Natural and anthropogenic radionuclides in karstic coastal area (Kaštela Bay, Adriatic Sea, Croatia) exposed to anthropogenic activities: Distribution, sources, and influencing factors

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Abstract.
^{40}K, ^{226}Ra, ^{232}Th, ^{238}U, and ^{137}Cs massic activities were determined by gamma-spectrometry in limestones, marls, stream sediments, and soils of Kaštela Bay (Adriatic Sea, Croatia) coastal area. Their distribution, sources and potential influencing factors were studied. The lowest ^{40}K, ^{226}Ra, ^{232}Th, and ^{238}U massic activities were determined in limestones and the highest in soils, with the following median values, respectively: 7.2 Bq/kg, 14 Bq/kg, 0.8 Bq/kg and 5.3 Bq/kg in limestones and 518 Bq/kg, 72 Bq/kg, 71 Bq/kg and 31 Bq/kg in soils. All four radionuclides were of natural origin and reflected background values of the karstic area influenced by flysch/marl and *terra rossa* soil. Local TENORM disposal site did not influence the study area, but it will be needed to study its potential influence on marine sediments. Strong disequilibrium between ^{226}Ra and ^{238}U was found in limestones s.l. and soils, but not in marls and only moderately in stream sediments. This implies that limestones are more susceptible to selective ^{238}U leaching than marls and soils more than stream sediments. ^{137}Cs was the only radionuclide of anthropogenic origin, with a global source only. It was detected in stream sediments and soils with median values of 5.4 Bq/kg and 31 Bq/kg, respectively. ^{137}Cs distribution was more heterogeneous in stream sediments than in soils, but soils generally presented higher activities. Soil is considered to be the most important reservoir of ^{137}Cs and its potential source.

Keywords: karst; limestones; marl; soil; stream sediment

Introduction

It is known that coastal and karstic areas are sensitive to anthropogenic activities, which may decrease quality of sediments (including soils) and surface and underground water, and human health accordingly. This is especially emphasised if such an area is (heavily) industrialised and urbanised and densely populated. One of such areas is Kaštela Bay (Adriatic Sea, Croatia), around which the largest urban agglomeration at the Croatian coast is formed. The centre of it is the City of Split that is the second most populous city in Croatia and the first in Dalmatia region [1].

Significant industrial, transport, and agricultural activities are present at the mainland around the whole Bay [2]. Čiovo Island is less affected by these activities, where only agricultural activities of smaller scale are present. However, the most important activity regarding radionuclides was the "Jugovinil/Adriavinil" chemical factory that operated in the 1950 – 1990 period, but whose legacy still remains actual. The factory used coal with elevated activities of natural radionuclides and it produced bottom and fly ash with elevated ^{238}U, ^{235}U, and ^{226}Ra massic activities. This material was, therefore, characterised as TENORM (technologically enhanced naturally occurring radioactive material) and it was deposited both on land and in the sea [1]. Part of it was deposited at a regulated disposal site and the rest was not. Additionally, TENORM from other power plants was deposited near the factory.

Taking the industrial past and present of Kaštela Bay into account, it may be assumed that it might have affected both terrestrial and marine environment. Indeed, many studies have been performed, encompassing numerous substances (including radionuclides) and various environmental compartments [1, 2 and references therein]. The emphasis was given to marine environment, while studies on terrestrial environment were much less represented and limited in their extent. Concerning the terrestrial area, mostly soils and the fly and bottom ash disposal site were studied [3–11]. However, only few studies encompassed the complete terrestrial area taking into account all relevant geological/lithological members and only two of them are related to radionuclides [1, 2, 12]. Therefore, the data for radionuclides in this area are still scarse. There are no compreshensive data on radionuclides distribution in all relevant lithological members and the radiological characterisation of the area is incomplete.

In order to obtain data regarding radionuclides in relevant lithological members of the studied area (limestones, marls, stream sediments, and soils), the research presented here was performed. The aim was to determine distribution of selected radionuclides (^{40}K, ^{226}Ra, ^{232}Th, ^{238}U, and ^{137}Cs), to determine their sources to studied sediments, but also to detect lithological members that could be the most probable source of radionuclides for marine sediments. Factors and mechanisms influencing distribution and possible natural and anthropogenic sources of radionuclides were discussed.

Results of this study may be useful both locally and globally. Locally, the area is radiologically characterised and the studied radionuclides baseline is established. This can serve as a basis for decision making concerning environmental radioactivity of the area. It will also show if the anthropogenic influence regarding radionuclides remained localised to (regulated and unregulated) disposal sites or if it spread to a wider area. Globally, since this is a typical karstic area, this study may be applied to other similar karstic areas, especially to the ones where pure carbonate rocks are associated with mixed carbonate/alumosilicate rocks (such as marls). This is even more important because studies of such or similar associations are rare [13]. Additionally, the data obtained for this karstic environment influenced by alumosilicates may be added to already existing data regarding part of the Earth's crust consisting of pure limestones or limestones influenced by noncarbonate sediments. Since only a small portion of the Earth's crust is built of limestones and carbonate rocks in general, it is important to collect the data for them to obtain reference values typical for these kind of rocks and sediments instead of using general reference data for the whole Earth's crust, which incorporate the data for various magmatic and metamofphic rocks as well.

Study area

Kaštela Bay is situated at the eastern coast of the central Adriatic Sea, Croatia (Figs. 1a) and 1b)). It is a semi-enclosed, lentil-shaped bay. It is bordered by the narrow coastal plain (1–3 km wide and covering approx. 14 500 ha) and mountains in the immediate hinterland to the north [14], by the Čiovo Island and by the City of Split and Marjan peninsula (Fig. 1c)).

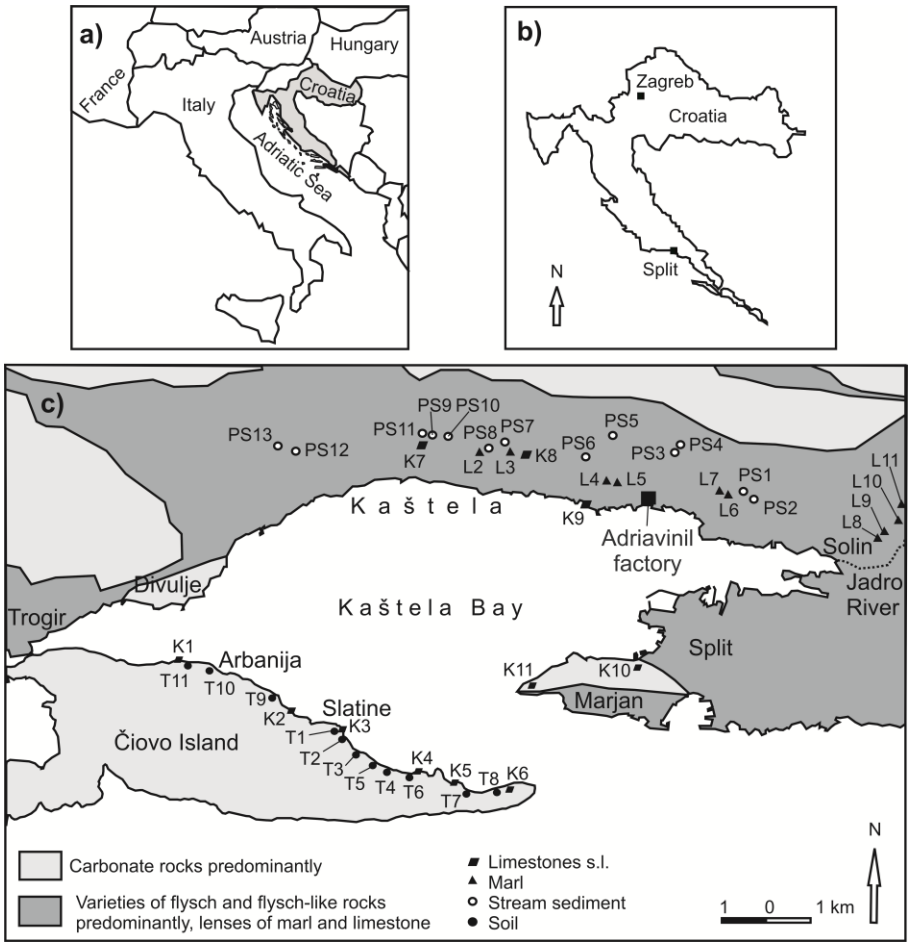

Fig. 1. Study area: a) Regional location of the study area; b) Location of the study area in Croatia; c) Simplified geological setting of Kaštela Bay area with sampling locations [after 1, 15, 16].

The Bay is 14.8 km long and 6.6 km wide. Its total surface is approx. 60 km^2, average depth is 23 m, and the maximum depth is 45–50 m at the Bay's entrance [17–19]. The coastal strip from the Trogir town to the City of Split forms an urban agglomeration. It is the biggest urban agglomeration at the Croatian coast.

Hydrographic net around the Bay reflects its geological history and its lithology. The whole area is intensively fractured and almost all surface water percolates underground. The only permanent surface stream flowing into Kaštela Bay is the Jadro River in the east part of the Bay. Numerous temporary streams form on the north coastal plain, depending on the amount of received precipitation [12]. They tend to dry up in dry periods, which happens regularly, even few years consecutively. No streams of any kind are present on the Čiovo Island.

Geological setting

Kaštela Bay and the surrounding area belong to a large Cretaceous-Tertiary sediment basin of the Outer Dinarides. The studied area is generally built from two types of sediments: carbonates and flysch/flysch-like rocks (Fig. 1). Carbonates encompass Cretaceous limestones and limestone dolomites found on Čiovo Island and in the Bay's hinterland, Eocene foraminiferal limestones found on Marjan hill, and Pleistocene breccias consisting of fragments of carbonate sediment bound by bauxitic matrix found around Divulje [15, 20]. The coastal area (including Split/Marjan peninsula) is mostly built from Eocene flysch and flysch-like rocks [15, 20–23]. Lenses of marl and limestone occur in these rocks. Alluvial deposits are of some significance only near the mouth of the Jadro River. They consist of accumulated and unbound Tertiary marls and breccias and of Cretaceous and Tertiary carbonates.

Materials and methods

Sampling

Samples of limestones s.l., marls, stream sediments, and soils were collected in 2005 – 2008. Forty-five samples were collected in total (11 limestones s.l., 10 marls, 13 stream sediments, 11 soils). In this study, the term limestones s.l. encompasses all rocks of limestone composition, irrespectively of their genesis. Soils are regarded as residual clastic sediments according to Tišljar [24]. Sampling locations are presented in Fig. 1 and their coordinates are given in Lovrenčić Mikelić et al. [2] and Lovrenčić Mikelić and Barišić [1].

Limestones s.l. and marls were sampled at open outcrops. Stream sediments on the north coast of Kaštela Bay were sampled up to 10 cm depth in brook beds. Surface samples of undisturbed soils were collected up to 10 cm depth on the Čiovo Island in places where soil transport by precipitation water was observed. Undisturbed soils were equivalent to stream sediments due to the same means of transport – precipitation water. All samples, except the T2 sample (which was brown soil), were *terra rossa*. More details regarding sampling are given in Lovrenčić Mikelić et al. [2, 12] and in Lovrenčić Mikelić and Barišić [1].

Gamma-spectrometry

Loose samples (stream sediment and soil) were first dried at 105 °C overnight to achieve constant mass, ground in a mill with agate spherules or in an agate mortar, and then homogenized. Lithified rocks (limestone s.l. and marl) were first crushed in a crusher and then dried overnight at 105 °C and homogenized. All samples were then filled into plastic containers of 125 cm^3 volume. Containers were closed with lids and weighted. The containers' lids were sealed with a self-adhesive tape and stored for at least four weeks to allow ingrowth of gaseous ^{222}Rn in order to achieve secular equilibrium between ^{222}Rn and its progenies.

HPGe coaxial detector with a relative efficiency of 25.3 % and with a resolution of 1.75 keV at 1332.5 keV (^{60}Co) and InSpector 2000 detector with a relative efficiency of 25.4 % and with a resolution of 1.80 keV at 1332.5 keV (^{60}Co) were used to perform gamma-spectrometric analyses. Both detectors were coupled with multichannel analysers with 8192 channels (Canberra Industries). Spectra were collected for 80 000 s and analysed with a Genie 2000 software package (Canberra Industries). All massic activities were recalculated to 6th June 2005. ^{40}K massic activity was determined from its 1460.75 keV peak. ^{226}Ra weighted mean activity was calculated using ^{214}Pb and ^{214}Bi activities obtained from the peaks at following energies: 295.21 keV and 351.92 keV for ^{214}Pb, and 609.31 keV, 1120.28 keV, and 1764.49 keV for ^{214}Bi. Secular equilibrium between ^{226}Ra and its progenies was assumed [25, 26]. ^{232}Th weighted mean activity was calculated using ^{212}Pb and ^{228}Ac activities obtained from the peaks at following energies: 238.63 keV for ^{212}Pb, and 338.32 keV, 911.20 keV, and 968.97 keV for ^{228}Ac. ^{238}U weighted mean activity was calculated from ^{234}Th 63.29 keV and 92.6 keV peaks assuming secular equilibrium between ^{238}U and ^{234}Th. Contribution of ^{232}Th gamma-rays to 63.29 keV peak was subtracted using ^{228}Ac peak at 338.32 keV [27]. Emission probability of 4.82 % was used for doublet peak at 92.6 keV. Contribution of ^{228}Ac Kα1 X-rays was subtracted from

92.6 keV peak. ^{137}Cs activity was determined from its 661.66 keV peak. Further information about gamma-spectrometry are given in Lovrenčić Mikelić et al. [28].

Results

Basic statistical parameters of ^{40}K, ^{226}Ra, ^{232}Th, ^{238}U, and ^{137}Cs massic activities in the studied rocks and sediments of Kaštela Bay costal area and their box and whisher plots are presented in Table 1 and Fig. 2, respectively. Box and whisker plot for ^{137}Cs is given only for stream sediments and soil because ^{137}Cs activities in limestones s.l. and marls were below the minimum detectable activity (MDA).

Table 1. Basic statistical parameters of ^{40}K, ^{226}Ra, ^{232}Th, ^{238}U, and ^{137}Cs massic activities in limestones s.l., marl, stream sediments, and soil of Kaštela Bay coastal area. $\bar{x}$ – mean value, SD – standard deviation.

Type of sample	Statistical parameter	^{40}K (Bq/kg)	^{226}Ra (Bq/kg)	^{232}Th (Bq/kg)	^{238}U (Bq/kg)	^{137}Cs (Bq/kg)
Limestones s.l.	Range	0.5 – 69	9.4 – 60	0.1 – 3.4	3.0 – 53	< 0.4 – 1.9
	$\bar{x}$	14	19	1.0	11	< 0.6
	SD	19	15	0.9	14	0.43
	Median	7.2	14	0.8	5.3	0.5
Marl	Range	148 – 284	8.1 – 20	8.6 – 17	4.6 – 17	< 0.1 – 2.6
	$\bar{x}$	215	14	11	13	< 0.8
	SD	54	4.3	3.2	4.1	0.8
	Median	194	14	9.9	13	0.4
Stream sediments	Range	46 – 310	8.2 – 47	4.8 – 36	8.5 – 31	< 0.8 – 111
	$\bar{x}$	193	23	17	17	25
	SD	89	11	9.4	6.1	34
	Median	212	21	15	16	5.4
Soil	Range	168 – 581	28 – 198	20 – 84	26 – 58	7.9 – 87
	$\bar{x}$	463	85	62	37	34
	SD	140	48	20	11	25
	Median	518	72	71	31	31

Generally, the lowest ^{40}K, ^{226}Ra, ^{232}Th and ^{238}U activities were determined in limestones s.l. or in marls and the highest activities were measured in soils (Table 1, Fig. 2). Maximum activities of individual radionuclides in different types of samples generally ascend in the following order: limestones, marls, stream sediments, and soil. Exception was found only for ^{226}Ra and ^{238}U activities in limestones s.l. and marls where they were higher in limestones s.l. than in marls. In limestones, the highest mean values and medians were found for ^{226}Ra, while in other sample types the highest mean values and medians were for ^{40}K (Table 1). Significant difference was observed between ^{226}Ra and ^{238}U activity medians in limestones s.l. and soils, where ^{226}Ra/^{238}U median activity ratios were 2.6 and 2.3, respectively (Table 1). This was also observed to a smaller extent in stream sediments where this ratio was 1.3 Table 1). ^{40}K and ^{232}Th showed the same distribution pattern between different types of samples (Fig. 2). Their distribution in marl and stream sediment is very similar, while limestones and soil are more differentiated from marl and stream sediment. ^{226}Ra and ^{238}U distributions between different types of samples do not show the same pattern, although there are some similarities (Fig. 2). ^{226}Ra distribution in limestones, marl, and stream sediment is generally very narrow and amost the same, while for ^{238}U, it is wider and an ascending trend exists. Soil is clearly differentiated from other types of samples for both ^{226}Ra and ^{238}U.

^{137}Cs massic activities were above the MDA only in stream sediments and soils, as they should be. They were below the MDA in limestones s.l. and marls because these rocks were lithified before ^{137}Cs was introduced into environment. The highest ^{137}Cs massic activity was determined in stream sediments (111 Bq/kg) but the median in soils (31 Bq/kg) was 5.7 times higher than the median in stream sediments (5.4 Bq/kg) (Table 1, Fig. 2). Both, stream sediment and soil tend to have some elevated ^{137}Cs activties, although it is more pronounced in stream sediment (Fig. 2).

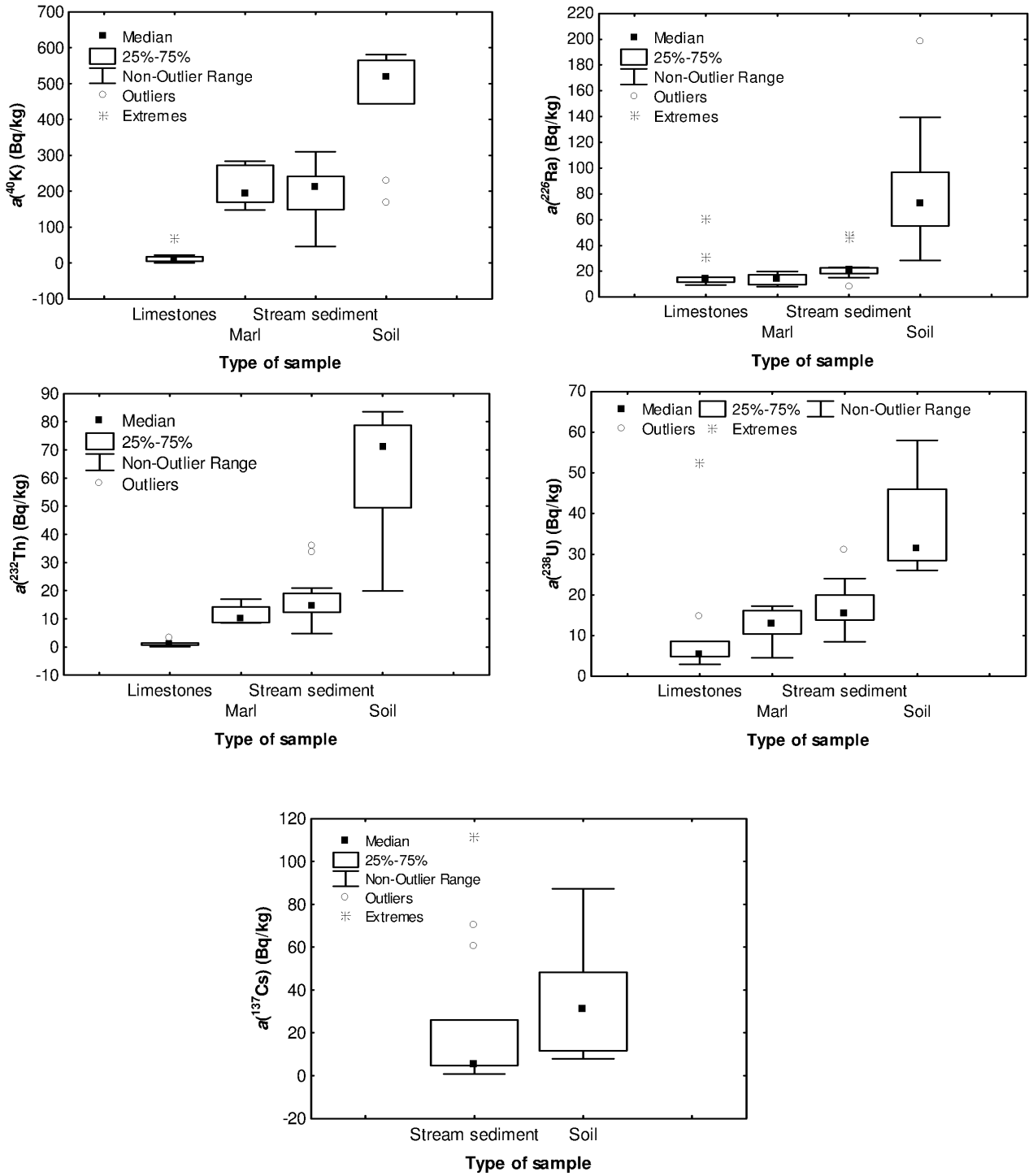

Fig. 2. Box and whisher plots of ^{40}K, ^{226}Ra, ^{232}Th, ^{238}U, and ^{137}Cs massic activities in limestones s.l., marl, stream sediment, and soil of Kaštela Bay coastal area.

Discussion

Natural radionuclides in limestones s.l.

^{40}K massic activities determined in limestones s.l. of Kaštela Bay are in accordance with activities reported by other authors (Table 2). Very low ^{232}Th massic activities were measured in Kaštela Bay limestones compared to

studies from other authors (Table 2). Such very low ^{232}Th and relatively low ^{40}K activities are not surprising in limestones since both radionuclides are preferably bound to detritic/terrestrial particles, which are not largely contained in limestones. Low ^{40}K and ^{232}Th activities make these limestones a weak source of ^{40}K and ^{232}Th for future sedimentation in Kaštela Bay or in the terrestrial stream sediments. Maximum ^{226}Ra massic activity in Kaštela Bay limestones was almost four times higher than the average ^{226}Ra activity in world limestones (Tables 1 and 2). However, its mean value was very close to the mean value given for world limestones (Tables 1 and 2). Maximum ^{238}U activity determined in Kaštela Bay limestones is approx. three times lower than the upper range value found by some authors (Tables 1 and 2). Relatively increased ^{238}U activities found in some Kaštela Bay samples represent a natural variability of ^{238}U distribution in limestones considering that ^{238}U activities may vary in the range of two orders of magnitude and that no special characteristics related to sampling sites specific only for these samples were observed. Activities of all four natural radionuclides in limestones s.l. showed natural background values.

Table 2. Comparison of ^{40}K, ^{232}Th, ^{226}Ra, and ^{238}U massic activity ranges and mean values in limestones s.l. from Kaštela Bay coastal area with the literature data.

Radionuclide (unit)	Kaštela / current study	World limestones	Reference
^{40}K (Bq/kg)	0.5 – 69 14±5.8	0 – 160	[29–31]
^{232}Th (Bq/kg)	0.1 – 3.4 1.0±0.3	0 – 13.8	[29–34]
^{226}Ra (Bq/kg)	9.4 – 60 19±4.5	15.4	[32]
^{238}U (Bq/kg)	3.0 – 53 11±4.3	2.9 – 150	[30, 31]

Strong disequilibrium between ^{238}U and ^{226}Ra activities in limestones s.l. was observed. Higher ^{226}Ra than ^{238}U activities imply higher ^{238}U mobility in limestones s.l., i.e. greater susceptibility of ^{238}U to chemical weathering processes such as preferential ^{238}U leaching [35, 36]. Uranium is very soluble in oxic waters and limestones are easily soluble rocks, thus facilitating preferential ^{238}U leaching. Additionally, high CO_2 concentrations produced by limestones (calcite) weathering enhance uranium solubility [35]. ^{40}K and ^{232}Th, on the other hand, will be more influenced by physical/mechanical weathering.

Natural radionuclides in marls

^{40}K and ^{232}Th massic activities in marls of Kaštela Bay were comparable with the values determined by Tzortzis et al. [30] for marls in Cyprus (Tables 1 and 3). Higher ^{40}K and ^{232}Th activities in Kaštela Bay marls than in limestones s.l. reflect natural differences in mineral composition between pure carbonate rocks and mixed carbonate/alumosilicate rocks such as marl having higher content of alumosilicate minerals, which serve as ^{40}K and ^{232}Th bearers. Muscovite was determined in Kaštela Bay marl samples as a considerably abundant mineral [12].

Table 3. Comparison of ^{40}K, ^{232}Th, ^{226}Ra, and ^{238}U massic activity ranges and mean values in marls from Kaštela Bay coastal area with the literature data.

Radionuclide (unit)	Kaštela / current study	World marls	Reference
^{40}K (Bq/kg)	148 – 284 215±17	187 – 434	[30]
^{232}Th (Bq/kg)	8.6 – 17 11±1.0	16.1	[30]
^{226}Ra (Bq/kg)	8.1 – 20 14±1.4	5 – 36 16.4	[37]
^{238}U (Bq/kg)	4.6 – 17 13±1.3	23.1	[30]

^{226}Ra activities in Kaštela Bay marls were in accordance with activities and mean values found by other authors in world marls (Tables 1 and 3). They reflect ^{238}U activities due to same origin of both radionuclides. ^{238}U massic activities in Kaštela Bay marls were lower than in world marls but still comparable with them (Tables 1 and 3).

Observed differences in mean values may be a consequence of variable marl composition, with different alumosilicate and carbonate minerals, oxides and oxyhydroxides content affecting radionuclides sorption, coprecipitation or accumulation [36, 38–42].

Activities of four studied natural radionuclides in marl showed natural background values. Considering that only ^{40}K, and to a lesser extent ^{232}Th, presented significantly higher activities in marls compared to activities in limestones s.l. (Table 1, Fig. 2), marls are considered an important source of ^{40}K and ^{232}Th for further sedimentation and weathering processes. Notably lower maximum ^{226}Ra and ^{238}U activities in marls than in limestones s.l. may be attributed to higher content of alumosilicate minerals in marls, primarily clay minerals that strongly bind ^{40}K and ^{232}Th, possibly preferably to ^{226}Ra and ^{238}U [2, 13]. However, clay minerals may also be assumed to reduce ^{238}U mobility in marls since, unlike in limestones, ^{226}Ra and ^{238}U were found to be in equilibrium in marls.

Natural radionuclides in stream sediments

A wide range of ^{40}K activities (Table 1) determined in Kaštela Bay stream sediments can be compared with activities of alluvial sediments ranging from 18 Bq/kg to 1047 Bq/kg determined by other authors [43– 46]. All four natural radionuclides activity ranges were wider in stream sediments than the corresponding ranges observed for marls, but only ^{40}K and ^{232}Th activity ranges in stream sediments were wider than the ones for limestones s.l. (Table 1, Fig. 2). This is associated with higher detritic component, clay minerals and/or organic matter content in stream sediments reflecting composition of the drained area and sediment accumulation. ^{226}Ra and ^{238}U activity ranges in stream sediments were narrower than in limestones s.l., with higher maxima in limestones but with higher mean values and medians in stream sediments (Table 1, Fig. 2). This implies more homogeneous ^{226}Ra and ^{238}U distribution in stream sediments than in limestones s.l. It was attributed to different mechanisms of genesis of these sedimentary rocks (limestones and stream sediments). ^{238}U activities in stream sediments of Kaštela Bay were similar to activities found by other authors in alluvial sediments (10 Bq/kg – 75 Bq/kg) [30, 42, 43, 45]. In stream sediments, as well as in alluvial sediments, ^{238}U can be bound to detritic material, clay minerals or organic matter [44] and thus increase ^{238}U activities in sediments.

Composition of stream sediments is influenced by geological background of the area drained by stream water flow such as flysch on one side and limestones and dolomites on the other side. Soil affects stream sediments‘ composition as well. Along with the composition of the nearby soils, meteorological conditions and anthropogenic activities such as soil cultivation or industrial activity may also have influence on composition of stream sediments [47]. No anthropogenic influence regarding ^{40}K, ^{232}Th, ^{226}Ra, and ^{238}U was detected in stream sediments of Kaštela Bay coastal area. All these influences, or lack of them, are revealed in a rather homogeneous distribution of all four studied natural radionuclides in stream sediments.

Natural radionuclides in soils

A wide range of ^{40}K massic activities was determined in world soils (Table 4) depending on the geological background that influences ^{40}K activities [13]. Activities up to 3200 Bq/kg were found is soils [48]. ^{40}K activities in soils of Kaštela Bay found in the current study were in accordance with activities determined in other studies referring to Croatian soils, *terra rossa* in Croatia and Kaštela Bay soils from the previous study (Table 4). However, ^{40}K activities from the current study are somewhat lower than activities reported for Mediterranean soils. This is attributed to normal variability of ^{40}K activities in soils of Mediterranean region, which is dependent on the local geological background on which soils are developed [8, 13]. Significantly increased ^{40}K activities were not expected in Kaštela Bay soils due to strong influence of carbonate rocks. ^{40}K activity outliers (decreased values) imply the same (Fig. 2).

^{232}Th activities determined in Kaštela Bay soils were comparable to the literature values for soils in Croatia and the world and to activities found in the previous Kaštela Bay study (Table 4). The range found in the current study was much narrower than the one reported for Mediterranean soils, but the mean values were almost the same. Some authors reported average ^{232}Th activities in soils between 30 Bq/kg and 40 Bq/kg [29, 57, 62], which is notably lower than the mean value obtained in the current study. It is, again, necessary to take into account variability of soil types and geological backgrounds on which soils were developed as well as local specific characteristics. Thorium is typically bound to terrestrial particles, i.e. it is preferentially accumulated in soils explaining the highest activities in soils compared to other studied types of samples [35, 41].

^{226}Ra massic activity mean value of Kaštela Bay soils was significantly higher than the mean value given by UNSCEAR [48] for world soils (Table 4). Vaupotič et al. [58] and Skoko et al. [8] also determined higher mean values for *terra rossa* soils in Croatia and for Kaštela Bay soils compared to world soils, respectively (Table 4). Studies performed in other countries also found some ^{226}Ra soil activities close to the ones found in the current study (Table 4). However, ^{226}Ra activities in world soils were found to vary in a wide range of three orders of magnitude (Table 4), which was not the case in Kaštela Bay area. Therefore, differences in observed ^{226}Ra activities are a result of variation of local characteristics such as geological background, organic matter, and clay minerals content, and exposure to water influence [13, 63].

Table 4. Comparison of ^{40}K, ^{232}Th, ^{226}Ra, and ^{238}U massic activity ranges and mean values in soils from the Čiovo Island (Kaštela Bay area) with the literature data.

Radionuclide (unit)	Čiovo Island (Kaštela) / current study	World soils	Mediterranean soils	Croatian soils	*Terra rossa* / locations in Croatia	Previous Kaštela Bay study
^{40}K (Bq/kg)	168 – 581 463±42	0 – 1800 [31, 49–56] 421 [48] 580 [57]	37 – 402 [8] 207±149 [8]	570 – 720 [8] 645±61 [8]	290 – 530 [58]	269 – 561 [8] 444±116 [8]
^{232}Th (Bq/kg)	20 – 84 62±6.1	 45 [48]	11 – 119 [8] 61±23 [8]	12 – 77 [8, 59] 45 [59] 62±13 [8]	–	26 – 73 [8] 47±20 [8]
^{226}Ra (Bq/kg)	28 – 198 85±14	8 – 210 [51, 53–56] 0 – 3700 [36, 51, 53, 56, 60] 32 [48]	–	51 – 86 [8] 73±16 [8]	49 – 84 [58] 65 [58]	33 – 120 [8] 58±33 [8]
^{238}U (Bq/kg)	26 – 58 37±3.2	10 – 50 [61] 35 [59] 33 [48] 30 [61]	11 – 53 [8] 32±9.1 [8]	78 – 140 [8] 107±26 [8]	49 – 74 [58]	24 – 92 [8] 54±24 [8]

^{238}U activities determined in Kaštela Bay soils are comparable to activities measured in Istrian *terra rossa* soils, Kaštela Bay soils from other studies, Mediterranean soils, and world soils (Table 4). However, they were significantly lower when compared with Croatian soils. Soils around Kaštela Bay are predominantly *terra rossa* soils typical for karstic area (including Croatian Adriatic Sea coast), while other soil types are predominant in non-karstic parts of Croatia. This explains the observed differences and variability of ^{238}U distribution in Croatian soils. ^{238}U activities from the current study were significantly lower than ^{226}Ra activities. It was explained by different mobility of two radionuclides. There is, often, a large excess of ^{226}Ra in relation to ^{238}U in soils and sediments due to ^{226}Ra cationic exchange binding or preferred ^{238}U leaching from soils and sediments, making radium relatively immobile in soils, in contrast to uranium [36].

Observed activities of all four natural radionuclides were the highest in soils when compared to other types of samples (Table 1, Fig. 2). Such activities are a result of soil composition originating from geological background on which the soil was developed (carbonate and mixed alumosilicate/carbonate rocks, i.e. limestones s.l. and marls) and of different soil genesis. The importance of geological background or parent materials such as limestones s.l. and marls for natural radionuclides massic activities in soils was also clearly shown by Gaspar et al. [13]. No anthropogenic influence regarding these radionuclides was determined in soils. Kaštela Bay soils can be a source of ^{40}K and ^{232}Th for further sedimentation via physical weathering mainly [38], while ^{238}U will be influenced by chemical weathering mostly.

Distribution of natural radionuclides between different types of samples

Distribution pattern of ^{40}K and ^{232}Th reflects prevailing influence of alumosilicate minerals on their distribution, while carbonates are of minor importance for their binding (Fig. 2). This is why their activities in limestones s.l. are very low and higher in other types of samples by an order of magnitude or more compared to limestones. Alumosilicate minerals are abundant in marls, stream sediments, and soil, but not in limestones. The most important among them would be clay minerals. In soils, organic matter would be another important factor facilitating radionculides binding. This may explain significant differentiation of soil from other types of samples. Very close relationship of ^{40}K and ^{232}Th in all types of studied samples, especially in limestones and marls, and their preferential association with alumosilicates have been confirmed earlier [2].

^{226}Ra and ^{238}U distributions are more complex than ^{40}K and ^{232}Th's. ^{238}U distribution is somewhat different from ^{226}Ra distribution and it may be attributed to disturbed equilibrium between ^{226}Ra and ^{238}U (Fig. 2). In both cases, soil is the most differentiated from other types of samples and it can be associated with more complex soil composition that enables both ^{226}Ra and ^{238}U binding [2]. It was suggested earlier that ^{226}Ra and ^{238}U might be strongly influenced by chemical weathering and preferential ^{238}U leaching, unlike ^{40}K and ^{232}Th [2]. It was also shown that relationship between ^{226}Ra and ^{238}U was not as close as between ^{40}K and ^{232}Th in both consolidated rocks (limestones and marls) and sediments (stream sediments and soils). This supports different ^{226}Ra and ^{238}U distributions observed in the current study.

^{137}Cs in stream sediments and soils

Wider range of ^{137}Cs massic activities was observed in stream sediments than in soils, while mean value and median were notably higher in soils (Table 1, Fig. 2). Skoko et al. [8] determined higher ^{137}Cs activities in Kaštela Bay soils (range: 13–100 Bq/kg, mean value: 44±37 Bq/kg), but still comparable with results presented in the current study. The results of both studies show variability of ^{137}Cs distribution in soils, i.e. ^{137}Cs is inhomogeneously distributed in soils. Stream sediments show even larger heterogeneity of ^{137}Cs distribution than soils (Fig. 2). It can be attributed to different genesis of stream sediments and soils. Stream sediments form by draining wide area of possibly various geological backgrounds, while soils depend on local geological background. In case of Kaštela Bay area, all sampled soils were developed on carbonate rocks but the water streams forming stream sediments may drain both carbonates and marls and, additionally, all soils developed on them. Thus, source material for soils is more uniform than for stream sediments, which reflects in their heterogeneity. Inhomogeneous ^{137}Cs distribution in soils may also depend on precipitation pattern at the time of ^{137}Cs atmospheric fallout, while distribution in stream sediments is influenced by the energy of water stream. Variations in water stream energy will define its ability to physically weather or erode rocks and sediments and to transport or accumulate particles. Considering that water streams around Kaštela Bay are of temporary nature and that they strongly depend on the amount of precipitation, their energy is very variable. In both stream sediments and soils, ^{137}Cs is easily bound to clay minerals and organic matter. This explains higher ^{137}Cs mean value and median in soils than in stream sediments because soils have higher content of clay minerals and organic matter and they will have larger capacity for ^{137}Cs binding. It was observed that ^{137}Cs activities were generally higher in soils than in stream sediments, irrespectively of some elevated activities in stream sediments (Table 1, Fig. 2). This also shows that soils of Kaštela Bay are the main storage for ^{137}Cs and possibly the main local source of it in future.

Conclusions

Although some outliers and/or extreme values were found, it was concluded that ^{40}K, ^{226}Ra, ^{232}Th, and ^{238}U massic activities represented natural background values of the local karstic area characterised by carbonate rocks, flysch/marl, and *terra rossa* soil. Activities of all four radionuclides generally increased in the following order: limestones s.l., marls, stream sediments, and soils. No anthropogenic source was determined for any of the four radionuclides. Local anthropogenic activities have not influenced researched terrestrial sediments regarding four studied radionuclides. It was not found that TENORM disposal site influenced the researched area. However, marine sediments will have to be studied separately to determine possible anthropogenic influence.

Pronounced disequilibrium between ^{226}Ra and ^{238}U was observed in limestones s.l. and soils due to possible strong ^{226}Ra cationic exchange binding and/or preferable ^{238}U leaching. In general, ^{226}Ra–^{238}U disequilibrium descended in the following order: limestones s.l., soil, stream sediment, and marl (in which there was no disequilibrium). It shows that limestones are significantly more susceptible to ^{238}U leaching than marls and soils more than stream sediments. This might be studied in detail in the future studies.

^{137}Cs was the only radionuclide of anthropogenic origin in Kaštela Bay coastal sediments and its sources were only global. This shows that global anthropogenic influence rearding radionuclides in the researched area is more present than the local influence, contrary to what might be expected. ^{137}Cs distribution in soils was mostly dependant on atmospheric fallout pattern, while the situation is more complex in stream sediments in which many influencing factors exist. ^{137}Cs massic activities were generally higher in soils, but distribution was more heterogeneous in stream sediments. Thus, soils may be considered the most important ^{137}Cs reservoir and a potential source of ^{137}Cs in future. Since ^{137}Cs was found in terrestrial sediments, it is expected that it will be found in marine sediments as well, in which its behaviour will be governed by other factors.

The data for ^{226}Ra clearly demonstrated that reference data used for comparison of different study areas should be carefully chosen and that care should be taken when using global data due to variability of the Earth's crust composition. Regional data should sometimes be preferably used over global data.

Acknowledgements. Gamma-spectrometry measurements were performed in the Laboratory for Radioecology of the Ruđer Bošković Institute (RBI) and the article was prepared in the Laboratory for Low-Level Radioactivities of the RBI. The work presented here was financially supported by the Ministry of Science, Education, and Sports of the Republic of Croatia through the "Radionuclides and trace elements in environmental systems" project (project number 098-0982934-2713).

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