., 2009). The town of Šibenik, located in the Krka River estuary, is the main Croatian port for phosphate ore transhipment, so localized anthropogenic input of ^{238}U explains the wide range of values observed across the estuary. In the Neretva Channel, anthropogenic input of ^{238}U and ^{232}Th radionuclides appears to be less pronounced. The mean values of ^{238}U and ^{232}Th activity concentrations in surface sediments of the Neretva Channel are 31 Bq kg^{-1} and 26 Bq kg^{-1}, respectively. These values are comparable to the world average value of 25 Bq kg^{-1} reported for these two radionuclides (UNSCEAR, 1988). Similar activity concentrations for ^{238}U (28 Bq kg^{-1}) and ^{232}Th (21 Bq kg^{-1}) were also reported in the Venice lagoon (DESIDERI et al., 2001). The use of fertilizers in the adjacent agricultural region of the Neretva River delta plain may contribute to slight enrichment in the Neretva Channel sediments of the ^{238}U and ^{232}Th radionuclides.

4.3. Distribution of radionuclides in core sediments

The distribution of ^{137}Cs in core sediments from stations K1–K3 is presented in Figure 4A. At station K1, activity concentrations of ^{137}Cs were constant (~ 9 Bq kg^{-1}) in the uppermost 12.5 cm of the sediment strata. The values started to decrease in deeper sediment layers and reached 0 Bq kg^{-1} at 32.5 cm depth. The nuclear weapon testing and the subsequent atmospheric fallout of the ^{137}Cs radionuclide reached

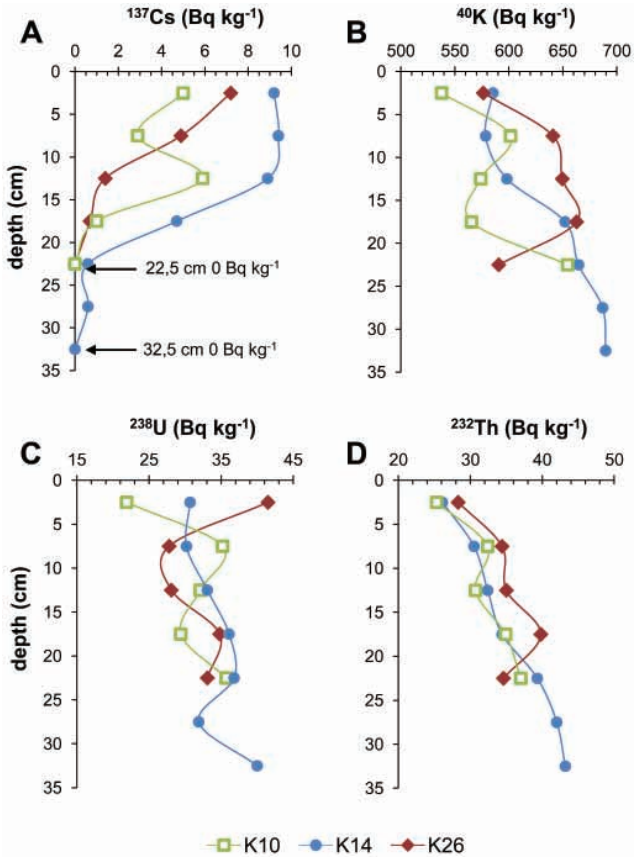

Figure 4. Activity concentrations distributions in the sediment cores from stations K1–K3: A) ^{137}Cs, B) ^{40}K, C) ^{238}U, D) ^{232}Th.

its maximum around 1963. The quantities of ^{137}Cs deposited in sediments prior to this were small and have been continuously reduced by radioactive decay up to the present day. For example, the amount of ^{137}Cs deposited in 1954 was reduced to half by 1984, and is reduced to about one quarter of the initial quantity by 2013. The detection limit of the gamma spectrometer used in this study was 0.3 Bq kg^{-1} for ^{137}Cs. RITCHIE & McHENRY (1990) argued that the determination of ^{137}Cs near the detection limits can cause inaccuracies in establishing the onset of accumulation. The quantity of this radionuclide deposited in the Neretva Channel sediments prior to the fallout maximum in 1963 was probably insufficient to be still reliably detectable. Therefore it is assumed that 1963 is taken as the onset for accumulation of ^{137}Cs in sediments and the sedimentation rate at station K1 is estimated to ~ 6 mm y^{-1}. At stations K2 and K3 the activity concentration of ^{137}Cs became undetectable at 22.5 cm depth. An estimated sedimentation rate at both stations is ~ 4 mm y^{-1}. The difference in the sedimentation rate between stations K1–K3 is due to their varying distances from the Neretva River mouth. It is expected that more sediment is deposited at station K1 located in front of the Neretva inlet, than at stations K2 and K3 which are in the central channel area. Nevertheless, considering the uncertainties of the measurements and estimated sedimentation rate, the observed difference of 2 mm y^{-1} is small. These results imply the significance of the fluvial input of sediments to the entire investigated area.

The vertical distribution of ^{137}Cs at station K2 was similar to the vertical distribution of this radionuclide at station K1; the maximum activity concentration was found at the surface (7.2 ± 1.5 Bq kg^{-1}) and values continuously decreased with depth. At station K3, the maximum activity concentration of ^{137}Cs (5.9 ± 1.0 Bq kg^{-1}) was observed at 12.5 cm sediment depth. This increase was attributed to the Chernobyl nuclear accident which occurred in 1986. The sedimentation rate, calculated based on this peak position, is ~ 4 mm y^{-1}, which is in agreement with the previously estimated sedimentation rate based on the onset of ^{137}Cs accumulation. The reason why this peak was only observed at station K3 is somewhat unclear. It is possible that disturbance of the sediments by bioturbation or some other process was less pronounced at Station K3 than in other areas of the Neretva Channel which allowed preservation of this distinct ^{137}Cs enrichment.

The vertical distribution of ^{40}K, ^{238}U and ^{232}Th activity concentrations are presented in Figure 4B–D. The activity concentrations of these three radionuclides in the core sediments were similar at all three sampling stations. Values ranged from 537.7 ± 62.6 to 689.6 ± 74.6 Bq kg^{-1} for ^{40}K, from 21.9 ± 6.7 to 41.5 ± 11.0 Bq kg^{-1} for ^{238}U and from 25.3 ± 5.3 to 43.2 ± 6.4 to 43.2 ± 6.4 Bq kg^{-1} for ^{232}Th. The vertical profiles of ^{40}K, ^{238}U and ^{232}Th activity concentrations revealed a similar accumulation pattern in core sediments for all three radionuclides, particularly at station K3. Considering the observed similarities in the temporal accumulation pattern of ^{238}U, ^{232}Th and ^{40}K, depth variations in these radionuclides activity concentrations can be attributed to differences in grain-size and mineralogy of the deposited sediments.

The only significant difference in the vertical accumulation trend of these radionuclides is an increase in ^{238}U activity concentration observed in surface sediments at station K2. This increase could be due to the penetration of seawater enriched with soluble ^{238}U in the surface sediment layers at this sampling station (PAPAEFTHYMIOU et al., 2007). An alternative explanation is differential bioturbation rates between the investigated stations. There are two mechanisms through which bioturbation processes can promote uranium release from sediments to the water column (ZHENG et al., 2002). Bioturbation can oxygenate sediment and/or stir them up, closer to the water-sediment interface. Since uranium is subject to remobilisation in oxidising conditions, either of these scenarios can be the explanation for the lower activity concentration of ^{238}U in surface sediments at stations K1 and K3. If bioturbation is less pronounced at station K2, removal of ^{238}U radionuclide from surface sediments layers should not occur.

5. CONCLUSIONS

1. The highest accumulation of ^{137}Cs occurred close to the river mouth, in the region of intensive deposition of organic matter of terrestrial origin, with amounts decreasing progressively seaward.
2. The sedimentation rates from 4 – 6 mm y^{-1} were estimated based on ^{137}Cs distribution in the core sediments.
3. The distribution of natural radionuclides ^{40}K, ^{238}U and ^{232}Th follows the accumulation pattern of the fine-grained sediment particles. This implies fine-grained sediment dispersal processes as the dominant factor governing the accumulation trend of these radionuclides.
4. Significant enrichment of ^{40}K in the Neretva Channel sediments could be explained by the use of fertilizers in the Neretva delta agricultural region, but further investigations are required. Anthropogenic input of ^{238}U and ^{232}Th appears to be negligible.

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