

# Distribution and origin of major, minor, and trace elements in sediments and sedimentary rocks of the Kaštela Bay (Croatia) coastal area

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## Highlights

- Three groups of elements distinguished according to preferred mineral component
- Three populations differentiated according to the type of sample and composition
- Elevated mass fractions of Cu, Zn, and Pb reflect possible anthropogenic influence
- Elevated Ni, Cr, and Zn in limestones possibly influenced by the Inner Dinaric area
- Elevated Ni and Zn in marls possibly influenced by the Inner Dinaric area

## Abstract

Mass fractions of Al, K, Ca, Fe, Ti, Mn, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Pb, and As were determined in the Cretaceous limestones, foraminiferal limestones, calcarenites, marls, stream sediments, and soils of the Kaštela Bay coastal area. Relationships between 18 studied elements and between the researched sediments and sedimentary rocks were established. The highest mass fractions of Ca and Sr were found in the limestones and calcarenites, while the highest contents of other elements were determined in marls, stream sediments, and soils. Possible influence of the heavy minerals assemblage originating from basic and ultrabasic rocks of the Dinaric area was reflected in elevated Ni, Cr, and Zn contents in limestones and elevated Ni and Zn contents in marls. Naturally higher mass fractions of Ti, Mn, V, Cr, Ni, Cu, Zn, Pb, and As were found in the *terra rossa* soils. Three groups of elements were distinguished: (1) carbonates bound elements; (2) elements reflecting possible anthropogenic influence or the specific mineralogical assemblages; (3) aluminosilicates bound elements. It was suggested that Sr was only partly bound to CaCO<sub>3</sub> and that Cu, Zn, and Pb were not primarily bound to any of the considered group of minerals. Three populations were differentiated according to their elemental composition and type of the sample: (1) samples with naturally higher mass fractions of Ca and Sr and lower mass fractions of other elements; (2) samples with naturally lower Ca and Sr mass fractions and higher mass fractions of other elements; (3) samples with elevated mass fractions of Cu, Zn, and/or Pb, reflecting possible anthropogenic influence.

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## **1. Introduction**

Kaštela Bay coastal area comprises the Split city and Solin, Kaštela, and Trogir towns which, during the time, merged into a single urban agglomeration, the largest on the Croatian coast. Since the 1950s this area was intensively industrialized and urbanized and the number of inhabitants multiplied very quickly, which resulted in a very high population density of the area. This can be illustrated with the data from the 2001 when 257 000 inhabitants lived in this area (Margeta, 2002). It was 5.8% of the total number of the Croatian population while the Kaštela Bay coastal area represented less than 2% of the territory of Croatia. Industrial as well as agricultural activities are intensive in this area. The industry is concentrated in the north-eastern part between the Solin and Kaštela towns and on the north-eastern coast of the Split peninsula. The main industrial facilities are former chemical factory "Adriavinil" (also called "Jugovinil" and "Inavinil"), cement-works, ironworks, shipyard, and electroplating facility. Agriculture is developed in the west part of the Bay area where the high capacity greenhouses were built. The airport is also situated in the west part of the Bay. As a consequence of the numerous human activities through decades and inadequate environmental protection, the Kaštela Bay became severely polluted (Margeta, 2002).

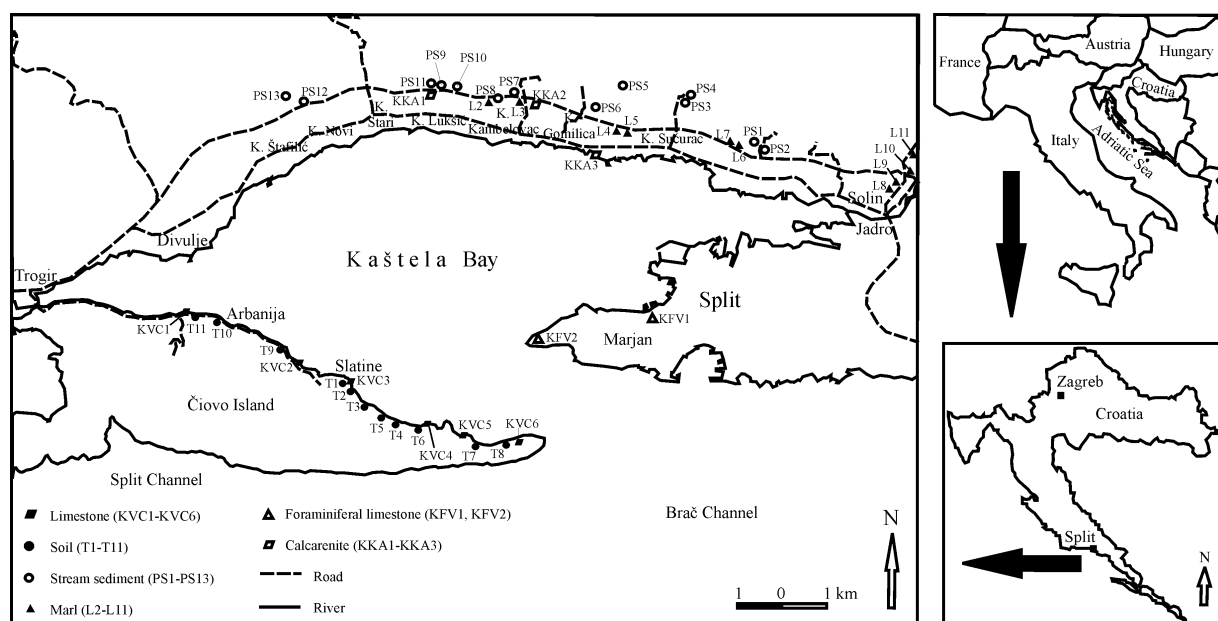
Simultaneously with the industrialization and urbanization of the area and the environment degradation, research interest for the area increased and various research studies concerning the Bay sediment, water or marine organisms were conducted (Barić et al., 1992; Bogner, 1996; Bogner et al., 1997, 1998, 1998a; Kljaković-Gašpić et al., 2006; Kwokal et al., 2002; Kwokal and Branica, 2000; Marasović et al., 2005; Mikac et al., 2006; Milun et al., 2004, 2006; Odžak et al., 2000, 2001; Orescanin et al., 2005; Tudor, 1993; Tudor et al., 1991; Ujević et al., 1998, 2000). However, although the Bay itself was very intensively researched, there were not many studies of the coastal area and the existing data are limited to only few most common metals (Cr, Ni, Cu, Zn, and Pb) of potentially anthropogenic origin in limestones and marl (Bogner, 1996; Bogner et al., 1998). As well as coastal marine sediments, coastal terrestrial sediments also reflect the condition of the environment including anthropogenic influence and the influence of the lithological members. Sediments and sedimentary rocks of the coastal area are expected to represent an important source material for sedimentation in the Kaštela Bay. Therefore, composition and condition of the marine sediment directly depends on the composition and the sedimentation pathways of the terrigenous material originating from terrestrial sediments and rocks.

Various sediments and sedimentary rocks, the most abundant in the Kaštela Bay surrounding area, representing different types of samples/matrices were sampled around the Kaštela Bay in order to determine which of the researched sample types will be the most probable source of the studied elements for sedimentation in the Bay, i.e. which elements are expected to originate from the respective sediments and rocks. The aim of this study was to determine relationships between the researched elements as well as between the researched sediments and rocks in terms of distribution of elements between different types of studied samples, and to establish the condition of the sediments in relation to the anthropogenic influence. Therefore, multielemental characterization of different sediments (soils and stream

sediments) and sedimentary rocks (three types of limestones and marl) of the Kaštela Bay coastal area was performed, selected samples were subjected to the phase analysis, and the results were statistically analysed. This study, together with the data for marine sediments of the Bay, will later enable the assessment of the influence of the source material on the sedimentation in the Kaštela Bay.

## 2. Study area

Kaštela Bay is situated on the east coast of the central Adriatic Sea close to the city of Split (Fig. 1). It is bordered by the narrow coastal plain in the north, Čiovo Island in the south-west and by the Split peninsula in the south-east. North from the coastal plain the mountains of the hinterland continue.

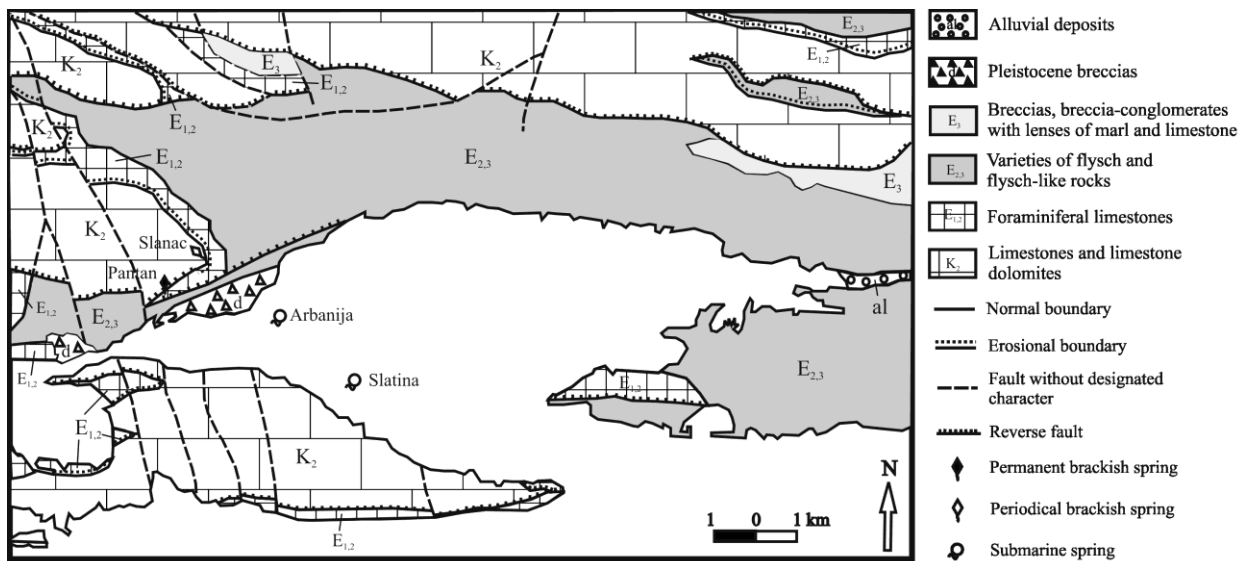


**Figure 1.** Location of the Kaštela Bay and the sampling stations of sediments and sedimentary rocks of the coastal area

Kaštela Bay and its wider area are a part of the big Cretaceous-Tertiary sedimentary basin of the Outer Dinarides. The researched area was a part of the Adriatic Carbonate Platform during the Cretaceous and was not characterized with a basinal sedimentation s.s. (Korbar, 2009; Vlahović et al., 2005). However, until the end of Cretaceous general emersion of the Platform and its final disintegration took place. The main characteristics of this basin are the high level of tectonic disturbance and an overthrust structure. The area around the Kaštela Bay is generally built of two types of sedimentary rocks (Fig. 2). The Bay's hinterland and the Čiovo Island are built of the Upper Cretaceous limestones, while the coastal area of the mainland is mostly built of flysch and flysch-like rocks deposited in Eocene (Komatina, 1968; Marinčić et al., 1971; Marjanac, 1996; Oluić et al., 1972). The Eocene flysch is very abundant around the Kaštela Bay and extends from the Trogir town, across the Kaštela town, to the Split city. The Quaternary sediments are built from firmly bound Pleistocene breccias and alluvial deposits (Borović, 1999; Magaš and Marinčić, 1973). Pleistocene breccias consist

of fragments of the Cretaceous and Paleogene carbonate sediments bound by bauxitic matrix. Alluvial deposits consist of accumulated and unbound Tertiary marls and breccias and of carbonate sediments of Cretaceous and Tertiary age.

Hydrographic net around the Bay reflects the geological history and the structure of the area. Due to an intensive karstification of the carbonate rocks in the hinterland and due to their high level of fracturing as a consequence of intensive tectonic activity, there are very few or none of the surface streams because almost all of the surface water percolates into the underground and forms bigger or smaller underground streams, which later appear on the surface as coastal or submarine springs (Fig. 2).



**Figure 2.** Simplified geological map of the Kaštela Bay area (after Fritz, 1994; Marinčić et al., 1971)

The only permanent surface stream which inflows into the Kaštela Bay is the Jadro River, which brings the majority of the freshwater into the Bay (Barić, 1995; Marasović et al., 2005; Margeta, 2002) and represents the most important water stream in this area. There are also numerous smaller brooks which inflow into the Bay, and whose outflow depends on the amount of the precipitation. It is not, therefore, unusual for many of them to dry up even more years in a row.

### 3. Material and methods

#### 3.1. Sampling

Sediments (stream sediments and soil) and sedimentary rocks (Cretaceous limestone, foraminiferal limestone, calcarenite and marl) of the Kaštela Bay coastal area were sampled (Fig. 1, Table 1). According to Tišljär (1994) soils are classified as the residual clastic sediment although they could be considered as a separate category due to their significantly different genesis compared to other clastic sediments. For this reason soils have been placed into sediments group of samples together with the stream sediments. Ten samples of marls were collected in October 2005, 11 soil samples and 13 stream sediments in April 2006 and

11 limestone samples (Cretaceous limestones, foraminiferal limestones, and calcarenites) in April 2008. In this study limestone is considered to be a sedimentary rock of the limestone composition irrespective of the rock genesis.

**Table 1.** Location of the samples of the Kaštela Bay coastal area

Sample	Sample coordinates	Type of sample	Geochronologic unit
KVC1	N 43°30'55.979", E 16°17'45.249"	Limestone	K <sub>2</sub>
KVC2	N 43°30'17.631", E 16°19'38.935"	Limestone	K <sub>2</sub>
KVC3	N 43°30'3.656", E 16°20'30.225"	Limestone	K <sub>2</sub>
KVC4	N 43°29'32.402", E 16°21'46.209"	Limestone	K <sub>2</sub>
KVC5	N 43°29'24.247", E 16°22'22.772"	Limestone	K <sub>2</sub>
KVC6	N 43°29'18.434", E 16°23'18.111"	Limestone	K <sub>2</sub>
KFV1	N 43°30'47.176", E 16°25'32.857"	Foraminiferal limestone	E <sub>1,2</sub>
KFV2	N 43°30'32.809", E 16°23'38.475"	Foraminiferal limestone	E <sub>1,2</sub>
KKA1	N 43°33'31.301", E 16°21'53.006"	Calcarenite	E <sub>2,3</sub>
KKA2	N 43°33'23.861", E 16°23'37.893"	Calcarenite	E <sub>2,3</sub>
KKA3	N 43°32'46.815", E 16°24'37.24"	Calcarenite	E <sub>2,3</sub>
L2	N 43°33'25.208", E 16°22'50.525"	Marl	E <sub>2,3</sub>
L3	N 43°33'25.345", E 16°23'21.656"	Marl	E <sub>2,3</sub>
L4	N 43°33'3.578", E 16°24'58.419"	Marl	E <sub>2,3</sub>
L5	N 43°33'2.414", E 16°25'9.356"	Marl	E <sub>2,3</sub>
L6	N 43°32'52.516", E 16°27'1.59"	Marl	E <sub>2,3</sub>
L7	N 43°32'55.461", E 16°26'52.466"	Marl	E <sub>2,3</sub>
L8	N 43°32'19.461", E 16°29'31.438"	Marl	E <sub>2,3</sub>
L9	N 43°32'24.521", E 16°29'37.928"	Marl	E <sub>2,3</sub>
L10	N 43°32'32.813", E 16°29'52.985"	Marl	E <sub>2,3</sub>
L11	N 43°32'43.834", E 16°29'56.087"	Marl	E <sub>2,3</sub>
PS1	N 43°32'55.409", E 16°27'16.868"	Stream sediment	–
PS2	N 43°32'49.102", E 16°27'27.326"	Stream sediment	–
PS3	N 43°33'24.32", E 16°26'7.881"	Stream sediment	–
PS4	N 43°33'29.907", E 16°26'13.673"	Stream sediment	–
PS5	N 43°33'37.441", E 16°25'5.934"	Stream sediment	–
PS6	N 43°33'21.59", E 16°24'37.264"	Stream sediment	–
PS7	N 43°33'33.125", E 16°23'16.528"	Stream sediment	–
PS8	N 43°33'28.689", E 16°23'0.509"	Stream sediment	–
PS9	N 43°33'38.632", E 16°22'3.784"	Stream sediment	–
PS10	N 43°33'37.678", E 16°22'18.973"	Stream sediment	–
PS11	N 43°33'40.306", E 16°21'52.855"	Stream sediment	–
PS12	N 43°33'27.915", E 16°19'45.588"	Stream sediment	–
PS13	N 43°33'31.982", E 16°19'27.637"	Stream sediment	–
T1	N 43°30'2.469", E 16°20'21.717"	<i>Terra rossa</i> soil	–
T2	N 43°29'55.953", E 16°20'28.994"	Brown soil	–
T3	N 43°29'44.989", E 16°20'42.533"	<i>Terra rossa</i> soil	–
T4	N 43°29'31.498", E 16°21'14.034"	<i>Terra rossa</i> soil	–
T5	N 43°29'37.584", E 16°20'59.683"	<i>Terra rossa</i> soil	–
T6	N 43°29'27.886", E 16°21'36.567"	<i>Terra rossa</i> soil	–
T7	N 43°29'15.628", E 16°22'33.529"	<i>Terra rossa</i> soil	–
T8	N 43°29'16.491", E 16°23'4.72"	<i>Terra rossa</i> soil	–
T9	N 43°30'26.87", E 16°19'18.639"	<i>Terra rossa</i> soil	–
T10	N 43°30'47.91", E 16°18'16.181"	<i>Terra rossa</i> soil	–
T11	N 43°30'51.249", E 16°17'53.984"	<i>Terra rossa</i> soil	–

Therefore, although calcarenite is a clastic carbonate rock s.s., i.e. detritic limestone (Tišljär, 1994), it was grouped together with other limestones according to their chemical composition. One to two kilograms of samples were taken on each sampling station. Samples were put in the labelled plastic bags and transported to the laboratory.

Different varieties of marls (L), according to the colour and consistency, were sampled on the open outcrops on the north coast of the Bay (Fig. 1). Stream sediments (PS) were sampled in beds of the periodic or permanent brooks on the north coast of the Bay (Fig. 1). According to the field observations, the majority of the stream sediments were fine grained, while the samples PS6, PS7, PS9, and PS13 were coarse grained with higher sand content. Since there are no surface water streams on the Čiovo Island which would generate and transport stream sediments representing one of the sources of the sedimentation material for the Kaštela Bay, precipitation water was considered as the most important medium of material transport to the Bay and the soils were presumed to be the main material available for transport and deposition in the Bay under the influence of the precipitation water. The effects of soil transport by precipitation water were observed by field prospection. Thus, although stream sediments and soils have completely different genesis, they are transported into the Bay in a very similar manner, i.e. by water, and they both represent a source material for deposition in the Bay. Samples of undisturbed soils (T) were taken in situ on the locations from which the transport by precipitation water was observed (Fig. 1). Soils on the Čiovo Island were almost exclusively the *terra rossa* soil. Only T2 sample was classified as brown soil. Cretaceous limestones (KVC) and the foraminiferal limestones (KfV) were sampled on the open outcrops on the north side of the Čiovo Island and on the north side of the Marjan hill, respectively (Fig. 1). Cretaceous limestones were present as white and yellowish varieties and foraminiferal limestones as yellowish and yellowish-greenish varieties. Calcarenites (KKA), which occur as lenses in the flysch, were sampled on the open outcrops on the north coast of the Kaštela Bay (Fig. 1).

### 3.2. Multielemental analysis

Samples were dried at 105°C to the constant mass, ground to powder in a stone-crusher, mill or agate mortar, homogenized, and prepared for analysis as thick targets. Total mass fractions of Al, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Rb, Sr, Y, and Pb were measured.

**Table 2.** Optimum measurement parameters for four groups of elements

Sequence	Voltage (kV)	Current (μA)	Filter	Filter thickness (μm)	Elements
<Na-Cl>	4	1000	–	–	Al
<K-V>	12	750	Al-thin	50	K, Ca, Ti, V
<Cr-Co>	20	300	Al	200	Cr, Mn, Fe, Co
<Ni-Ag>	30	300	Ag	100	Ni, Cu, Zn, Ga, As, Pb, Rb, Sr, Y

All targets were analysed by energy dispersive X-ray fluorescence (EDXRF) technique using MiniPal 4 spectrometer (PANalytical, Almelo, Nederland) according to the method described

in Oreščanin et al. (2008). Four sequences were defined to measure 18 elements of interest. Measurement time of each sequence was 200 s. Optimum measurement parameters for four groups of elements are shown in Table 2.

Calibration model for qualitative and quantitative analyses and quality control of the measurements were performed as presented in Oreščanin et al. (2008). Quality control was also performed by daily measurements of the IAEA-SL1 (lake sediment) standard reference material as unknown sample.

### 3.3. Phase analysis

Samples were dried overnight at 105°C in a drier, ground to powder in a stone-crusher, mill or agate mortar, homogenized, placed into aluminium holders, and analysed as described in Oreščanin et al. (2005).

### 3.4. Statistical analysis

Statistical analyses were performed using a programme package Statistica 6.0 (StatSoft, Inc.).

Correlation analysis was performed by calculating the product-moment correlation coefficient or Pearson's correlation coefficient to express the level of systematic linear correlation between mass fractions of the researched elements. Obtained values were statistically significant at  $p < 0.05$ .

Relationships between variables (18 elements) were determined by principal component analysis (PCA). Two principal components were extracted and projected on a factor-plane.

Factor analysis (FA) was used to obtain the scatter plot for different types of samples. Factors were extracted by the principal component analysis method. Maximum allowed number of factors was five and the selection of the number of factors was based on the eigenvalues and scree plots. Factors with eigenvalues greater than one were retained, while factors with eigenvalues less than one were retained if it was suggested by the scree plot. Residual correlations were also taken into account. They should have been as low as possible, if possible less than |0,1|. Obtained factors were rotated by varimax normalized method.

## 4. Results

### 4.1. Multielemental characterization

Basic statistical parameters of mass fractions of 18 researched elements (Al, K, Ca, Fe, Ti, Mn, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Sr, Y, Pb, and As) in sediments and sedimentary rocks of the Kaštela Bay coastal area are given in Table 3. Comparing the mean values, medians or ranges for different sample types, seven categories of elements can be differentiated according to their distribution between the researched sediments and rocks.

Two groups of samples were separated for Al and K. Al and K mass fractions increased in the following order: (KKA, KVC, KVV) < (L, PS, T). Carbonate rocks were defined as one group of samples with lower mass fractions, while marls, stream sediments, and soils were separated as the second group with higher values.

**Table 3.** Basic statistical parameters of mass fractions of metals and arsenic in sediments and sedimentary rocks of the Kaštela Bay coastal area; Mass fractions are expressed in mg/kg. KVC – limestone, KfV – foraminiferal limestone, KKA – calcarenite, L – marl, PS – stream sediment, T – soil,  $\bar{x}$  – mean value, N – number of results, SD – standard deviation

Sample type	Statistical parameter	Al	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Pb	As
KVC	$\bar{x}$	19000	1333	416000	1319	35	13	157	8400	3.6	15	< 2.0	34	2.3	2.6	144	< 1.0	< 1.6	< 1.0
	N	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6	6
	SD	0	539	10900	2.1	2.4	13	37	52	3.8	3.3	0	2.1	0.28	0.31	45	0	0	0
	Minimum	19000	800	398000	1317	32	< 1.0	130	8300	< 0.10	12	< 2.0	31	2.0	2.2	101	< 1.0	< 1.6	< 1.0
	Maximum	19000	2000	431000	1322	38	25	210	8440	7.3	21	< 2.0	36	2.7	3.0	218	< 1.0	< 1.6	< 1.0
	Median	19000	1200	418000	1318	35	12	137	8415	3.5	15	< 2.0	34	2.2	2.5	129	< 1.0	< 1.6	< 1.0
KfV	$\bar{x}$	22000	3000	392000	1406	38	30	157	9595	7.5	22	2.3	41	2.9	8.4	321	< 1.0	< 1.6	< 1.0
	N	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
	SD	4200	3394	22600	79	1.8	6.0	21	1039	0.28	6.4	0.35	0.71	0.57	5.1	31	0	0	0
	Minimum	19000	600	376000	1350	37	25	142	8860	7.3	18	< 2.0	41	2.5	4.8	299	< 1.0	< 1.6	< 1.0
	Maximum	25000	5400	408000	1462	40	34	171	10330	7.7	27	2.5	42	3.3	12	343	< 1.0	< 1.6	< 1.0
	Median	22000	3000	392000	1406	38	30	157	9595	7.5	22	2.3	41	2.9	8.4	321	< 1.0	< 1.6	< 1.0
KKA	$\bar{x}$	18700	2467	416000	1357	35	27	177	9033	7.2	18	3.6	35	2.5	4.2	252	< 1.0	< 1.6	< 1.0
	N	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3	3
	SD	580	462	5500	9.1	1.3	1.4	12	137	0.10	9.1	0.96	3.0	0.53	1.3	45	0	0	0
	Minimum	18000	2200	410000	1350	34	26	166	8940	7.1	12	2.9	32	1.9	3.0	200	< 1.0	< 1.6	< 1.0
	Maximum	19000	3000	420000	1367	36	28	189	9190	7.3	28	4.7	38	2.9	5.6	282	< 1.0	< 1.6	< 1.0
	Median	19000	2200	419000	1353	36	28	175	8970	7.2	13	3.2	37	2.7	4.1	274	< 1.0	< 1.6	< 1.0
L	$\bar{x}$	26800	8600	221640	1944	51	55	474	16063	7.7	68	17	69	5.4	37	273	3.9	10	3.1
	N	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10	10
	SD	2098	1485	31404	179	5.0	9.5	89	1816	0.36	17	4.5	14	1.4	11	58	5.9	15	4.5
	Minimum	24000	6000	176800	1680	44	45	338	13790	7.3	51	13	54	3.9	23	193	< 1.0	< 1.6	< 1.0
	Maximum	30000	10800	262100	2149	60	76	630	18990	8.4	104	27	101	7.6	52	368	15	41	14
	Median	26500	8200	224700	1930	50	54	490	15795	7.7	67	16	64	5.1	33	271	< 1.0	< 1.6	0.75

Sample type	Statistical parameter	Al	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Pb	As
PS	$\bar{x}$	28923	9000	226331	2252	54	62	573	18238	8.2	51	57	94	6.0	47	199	22	32	5.6
	N	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13	13
	SD	4555	2551	57448	380	12	15	168	4158	0.79	11	69	26	2.5	26	32	17	59	4.9
	Minimum	19000	4500	146100	1530	36	38	261	11470	7.0	32	17	57	2.2	11	163	< 1.0	< 1.6	< 1.0
	Maximum	37000	14100	343200	2855	73	84	807	25180	9.6	68	277	147	10	93	266	51	223	19
	Median	30000	9000	208600	2213	56	63	575	17800	8.1	54	36	92	5.8	42	196	23	14	4.9
T	$\bar{x}$	43364	12843	66873	4140	113	109	1609	37509	13	75	77	152	16	139	137	111	76	23
	N	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11	11
	SD	7173	4687	73178	947	37	27	564	9528	2.5	16	37	51	5.2	47	44	47	48	7.9
	Minimum	26000	1870	10400	2233	45	55	600	17640	8.0	40	41	98	4.0	40	98	15	22	14
	Maximum	50000	16700	240400	5272	193	150	2476	49940	16	98	141	298	22	193	247	160	200	42
	Median	46000	14800	32700	4453	111	114	1631	40060	14	81	81	136	17	157	117	128	65	24
Range of all data (minimum and maximum)		18000 50000	600 16700	10400 431000	1317 5272	32 193	< 1.0 150	130 2476	8300 49940	< 0.10 16	12 104	< 2.0 277	31 298	1.9 22	2.2 193	98 368	< 1.0 160	< 1.6 223	< 1.0 42

Two same groups of samples were also distinguished for Ca but with the opposite characteristics compared to Al and K. The first group of samples (KKA, KVC, KVV) had higher Ca mass fractions and the second (L, PS, T) lower. Theoretically, maximum possible Ca mass fraction in the pure  $\text{CaCO}_3$  is 400 000 mg/kg. Measured fractions in this research higher than the theoretical value were attributed to the measurement uncertainty.

The largest category of elements comprised Fe, Ti, Mn, V, Cr, Zn, Ga, Rb, Y, and As. Three groups of samples were distinguished here with an increasing content of aforementioned elements as follows: (KVC, KVV, KKA) < (L, PS) < T. Very low mass fractions of these elements were determined in the carbonate rocks. Thus, Y and As mass fractions in all samples of the carbonate rocks were below the lower limit of detection, i.e. < 1.0 mg/kg for both elements. Marls and stream sediments showed significantly higher elements contents and the highest values were obtained for soil samples which also frequently showed the widest ranges of the studied elements.

Co was separated alone in a special category because only soil samples showed significantly higher mass fractions compared to the other sample types. There was not very distinctive difference between Co mass fractions in KVC, KVV, KKA, L, and PS samples.

Ni was also separated as the only element in its category in which Ni mass fractions increased in the following order: (KVC, KVV, KKA) < PS < (L, T). It can be observed that Ni was similarly distributed between different sample types as Fe and other elements of that category. The difference is that high mass fractions of Ni were observed in both marls and soils while significantly higher mass fractions of Fe and associated elements were observed only in the soil samples.

Cu and Pb mass fractions in different types of the studied samples increased in the following order: (KVC, KVV, KKA) < L < (PS, T). Mass fractions in marls, and especially in stream sediments and soils, were significantly higher than in the carbonate rocks. All KVC samples showed Cu mass fractions below the lower level of detection (< 2.0 mg/kg). KVV and KKA samples had a very low Cu content as well; maximum value was 4.7 mg/kg. Other sample types showed significantly higher Cu contents. In all samples of the carbonate rocks Pb mass fractions were below the lower level of detection (< 1.6 mg/kg). In the marl samples the majority of the samples had < 1.6 mg/kg of Pb. Only three samples had mass fractions > 1.6 mg/kg: L2 ( $17.1 \pm 2.0$  mg/kg), L4 ( $40.6 \pm 4.7$  mg/kg), and L7 ( $31.4 \pm 3.6$  mg/kg). Only two samples of stream sediments had Pb mass fractions < 1.6 mg/kg, while in the rest of the samples Pb content varied up to 223 mg/kg. There were no Pb mass fractions below the lower level of detection in the soil samples.

Sr mass fractions did not significantly vary between different types of the researched sediments and sedimentary rocks although Sr distribution was similar to the Ca distribution to some extent. The highest Sr mean value was determined for KVV and the lowest for soils.

#### *4.2. Mineral (phase) composition*

Results of the mineral (phase) analysis of the selected samples are given in Table 4. Two main groups of minerals were distinguished: carbonate and aluminosilicate minerals. The most abundant minerals were calcite, quartz, and muscovite.

**Table 4.** Mineral (phase) composition of the selected samples of sediments and sedimentary rocks of the Kaštela Bay coastal area; ++++ very abundant (> 40%), +++ abundant (approximately 25–40%), ++ considerable (approximately 10–25%), + subordinate to accessory (< 10%), blank spaces – not present

Mineral (phase) / chemical formula	Sample										
	KVC4	KKA1	KFV2	L2	L5	L8	PS3	PS5	PS9	T2	T11
Calcite / $\text{CaCO}_3$	++++	++++	++++	++++	++++	++++	++	++	++++	++	+
Quartz / $\text{SiO}_2$		+	+	++	+	++	++++	++	+++	++++	+++
Muscovite / $\text{KAl}_2(\text{AlSiO}_3\text{O}_{10})(\text{OH})_2$				++	++	++	+++	++	++	++	++++
Boehmite / $\text{AlO}(\text{OH})$											+
Kaolinite / $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$							+				+
Plagioclase / $\text{Na}_{0.986}(\text{Al}_{1.005}\text{Si}_{2.995}\text{O}_8)$											+
Almandine / $\text{Fe}_3\text{Al}_2(\text{SiO}_4)_3$										+	
Microcline / $\text{K}(\text{Si}_{0.75}\text{Al}_{0.25})_4\text{O}_8$								+++			
Cristobalite / $\text{SiO}_2$								+			
Dolomite / $\text{CaMg}_{0.77}\text{Fe}_{0.23}(\text{CO}_3)_2$									+		
Clinocllore / $(\text{Mg}_{2.96}\text{Fe}_{1.55}\text{Fe}_{0.136}\text{Al}_{1.275})(\text{Si}_{2.622}\text{Al}_{1.376}\text{O}_{10})(\text{OH})_8$					+						

**Table 5.** Correlation coefficients for mass fractions of 18 elements in sediments and sedimentary rocks of the Kaštela Bay coastal area; Marked correlations are significant at  $p < 0.05$ ; N = 45

	Al	K	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Rb	Sr	Y	Pb	As
Al	1.00																	
K	<b>0.83</b>	1.00																
Ca	<b>-0.94</b>	<b>-0.86</b>	1.00															
Ti	<b>0.98</b>	<b>0.76</b>	<b>-0.91</b>	1.00														
V	<b>0.93</b>	<b>0.73</b>	<b>-0.85</b>	<b>0.96</b>	1.00													
Cr	<b>0.95</b>	<b>0.81</b>	<b>-0.94</b>	<b>0.95</b>	<b>0.91</b>	1.00												
Mn	<b>0.94</b>	<b>0.77</b>	<b>-0.88</b>	<b>0.96</b>	<b>0.91</b>	<b>0.89</b>	1.00											
Fe	<b>0.98</b>	<b>0.77</b>	<b>-0.92</b>	<b>1.00</b>	<b>0.97</b>	<b>0.95</b>	<b>0.96</b>	1.00										
Co	<b>0.87</b>	<b>0.71</b>	<b>-0.84</b>	<b>0.88</b>	<b>0.85</b>	<b>0.92</b>	<b>0.86</b>	<b>0.89</b>	1.00									
Ni	<b>0.79</b>	<b>0.81</b>	<b>-0.88</b>	<b>0.75</b>	<b>0.72</b>	<b>0.83</b>	<b>0.71</b>	<b>0.77</b>	<b>0.70</b>	1.00								
Cu	<b>0.34</b>	<b>0.38</b>	<b>-0.37</b>	<b>0.38</b>	<b>0.32</b>	<b>0.38</b>	<b>0.43</b>	<b>0.38</b>	<b>0.37</b>	0.26	1.00							
Zn	<b>0.61</b>	<b>0.57</b>	<b>-0.63</b>	<b>0.63</b>	<b>0.55</b>	<b>0.63</b>	<b>0.62</b>	<b>0.62</b>	<b>0.58</b>	<b>0.50</b>	<b>0.71</b>	1.00						
Ga	<b>0.96</b>	<b>0.76</b>	<b>-0.90</b>	<b>0.98</b>	<b>0.96</b>	<b>0.92</b>	<b>0.96</b>	<b>0.99</b>	<b>0.87</b>	<b>0.73</b>	<b>0.32</b>	<b>0.54</b>	1.00					
Rb	<b>0.96</b>	<b>0.77</b>	<b>-0.92</b>	<b>0.98</b>	<b>0.93</b>	<b>0.92</b>	<b>0.97</b>	<b>0.98</b>	<b>0.87</b>	<b>0.74</b>	<b>0.39</b>	<b>0.59</b>	<b>0.98</b>	1.00				
Sr	<b>-0.43</b>	-0.28	<b>0.31</b>	<b>-0.46</b>	<b>-0.44</b>	<b>-0.33</b>	<b>-0.40</b>	<b>-0.44</b>	-0.17	-0.08	-0.16	<b>-0.32</b>	<b>-0.45</b>	<b>-0.43</b>	1.00			
Y	<b>0.90</b>	<b>0.62</b>	<b>-0.78</b>	<b>0.94</b>	<b>0.93</b>	<b>0.86</b>	<b>0.92</b>	<b>0.93</b>	<b>0.82</b>	<b>0.58</b>	<b>0.34</b>	<b>0.52</b>	<b>0.94</b>	<b>0.93</b>	<b>-0.48</b>	1.00		
Pb	<b>0.44</b>	<b>0.38</b>	<b>-0.46</b>	<b>0.48</b>	<b>0.46</b>	<b>0.50</b>	<b>0.44</b>	<b>0.48</b>	<b>0.42</b>	<b>0.33</b>	<b>0.33</b>	<b>0.67</b>	<b>0.45</b>	<b>0.44</b>	<b>-0.34</b>	<b>0.41</b>	1.00	
As	<b>0.87</b>	<b>0.62</b>	<b>-0.79</b>	<b>0.91</b>	<b>0.92</b>	<b>0.88</b>	<b>0.87</b>	<b>0.91</b>	<b>0.80</b>	<b>0.67</b>	<b>0.38</b>	<b>0.65</b>	<b>0.89</b>	<b>0.87</b>	<b>-0.46</b>	<b>0.88</b>	<b>0.69</b>	1.00

In all samples of the marl, stream sediment, and soil samples they were generally significantly present while in the limestone samples calcite was almost the only mineral detected and quartz was subordinate to accessory. The only additional mineral found to be abundant in any of the samples was microcline in the PS5 sample. The other minerals were subordinate to accessory in some marl, stream sediment, and soil samples. Also, the presence of the swelling clays was detected in the L8 sample and probably in the L2 sample but it could not be determined with confidence.

#### 4.3. Correlation analysis

Results of the correlation analysis between 18 elements in the researched sample types are given in Table 5. The majority of the elements mass fractions were highly or very highly correlated with each other. The results for the characteristic elements are commented below.

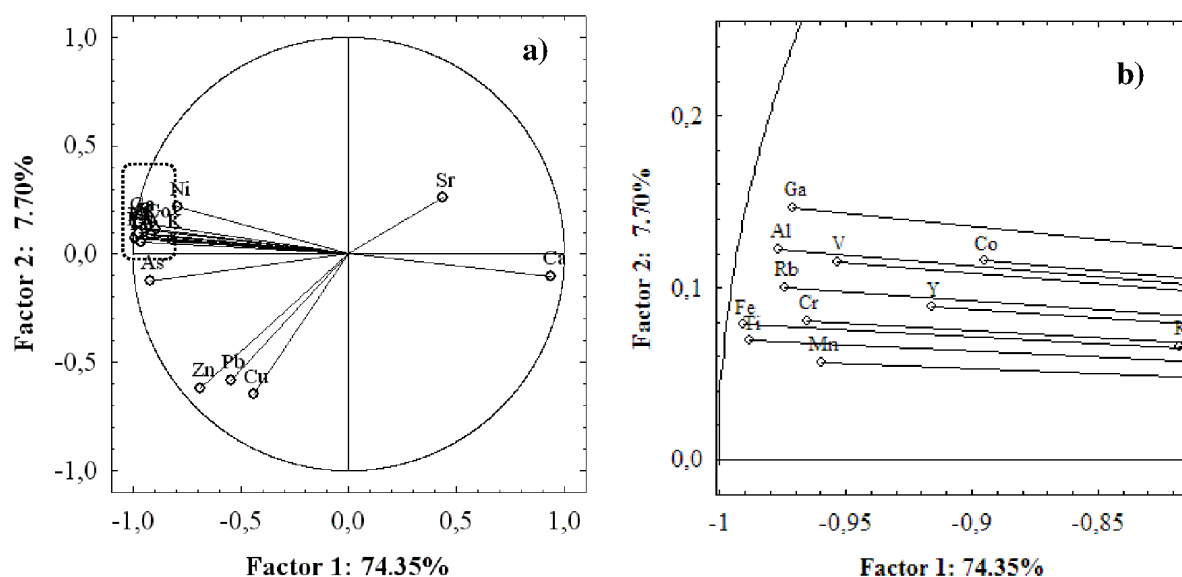
Al, K, and Ti showed high or very high positive correlations with V, Cr, Mn, Fe, Co, Ni, Ga, and Rb ( $r = 0.71 - 1.00$ ). Al and Ti also showed such correlations with Y and As ( $r = 0.87 - 0.94$ ) while K correlations with these two elements were lower (both  $r = 0.61$ ) and classified as the real significant correlation. Mn was very highly positively correlated with Fe ( $r = 0.96$ ) and both elements showed high or very high positive correlations with the following elements: V, Cr, Co, Ni, Ga, Rb, Y, and As ( $r = 0.71 - 0.99$ ) as well as with Al, K, and Ti ( $r = 0.77 - 1.00$ ). Ga and Rb, as another elements characteristic for aluminosilicate minerals, were also very highly positively correlated with each other ( $r = 0.98$ ) and both showed high or very high positive correlations with all elements ( $r = 0.73 - 0.99$ ) except with Ca, Sr, Cu, Zn, and Pb.

The only elements showing negative correlations were Ca and Sr. However, they were weakly positively correlated with each other ( $r = 0.31$ ). Ca showed very high negative correlations with all elements ( $r = -0.78$  to  $-0.94$ ) except with Cu, Zn, and Pb with which the correlations were lower ( $-0.37$  to  $-0.63$ , i.e. weak to real significant correlation). On the other hand, Sr showed no high (negative) correlations with any of the researched elements ( $r = -0.32$  to  $-0.48$ ).

Another distinctive group of elements were Cu, Zn, and Pb which generally showed only weak to real significant positive correlations with each other (Cu-Pb:  $r = 0.33$ , Zn-Pb:  $r = 0.67$ , Cu-Zn:  $r = 0.71$ ) and with other elements ( $r = 0.32 - 0.65$ ). The only exception was the correlation between Cu and Zn which was high ( $r = 0.71$ ). Cu generally showed the lowest correlations with other elements compared with Zn and Pb ( $r = 0.32 - 0.43$ ).

#### 4.4. Principal component analysis

Results of the PCA showing the relationships between the researched elements are given in Fig. 3. Three groups were distinguished: the first group comprising Ca and Sr although they were not highly correlated, the second comprising Zn, Pb, and Cu, and the third comprising all the other elements. The first group represented the carbonate component of the mineral composition of the samples, the second represented elements whose content might have been influenced by anthropogenic activity or by specific mineralogical assemblages found in the geological members of the area, and the third represented elements bound to the aluminosilicate component of the samples (primarily to the clay minerals).



**Figure 3. a)** Relationships between 18 elements in sediments and sedimentary rocks of the Kaštela Bay coastal area obtained by the principal component analysis; **b)** Magnification of the area bordered by the dashed rectangle

#### 4.5. Factor analysis

Relationships between different types of samples were studied by FA and the results are shown in Tables 6 and 7 and in Fig. 4. Two factors, which explain 82.05% of the total variance, were extracted (Table 6). Only the first factor alone explained more than 60% of the total variance. Two extracted factors did not explain all variables (Table 7). Only Sr was not explained by any of the two factors. Factor 1 explained K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Ga, Rb, Y, and As. Factor 2 explained Cu, Zn, and Pb. It was suggested that factor 1 explained elements of natural origin, while factor 2 explained elements which could significantly reflect anthropogenic influence on sediments.

**Table 6.** Results of the factor analysis of mass fractions of 18 elements in sediments and sedimentary rocks of the Kaštela Bay coastal area

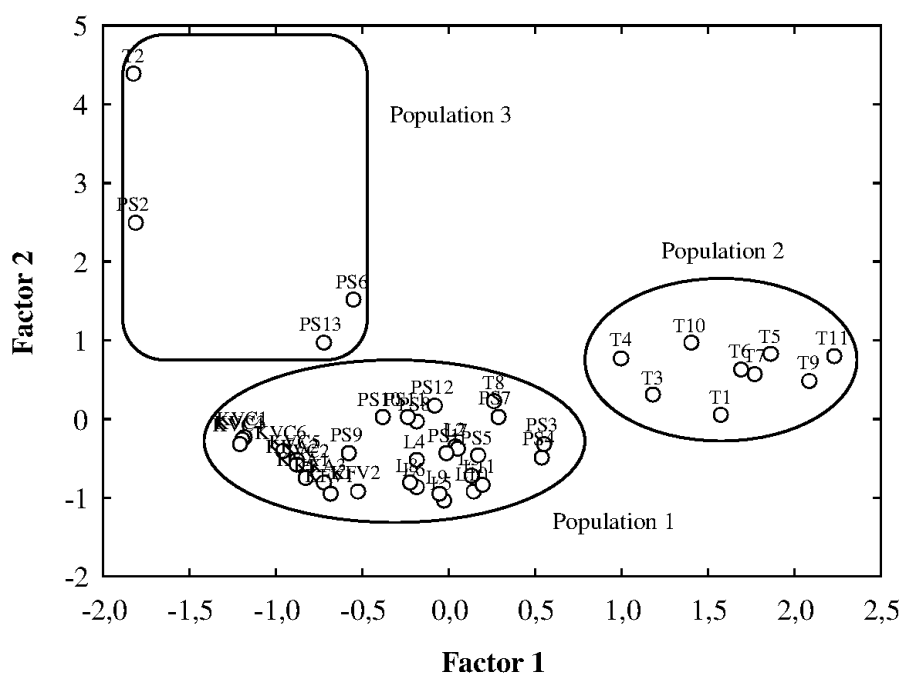
Factor	Eigenvalue	Total variance (%)	Cumulative eigenvalue	Cumulative variance (%)
1	13.38	74.35	13.38	74.35
2	1.39	7.70	14.77	82.05

Projections of the mass fractions of metals and arsenic on the factor-plane are shown in Fig. 4. Grouping of samples in relation to the factor 1 and separation of a few single samples in relation to the factor 2 was observed. There were two populations of samples in relation to the factor 1. The majority of the samples were in the population 1, which contained all samples of KVC, KVV, KKA, and L, almost all samples of stream sediments and one soil sample. Population 2 consisted only of the soil samples, which were grouped together due to naturally higher mass fractions of Al, K, Fe, Ti, Mn, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Y, Pb,

and As and due to naturally lower Ca and Sr mass fractions compared to other types of samples. In relation to the factor 2, population 3 was also observed.

**Table 7.** Factor loadings for 18 elements in sediments and sedimentary rocks of the Kaštela Bay coastal area; Values in bold numbers are > 0.7.

Variable	Factor 1	Factor 2
Al	<b>0.94</b>	0.31
K	<b>0.77</b>	0.29
Ca	<b>-0.89</b>	-0.31
Ti	<b>0.92</b>	0.36
V	<b>0.91</b>	0.30
Cr	<b>0.91</b>	0.34
Mn	<b>0.89</b>	0.36
Fe	<b>0.93</b>	0.35
Co	<b>0.86</b>	0.28
Ni	<b>0.81</b>	0.14
Cu	0.12	<b>0.78</b>
Zn	0.36	<b>0.85</b>
Ga	<b>0.94</b>	0.28
Rb	<b>0.92</b>	0.33
Sr	-0.28	-0.42
Y	<b>0.87</b>	0.31
Pb	0.24	<b>0.76</b>
As	<b>0.78</b>	0.51



**Figure 4.** Results of the factor analysis of mass fractions of metals and arsenic in sediments and sedimentary rocks of the Kaštela Bay coastal area; KVC – limestone, KKV – foraminiferal limestone, KKA – calcarenite, L – marl, PS – stream sediment, T – soil

This population contained few stream sediment samples and a soil sample in which elevated mass fractions of Cu, Zn, and/or Pb were determined. Elevated mass fractions of all three

metals were measured in the T2 sample. Mass fractions of Cu and Zn were elevated in the PS2 sample, while Zn and Pb were elevated in the PS6 and PS13 samples.

## 5. Discussion

### 5.1. Major elements

Higher Al and K mass fractions in samples of the marls, stream sediments, and soils (Table 3) were explained by the naturally significantly higher content of aluminosilicate minerals, including the clay minerals (Table 4), in whose composition Al and K are typical elements and accompany each other. This was supported by the results presented in Table 5 where Al showed high positive correlation with K ( $r = 0.83$ ). Marls consist of clay and carbonate minerals and it was expected to obtain higher Al and K contents compared to the almost pure carbonate rocks (Table 4). Periodical brooks on the north coast of the Kaštela Bay drain the Eocene flysch and flysch-like rocks and possibly the Cretaceous limestones in the hinterland. High Al and K mass fractions in the stream sediments were attributed to drainage of the marls from the flysch sequence. Clay minerals, and hence Al and K, are abundant in the soils as the secondary minerals (van Breemen and Buurman, 2003). Al can also occur in the form of  $\text{Al}(\text{OH})_3$  in the *terra rossa* soils (Yokel, 2004). Therefore, the identical distribution of K and Al between the researched types of samples was generally a result of the presence/absence of the same aluminosilicate minerals in the samples and can be explained by the same processes for both elements. This was confirmed by the results of the PCA presented in Fig. 3 where Al and K were in the same group of elements projected on the factor-plane.

Distribution of Fe in the various types of samples was similar to the distributions of Al and K (Table 3, Fig. 3). It was suggested that Fe in marls, stream sediments, and soils was associated with aluminosilicates (Table 4). It was in accordance with high or very high positive correlations of Fe with Al, K, Ga, and Rb ( $r = 0.98$ ,  $r = 0.77$ ,  $r = 0.99$ , and  $r = 0.98$ , respectively) (Table 5). Low Fe mass fractions in the carbonate rocks were in accordance with the very high negative correlation between Fe and Ca ( $r = -0.92$ ) (Table 5) and with Ca being positioned in a separate group, opposite to the group with Fe, on the factor-plane in Fig. 3.

Very high negative correlations of Ca with Al and K,  $r = -0.94$  and  $r = -0.86$ , respectively, (Table 5) were in accordance with the presence of two main groups of minerals (carbonate and aluminosilicate) (Table 4) of different origin and characteristics in sediments and rocks of the researched area (Fig. 3). While Al and K are preferably bound in the aluminosilicate minerals, Ca is preferably bound in the carbonate minerals. It is understandable that high Ca fractions were measured in the samples of the KVC, KVV, and KKA (Table 3) considering that these rocks were composed of almost pure  $\text{CaCO}_3$  (Table 4). Lower, but still relatively high, Ca mass fractions in the marls, stream sediments, and soils were a result of the mineralogical composition of the samples comprising the mixture of carbonate and aluminosilicate minerals (Table 4).

Comparison of the results for Al, K, Fe, and Ca in carbonate rocks and soils obtained in this study with the data found in the literature was given in Tables 8 and 9. In carbonate rocks only Al and Ca showed significantly higher values compared to the world carbonate rocks. Influence of the geological bedrock on the composition of the sediment forming on it or from it was clearly visible in the studied soils. Ca mean value of the sampled soils was

significantly higher than the mean values for the world and Croatian soils but the range was still within the range observed for Croatian soils. This was attributed to the influence of the carbonate bedrock on which the soils on the Čiovo Island are developed.

**Table 8.** Comparison of the mass fraction ranges of 18 elements in carbonate rocks (KVC, KfV, KKA) from the Kaštela Bay coastal area with the data from the literature; All values are expressed in mg/kg. A, B – world carbonate rocks, C – world limestones, D – limestones from the locations around the world, E – limestones from the previous Kaštela studies

Element	Kaštela / current study	A <sup>a</sup>	B <sup>b</sup>	C <sup>c</sup>	D <sup>d</sup>	E <sup>d</sup>
Al	18000 – 25000	10300	4000	–	–	–
K	600 – 5400	4700	2700	–	–	–
Ca	376000 – 431000	315000	300000 <sup>e</sup>	–	–	–
Ti	1317 – 1462	400	400	400	–	–
V	34 – 40	20	20	20	10 – 45 <sup>e,f</sup>	–
Cr	< 1.0 – 34	11	< 10	11	–	26.9 <sup>j</sup>
Mn	130 – 210	700	700	700	–	–
Fe	8300 – 10330	14600	4000	15000	–	–
Co	< 0.10 – 7.7	2	2	2	< 0.3 – 2.0 <sup>g</sup> 0.1 <sup>h</sup>	–
Ni	12 – 28	15	10	15	–	3.7 – 4.8 <sup>j,k</sup>
Cu	< 2.0 – 4.7	4	4	4	–	2.7 – 2.8 <sup>k</sup>
Zn	31 – 42	23	21	23	≤ 50 <sup>g</sup>	5.4 – 7.1 <sup>k</sup>
Ga	1.9 – 3.3	2.5	–	–	≤ 3.7 <sup>g</sup>	–
Rb	2.2 – 12	11	–	–	–	–
Sr	101 – 343	450	610	–	–	–
Y	< 1.0	3.8	4	–	4 <sup>i</sup>	–
Pb	< 1.6	9	9	5	5 – 1 <sup>g</sup>	0.6 – 1.0 <sup>k</sup>
As	< 1.0	1	1	2.5	–	–

<sup>a</sup> Prohić (1998), <sup>b</sup> Halamić and Miko (2009), <sup>c</sup> Wedepohl (2004), <sup>d</sup> various authors, <sup>e</sup> average values, <sup>f</sup> Anke (2004), <sup>g</sup> Rankama and Sahama (1968), <sup>h</sup> Schrauzer (2004), <sup>i</sup> Dobrowolski (2004), <sup>j</sup> Bogner et al. (1998), <sup>k</sup> Bogner (1996)

**Table 9.** Comparison of the mass fraction ranges and mean values of V, Ga, Rb, Y, Co, Sr, and As in marls from the Kaštela Bay coastal area with the average mass fractions in the Earth's crust; All values are expressed in mg/kg.

Element	Kaštela / current study	Earth's crust
V	44 – 60 / 51	150 <sup>a</sup> 110 <sup>b</sup>
Ga	3.9 – 7.6 / 5.4	18 <sup>b</sup>
Rb	23 – 52 / 37	310 <sup>a,c</sup> 90 <sup>b</sup>
Y	< 1.0 – 15 / 3.9	20 <sup>d</sup>
Co	7.3 – 8.4 / 7.7	24 <sup>e</sup>
Sr	193 – 368 / 273	300 <sup>a</sup> 375 <sup>b</sup>
As	< 1.0 – 14 / 3.1	3.1 <sup>e</sup>

<sup>a</sup> Mason (1956), <sup>b</sup> Prohić (1998), <sup>c</sup> Anke and Angelov (2004), <sup>d</sup> Dobrowolski (2004), <sup>e</sup> Wedepohl (2004)

## 5.2. Minor elements

Distribution of Ti and Mn in the studied samples showed the same pattern as the distribution of Fe (Table 3) and it implied that Ti and Mn were associated with aluminosilicates in marls, stream sediments, and especially in soils (Table 4). It was also assumed that Mn, as well as Fe, might be contained in the Fe- and/or Mn-oxyhydroxides associated with clay minerals but it was not supported by the phase analysis because neither Fe- nor Mn-oxyhydroxides were detected in any of the samples (Table 4). Ti and Mn association with aluminosilicates was supported by the results presented in Fig. 3 in which Ti and Mn were projected in the same group of elements as Al, K, and Fe, and by the results in Table 5 where Ti was highly or very highly positively correlated with Al, K, Fe, and Mn ( $r = 0.98$ ,  $r = 0.76$ ,  $r = 1.00$ , and  $r = 0.96$ , respectively) and Mn with Al, K, and Fe ( $r = 0.94$ ,  $r = 0.77$ , and  $r = 0.96$ , respectively).

Ti mass fractions in the carbonate rocks of the Kaštela area were higher than the average values for the world carbonate rocks/limestones while Mn were significantly lower (Table 8). The highest Ti mass fractions were found in soils due to high stability of titanium minerals in the soils. Titanium minerals have a low solubility and are the most stable minerals in the soils (Anke and Seifert, 2004). Due to weathering of the soils, Ti content in the higher horizons of the soils increases. Ti mass fractions in the researched soils were in accordance with the literature values for the world and Croatian soils (Table 9). Very high Mn content was found in the studied soils. The determined mean value was 1.6 – 3.7 times higher than the average Mn content in the world soils given by the various authors, 3.1 times higher than the mean value for European soils, and 2 times higher than the mean value for the Croatian soils (Table 9). However, the measured range was within the ranges for world, European, and Croatian soils. High contents of Ti and Mn in the soil samples can be connected to the type of soil and are often found in the *terra rossa* soils (Feng, 2011; Gurhan Yalcin and Ilhan, 2008; Miko et al., 2003; Obhodaš et al., 2006).

## 5.3. Trace elements

### 5.3.1. Relationships between elements

Significantly higher V, Ga, Rb, Y, As, Cr, Ni, and Co contents in marls, stream sediments, and soils compared to all types of limestones of the Kaštela Bay coastal area (Table 3) were attributed to higher aluminosilicate minerals content (including clay minerals) in marls, stream sediments, and soils (Table 4). This was supported by the results presented in Fig. 3, where all these elements were grouped with the elements representing silicate component, and by their significant, high or very high positive correlations with Al, K, and Ti (Table 5). V correlations with Al, K, and Ti were as follows:  $r = 0.93$ ,  $r = 0.73$ , and  $r = 0.96$ , respectively. Vanadium mass fractions in sediments and rocks depend on the content of clay minerals and organic matter because V is built into the clay minerals and organic matter or bound to them (Rankama and Sahama, 1968). In sediment rocks V replaces Al mostly in the clay minerals. Ga correlations with Al, Mn, and Fe were very high ( $r = 0.96$ ,  $r = 0.96$ , and  $r = 0.99$ , respectively), while with K it was somewhat lower ( $r = 0.76$ ). It suggested that Ga was preferably bound to the aluminium bearing minerals but that it could also be easily bound to potassium bearing minerals. Since Rb is preferably bound to potassium bearing minerals it

was expected to obtain high positive correlation of Rb with K ( $r = 0.77$ ). It was also very highly positively correlated with Al, Mn, and Fe ( $r = 0.96$ ,  $r = 0.97$ , and  $r = 0.98$ , respectively), and very highly negatively correlated with Ca ( $r = -0.92$ ). Y was significantly positively correlated with K ( $r = 0.62$ ), very highly positively correlated with Al, Mn, and Fe ( $r = 0.90$ ,  $r = 0.92$ , and  $r = 0.93$ , respectively), and highly negatively correlated with Ca ( $r = -0.78$ ). Arsenic showed very high positive correlation with Al, Mn, and Fe ( $r = 0.87$ ,  $r = 0.87$ , and  $r = 0.91$ , respectively) and a significant positive correlation with K ( $r = 0.62$ ). Very high positive correlations of Cr with Al, K, Ga, and Rb, i.e. elements representing silicate minerals, were observed ( $r = 0.95$ ,  $r = 0.81$ ,  $r = 0.92$ , and  $r = 0.92$ , respectively). Also, very high positive correlations of Cr with Mn ( $r = 0.89$ ) and Fe ( $r = 0.95$ ) were observed. Correlations of Ni with Al, K, Mn, Fe, Ga, and Rb were as follows:  $r = 0.79$ ,  $r = 0.81$ ,  $r = 0.71$ ,  $r = 0.77$ ,  $r = 0.73$ , and  $r = 0.74$ , respectively. High positive correlation between Co and K ( $r = 0.71$ ) and very high positive correlations between Co and Al, Mn, Fe, Ga, and Rb ( $r = 0.87$ ,  $r = 0.86$ ,  $r = 0.89$ ,  $r = 0.87$ , and  $r = 0.87$ , respectively) were observed.

Considering that the highest Zn, Cu, and Pb contents were determined in marls, stream sediments and soils, it could be assumed that their content would be dependant on the clay minerals and/or organic matter content. However, this was not supported by the results in Fig. 3 where Zn, Cu, and Pb were differentiated as a separate group of elements. This indicated that these three elements were not primarily bound to silicate or carbonate minerals in the researched sediments and sedimentary rocks. It suggested that Zn, Cu, and Pb in the studied sediments and rocks were of different origin than other elements or that they accumulated by different processes. It was supported by weak positive correlations of Cu with Al, K, Fe, Ga, and Rb ( $r = 0.34$ ,  $r = 0.38$ ,  $r = 0.38$ ,  $r = 0.32$ , and  $r = 0.39$ , respectively), somewhat higher correlation with Mn ( $r = 0.43$ ), and a weak negative correlation with Ca ( $r = -0.37$ ) (Table 5). Negative correlation with Sr was not statistically significant. Also, high positive correlation between Cu and Zn was observed ( $r = 0.71$ ), while correlation with Pb was weak ( $r = 0.33$ ) (Table 5). However, Zn showed higher correlations with Al, K, Mn, Fe, Ga, Rb, Ca, and Sr than Cu. Correlations were as follows: 0.61, 0.57, 0.62, 0.62, 0.54, 0.59, -0.63, and -0.32, respectively (Table 5). Pb showed significant positive correlations with Al, Mn, Fe, Ga, and Rb ( $r = 0.44$ ,  $r = 0.44$ ,  $r = 0.48$ ,  $r = 0.45$ , and  $r = 0.44$ , respectively) and a weak positive correlation with K ( $r = 0.38$ ) (Table 5).

Although Sr was grouped in the same group with Ca (Fig. 3), it was only weakly positively correlated with Ca ( $r = 0.31$ ) (Table 5). It suggested that Sr was only partly bound to  $\text{CaCO}_3$ . This was attributed to different precipitation conditions of  $\text{CaCO}_3$  and  $\text{SrCO}_3$  which resulted in non-simultaneous precipitation of two compounds.

### 5.3.2. Trace elements in limestones

V, Ga, and Cu mass fractions in the Kaštela Bay coastal area limestones were in accordance with the average values for limestones given in the literature (Table 8). Cu content was also similar to the mass fractions determined in the previous research of the Kaštela area (Bogner, 1996) (Table 8). Rb, Y, As, Sr, and Pb mass fractions were lower than the data given in the literature (Table 8). However, the results for Pb in limestones obtained in the current study were in accordance with the results obtained by Bogner (1996) (Table 8). Co, Ni, Cr,

and Zn showed mass fractions higher than the mean values for the limestones cited in the literature by different authors (Table 8). Ni mass fractions in the limestones of the Kaštela Bay surrounding area obtained by the current study were significantly higher compared to the previous research (Bogner, 1996; Bogner et al., 1998) (Table 8). The difference between the results of these two studies could be a consequence of the methods used for sample preparation and analyses. Bogner (1996) and Bogner et al. (1998) used a mixture of HF, HNO<sub>3</sub>, and HClO<sub>4</sub> to digest and dissolve the samples and the electrothermic atomic-absorption spectrometry (ETAAS) and graphite-furnace atomic-absorption spectrophotometry (GFAAS), respectively, to determine chemical composition of the samples. Such sample preparation could produce an undissolved residual fraction, which could not be analysed by the used analytical methods. Therefore, the results obtained by these methods could be lower than the results obtained by the XRF method used in the current study because the sample preparation for the XRF analysis allowed no loss of any fraction of the sample and the analysis gives a total chemical composition of the sample. Higher Ni mass fractions determined in the limestones could be a consequence of the influence of the heavy minerals assemblage originating from the basic and ultrabasic rocks although analysis of heavy minerals assemblage of the Kaštela Bay samples would be needed to support this assumption. According to Prohić and Juračić (1989) enrichment with Ni was observed in the whole Dinaric karstic area. They determined 41 mg/kg of Ni in the Upper Cretaceous limestones from the Krka River watershed (Prohić and Juračić, 1989). Cr mean value of the KVC (13 mg/kg) obtained in this study was lower than the Cr mass fraction obtained in the previous study by Bogner et al. (1998) (Table 8). However, mean values for the KVV (30 mg/kg) and KKA (27 mg/kg) were very close to the fraction determined in the previous study and significantly higher than the Cr mean value in the limestones found in the literature (Table 8). Zn mass fractions obtained in the current study were significantly higher than the ones determined by Bogner (1996) in limestones around the Kaštela Bay (Table 8). The significantly lower values from Bogner (1996) can be attributed to the methods of sample preparation and analysis as discussed earlier for Ni. However, the difference between the values obtained in the current research and the average Zn mass fractions in the limestones found in the literature was less pronounced (Table 8). Elevated Zn content in the limestones could also be connected with the influence of the basic and ultrabasic eruptive rocks on the mineral composition. Enrichment with Zn was observed in the whole area of the Dinaric karst (Prohić and Juračić, 1989). In the Upper Cretaceous limestones of the Krka River watershed, 30 mg/kg of Zn was determined (Prohić and Juračić, 1989).

### 5.3.3. Trace elements in marls

Mass fractions and/or mean values of V, Ga, Rb, Y, Co, and Sr in marls of the Kaštela Bay surrounding area were lower than the average values for the Earth's crust while As mean value was in accordance with the average As content in the continental crust (Table 9). The observed differences can be attributed to the local variations of the composition of the geological bedrock, i.e. variability of the composition of the Earth's crust. Significant part of the geological bedrock of the Kaštela Bay area is of carbonate composition, while in the Earth's crust as a whole carbonates are weakly represented compared to other sediments. Cu

mass fractions for marls observed in the current study were close to the values determined in the previous research by Bogner (1996) (Table 10).

**Table 10.** Comparison of the mass fraction ranges and mean values of Cr, Ni, Cu, Pb, and Zn in marls from the Kaštela Bay coastal area with the data from the literature; All values are expressed in mg/kg. A – marls from the previous Kaštela studies, B – marls from the Krka River watershed

Element	Kaštela / current study	A	B
Cr	45 – 76 55	61 – 122 <sup>a</sup>	400 <sup>c</sup>
Ni	51 – 104 68	37 – 50 <sup>a,b</sup>	200 <sup>c</sup>
Cu	13 – 27 17	23 – 25 <sup>b</sup>	–
Pb	< 1.6 – 41 10	7.1 – 10.8 <sup>b</sup>	–
Zn	54 – 101 69	28 – 69 <sup>b</sup>	90 <sup>c</sup>

<sup>a</sup> Bogner et al. (1998), <sup>b</sup> Bogner (1996), <sup>c</sup> Prohić and Juračić (1989)

Ni and Zn contents in the marls of the Kaštela area obtained by the current study were generally higher than the mass fractions determined in the previous researches (Bogner, 1996; Bogner et al., 1998) (Table 10). Ni mean value was also higher than the average value for the continental crust (56 mg/kg) (Wedepohl, 2004). Maximum Zn value (101 mg/kg) obtained in the current study was significantly higher than the values reported by Bogner (1996) but the mean value (69 mg/kg) and median (64 mg/kg) were very close to the maximum value obtained by Bogner (1996). Higher Ni and Zn contents in marls were attributed to the possible influence of the heavy minerals assemblage originating from basic and ultrabasic rocks on the mineral composition of the flysch deposits (Korbar, 2009; Prohić and Juračić, 1989). It was recently reported that the minerals originating from the Inner Dinarides, which include the ophiolitic masses, were found in the Eocene flysch of the Outer Dinarides (Korbar, 2009). It is very likely that these minerals would also be found in the Eocene marls of the Kaštela area. However, the analysis of heavy minerals assemblage would be needed to entirely validate this conclusion. Pronounced influence of the basic and ultrabasic rocks on the mineral composition of the marls is clearly visible in high Ni and Zn mass fractions (200 mg/kg and 90 mg/kg, respectively) measured in the Upper Eocene marl from the Krka River watershed (Prohić and Juračić, 1989) (Table 10). Cr and Pb mass fractions in marls obtained in the current study were generally lower than the mass fractions determined in the earlier studies from the Kaštela area (Bogner, 1996; Bogner et al., 1998) (Table 10). However, high Cr content and high Cr distribution variability can be expected in marls (Bogner et al., 1998a; Prohić and Juračić, 1989). Thus, Prohić and Juračić (1989) determined 400 mg/kg of Cr in the Upper Eocene marl of the flysch series from the Krka River watershed. Samples L2, L4, and L7 were the exceptions in which Pb mass fractions were higher than the maximum values from Bogner (1996). Pb mass fractions in marls obtained by Bogner (1996) could possibly be

even higher but the loss of a sample fraction may have occurred due to characteristics of the methods used for sample digestion and analysis.

#### 5.3.4. Trace elements in stream sediments

V, Ga, Rb, Sr, and Cr mass fractions in stream sediments of the Kaštela Bay area were lower than the average mass fractions in the Earth's crust, i.e. lower than 110 mg/kg, 18 mg/kg, 310 mg/kg, 300 mg/kg, and 100 mg/kg, respectively (Anke and Angelov, 2004; Mason, 1956; Prohić, 1998). The observed differences can be attributed to the variability of the composition of the Earth's crust. Co and Ni mass fractions were lower than the average values for the continental crust (24 mg/kg and 75 mg/kg, respectively) (Prohić, 1998; Wedepohl, 2004). Ni content in stream sediments reflected lithological composition of the drained geological bedrock, mainly built from flysch deposits and limestones. Y and As mean values for stream sediments were close to the mean values for continental crust (20 mg/kg and 3.1 mg/kg, respectively) (Dobrowolski, 2004; Wedepohl, 2004). Mean values for Zn, Cu, and Pb in stream sediments were higher than the average contents in the continental crust (65 mg/kg, 25 mg/kg, and 15 mg/kg, respectively) (Wedepohl, 2004). However, Zn mean value was lower than the average Zn content in the superficial rocks of the world (127 mg/kg) (Baptista Neto et al., 2006) and median of Pb mass fractions was almost equal to the average Pb content in the continental crust. It can be assumed that the Zn and Cu contents in stream sediments were largely dependant on the Zn and Cu contents in the drained soils.

#### 5.3.5. Trace elements in soils

The majority of the trace elements in the researched soils of the Kaštela Bay area showed higher mean values than the average values of the respective elements found in the literature for the soils of the world. These elements were: Rb, Y, As, Cr, Zn, Cu, Pb, and Co. Only Ga and Sr showed lower mean values compared to the found data and only V mean value showed no significant difference compared to the soils of different parts of the world. V mean value determined for studied soils from the Čiovo Island was generally close to the average V content found in the literature (Table 11) although it was almost twice higher than the mean value for the soils of Europe according to Melegy et al. (2010) (Table 11). Variations of the geological bedrock on which the soil is developed and the type of the soil should be taken into account. Soils around the Kaštela Bay are mostly the *terra rossa* soils developed on the carbonate bedrock. Vanadium is typically accumulated in soils developed on the carbonate bedrock (Miko et al., 2003) and high V mass fractions in the analysed soils should not necessarily be attributed to an anthropogenic influence. Thus, Miko et al. (2003, 2003a) determined high V mean values in soils of Istria and around the Vransko Lake on the Cres Island in Croatia (Table 11). Sr mean value for the researched soils was lower than the average Sr mass fraction in the world soils (Table 11), very close to the value for European soils, and somewhat higher than the value for Croatian soils. However, the observed range was in accordance with the literature data (Table 11). Ga mean value for soils from the Čiovo Island was almost two times lower than the average Ga mass fraction in the world soils reported in the literature (Prohić, 1998) (Table 11).

**Table 11.** Comparison of the mass fraction ranges and mean values of 18 elements in soils from the Čiovo Island (Kaštela Bay area) with the data from the literature; All values are expressed in mg/kg. A, B, C – world soils, D – European soils, E – Croatian soils, F – *terra rossa* from the locations in Croatia, G – *terra rossa* from the locations around the world, H – maximum allowed value (MAV) prescribed by the Croatian regulation

Element	Čiovo Island (Kaštela) / current study	A <sup>a</sup>	B <sup>b</sup>	C <sup>c</sup>	D <sup>d</sup>	E <sup>a</sup>	F <sup>c</sup>	G <sup>c</sup>	H <sup>ae</sup>
Al	26000 – 50000 43364	70000	–	700 – 300000 71000 <sup>e</sup>	–	11000 – 140400 69600	–	–	–
K	1870 – 16700 12843	500 – 90000 16800	14000	< 30 – (> 200) <sup>f</sup>	–	1800 – 37900 14900	–	–	–
Ca	10400 – 240400 66873	to 20000	13700	–	–	700 – 287300 21300	–	–	–
Ti	2233 – 5272 4140	1000 – 10000 5000	5000	1000 – 9000 3300 <sup>g</sup>	–	600 – 11260 4050	–	–	–
V	45 – 193 113	3 – 500 90	100	to 460 18 – 115 <sup>h</sup>	2.71 – 537 68.1 <sup>t</sup>	9 – 473 119	128 – 332 <sup>u,v</sup> 149 <sup>u,w</sup>	–	–
Cr	55 – 150 109	5 – 1000	100	10 – 5000 <sup>i</sup>	< 3.0 – 6230 94.8	18 – 524 97	10 – 140 <sup>v,x</sup> 86 <sup>v,x</sup> 67 – 278 <sup>x,y</sup> 146 <sup>x,y</sup>	166 – 255 <sup>aa,ab</sup> 203 <sup>aa,ab</sup> ≈ 160 <sup>ac,ad</sup>	80 – 120
Mn	600 – 2476 1609	20 – 10000 1000	850	437 <sup>j</sup>	< 10.0 – 6480 524	96 – 5619 808	–	–	–
Fe	17640 – 49940 37509	21000	–	< 10000 – few 10000 <sup>k</sup>	700 – 152000 21700	5500 – 80200 35100	–	–	–
Co	8.0 – 16 13	2 – 40	8	8 <sup>l</sup>	< 3.0 – 249 10.4	3 – 120 14	–	–	–
Ni	40 – 98 75	5 – 500 40	40	5 – 1000 <sup>m</sup>	< 2.0 – 2690 37.3	9 – 427 55	82 <sup>u,w,x</sup> 20 – 300 <sup>v,x</sup> 57 <sup>v,x</sup> 43 – 330 <sup>x,y</sup> 128 <sup>x,y</sup>	–	50 – 75
Cu	41 – 141 77	2 – 250 30	20	2 – 250 30 <sup>n</sup>	0.81 – 256 17.3	3 – 429 30	–	–	90 – 120
Zn	98 – 298	1 – 900	50	10 – 300 <sup>o</sup>	< 3.0 – 2900	23 – 1432	40 – 200 <sup>v,x</sup>	–	150 – 200

Element	Čiovo Island (Kaštela) / current study	A <sup>a</sup>	B <sup>b</sup>	C <sup>c</sup>	D <sup>d</sup>	E <sup>a</sup>	F <sup>c</sup>	G <sup>c</sup>	H <sup>ae</sup>
	152	90			68.1	99	86 <sup>v,x</sup> 61 – 506 <sup>x,y</sup> 173 <sup>x,y</sup> 122 <sup>w,z</sup>		
Ga	4.0 – 22 16	–	30	–	0.54 – 34.3 13.1	–	–	–	–
Rb	40 – 193 139	–	100	< 20 – 400 <sup>p</sup>	< 2.0 – 390 86.8	–	–	–	–
Sr	98 – 247 137	300	300	–	8.00 – 3120 130	22 – 1090 108	–	–	–
Y	15 – 160 111	50	50	to 500 <sup>i</sup>	< 3.0 – 267 22.7	3 – 201 22	–	–	–
Pb	22 – 200 76	2.6 – 83 14	10	to 1000 <sup>i</sup> ≤ 40 <sup>r</sup>	5.32 – 970 32.6	10 – 699 38	18 – 150 <sup>v,x</sup> 55 <sup>v,x</sup> 21 – 113 <sup>x,y</sup> 59 <sup>x,y</sup>	–	100 – 150
As	14 – 42 23	6	6	< 5 <sup>s</sup>	0.32 – 282 11.6	0.5 – 105 13	–	–	–

<sup>a</sup> Halamić and Miko (2009), <sup>b</sup> Prohić (1998), <sup>c</sup> various authors, <sup>d</sup> Salminen et al. (2005), <sup>e</sup> Yokel (2004), <sup>f</sup> Anke (2004), <sup>g</sup> Anke and Seifert (2004), <sup>h</sup> Anke (2004a), <sup>i</sup> Rankama and Sahama (1968), <sup>j</sup> Schäfer (2004), <sup>k</sup> Schumann and Elsenhans (2004), <sup>l</sup> Schrauzer (2004), <sup>m</sup> Sunderman Jr. (2004), <sup>n</sup> Wedepohl (2004), <sup>o</sup> Peganova and Eder (2004), <sup>p</sup> Anke and Angelov (2004), <sup>r</sup> Gerhardsson (2004), <sup>s</sup> Stoeppler (2004), <sup>t</sup> also in Melegy et al. (2010), <sup>u</sup> Miko et al. (2003), <sup>v</sup> from Istria, <sup>w</sup> from Cres Island, <sup>x</sup> Miko et al. (1999), <sup>y</sup> from Sinsko polje, <sup>z</sup> Miko et al. (2003a), <sup>aa</sup> Gurhan Yalcin and Ilhan (2008), <sup>ab</sup> from Turkey, <sup>ac</sup> Feng (2011), <sup>ad</sup> SW China, <sup>ae</sup> Narodne novine 32/10 (2010)

Such difference can also be explained by the local variations of the composition of the geological bedrock because soil composition is directly dependant on its composition. However, Ga range and mean value for the studied soils were in accordance with the values given for European soils (Table 11). Variability of the composition of the geological bedrock is especially important for Rb which is very dispersed in the Earth's crust and whose soil content largely depends on the composition of the geological bedrock. It was reflected in differences between the Rb mass fractions and mean values obtained for different sample types in this research and the literature values (Table 11). Rb mean value and median for soils analysed in the current study were higher than the average Rb content in soils (Table 11). However, due to the large variability of Rb content in soils, the range observed in soils of the Kaštela Bay area was in accordance with the literature data for the world and European soils. Y mean value and median for studied soils from the Čiovo Island were significantly above the average Y content in European and Croatian soils (Table 11). However, it was also found that Y content in soils can be as high as 500 mg/kg (Rankama and Sahama, 1968). Mass fractions measured in the Kaštela Bay soils were in accordance with this value and with the ranges found for European and Croatian soils (Table 11). Soils from the Čiovo Island exhibited higher Co mean value than the average soil content in the world and Europe, but it was in accordance with the mean value for Croatian soils. The obtained ranges were also in accordance with the literature data (Table 11). Cr, Ni, Zn, Cu, Pb, and As mean values were higher than the respective mean values for the soils on a world, European, and Croatian level but all ranges were in accordance with the literature data (Table 11). Local variations of the geological bedrock and the type of the soil should be taken into consideration since Cr and Ni contents in soils were found to vary in the wide range (Table 11). Studied soils from the Kaštela Bay area are mostly the *terra rossa* soils developed on the limestones and they have naturally higher Cr, Ni, Zn, Cu, Pb, and As contents than other types of soils (Feng, 2011; Gurhan Yalcin and Ilhan, 2008; Miko et al., 1999, 2003, 2003a). It was found that soils developed on the carbonate bedrock often have higher Pb content and higher median values of Cu were also determined in such soils compared to the soils developed on the non-carbonate bedrock (Miko et al., 2003). High mass fractions of Cr, Ni, Zn, Cu, and Pb were found in more locations in Croatia as well as in the world (Table 11). Cr mass fractions, ranging from approximately 160 mg/kg to almost 300 mg/kg, were determined in the *terra rossa* from Croatia (Miko et al., 1999), Turkey (Gurhan Yalcin and Ilhan, 2008), and SW China (Feng, 2011) (Table 11). These values were significantly higher than the average value for the upper continental crust (app. 40 mg/kg) (Feng, 2011). Due to the high Cr content determined in the marls of the Dinaric karst (Prohić and Juračić, 1989), naturally high Cr content can be expected to be detected in soils developed on them. Ni mean value of 82 mg/kg, which is very close to the mean value and median obtained for soils in the current research, was determined for soils around the Vransko Lake on the Cres Island (Croatia) (Table 11). Wider ranges and variable mean values for Ni were determined in the superficial layers (0 – 15 cm) of the *terra rossa* soils in Istria and Sinjsko polje (Croatia) compared to the Kaštela area (Miko et al., 1999). Pb mass fractions similar to the ones found in the Kaštela Bay area were determined in the upper 15 cm of the *terra rossa* soil in Istria (Croatia) and in the Sinjsko polje (Croatia) (Miko et al., 1999) (Table 11). High Cu content in soils can also be a consequence of the use

of copper based pesticides frequently used in the vineyards (Miko et al., 2003; Prohić and Juračić, 1989). Arsenic mean value for soils from the Čiovo Island was more than 3.8 times higher than the average As content in the world soils found in the literature, 1.9 times than the European soils, and 1.8 times than the Croatian soils (Table 11). However, the range was in accordance with the ranges for European and Croatian soils. High As content was the most probably connected to the type of soil since it was already found that the *terra rossa* soils have high As contents (Gurhan Yalcin and Ilhan, 2008; Miko et al., 2003). Arsenic could also be of anthropogenic origin due to its use in pesticides, herbicides, and defoliants, or it could also originate from the smelter. However, soil sampling locations should be taken into account. All soils were sampled on the coast of the Čiovo Island, where there is no intensive agricultural or metallurgic activities. It was, therefore, assumed that the majority of As in the soils was of natural origin and that only a minor portion of As was from anthropogenic sources such as agricultural activity of the local inhabitants.

Comparison of the ranges and mean values for Cr, Ni, Cu, Zn, and Pb with the maximum allowed values (MAVs) for clayey soils prescribed by the Croatian regulation (NN 32/10) is given in Table 11. Maximum values of all these elements were higher than the respective MAVs. The only soil sample in which the MAVs for Zn and Pb were exceeded was the T2 sample with the respective mass fractions of  $298 \pm 15$  mg/kg and  $200 \pm 23$  mg/kg. Also, Ni median value was higher than the MAV.

#### 5.4. Relationships between different types of samples

It can be concluded that differentiation of the studied samples into populations 1 and 2 (Fig. 4) occurred due to natural variations of mass fractions of the studied elements in different types of sediments and sedimentary rocks, while the population 3 could be a consequence of possible anthropogenic influence. It is unlikely that the elemental composition of the samples in this population would be the result of the influence of the source rocks only. In that case it would be expected to have the majority of the soil and stream samples in the population 3 due to large areas influenced by the same lithological members. The results in Fig. 4 also suggest that, in terms of the multielemental composition, stream sediments were more similar to the source rocks, limestones and marls, than soils which were more differentiated during the pedogenesis process.

## 6. Conclusions

The highest mass fractions of Ca and Sr were found in three types of limestones s.l., while the highest fractions of Al, K, Fe, Ti, Mn, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Y, Pb, and As were determined in marls, stream sediments, and, especially, in soils. Elevated Ni, Cr, and Zn contents in limestones and elevated Ni and Zn contents in marls were attributed to the possible influence of the heavy minerals assemblage originating from basic and ultrabasic rocks of the Inner Dinaric area. Ti, Mn, V, Cr, Ni, Cu, Zn, Pb, and As mass fractions were elevated in soils. It was explained by naturally higher contents of these elements in the *terra rossa* soils developed on the carbonate bedrock.

Three groups of elements were distinguished by the PCA: (1) Ca and Sr, representing the carbonate component of the mineral composition; (2) Zn, Pb, and Cu, representing possible anthropogenic influence or the specific mineralogical assemblages found in the

geological members of the area; (3) Al, K, Fe, Ti, Mn, V, Cr, Co, Ni, Ga, Rb, Y, and As, representing the aluminosilicate component of the mineral composition. Weak positive correlation of Sr with Ca suggests that Sr was only partly bound to  $\text{CaCO}_3$ . Sr distribution between different types of samples resembled to the Ca distribution, but Sr variations were much less pronounced. Group 2 implies that Cu, Zn, and Pb were not primarily bound to the silicate or carbonate minerals.

FA showed differentiation of the samples according to their elemental composition and the type of the sample. Three populations were separated: (1) all samples of KVC, KVV, KKA, and L, almost all samples of stream sediments, and one soil sample (T8), representing sediments and sedimentary rocks with naturally higher mass fractions of Ca and Sr and lower mass fractions of Al, K, Fe, Ti, Mn, V, Cr, Co, Ni, Cu, Zn, Ga, Rb, Y, Pb, and As; (2) all soil samples but the T8, representing sediment type with naturally lower Ca and Sr mass fractions and higher mass fractions of the other studied elements compared to other types of samples; (3) three stream sediment samples and one soil sample with elevated mass fractions of Cu, Zn, and/or Pb, representing possible anthropogenic influence. It was established that the multielemental composition of stream sediments reflects the source rocks better than the multielemental composition of soils.

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