^{40}K, ^{226}Ra, ^{232}Th, ^{238}U and ^{137}Cs relationships and behaviour in sedimentary rocks and sediments of a karstic coastal area (Kaštela Bay, Croatia) and related rocks and sediments' differentiation

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Abstract

Natural (^{40}K, ^{226}Ra, ^{232}Th, ^{238}U) and anthropogenic (^{137}Cs) radionuclides in consolidated sedimentary rocks (limestones s.l. and marls) and unconsolidated sediments (stream sediments and soils) of the Kaštela Bay (Adriatic Sea, Croatia) coastal area were studied. Kaštela Bay is a typical karstic environment and it is under strong anthropogenic influence due to industrialisation and urbanization. Relationships between radionuclides, their behaviour in different types of samples and possible influencing factors were studied. Radionuclides were also studied in relation to selected metals (Al, K, Ca, Fe, Ti, Mn, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Pb, and As) and distribution in limestones s.l., marls, stream sediments and soils. Radionuclides' massic activities were determined by gamma-spectrometry and metals mass fractions were measured by EDXRF technique. Relationships were studied using statistical tools (principal component analysis, factor analysis). It was found that stream sediments were more similar to source rocks (limestones s.l. and marl) than to soils in terms of natural radionuclides' activities. ^{40}K and ^{232}Th in consolidated rocks were preferentially bound to alumosilicates and associated with the majority of studied metals. However, this was not the case with ^{226}Ra and ^{238}U, which did not show any preferences regarding binding to mineral components or associating with metals. On the other hand, all four natural radionuclides presented the same behaviour in unconsolidated sediments, i.e. they were all preferentially bound to alumosilicates and associated with the majority of metals. ^{137}Cs did not associate with any of the metals or other radionuclides in sediments. The statistical approach applied in this study revealed differences in radionuclides' relationships and behaviour in a karstic environment and implied possible influencing processes or factors. This approach can be applied in other types of environments as well to study preferential radionuclides' binding to certain mineral components that influences radionuclides' mobility and transport to other environmental compartments.

Keywords: Adriatic Sea; limestones; marl; radionuclides; soil; stream sediment

Introduction

Kaštela Bay coastal area is the largest urban agglomeration on the east coast of the Adriatic Sea comprising the towns of Trogir, Kaštela, and Solin and the city of Split. Čiovo Island, which is connected to the mainland with a bridge, is closely connected to the densely

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populated agglomeration. The coastal area was intensively industrialized and urbanized from the 1950s to 1980s causing significant pollution of the Kaštela Bay (Barić et al. 1992; Knezić and Margeta 2001, 2002; Kranjčević et al. 2014; Margeta 2002). Industrial activities included or still include the following: chemical factory ("Jugovinil"/"Adriavinil", operating in the 1950-1990 period), cementworks, ironworks, electroplating facility, and shipyard. They are mostly located in the eastern part of the Bay. The airport and the high capacity greenhouses are located in the western part of the coastal area. TENORM, bottom and fly ash resulting from coal burning in the thermoelectric power-plant of the "Jugovinil"/"Adriavinil" factory, with increased ^{235}U, ^{238}U and ^{226}Ra massic activities was also deposited in the coastal area, both on land and in the sea (Lovrencic et al. 2007; Orescanin et al. 2005). It was deposited both in a regulated and unregulated manner during almost 50 years of the factory production.

Concerns raised by contamination or pollution of the Kaštela Bay initiated numerous researches dealing with various contaminants/pollutants (including radionuclides) influencing marine sediment (Andelic et al. 2015; Anđelić et al. 2020; Blanco et al. 2018; Bogner et al. 1997, 1998a, 1998b; Buljac et al. 2011; Lovrencic et al. 2005; Mandić et al. 2018; Mikac et al. 2006; Milun et al. 2006; Orescanin et al. 2005; Tudor 1993; Ujević et al. 1998a, 1998b, 2000), water (Kwokal and Branica 2000; Kwokal et al. 2002; Marasović et al. 2005; Marovic and Sencar 1999; Marović et al. 2006; Tudor 1993; Tudor et al. 1991), and marine organisms (Anđelić et al. 2020; Bužančić et al. 2016; Custovic et al. 2014; Filipovic Marijic and Raspor 2007; Klobučar et al. 2008; Kljaković-Gašpić et al. 2006; Marasović et al. 2005; Milun et al. 2004, 2016; Odžak et al. 2000, 2001; Rada et al. 2012; Rozmaric et al. 2013). Studies related to terrestrial coastal Kaštela Bay area were limited mostly to the fly and bottom ash disposal site associated with the former "Adriavinil" factory. Performed studies considered elemental and/or radiological characterization of the site (Lovrencic et al. 2005, 2007; Oreščanin et al. 2006; Skoko et al. 2017), plant uptake of radionuclides from the site (Skoko et al. 2017) and radiological risk assessment (Marović and Senčar 1999; Marović et al. 2006; Skoko et al. 2019). However, studies concerning complete surrounding terrestrial coastal area are still scarce and mostly limited to research of metals in sediments and rocks. Bogner (1996) and Bogner et al. (1998a) studied selected metals in marls and limestones and Lovrenčić Mikelić et al. (2013) studied metals in a variety of limestones, marl, stream sediments, and soils. Miloš and Bensa (2019) studied Cd, Cu, Pb and Zn in topsoil (0-25 cm depth) on flysch deposits of the Kaštela Bay coastal area. Radionuclides in soils of the Kaštela Bay coastal area (mainly from the Čiovo Island) were studied only relatively recently (Skoko et al. 2014), but other sediments and rocks (e.g. limestones, marls, stream sediments) have not been researched and the entire coastal area was not encompassed. Similarly, Vaupotič et al. (2007) studied radionuclides only in soils of the karstic area in Croatia and Slovenia. Since other sediments and rocks were not studied in these two studies (Skoko et al. 2014; Vaupotič et al. 2007), these researches do not represent potential complete models of terrestrial karstic environment for studying radionuclides' relationships and behaviour in different rocks and sediments.

Kaštela Bay and its coastal area are a typical karstic environment. Considering that: i) karstic environments are sensitive to anthropogenic activities, especially coastal areas; ii) data about radionuclides in terrestrial sediments and rocks of the Kaštela Bay coastal area are scarce; iii) TENORM history in the Kaštela Bay area exists; Kaštela Bay was selected as an example model area and the study presented in this paper was conducted.

This study is focused on natural and anthropogenic radionuclides (including possible TENORM radionuclides) in consolidated rocks (limestones s.l. and marl) and unconsolidated sediments (stream sediments and soils) of the coastal karstic environment. Its aim is to give insights into relationships and behaviour of studied radionuclides within the studied system. This was done by: i) studying relationships between radionuclides themselves and between radionuclides and metals; ii) studying radionuclides' behaviour in different karstic rocks and sediments and detecting related processes or influencing parameters. Tools used to achieve the aims are statistical methods of clustering. Obtained data and findings can have both local and global importance. Locally, this study will identify the type of samples with the highest massic activities of certain radionuclides. It will also identify sediments with the highest potential for accumulation of studied radionuclides, which is especially important for anthropogenic radionuclides. Additionally, this study may serve as a guideline in land use planning taking into account different radionuclides' behaviour in different rocks and sediments. Globally, the researched system may serve as a preliminary model for radionuclides' behaviour in karstic environments. This study also indicates pathways of radionuclides' introduction from terrestrial karstic environment into marine environment.

Material and methods

Study area

Kaštela Bay is located in the central part of the eastern coast of the Adriatic Sea (Fig. 1). It is bordered by the Čiovo Island, peninsula with the City of Split, and by the narrow coastal plain bordered by the mountains in the north and stretching from the Trogir town, across the Kaštela town (comprising seven Kaštelas) to the Solin town.

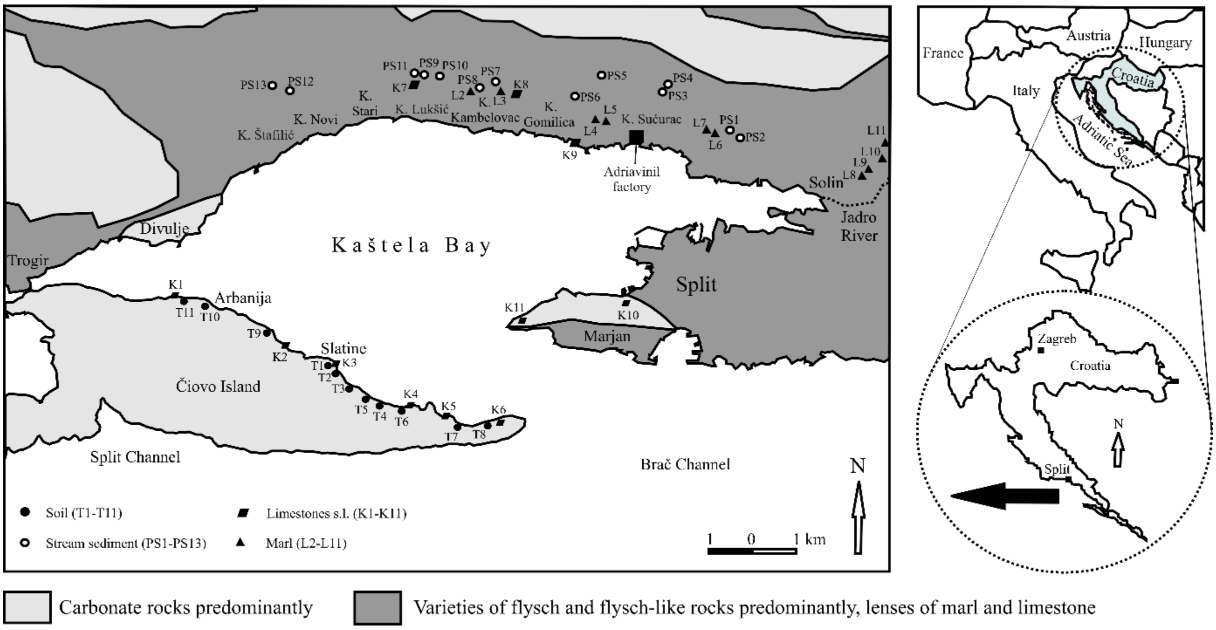

Fig. 1 Location and simplified lithological setting of the Kaštela Bay area with sampling stations of sediments and sedimentary rocks of the coastal area (after Fritz 1994; Marinčić et al. 1971)

The only permanent surface stream inflowing into the Kaštela Bay is the Jadro River in the easternmost part of the Bay. Temporary streams appear on the north coast (coastal plain) in the form of brooks, but they significantly depend on the amount of precipitation causing them to dry up frequently (Lovrenčić Mikelić et al. 2013).

The coastal area is generally built of two types of rocks: i) carbonate rocks, ii) Eocene flysch and flysch-like rocks with lenses of marl and limestone (Fig. 1) (Magaš and Marinčić 1973; Marinčić et al. 1971). Carbonate rocks comprise Cretaceous limestones and limestone dolomites at the Čiovo Island, Eocene foraminiferal limestones at the Marjan hill, and Pleistocene breccias around Divulje consisting of fragments of carbonate sediment bound by bauxitic matrix (Magaš and Marinčić 1973; Marinčić et al. 1971). Flysch and flysch-like rocks are abundant and they are extensively present from the Trogir town to the City of Split. Calcarenites occur as lenses in flysch (Lovrenčić Mikelić et al. 2013). Alluvial deposits are found along the Jadro River, but are not shown in the Fig. 1 due to their small extent. They are a mixture of marls, breccias, and carbonate sediments (Magaš and Marinčić 1973).

Sampling

Sediments and sedimentary rocks of the Kaštela Bay coastal area were collected between 2005 and 2008. In total, 45 samples were collected. Sampling locations and their coordinates are presented in Fig. 1 and Table 1, respectively.

Table 1. Sampling locations of the Kaštela Bay coastal area; Types of samples: K – limestones s.l., L – marl, PS – stream sediment, T – soil

Sample	Sampling location coordinates	Sample	Sampling location coordinates
K1	N 43°30'55.979", E 16°17'45.249"	PS3	N 43°33'24.32", E 16°26'7.881"
K2	N 43°30'17.631", E 16°19'38.935"	PS4	N 43°33'29.907", E 16°26'13.673"
K3	N 43°30'3.656", E 16°20'30.225"	PS5	N 43°33'37.441", E 16°25'5.934"
K4	N 43°29'32.402", E 16°21'46.209"	PS6	N 43°33'21.59", E 16°24'37.264"
K5	N 43°29'24.247", E 16°22'22.772"	PS7	N 43°33'33.125", E 16°23'16.528"
K6	N 43°29'18.434", E 16°23'18.111"	PS8	N 43°33'28.689", E 16°23'0.509"
K7	N 43°33'31.301", E 16°21'53.006"	PS9	N 43°33'38.632", E 16°22'3.784"
K8	N 43°33'23.861", E 16°23'37.893"	PS10	N 43°33'37.678", E 16°22'18.973"
K9	N 43°32'46.815", E 16°24'37.24"	PS11	N 43°33'40.306", E 16°21'52.855"
K10	N 43°30'47.176", E 16°25'32.857"	PS12	N 43°33'27.915", E 16°19'45.588"
K11	N 43°30'32.809", E 16°23'38.475"	PS13	N 43°33'31.982", E 16°19'27.637"
L2	N 43°33'25.208", E 16°22'50.525"	T1	N 43°30'2.469", E 16°20'21.717"
L3	N 43°33'25.345", E 16°23'21.656"	T2	N 43°29'55.953", E 16°20'28.994"
L4	N 43°33'3.578", E 16°24'58.419"	T3	N 43°29'44.989", E 16°20'42.533"
L5	N 43°33'2.414", E 16°25'9.356"	T4	N 43°29'31.498", E 16°21'14.034"
L6	N 43°32'52.516", E 16°27'1.59"	T5	N 43°29'37.584", E 16°20'59.683"
L7	N 43°32'55.461", E 16°26'52.466"	T6	N 43°29'27.886", E 16°21'36.567"
L8	N 43°32'19.461", E 16°29'31.438"	T7	N 43°29'15.628", E 16°22'33.529"
L9	N 43°32'24.521", E 16°29'37.928"	T8	N 43°29'16.491", E 16°23'4.72"
L10	N 43°32'32.813", E 16°29'52.985"	T9	N 43°30'26.87", E 16°19'18.639"
L11	N 43°32'43.834", E 16°29'56.087"	T10	N 43°30'47.91", E 16°18'16.181"
PS1	N 43°32'55.409", E 16°27'16.868"	T11	N 43°30'51.249", E 16°17'53.984"
PS2	N 43°32'49.102", E 16°27'27.326"		

Stream sediments (PS) and soils (T) are both considered as sediments although they have different genesis, which is in accordance with the classification given by Tišljar (1994) where soils are classified as a residual clastic sediment. Sampled consolidated sedimentary rocks are limestones s.l. (K) and marl (L). Limestones s.l. encompass a group of carbonate rocks (or carbonates), i.e. Cretaceous limestones, Eocene calcarenites and Eocene foraminiferal limestones, due to their limestone composition irrespective of the rock genesis.

At each sampling location, 1–2 kg of samples were collected, placed into labelled plastic bags and transported to laboratory. Marls and limestones s.l. were sampled on open outcrops. Stream sediments were sampled in beds of brooks at a depth of 0 – 10 cm. Stream sediments were not collected at the Čiovo Island because there are no surface streams (brooks or rivers) on the island. Instead, surface (0 – 10 cm depth) samples of undisturbed soils were collected at locations where transport of soil to the sea by precipitation water was observed. In such a way, soil transported by precipitation water, is analogous to stream sediments from the north coast of the Bay. They share several common characteristics: i) they are both unconsolidated sediments; ii) they are transported to the Bay by the same medium (water); iii) they are expected to be a significant source of sedimentation material in the Bay (Lovrenčić Mikelić et al. 2013). All soil samples were *terra rossa*, except the T2 sample, which was brown soil. More details on sampling are given in Lovrenčić Mikelić et al. (2013).

Gamma-spectrometric analysis

Sediment samples were first dried at 105 °C overnight to achieve constant mass, then ground in a mill with agate spherules or in an agate mortar, and homogenized. Rock samples were first crushed in a crusher, then dried overnight at 105 °C, and homogenized. After homogenization, all samples were stored in plastic containers of 125 cm^3 volume, closed with lids and weighted. The containers' lids were additionally sealed with a self-adhesive tape and stored for at least four weeks to allow ingrowth of gaseous ^{222}Rn from the ^{238}U radioactive decay chain and to ensure secular equilibrium between ^{226}Ra and its progenies.

Gamma-spectrometric analysis was preformed using HPGe coaxial and InSpector 2000 detectors with 25.3 % and 25.4 % relative efficiencies, respectively. Detectors were coupled with multichannel analysers with 8192 channels (Canberra Industries). Resolution at 1332.5 keV (^{60}Co) was 1.75 keV for the coaxial detector and 1.80 keV for the InSpector 2000. Spectra were collected for 80 000 s and analysed with a Genie 2000 software package (Canberra Industries). All massic activities were recalculated to the same reference date (6th June 2005) due to a relatively short half-life of ^{137}Cs. Energy and efficiency calibrations and quality control were performed as described in Lovrenčić Mikelić et al. (2017).

^{40}K and ^{137}Cs massic activities were determined directly from their characteristic spectrum peaks at 1460.75 keV and 661.66 keV, respectively. ^{226}Ra activity was determined indirectly through ^{214}Pb and ^{214}Bi, assuming secular equilibrium between ^{226}Ra and its progenies. ^{214}Pb activity was determined using peaks at 295.21 keV and 351.92 keV, while for ^{214}Bi activity peaks at 609.31 keV, 1120.28 keV, and 1764.49 keV were used. ^{226}Ra weighted mean activity was then calculated from five activities obtained through ^{214}Pb and ^{214}Bi (Canberra Industries 2006; Saïdou et al. 2008). ^{232}Th activity was calculated as a weighted mean activity from the ^{212}Pb peak at 238.63 keV and ^{228}Ac peaks at 338.32 keV, 911.20 keV, and 968.97 keV. ^{238}U activity was calculated using ^{234}Th activity under the assumption of existing secular equilibrium between the two radionuclides. ^{234}Th peaks at 63.29 keV and 92.6 keV were used to calculate ^{238}U weighted mean activity. Interfering contribution of ^{232}Th gamma-rays to the 63.29 keV peak was subtracted using the ^{228}Ac peak at 338.32 keV (Papachristodoulou et al. 2003). Emission probability of 4.82 % was used for ^{234}Th doublet peak at 92.6 keV in this study. Contribution of ^{228}Ac Kα_1 X-rays was subtracted from the 92.6 keV peak.

Mutlielemental analysis

All samples were analysed for total mass fractions of Al, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, and Pb by energy dispersive X-ray fluorescence (EDXRF) technique using MiniPal 4 spectrometer (PANalytical, Almelo, Netherland). The results of multielemental analyses were previously presented in Lovrenčić Mikelić et al. (2013) and are used here only as an aid for environmental behaviour interpretation of radionuclides and to study the relationships of radionuclides with metals. Therefore, all details regarding sample preparation, measurement, instrument calibration, and quality control for multielemental analysis were given in Lovrenčić Mikelić et al. (2013) and references therein.

Statistical analysis

Statistical analyses were performed with a Statistica 7.0 (StatSoft, Inc.) programme package.

Pearson’s correlation coefficients were calculated for radionuclides and 18 metals in consolidated rocks and sediments separately. Consolidated rocks (K, L) and unconsolidated sediments (PS, T) were analysed separately because of different occurrence of ^{137}Cs in them, i.e. it should be detected in unconsolidated sediments only. Obtained values were statistically significant at $p<0.05$.

Principal component analysis (PCA) was used to determine relationships between radionuclides and between radionuclides and 18 metals. Consolidated rocks and sediments were again analysed separately due to different ^{137}Cs occurrence. Two principal components were extracted and projected on factor-planes.

Factor analysis (FA) was used to determine relationships between different types of studied samples, i.e. radionuclides behaviour in different rocks and sediments. The analysis was first performed on data for all samples to obtain information about radionuclides’ distribution between two main groups of samples. ^{137}Cs was taken into account for all samples in this analysis. In samples where ^{137}Cs massic activity was below minimum detectable activity (MDA), or not present, the MDA was taken as the activity to enable performance of the analysis. Afterwards, the analysis was performed for consolidated rocks and sediments separately, considering ^{137}Cs only in sediments, to gain information about radionuclides’ distribution inside these groups. Factors were extracted by the principal component analysis method. Maximum allowed number of factors was three. Factors were selected based on eigenvalues and scree plots. Whenever possible, only factors with eigenvalues greater than one were retained, but factors lower than one were also retained if they were the second factor or if they further explained the data. Obtained factors were rotated by varimax normalized method and projected on factor-planes.

Results

Radionuclides’ massic activities

Basic statistical parameters of radionuclides’ massic activities in four different types of samples are given in Table 2.

Table 2. Basic statistical parameters of radionuclides’ massic activities in sediments and sedimentary rocks of the Kaštela Bay coastal area; Massic activities are expressed in Bq/kg. K – limestones s.l., L – marl, PS – stream sediment, T – soil, $\bar{x}$ – mean value, SDM – standard deviation of the mean, SD – standard deviation, N – number of samples

Type of sample	Statistical parameter	^{40}K	^{226}Ra	^{232}Th	^{238}U	^{137}Cs
K	$\bar{x}$	14	19	1.0	11	< 0.6
	SDM	5.8	4.5	0.3	4.3	0.1
	SD	19	15	0.9	14	0.43
	N	11	11	11	11	11
	Minimum	0.5	9.4	0.1	3.0	< 0.4
	Maximum	69	60	3.4	53	1.9
	Median	7.2	14	0.8	5.3	0.5
L	$\bar{x}$	215	14	11	13	< 0.8
	SDM	17	1.4	1.0	1.3	0.3
	SD	54	4.3	3.2	4.1	0.8
	N	10	10	10	10	10
	Minimum	148	8.1	8.6	4.6	< 0.1
	Maximum	284	20	17	17	2.6
	Median	194	14	9.9	13	0.4
PS	$\bar{x}$	193	23	17	17	25
	SDM	25	3.1	2.6	1.7	9.6
	SD	89	11	9.4	6.1	34
	N	13	13	13	13	13
	Minimum	46	8.2	4.8	8.5	< 0.8
	Maximum	310	47	36	31	111
	Median	212	21	15	16	5.4
T	$\bar{x}$	463	85	62	37	34
	SDM	42	14	6.1	3.2	7.6
	SD	140	48	20	11	25
	N	11	11	11	11	11
	Minimum	168	28	20	26	7.9
	Maximum	581	198	84	58	87
	Median	518	72	71	31	31

It should be noted that ^{137}Cs massic activities were below minimum detectable activity in consolidated rocks (as they should be because these rocks were lithified before the ^{137}Cs atmospheric fallout occurred).

Correlation analysis

Detailed results concerning metals were presented and discussed earlier in Lovrenčić Mikelić et al. (2013). Results of correlation analyses of radionuclides massic activities and mass fractions of 18 elements in consolidated rocks and in sediments are given in Tables 3 and 4, respectively.

Two main characteristics were observed in Table 3. ^{238}U and ^{226}Ra in consolidated rocks are statistically significantly correlated only one to another with high or very high positive correlation. No statistically significant correlations were determined neither with other radionuclides nor with metals. Contrary to them, ^{40}K and ^{232}Th showed high or very high positive correlations with the majority of metals. Correlations with Ca were negative.

Correlations between radionuclides and 18 elements in sediments (Table 4) showed a different pattern. Four natural radionuclides (^{40}K, ^{226}Ra, ^{232}Th, ^{238}U) were all significantly positively correlated one to another with almost all correlations being high or very high. The only exception was a correlation between ^{226}Ra and ^{238}U, which was lower and was opposed to their correlation in consolidated rocks where it was the only statistically significant correlation of these radionuclides and it was much higher. All natural radionuclides showed no statistically significant correlations with Cu, Zn, and Pb. Correlations of natural radionuclides with other elements (Al, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Ga, Rb, Y, As) were statistically significant and were mostly high or very high positive correlations. The only statistically significant negative correlations between natural radionuclides and 18 elements were correlations with Ca and Sr. It was also clearly determined that ^{137}Cs was not statistically significantly correlated to any of the radionuclides or 18 elements.

Table 3. Correlation coefficients for massic activities of natural radionuclides and mass fractions of 18 elements in consolidated rocks (carbonate rocks, flysch, and flysch-like rocks) of the Kaštela Bay coastal area; Marked correlations are significant at $p<0.05$; N=21; 0.00 to ± 0.20: no or slightly correlated, ± 0.20 to ± 0.40: weak correlation, ± 0.40 to ± 0.70: real significant correlation, ± 0.70 to ± 1.00: high or very high correlation

	^{40}K	**^{226}Ra**	**^{232}Th**	**^{238}U**	**Al**	**K**	**Ca**	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**	**Ga**	**Rb**	**Sr**	**Y**	**Pb**	**As**
^{40}K	1.00																					
^{226}Ra	-0.18	1.00																				
^{232}Th	**0.99**	-0.16	1.00																			
^{238}U	0.13	**0.92**	0.14	1.00																		
Al	**0.96**	-0.20	**0.95**	0.12	1.00																	
K	**0.98**	-0.24	**0.96**	0.08	**0.96**	1.00																
Ca	**-0.98**	0.21	**-0.97**	-0.10	**-0.94**	**-0.95**	1.00															
Ti	**0.98**	-0.17	**0.98**	0.13	**0.96**	**0.96**	**-0.96**	1.00														
V	**0.97**	-0.10	**0.96**	0.21	**0.94**	**0.94**	**-0.95**	**0.97**	1.00													
Cr	**0.86**	-0.19	**0.86**	0.13	**0.88**	**0.87**	**-0.86**	**0.90**	**0.87**	1.00												
Mn	**0.83**	-0.22	**0.80**	0.10	**0.80**	**0.85**	**-0.87**	**0.85**	**0.84**	**0.83**	1.00											
Fe	**0.98**	-0.20	**0.97**	0.11	**0.96**	**0.97**	**-0.96**	**0.99**	**0.97**	**0.89**	**0.88**	1.00										
Co	**0.49**	-0.06	**0.48**	0.17	**0.47**	**0.50**	**-0.48**	**0.48**	**0.52**	**0.76**	**0.52**	**0.50**	1.00									
Ni	**0.87**	-0.24	**0.84**	0.06	**0.88**	**0.87**	**-0.90**	**0.92**	**0.86**	**0.87**	**0.88**	**0.90**	**0.44**	1.00								
Cu	**0.85**	-0.26	**0.83**	0.05	**0.85**	**0.85**	**-0.87**	**0.89**	**0.86**	**0.88**	**0.94**	**0.90**	**0.46**	**0.93**	1.00							
Zn	**0.81**	-0.20	**0.79**	0.09	**0.85**	**0.82**	**-0.83**	**0.89**	**0.86**	**0.87**	**0.89**	**0.88**	**0.45**	**0.94**	**0.96**	1.00						
Ga	**0.94**	-0.17	**0.96**	0.10	**0.92**	**0.90**	**-0.91**	**0.92**	**0.92**	**0.79**	**0.71**	**0.93**	**0.45**	**0.73**	**0.74**	**0.71**	1.00					
Rb	**0.99**	-0.17	**0.99**	0.13	**0.94**	**0.96**	**-0.96**	**0.97**	**0.96**	**0.83**	**0.80**	**0.97**	**0.48**	**0.83**	**0.81**	**0.77**	**0.96**	1.00				
Sr	0.34	-0.32	0.30	-0.12	0.34	0.38	-0.40	0.32	0.38	**0.54**	**0.57**	0.37	**0.68**	0.42	**0.45**	**0.45**	0.25	0.32	1.00			
Y	-0.24	0.27	-0.21	0.16	-0.23	-0.37	0.24	-0.21	-0.12	-0.15	-0.28	-0.23	0.04	-0.26	-0.24	-0.13	-0.14	-0.21	0.04	1.00		
Pb	0.35	-0.11	0.34	0.04	0.37	0.36	-0.39	0.41	**0.47**	0.37	**0.48**	0.41	0.20	**0.45**	**0.54**	**0.64**	0.27	0.35	0.26	-0.05	1.00	
As	0.25	-0.11	0.24	0.01	0.38	0.29	-0.31	0.41	0.35	**0.50**	**0.48**	0.38	0.17	**0.59**	**0.62**	**0.75**	0.14	0.19	0.22	-0.04	**0.69**	1.00

Table 4. Correlation coefficients for massic activities of radionuclides and mass fractions of 18 elements in sediments (stream sediments and soils) of the Kaštela Bay coastal area; Marked correlations are significant at $p < 0.05$; N = 24; 0.00 to ± 0.20: no or slightly correlated, ± 0.20 to ± 0.40: weak correlation, ± 0.40 to ± 0.70: real significant correlation, ± 0.70 to ± 1.00: high or very high correlation

	^{40}K	^{137}Cs	^{226}Ra	^{232}Th	^{238}U	Al	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Pb	As
^{40}K	1.00																						
^{137}Cs	0.26	1.00																					
^{226}Ra	**0.73**	0.26	1.00																				
^{232}Th	**0.95**	0.26	**0.85**	1.00																			
^{238}U	**0.82**	0.22	**0.57**	**0.86**	1.00																		
Al	**0.95**	0.25	**0.80**	**0.94**	**0.77**	1.00																	
K	**0.65**	0.29	**0.55**	**0.59**	**0.48**	**0.68**	1.00																
Ca	**-0.95**	-0.35	**-0.79**	**-0.96**	**-0.80**	**-0.95**	**-0.64**	1.00															
Ti	**0.95**	0.24	**0.86**	**0.98**	**0.80**	**0.97**	**0.60**	**-0.96**	1.00														
V	**0.85**	0.23	**0.95**	**0.93**	**0.68**	**0.92**	**0.63**	**-0.89**	**0.95**	1.00													
Cr	**0.91**	0.27	**0.86**	**0.93**	**0.74**	**0.94**	**0.61**	**-0.95**	**0.97**	**0.93**	1.00												
Mn	**0.94**	0.17	**0.75**	**0.96**	**0.86**	**0.93**	**0.68**	**-0.93**	**0.95**	**0.87**	**0.87**	1.00											
Fe	**0.94**	0.24	**0.87**	**0.98**	**0.80**	**0.97**	**0.62**	**-0.96**	**1.00**	**0.96**	**0.95**	**0.95**	1.00	1.00									
Co	**0.94**	0.21	**0.87**	**0.98**	**0.81**	**0.96**	**0.60**	**-0.95**	**1.00**	**0.96**	**0.95**	**0.95**	**1.00**	1.00									
Ni	**0.92**	0.39	**0.87**	**0.92**	**0.70**	**0.94**	**0.72**	**-0.93**	**0.94**	**0.94**	**0.93**	**0.87**	**0.95**	**0.93**	1.00								
Cu	-0.02	-0.15	0.03	0.06	0.33	-0.10	-0.02	0.11	-0.02	-0.01	-0.07	0.09	-0.00	0.03	-0.11	1.00							
Zn	0.23	-0.16	0.25	0.29	0.38	0.20	0.14	-0.21	0.28	0.24	0.20	0.30	0.27	0.28	0.11	**0.52**	1.00						
Ga	**0.96**	0.28	**0.84**	**0.98**	**0.80**	**0.96**	**0.66**	**-0.96**	**0.98**	**0.95**	**0.94**	**0.95**	**0.99**	**0.98**	**0.95**	-0.04	0.19	1.00					
Rb	**0.98**	0.30	**0.79**	**0.98**	**0.86**	**0.95**	**0.64**	**-0.97**	**0.97**	**0.89**	**0.91**	**0.97**	**0.97**	**0.97**	**0.93**	0.03	0.24	**0.98**	1.00				
Sr	**-0.48**	-0.21	**-0.53**	**-0.54**	-0.33	**-0.57**	**-0.49**	**0.58**	**-0.58**	**-0.58**	**-0.58**	**-0.51**	**-0.57**	**-0.55**	**-0.52**	0.19	-0.27	**-0.56**	**-0.51**	1.00			
Y	**0.95**	0.26	**0.88**	**0.98**	**0.81**	**0.96**	**0.64**	**-0.95**	**0.99**	**0.95**	**0.96**	**0.95**	**0.98**	**0.98**	**0.94**	0.05	0.26	**0.97**	**0.97**	**-0.56**	1.00		
Pb	0.20	-0.19	0.29	0.25	0.21	0.18	0.11	-0.24	0.24	0.26	0.29	0.20	0.25	0.24	0.18	0.07	**0.53**	0.23	0.20	-0.34	0.20	1.00	
As	**0.81**	0.13	**0.90**	**0.90**	**0.71**	**0.84**	**0.50**	**-0.85**	**0.90**	**0.92**	**0.90**	**0.82**	**0.91**	**0.90**	**0.85**	0.05	0.39	**0.89**	**0.84**	**-0.58**	**0.88**	**0.57**	1.00

Principal component analysis

Results of the PCA showing relationships between radionuclides in consolidated rocks and sediments are given in Fig. 2.

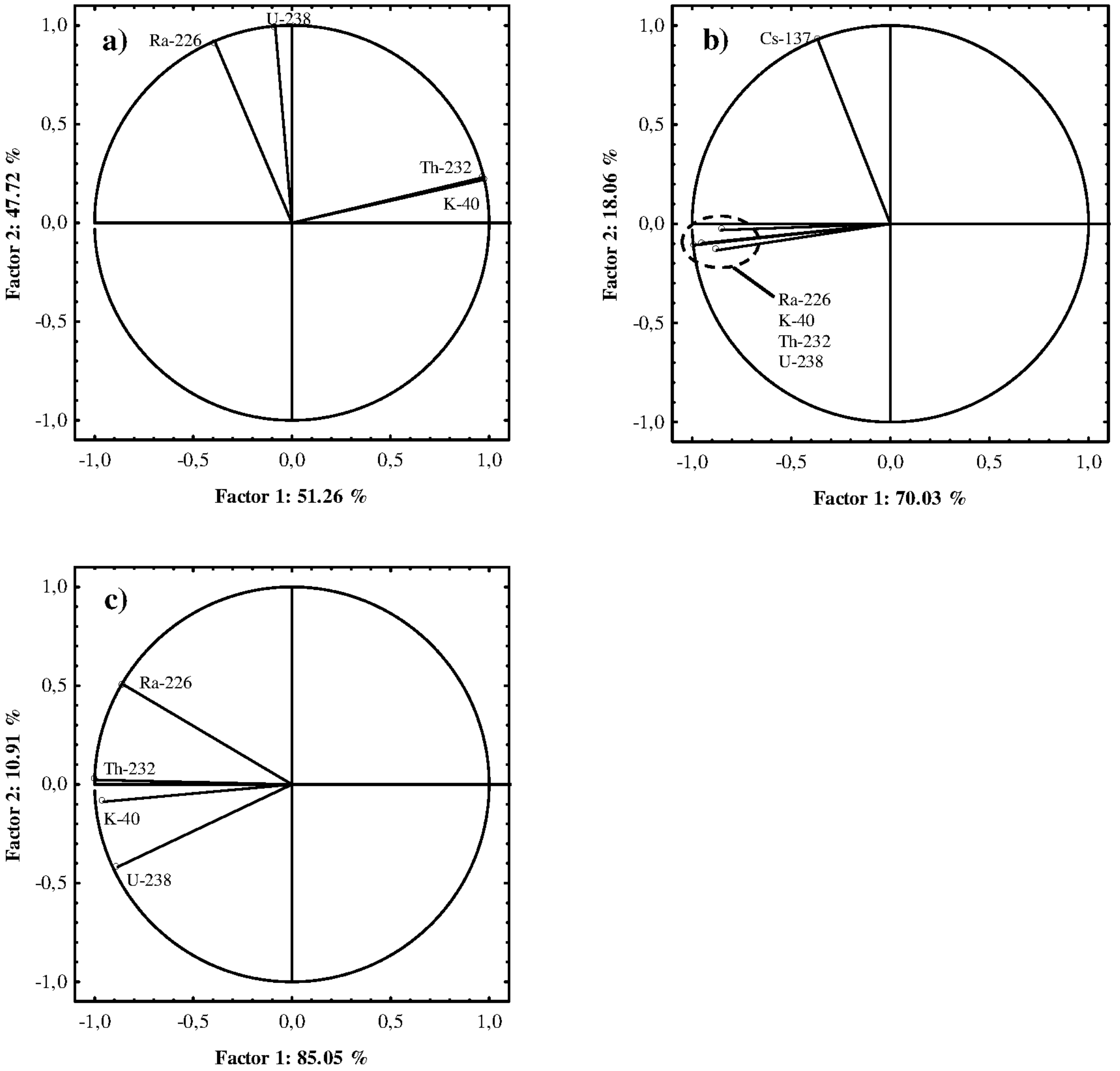

Fig. 2 Relationships between radionuclides in sedimentary rocks and sediments of the Kaštela Bay coastal area obtained by principal component analysis: a) In consolidated rocks (carbonate rocks, flysch, and flysch-like rocks) with ^{137}Cs excluded from analysis; b) In sediments (stream sediments and soils) with ^{137}Cs included in analysis; c) In sediments (stream sediments and soils) with ^{137}Cs excluded from analysis

^{40}K and ^{232}Th in consolidated rocks were grouped very closely, while ^{226}Ra and ^{238}U were in another group, but not so closely grouped (Fig. 2a). Relationships in sediments showed a significant influence of ^{137}Cs (Fig. 2b). When including ^{137}Cs in the analysis, all natural radionuclides were grouped closely and ^{137}Cs was clearly separated from other radionuclides. However, analysis without ^{137}Cs (Fig. 2c) showed some similarities to relationships in consolidated rocks. ^{40}K and ^{232}Th were grouped very closely, as in the consolidated rocks, but the second group with ^{226}Ra and ^{238}U was not so clearly defined.

Fig. 3 presents relationships between radionuclides and 18 elements in consolidated rocks and sediments. Ca and Sr represent carbonate component of the sediment, while the opposite group with the majority of metals and natural radionuclides represent silicate component and elements bound to it (Lovrenčić Mikelić et al. 2013). ^{226}Ra and ^{238}U were again separated in a single group in consolidated rocks, while ^{40}K and ^{232}Th were grouped with the majority of metals (Fig. 3a). In sediments, only ^{137}Cs was separated from other radionuclides and metals, while all natural radionuclides were grouped with the majority of metals (Fig. 3b).

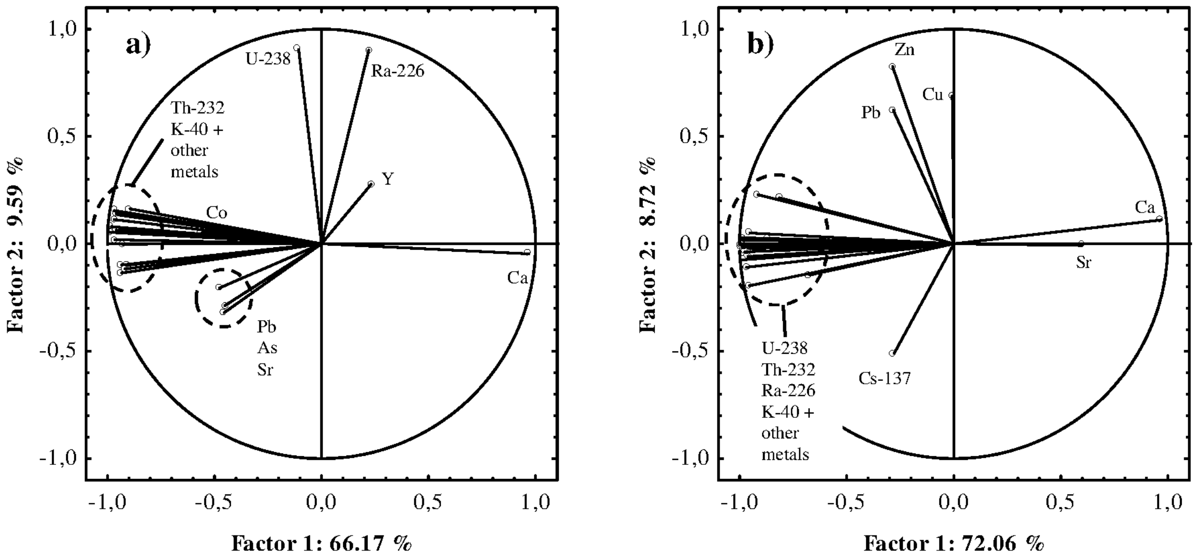

Fig. 3 Relationships between radionuclides and 18 elements in sedimentary rocks and sediments of the Kaštela Bay coastal area obtained by principal component analysis: a) In consolidated rocks (carbonate rocks, flysch, and flysch-like rocks) with ^{137}Cs excluded from analysis; b) In sediments (stream sediments and soils) with ^{137}Cs included in analysis

Factor analysis

Results of the FA are presented in Figs. 4–6. Analysing all studied types of samples together (Fig. 4), two factors were extracted. Factor 1 explained all natural radionuclides, while factor 2 explained only ^{137}Cs. The majority of samples were within the population 1. Differentiation between populations 1 and 2 is based on natural radionuclides’ massic activities. Their activities are generally lower in population 1 (Table 2). Population 3 is characterised by increased ^{137}Cs massic activities in stream sediments and soils (Table 2).

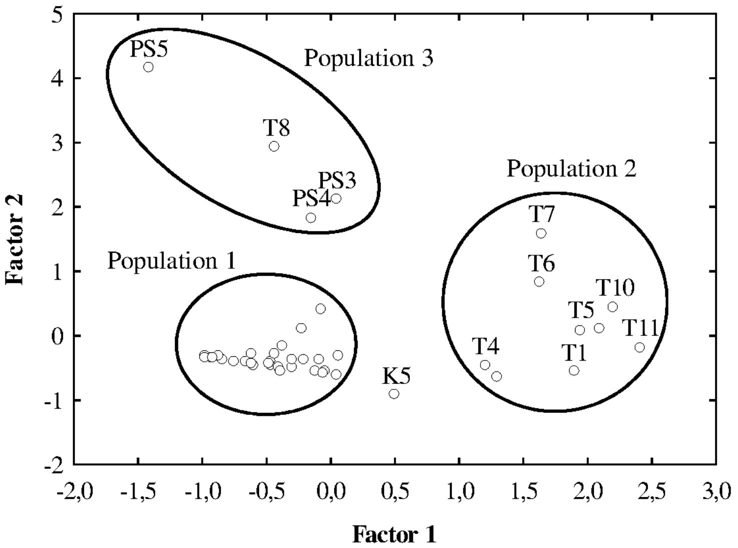

Fig. 4 Relationships between all sediments and sedimentary rocks of the Kaštela Bay coastal area obtained by factor analysis of radionuclides' massic activities; K – limestones s.l., L – marl, PS – stream sediment, T – soil; ^{137}Cs included in analysis

FA of natural radionuclides' massic activities in consolidated rocks also extracted two factors. Factor 1 explained ^{40}K and ^{232}Th and factor 2 explained ^{226}Ra and ^{238}U (Fig. 5, Table 2). Two populations were observed in relation to factor 1. Population 1 is very homogenous and comprises carbonates. All L samples are comprised by the population 2, which is, contrary to the population 1, heterogeneous and shows higher massic activities of ^{40}K and ^{232}Th (Table 2).

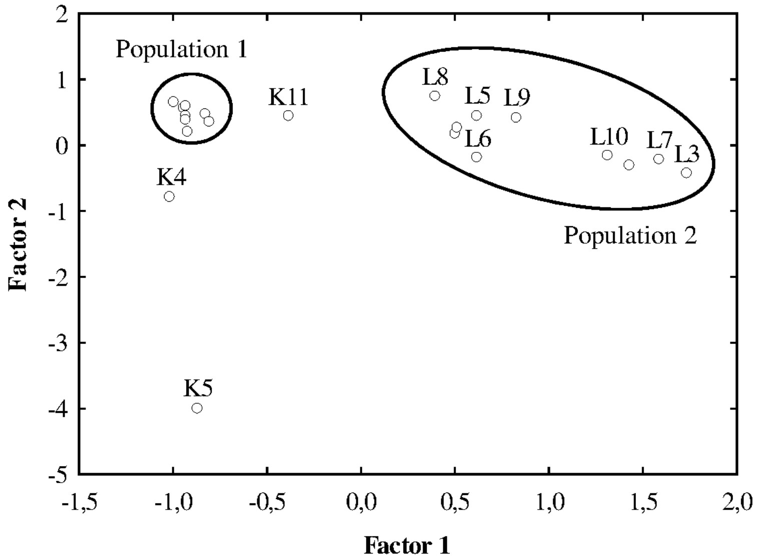

Fig. 5 Relationships between consolidated rocks (carbonate rocks, flysch, and flysch-like rocks) of the Kaštela Bay coastal area obtained by factor analysis of radionuclides' massic activities; K – limestones s.l., L – marl; ^{137}Cs excluded from analysis

FA of all studied radionuclides in sediments extracted three factors. Factor 1 explained ^{40}K, ^{232}Th, and ^{238}U, factor 2 explained ^{137}Cs and factor 3 explained ^{226}Ra (Fig. 6, Table 2). Two populations were defined in relation to factor 1 (Fig. 6a).

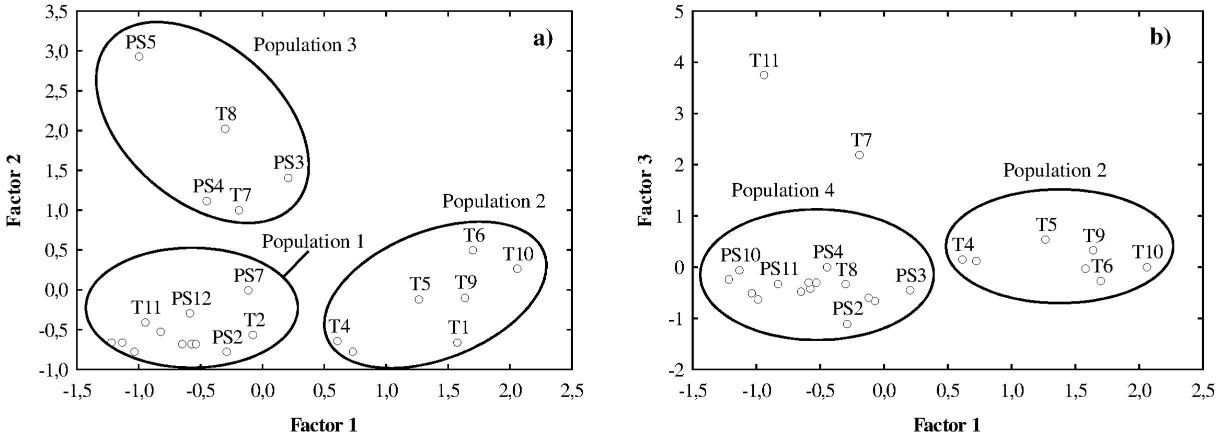

Fig. 6 Relationships between sediments (stream sediments and soils) of the Kaštela Bay coastal area obtained by factor analysis of radionuclides' massic activities; PS – stream sediment, T – soil; ^{137}Cs included in analysis: a) Relationships defined by factor 1 (^{40}K, ^{232}Th, ^{238}U) and factor 2 (^{137}Cs); b) Relationships defined by factor 1 (^{40}K, ^{232}Th, ^{238}U) and factor 3 (^{226}Ra)

Population 1 is characterised by lower ^{40}K, ^{232}Th, and ^{238}U activities (Table 2) compared to population 2 and it is relatively homogeneous. Population 3 reflects increased ^{137}Cs activities in stream sediments and soils (Table 2). Projection on the factor-plane regarding factor 1 and factor 3 did not reveal a new population, although a population 4 was shown (Fig. 6b). In fact, population 4 is a combination of populations 1 and 3, which are characterised by low ^{40}K, ^{232}Th, and ^{238}U activities (Table 2). Factor 3 revealed outliers with respect to increased ^{226}Ra massic activities (samples T7 and T11).

Discussion

Radionuclides' relationships and behaviour in consolidated rocks and influencing factors

Positive correlations of ^{40}K and ^{232}Th with almost all studied elements and negative correlations with Ca in consolidated rocks (Table 3) indicate that they are associated with elements representing silicate component of the rocks and that they are bound to alumosilicates, which include clay minerals. Potassium is usually found in silicates and alumosilicates such as feldspars, feldspathoids, micas, clays and zeolites (Anke 2004; IAEA 2003; Rankama and Sahama 1968). Silicate minerals are the main bearers of potassium in rocks. Micas, clays and feldspars were determined in various abundances in the Kaštela Bay coastal samples (Lovrenčić Mikelić et al. 2013). Correlation between ^{40}K and ^{232}Th suggests their same preferences regarding binding to particulate matter. They are both preferably bound to terrestrial particles, especially to fine grained fraction such as clay and silt (Cocco et al. 1972; Gascoyne 1982; Navas et al. 2002; Powell et al. 2007; Rankama and Sahama 1968; Sakaguchi et al. 2006; Seddeek et al. 2005; Shetty et al. 2006; van der Graaf et al. 2007). Preferable binding to the same type or size of particles was supported by the PCA (Fig. 2a) where ^{40}K and ^{232}Th were projected in almost the same point on the factor-plane. It also implies that the same processes affect both radionuclides equally and/or that they share the same origin (source rock or soil). The association of ^{40}K and ^{232}Th with alumosilicates was also confirmed by the PCA when metals were analysed with radionuclides (Fig. 3a). ^{40}K and ^{232}Th were found in a large group of elements comprising K, Al, and Ti among other elements, which are typical for alumosilicates. On the other side of the factor-plane, Ca was separated, which shows a clear distinction between silicate and carbonate component of rocks and related silicate and carbonate bound elements/radionuclides.

Absence of statistically significant correlations of ^{226}Ra and ^{238}U with the studied elements in consolidated rocks (Table 3) as well as their lack of association with the PCA factor representing the main mineral rock components (Figs. 2a and 3a) imply that ^{226}Ra and ^{238}U are not preferably bound to any of the rock components (silicate or carbonate minerals). They are influenced by some parameter(s) other than the mineral composition, represented as factor 2 (Figs. 2a and 3a). It is assumed that those parameters might be the chemical weathering processes or presence of other particulate matter such as organic matter. However, if organic matter would be the main influential parameter, it would be expected to see its influence on ^{40}K and ^{232}Th as well, but this was not observed. It is suggested that chemical weathering processes would have greater influence on ^{226}Ra and ^{238}U than on ^{40}K and ^{232}Th, due to strong binding of ^{40}K and ^{232}Th to minerals and particulate matter and due to higher mobility of ^{226}Ra and ^{238}U, especially in carbonate rocks (Cowart and Burnett 1994; Dowdall and O'Dea 1999; von Gunten et al. 1996). Their mobility may be enhanced by dissolution of limestones facilitated by rainwater circulation (Orescanin et al. 2005). A common parameter influencing both ^{226}Ra and ^{238}U was also suggested by their high positive mutual correlation (Table 3).

Radionuclides' relationships and behaviour in sediments and influencing factors

Differently from consolidated rocks, all four natural radionuclides showed the same or very similar behaviour in sediments (stream sediments and soils). They presented positive correlations with the majority of other elements (Table 4) and they were very closely grouped by the PCA with each other (Fig. 2b) and with alumosilicate bound elements (Fig. 3b). They were also strongly influenced by the PCA factor 1 representing silicate/carbonate rock component (Figs. 2b and 3b). All this points out to their preferred binding to alumosilicates as a predominant parameter influencing their distribution in soils and stream sediments. It also implies a common origin of natural radionuclides and the majority of studied metals. Organic matter might also be encompassed by factor 1, together with mineral composition, considering that all four natural radionuclides showed strong dependency regarding factor 1. If the only influential parameter would be the mineral composition, it would be expected to observe a situation similar to the one in consolidated rocks (Figs. 2a and 3a), where ^{226}Ra and ^{238}U were not dependent on mineral composition. Soils and sediments contain significantly more organic matter than limestones and marls and, therefore, it is expected that more ^{226}Ra and ^{238}U will be bound to organic matter, along with ^{40}K and ^{232}Th. It is known that ^{226}Ra is adsorbed to clays, organic matter and Fe oxides in soils and sediments, with cation exchange being an important mechanism (Dowdall and O'Dea 1999; Gascoyne 1982; IAEA 1986). Uranium is also adsorbed to organic matter and Fe oxides (Cowart and Burnett 1994; Dowdall and O'Dea 1999;

Sakaguchi et al. 2006; Silva et al. 2006). However, Fig. 2c reveals that ^{226}Ra and ^{238}U were differentiated from ^{40}K and ^{232}Th and from each other. Differentiation between ^{226}Ra and ^{238}U was more pronounced in sediments than in consolidated rocks. On the contrary, ^{40}K and ^{232}Th were still close together on the factor-plane and not influenced by the parameter represented by factor 2. This suggests existence of an additional parameter influencing only ^{226}Ra and ^{238}U, but not ^{40}K and ^{232}Th distribution. Since ^{226}Ra and ^{238}U showed opposite behaviours on the factor-plane (Fig. 2c) and only a real significant positive correlation (Table 4), the additional parameter could be a preferential leaching of ^{238}U from soils and stream sediments considering that oxidizing conditions significantly increase uranium mobility. Uranium mobility is especially facilitated in soils containing calcite by its chemical weathering, releasing uranium as stable and soluble carbonate complexes (von Gunten et al. 1996). The same principle can be applied to stream sediments containing calcite. It also points out to negligible leaching influence on ^{40}K and ^{232}Th, which is in accordance to their preferred strong binding to particulate matter.

Another distinguishable group of elements in Fig. 3b are Pb, Zn, and Cu. They were separated in one group as possibly anthropogenic or characteristic of specific mineralogical assemblages of lithological members and were discussed in the earlier study (Lovrenčić Mikelić et al. 2013). Naturally increased mass fractions of Pb, Zn, and Cu were earlier found in *terra rossa* soils developed on the carbonate bedrock, as is the case in the Kaštela Bay (Feng 2011; Gurhan Yalcin and Ilhan 2008; Miko et al. 2003). These metals may also have been introduced into the Kaštela Bay or in sediments and soils of the coastal area via agricultural and urban runoff (Ujević et al. 2000).

The only radionuclide showing significantly different characteristics in sediments was ^{137}Cs (Figs. 2b and 3b, Table 4). This is a consequence of its anthropogenic origin and a different mode of introduction (atmospheric fallout) into soils and stream sediments. ^{137}Cs shows some tendency to bind to alumosilicates, but less pronounced than that of other radionuclides (Figs. 2b and 3b). Therefore, ^{137}Cs distribution in soils and stream sediments is primarily dependant on its global anthropogenic origin and atmospheric fallout and not on its preferred binding to any group of minerals or particles. Atmospheric fallout and deposition of radionuclides from air are influenced by the precipitation pattern during the fallout period (Pálsson et al. 2006). This is especially important in the case of Chernobyl accident because of the short duration of radionuclides' release event into the atmosphere. This largely contributed to inhomogeneous ^{137}Cs distribution in soils and sediments (Table 2). ^{137}Cs was also separated from Pb, Zn, and Cu, which were also partly of anthropogenic origin, but were introduced into sediments from different sources and in a different manner compared to ^{137}Cs. Pb, Zn, and Cu were introduced into sediments via surface runoff or wet and dry deposition following their emission into the air (Orescanin et al. 2005; Ujević et al. 2000). Source of ^{137}Cs in the Kaštela Bay area is global (nuclear tests and Chernobyl accident), while anthropogenic sources of Pb, Zn, and Cu are local agricultural and industrial activities.

Differentiation of consolidated rocks and sediments in relation to radionuclides

Different types of samples are primarily differentiated based on the content of carbonate and alumosilicate minerals and of organic matter (populations 1 and 2) (Fig. 4), i.e. differentiation depends on geological background and natural variability of radionuclides' massic activities in carbonate and mixed carbonate/alumosilicate samples. Population 1 comprises mostly samples with higher content of carbonate component. Most of the studied soils were separated in population 2 because they have significantly higher content of alumosilicate minerals and organic matter and higher natural radionuclides' activities. It is observed that soils were more heterogeneous than other sample types regarding natural radionuclides due to differentiation during paedogenesis process. Stream sediments were more similar to the source carbonate rocks and marls than soils in terms of radionuclides' activities and more heterogeneous regarding ^{137}Cs distribution. The same was shown earlier for metals in these rocks and sediments (Lovrenčić Mikelić et al. 2013). Increased ^{137}Cs activities are dominant parameter influencing some sediment samples (population 3) in which anthropogenic influence is the most pronounced.

The main differentiating parameter between limestones s.l. and marls (Fig. 5) are ^{40}K and ^{232}Th massic activities or alumosilicate minerals' content. Marls were found in a separate population because they consist of clay and carbonate minerals while other studied rocks are formed of carbonate minerals predominantly. Differentiation between carbonate rocks and marls reflects the natural variability of ^{40}K and ^{232}Th massic activities in these rocks.

Soils and stream sediments are clearly differentiated regarding ^{40}K, ^{232}Th, and ^{238}U activities, where soils generally have higher activities (factor 1) (Fig. 6a). Week differentiation of soils regarding ^{226}Ra (factor 3) (Fig. 6b) may indicate that some process influences only ^{226}Ra distribution and possibly ^{238}U distribution, but it is not possible to determine it reliably based on the available data. Natural variations of ^{40}K, ^{232}Th, ^{226}Ra, and ^{238}U massic activities in stream sediments and soils generally reflect carbonate and alumosilicate components of sediments, while ^{137}Cs distribution reflects its anthropogenic origin and atmospheric fallout input mode.

Conclusions

^{40}K and ^{232}Th in consolidated rocks presented preferential binding to alumosilicates, while ^{226}Ra and ^{238}U were not preferably bound to any of the main mineral components (silicate or carbonate). Unlike in consolidated rocks, all four natural radionuclides showed preferential binding to alumosilicates in stream sediments and soils. Differentiation between ^{226}Ra and ^{238}U was more pronounced in stream sediments and soils than in consolidated rocks. ^{137}Cs relationships in sediments differ from other studied radionuclides because the main influencing factors are its source and introduction manner into sediments. Its anthropogenic origin is strongly distinguishable. It was established that stream sediments were more similar to source rocks (limestones s.l. and marl) than soils in terms of ^{40}K, ^{226}Ra, ^{232}Th, and ^{238}U massic activities. The greatest heterogeneity of natural radionuclides' distribution was observed in soils, while for ^{137}Cs, it was in stream sediments.

The collected data and findings of this study could be a useful tool to support the authorities in decision-making and the researchers in future studies of karstic areas, taking the observed differences in radionuclides' behaviour in the same or different rocks and sediments into account. The applied statistical approach could also be applied to environments other than karstic.

Declarations

Ethics approval and consent to participate: Not applicable.

Consent for publication: Not applicable.

Availability of data and materials: The datasets used and analysed during the current study are available from the corresponding author on reasonable request.

Competing interests: The authors declare that they have no competing interests.

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Authors’ contributions: ILM – Conceptualization, methodology, sampling, data collection and analysis, interpretation of data, preparation and writing of the article; VO – Data analysis, interpretation of data; DB – Conceptualization, methodology, sampling. All authors read and approved the final manuscript.

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