Geochemical characterization and environmental status of Makirina Bay sediments (northern Dalmatia, Republic of Croatia)

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ABSTRACT

This research focuses on determination of the mineralogical composition, geochemical characteristics and evaluation of pollution status of the Makirina Bay sediments. Calculated enrichment factor (EF) values show no enrichment (< 1) for Cd, Ni, and Zn, minor enrichment (< 3) for As, Cu, and Pb, and minor to moderate enrichment for Mo. The results of the sequential leaching procedure for the aforementioned potentially toxic elements (PTE) indicates that the mobility and bioavailability characteristics of the PTE studied declined in the following order: Mo > Cd > Pb > Ni > Zn > Cu > As. Principal component analysis (PCA) and correlation analysis confirmed the PTE distribution depends mainly on the geogenic mineral components and anthropogenic activities in the areas surrounding the bay. Calculated transfer factor (TF) values from sediment to seagrass *Cymodocea nodosa* (*C. nodosa*) were < 1, showing that despite the results of the sequential extraction procedure, PTE transfer from sediment to roots was not effective.

Keywords: Makirina Bay sediments (Republic of Croatia), Potentially toxic elements (PTE), Enrichment factor (EF), Sequential extraction procedure, Transfer factor (TF), seagrass *Cymodocea nodosa*

1. INTRODUCTION

Sediments in aquatic ecosystems serve as one of the major reservoirs for various pollutants including essential and non-essential trace elements (EBRAHIMPOUR & MUSHRI-FAH, 2008, AHMED et al., 2010, GAO et al., 2010, LIU et al., 2011, SATPATHY et al., 2012, ZHANG et al., 2012). Trace elements are among the most persistent contaminants in sediments and potentially toxic elements (PTE), in particular, have the potential to be toxic to biota (EBRAHIM-POUR & MUSHRIFAH, 2008, AHMED et al., 2010). PTE

can bioaccumulate in living tissue and might pose a risk to organisms in higher concentrations. PTE such as Cu, Mo, Ni, and Zn are considered to be essential for the growth of organisms, but can produce a toxic effect when their intake is excessive, whereas As, Cd, and Pb are PTE with no biological function and are toxic even in trace amounts (ÖZTÜRK et al., 2009, QUI et al., 2011, PEREIRA MAJER et al., 2014). Geochemical studies of marine sediments are therefore necessary to determine the extent of PTE contamination and to estimate the quality of the entire aquatic environment.
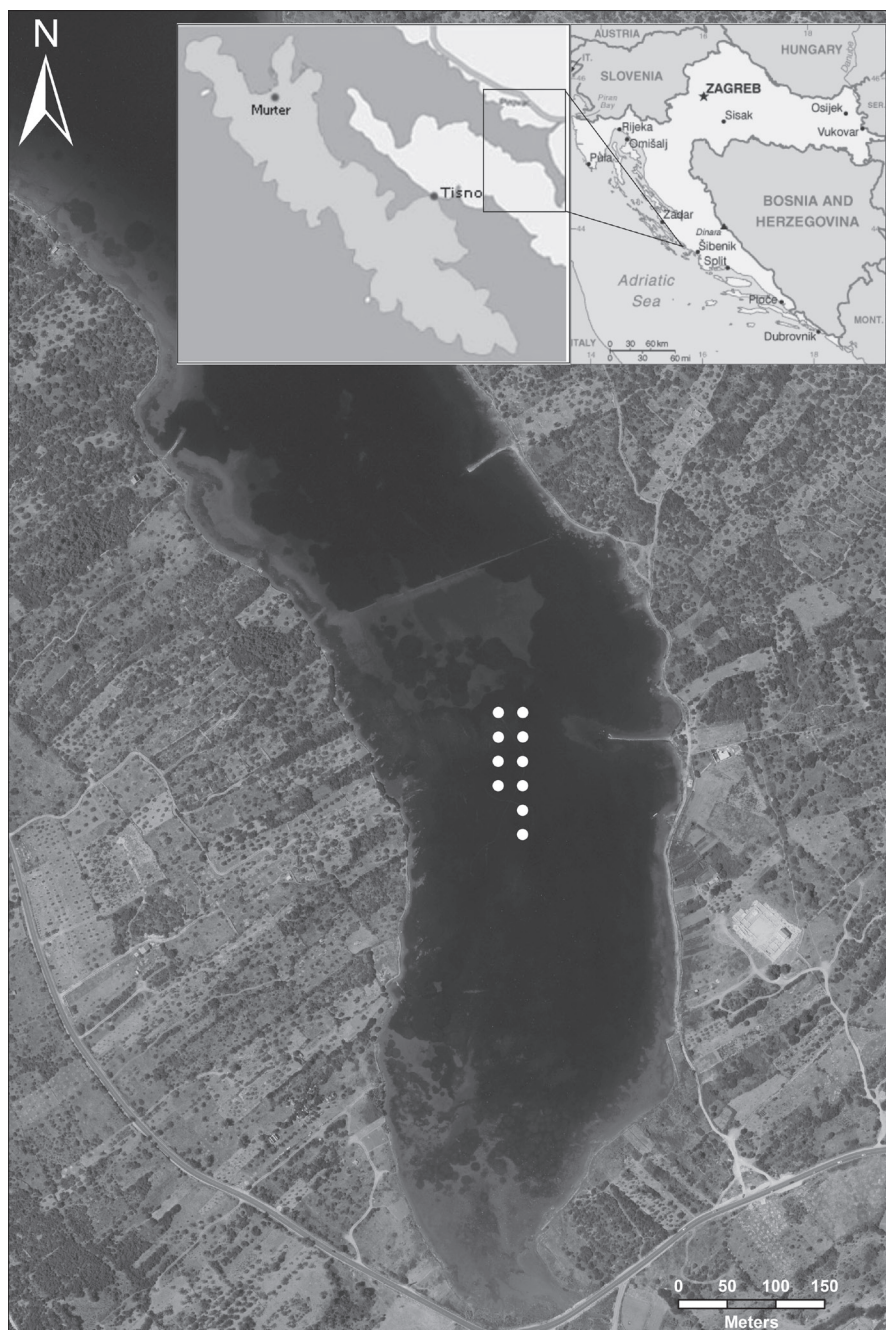
The physical and chemical behaviour of PTE in the environment strongly depends on their chemical forms or binding type (TESSIER et al., 1979, LI et al., 2000, YU et al., 2001, YUAN et al., 2004, EBRAHIMPOUR & MUSHRIFAH, 2008, YAN et al., 2010) and can be determined by various sequential extraction procedures (TESSIER et al., 1979, FILGUEIRAS et al., 2002, SAHUQUILLO et al., 2003, DEAN, 2007, RAO et al., 2008). The results obtained from the sequential leaching procedure provide important information about the mobility of PTE in sediments (LI et al., 2001).

Several geochemical studies of Makirina Bay (Republic of Croatia) sediments have been undertaken in previous years (ŠPARICA et al., 1989, VREČA, 1998, DOLENEC et al., 2002, LOJEN et al., 2004, VREČA & DOLENEC, 2005, ŠPARICA et al., 2005, MIKO et al., 2007, MIKO et al., 2008). According to their organoleptic properties these sediments are treated as peloid or healing mud and could be used as a virgin material for various therapeutic purposes (ŠPARICA et al., 1989). The previous researches were mainly focused on measurements of the total element concentrations in surface (0–5 cm) sediments.Unfortunately, determination of the total element content in sediments cannot provide sufficient information about PTE mobility, bioavailability, and consequently the assessment of the environmental risk to the marine ecosystem (LI et al., 2001, EBRAHIMPOUR & MUSHRIFAH, 2008, GAO et al., 2010, ZHANG et al., 2012).

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Therefore the main aims of our research were (1) to determine the basic physico-chemical characteristics of the Makirina Bay sediments, (2) to determine the total major and trace element concentrations in sediment cores (0–25 cm), (3) to analyse PTE chemical speciation, (4) to calculate PTE enrichment factors (EF), and (5) to define the PTE transfer factor (TF) from sediment to seagrass *C. nodosa*.

2. MATERIAL AND METHODS

2.1. Study area

Makirina Bay is located in N Dalmatia (Republic of Croatia), 18 km NW of Šibenik city (Fig. 1). It is a relatively small bay, approximately 1250 m in length and 300 m in width. The depth of the sea rarely exceeds 0.5 m in the southern part of the bay and increases in the seaward direction to a depth of 4.5 m. The surroundings of the bay are cultivated (olives, gardens, vineyards) and sparsely populated. The only larger settlement near Makirina Bay is Pirovac city, with approximately 2000 inhabitants, located on the E side of Pirovac bay. Along the S coast of the bay, the road connects the main land and Murter Island. The wider area of Makirina is mostly composed of Early and Late Cretaceous carbonate rocks and Quaternary sediments (ŠPARICA et al., 1989).

2.2. Sampling

Sediment core samples were taken in summer 2010 from 10 different sites in the central part of the bay (Fig. 1). Samples were collected with hand-driven plexiglass core samplers (50 cm long, 5 cm inner diameter) and were immediately frozen until further analysis was possible. In the laboratory, cores were divided into 5-cm-long sections and air-dried. Before the mineralogical and geochemical analyses, non-representative debris (large rocks and organic debris) was removed by wet sieving. Samples were homogenized to a fine powder (<63 μm) in an agate mortar.

Samples of seagrass *C. nodosa* were handpicked in the central part of the bay in the same location as the sediment cores (Fig. 1) at a depth of about 0.5 m and transferred to polyethylene bags. In the laboratory, seagrass samples were washed in distilled water. Sediments and epiphytes were carefully removed from the samples with a nylon brush. Seagrass individuals were dissected into two different compartments: belowground (roots and rhizomes) and above ground biomass (leaves). Plant samples were dried to a constant weight and then ground and homogenized to a fine powder in an agate mill.

2.3. Analysis

2.3.1. Grain size analysis

The granulometric composition of the sediment was determined by a combination of wet sieving and laser diffractometry with a Malvern Mastersizer S (fraction<125 μm) at Salonit Anhovo d.d., Slovenia. Grain size boundaries were calculated using the GRADISTAT 8.0 program developed by BLOTT & PYE (2001, 2012).

2.3.2. pH, Eh,and elemental (TC, C_{org}, TS) analysis

pH and redox potential (Eh) were measured in a separate core immediately after coring. A combined glass electrode connected to a pH-Eh meter (Mettler Toledo, pH ±0.01) was used for pH measurements and an InLab Redox micro-electrode for Eh measurements.

Total carbon (TC), sulfur (TS), and organic carbon (C_{org}) contents were analysed by a LECO Carbon-Sulfur analyser in a certified commercial Canadian laboratory (Acme Analytical Laboratories). Loss on ignition (LOI) is by weight difference after ignition at 1000°C.

2.3.3. Mineralogical analysis

The mineralogical composition of sediments was carried out at the Faculty of Natural Sciences and Engineering, Department of Geology, Ljubljana (Slovenia) via X-Ray Powder Diffraction (XRD) using a Philips PW3710 X-ray diffractometer. Diffraction patterns were identified with the X'Pert HighScore Plus program and Rietveld method.

2.3.4. Major and trace element concentrations in sediment and seagrass

Geochemical analysis of sediments was carried out in a certified commercial Canadian laboratory (Acme Analytical Laboratories) by extraction for 1 h with 2-2-2-HCl-HNO₃-H₂O at 95°C by Inductively Coupled Plasma mass spectrometry (ICP-MS). The analytical precision and accuracy were better than ±5% for the investigated elements. This was assessed with in-house reference materials (STD SO-18) and by the results of the duplicate measurements of six sediment samples as well as duplicate measurements of reference material samples.

The geochemical composition of seagrass samples was determined in the certified commercial laboratory Actlabs (Activation Laboratories, Canada) by high resolution ICP-MS and microwave digestion. Dry, ashed samples were dissolved in acid (Aqua Regia solution). The quality of the analysis was assessed using standard materials NIST 1575a. Measurements of samples were also duplicated. The results indicated that the analytical precision and accuracy were within ±10% for the analysed elements.

2.3.5. Assessment of sediment pollution

The extent of sediment contamination with PTE was assessed by the enrichment factor (EF) calculation (BIRTH, 2003, CHEN et al., 2007, VAROL, 2011, GHREFAT et al., 2011). EF is defined as follows: EF=(PTE/Al)$_{sample}$/(PTE/Al)$_{background}$.

EF values were interpreted as suggested by BIRTH (2003) and CHEN et al. (2007) (Table 1). In this study aluminium (Al) was used as the reference element for geochemical normalization. PTE to Al ratios are widely adopted, presumably because the concentrations of Al in weathering products and their parent material are generally comparable (ZHANG & LIU, 2002). For background values, mean concentrations of PTE in the surficial sediment of the Central Adriatic were applied (DOLENEC et al., 1998, ŽVAB ROŽIČ et al., 2012).

Table 1: Enrichment categories.

EF value	Extent of enrichment according to calculated EF
EF < 1	No enrichment
EF< 3	Minor enrichment
3 < EF < 5	Moderate enrichment
5 < EF < 10	Moderately severe enrichment
10 < EF < 25	Severe enrichment
25 < EF < 50	Very severe enrichment
EF > 50	Extremely severe enrichment

2.3.6. Sequential extraction procedure

One sediment core was selected for the chemical partitioning analysis of As, Cd, Cu, Pb, Mo, Ni, and Zn by employing an sequential extraction procedure in Acme Analytical Laboratories, Canada.

The sediment samples, weighing 1 g, were placed in screw-top test tubes. To each sample, 10 ml of leaching solution was added. Afterwards, the caps were screwed on and the tubes were subjected to the appropriate extraction procedure, depending on the stage of the leaching. Within this procedure the sequential extraction scheme included a water soluble fraction (F1), an exchangeable and carbonate bound fraction (F2), an organic (oxidizable) fraction (F3), a reducible fraction (F4) and a reducible + residual fraction (F5). Reagents used per one gram of sample were F1 – demineralized water, F2 – 1M ammonium acetate, F3 – 0.1M sodium pyrophosphate, F4 – 0.1M (cold) hydroxylamine hydrochloride and F5 – 0.25M (hot) hydroxylamine hydrochloride.

After the sequential extraction procedure, the concentration of the analysed elements in the solutions was measured by Perkin Elan 6000 ICP-MS for the determination of 60 or more elements. A QA/QC protocol incorporated a sample duplicate to monitor the analytical precision, a reagent blank was used to measure the background, and an aliquot of in-house reference material to monitor appropriate accuracy.

For sketching the graphs we replaced the values below the detection limit (LOD) with $LOD/\sqrt{2}$ (VERBOVŠEK, 2011).

2.3.7. Transfer factor (TF) calculation

To evaluate the transfer of PTE from sediment to seagrass *C. nodosa*, the transfer factor (TF) was calculated as follows: $TF=C_{plant}/C_{sediment\ or\ water}$ (DEAN, 2007). The higher the TF value, the more mobile and available the PTE (DEAN, 2007). According to KALFAKAKOU & AKRIDA-DEMERTZI (2000), TF >1 indicates PTE bioaccumulation.

2.3.8. Statistical test

Pearson R correlation analyses were applied to ascertain any associations between elements determined in the Makirina Bay sediments. Basic statistical analyses, box plots, and statistical calculations mentioned above were performed using the STATISTICA 10 software program.

A principal component analysis (PCA) was conducted in order to group major and trace elements. AITCHISON (1981, 1986) showed that the effects of the Constant-Sum Constrain (CSC) on covariance and correlation matrices disappear if the raw percentage data are expressed as logarithms of ratios. Consequently we used centred log-ratio transformation.
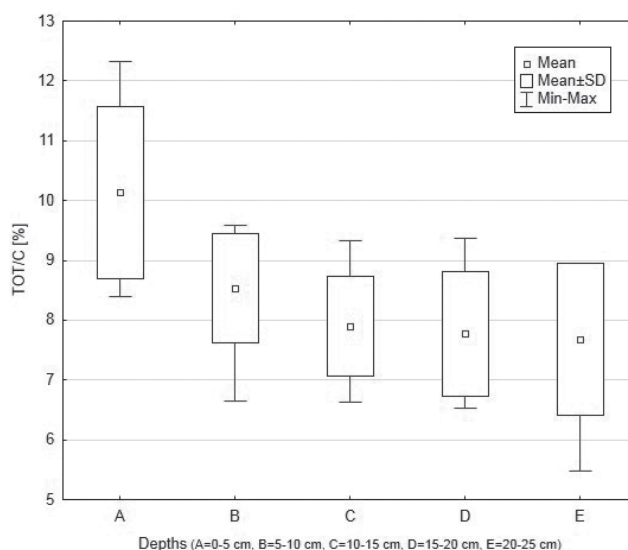
3. RESULTS AND DISCUSSION

3.1. Basic sediment characteristics

3.1.1. C_{org}, TC, TS, pH and Eh

The C_{org} content in the Makirina Bay sediments varies from 4.08 to 5.53%. In the surface sediment of the Central Adriatic, the value of C_{org} is estimated to be 0.95% (DOLENEC et al., 1998). Relatively high C_{org} concentrations in the Makirina Bay sediments are related to the accumulation of organic material associated with the decomposition of aquatic plants abundant in the Makirina Bay (VREČA et al., 1998). C_{org} does not show any specific trend with depth in sediment cores, while TC concentrations (5.47 to 12.32%) show a general decrease (Fig. 2) associated with higher quantities of the detrital fraction in the upper part of sediment cores. TS concentrations are also very high (1.22–2.59%), indicating a general increase with depth (Fig. 3), similar to the presence of the mineral pyrite in sediments. Results of Eh measurement showed a highly reductive sedimentary environment even at the sediment/water interference (Eh= –430 mV). Negative Eh values and slightly decreasing pH (ranging from 7.95 to 6.94), are attributed to processes accompanying the decomposition of sedimentary organic matter (LOJEN et al., 2004). In recent anoxic marine sediment, pH is also controlled by the precipitation of metal sulfides (BEN-YAAKOV, 1973), pyrite in the case of the Makirina Bay sediments.

3.1.2. Grain size distribution

The granulometric analysis of the Makirina Bay sediments showed that they are mostly represented by very poorly sorted

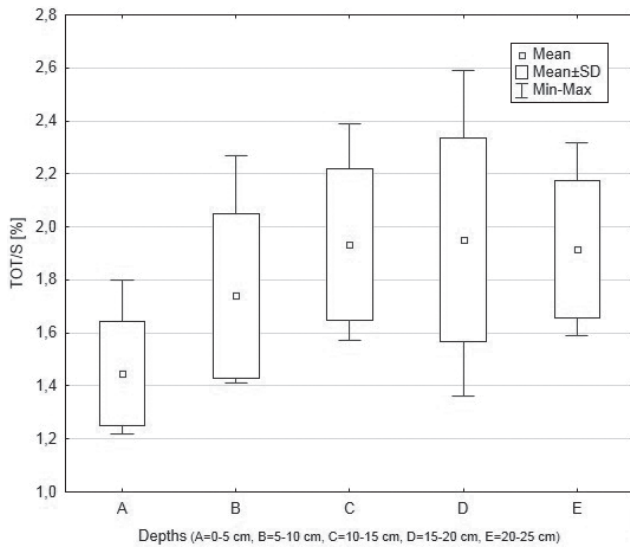**Figure 2:** Vertical distribution of TC concentrations.

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Figure 3: Vertical distribution of TS concentrations.

sandy silt (Fig. 4). In all sediment samples, mud (silt+clay) dominates over sand, indicating a relatively calm depositional environment (ŠPARICA et al., 1989, ŠPARICA et al., 2005). The average sand content is 27% with the major proportion (41%) in the top 5 cm of sediment cores while the average content of mud is 73% with the minor proportion (59%) in the top 5 cm of sediment cores. Mean values of grain sizes ranged from 40 μm (top 5 cm of sediment cores) to 20 μm (bottom 5 cm of sediment cores).

3.1.3. Mineralogy

According to XRD analysis, the mineral composition of the Makirina Bay sediments is characterized by high quantities of dolomite and quartz, followed by illite/muscovite, aragonite, halite, calcite, and pyrite. In some sediment samples, magnesium calcite, plagioclase, gypsum, and clinochlore were also determined. Carbonate minerals predominate among the established mineral assemblage, which is in accordance with the catchment geology of the study area, where Ivinj dolomites, Makirina limestones and dolomites, Kamena rudist limestones and Ivinj Draga deluvial deposits lithostratigraphic units may be discerned (ŠPARICA et al., 1989, ŠPARICA et al., 2005).

4. CORE SEDIMENT GEOCHEMISTRY

4.1. Major elements

Mean concentrations of major elements are presented in Table 2.

The concentration of **Si** in the Makirina Bay sediments ranges from 9.34 to 21.84% and indicates a slightly increasing trend with depth in the sediment cores, visible mostly in
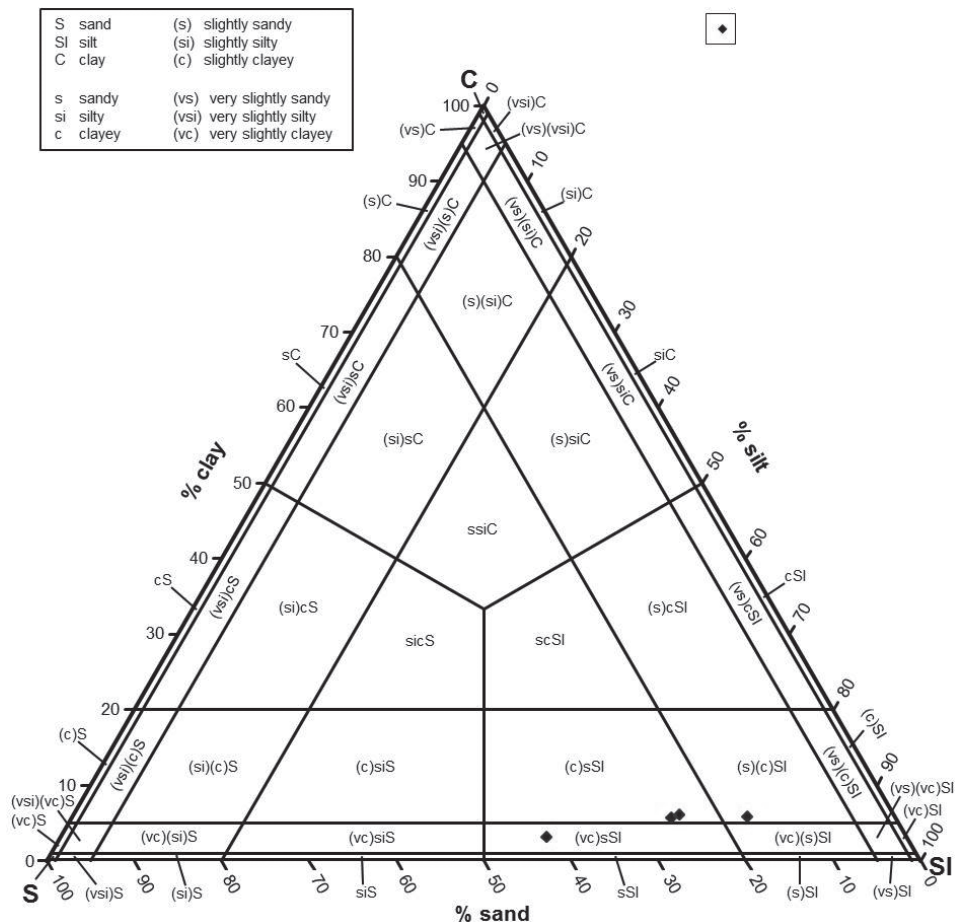

Figure 4: Granulometric composition of the Makirina Bay sediments, diagram developed by Blott & Pye (2001, 2012).

Table 2: Mean concentrations of major and trace elements in Makirina Bay sediments. Concentrations in italic letters represent minimum values, concentrations in bold letters represent maximum values (*DOLENEC et al, 1998, ** ŽVAB ROŽIČ et al., 2012).

Depth [cm]	Si [%]	Al [%]	K [%]	Ca [%]	Mg [%]	Fe [%]	Na [%]	Mn [%]	P [%]	Ti [%]
0–5	*12.65*	*4.33*	*1.23*	**11.32**	3.11	*2.26*	2.45	*0.02*	**0.03**	*0.26*
5–10	14.66	5.32	1.38	9.11	**3.30**	2.80	**2.46**	*0.02*	**0.03**	0.32
10–15	15.65	5.92	1.49	*8.25*	3.20	3.11	2.07	**0.03**	**0.03**	**0.35**
15–20	15.54	**5.93**	**1.50**	8.57	*2.95*	**3.15**	1.91	**0.03**	**0.03**	**0.35**
20–25	**15.98**	5.80	1.46	9.29	2.97	3.08	*1.90*	**0.03**	**0.03**	**0.35**
Mean	14.9	5.46	1.41	9.31	3.11	2.88	2.16	0.03	0.03	0.33
Central Adriatic* Mean value		4.35	1.41	12.56	2.32	2.62		0.12	0.05	0.2
Central Adriatic** Mean value	3.73	0.77					1.23			

Depth	Ag [ppm]	As [ppm]	Au [ppb]	Ba [ppm]	Be [ppm]	Bi [ppm]	Cd [ppm]	Co [ppm]	Cr [ppm]	Cu [ppm]	Cs [ppm]	Ga [ppm]	Hf [ppm]	Hg [ppm]	Mo [ppm]	Ni [ppm]
0–5	*0.08*	*14.47*	1.62	*142.94*	1.60	*0.19*	0.27	*7.05*	*82.10*	27.64	*4.87*	*8.32*	*3.38*	**0.07**	*13.82*	*26.51*
5–10	**0.09**	15.59	*1.47*	168.31	*1.48*	0.26	*0.25*	8.79	96.64	30.74	5.51	10.09	4.23	**0.07**	22.56	31.86
10–15	**0.09**	16.45	2.18	185.63	2.14	0.31	0.31	9.95	105.19	**34.10**	6.20	11.38	4.33	**0.07**	25.14	34.93
15–20	*0.08*	**17.41**	1.86	**189.00**	**3.00**	**0.33**	**0.33**	**10.78**	**119.73**	31.29	**6.38**	**11.83**	4.31	**0.07**	31.54	**37.86**
20–25	*0.08*	17.37	**3.47**	184.43	2.10	0.26	0.27	10.04	113.38	23.06	6.13	10.93	**4.43**	0.07	**32.69**	35.27
Mean	0.08	16.26	2.12	174.06	2.06	0.27	0.28	9.32	103.41	29.36	5.82	10.51	4.14	0.07	25.15	33.29
Central Adriatic* Mean value	0.8	10.5		190	1.9			16	115	24.7				0.113		111
Central Adriatic** Mean value							0.07								1.06	

Depth	Pb [ppm]	Rb [ppm]	Sb [ppb]	Sc [ppm]	Se [ppm]	Sn [ppm]	Sr[ppm]	Ta [ppm]	Th [ppm]	Tl [ppm]	U [ppm]	V [ppm]	W [ppm]	Y [ppm]	Zn [ppm]	Zr [ppm]
0–5	*23.74*	*68.88*	*0.28*	*7.23*	**1.18**	*2.36*	**496.44**	*0.72*	*8.60*	*0.45*	*6.16*	*80.23*	*1.01*	*17.20*	47.67	*120.29*
5–10	27.01	84.79	0.34	8.94	1.14	2.75	335.28	0.89	10.86	0.58	9.01	103.38	1.53	21.33	48.50	150.02
10–15	27.29	93.44	0.34	**10.00**	1.16	2.63	*300.15*	**0.94**	11.83	0.63	9.70	111.13	**1.56**	23.58	**50.63**	160.58
15–20	**27.35**	**96.69**	0.39	9.88	1.04	2.75	328.95	**0.94**	**12.09**	**0.66**	10.80	**113.88**	**1.56**	23.88	**50.63**	161.01
20–25	25.31	92.06	**0.43**	**10.00**	*0.91*	**3.71**	368.86	0.87	11.77	0.65	**10.89**	110.00	1.51	**24.37**	*46.57*	**166.89**
Mean	26.14	87.17	0.35	9.21	1.09	2.84	365.94	0.87	11.03	0.60	9.31	103.72	1.43	22.07	48.80	151.76
Central Adriatic* Mean value	11			9.6			584		6.4		2.1	89			73	38.9

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the upper 15 cm. Si levels in the sediment are higher than Si concentrations in the surface sediments of the Central Adriatic (ŽVAB ROŽIČ et al., 2012). Relatively high concentrations of SiO_2 are related to the presence of quartz originating from the Eocene flysch located approximately 6 km NE of Makirina (ŠPARICA et al., 2005). This is supported by a positive correlation of Si, Zr, and Cr (Table 3), showing their common source. Si in the sediment could also originate from "terra rossa", a typical Mediterranean red soil developed in the surroundings of the bay (VREČA, 1998).

Al and **K** concentrations in the Makirina Bay sediments range from 2.99 to 8.31% and from 0.99 to 2.11%, respectively. Concentrations of Al and K in the Makirina Bay sediments are higher than their respective concentrations in the surface sediments of the Central Adriatic (DOLENEC et al., 1998). The distribution of Al and K and a strong positive correlation between the Al and K concentrations (Table 3) suggest that these two elements have similar origins and depositional characteristics. Concentrations of both elements indicate a slightly increasing trend with depth of the sediment cores, visible mostly in the upper 15 cm, confirming the presence and distribution of clay minerals (illite/muscovite and clinochlore) in these cores.

The concentration of **Ca** and **Mg** in the Makirina Bay sediments varies from 3.67 to 14.84% and from 2.07 to 3.90%, respectively. Concentrations are more or less the same as the concentration of Ca and Mg in the surface sediments of the Central Adriatic (DOLENEC et al., 1998). Relatively high concentrations of Ca and Mg in the sediments of the Central Adriatic probably suggest the enrichment of sediments with predominantly detrital calcite and dolomite, carried into the basin from the land (DOLENEC et al., 1998). Ca has a strong positive correlation with Sr (Table 3) which is related to their similar geochemical behaviour. Sr is often a substitute for Ca because their ionic radii are fairly similar. A negative correlation or lack of correlation between Ca, Mg, and the majority of the trace elements (Table 3) confirms the important role of other minerals (for example silicates) as the geochemical carrier phase of trace elements.

Fe concentrationsin the Makirina Bay sediments varied from 1.59 to 4.35%. The Fe content in sediments is higher than that in the surface sediment of the Central Adriatic (DOLENEC et al., 1998).The vertical profiles of Fe in the sediments show exactly the same pattern as Al. A strong positive correlation between Fe, Al, and K (Table 3) suggests that Fe is principally associated with the clay minerals. Iron is also present in sulfide form as authigenic pyrite, which is also supported by the positive correlation between Fe and TS (Table 3).

Na concentrations in the Makirina Bay sediments range between 0.78 and 3.78%. Na content in the sediments is related to the presence of the halite mineral. Concentrations of Na in the Makirina Bay sediments are higher than the Na content in surface sediments of the Central Adriatic (ŽVAB ROŽIČ et al., 2012) because of the semi-enclosed character and evaporitic environment of the study area (DOLENEC et al., 2002).

The concentrations of **Mn** range between 0.02 and 0.04%. Concentrations obtained in this study are lower than those in the surface sediments of the Central Adriatic (DOLENEC et al., 1998). Its concentrations reflect redox conditions. In oxygen rich sediments, manganese is accumulated as oxides, whereas in oxygen depleted sediment the reduction and solubilization of these oxides can release Mn to pore waters (MONTEIRO et al., 2012).

The concentrations of total **P** varied from 0.02 to 0.05%. These concentrations are more or less the same as the concentrations of P in the surface sediment of the Central Adriatic (DOLENEC et al., 1998). There is no significant correlation between P and other elements present (Table 3). P enrichment in the top 5 cm of sediment cores could be related to the phosphorus fertilizers applied in the surroundings of the bay. P may be present in marine sediments either as a detrital inorganic phosphate mineral or as phosphate ions in association with various sediment compounds. Concentrations of P could also be related to the presence of the mineral apatite in the Makirina Bay sediments (ŠPARICA et al., 2005).

The content of **Ti** in the Makirina Bay sediments varied from 0.17 to 0.47%. The concentrations are higher than their respective concentrations in the surface sediments from the Central Adriatic (DOLENEC et al., 1998). The high positive correlation with Al and K (Table 3) indicates its relationship with clay minerals. Ti concentrations indicate a downcore increase that coincides with the vertical profile of the clay minerals. Concentrations of Ti in the sediments could also be related to the presence of the mineral rutile (ŠPARICA et al., 2005).

4.2. Trace elements

The mean concentrations of trace elements in sediment profiles are presented in Table 2.

Concentrations of most trace elements are generally higher in the bottom (20–25 cm) than in the top (0–5 cm) of the sediment cores. Mean concentrations of Ag, Co, Cr, Hg, Ni, Sc, Sr, and Zn in the Makirina Bay sediments do not exceed their respective concentrations in the surface sediments of the Central Adriatic, while the mean values of As, Be, Cu, Pb, Th, U, V, and Zr do exceed them (DOLENEC et al., 1998). This is related to the different source materials of the sediments (Be, Th, Zr), anoxic conditions in Makirina Bay sediments (V, U), agricultural activity surrounding the Makirina Bay (As, Cu), and the vicinity of the main road (Pb). Higher values of trace elements in the Makirina Bay sediments in comparison to the surface sediment of the Central Adriatic (DOLENEC et al., 1998, ŽVAB ROŽIČ et al., 2012) could also be attributed to the calm depositional environment in Makirina Bay.

Downcore concentrations of the majority of trace elements, including Ba, Co, Ni, V, and Zr (Table 2), indicate a similar distribution to Al, K, and Fe, suggesting their associations with clay minerals. This is supported by the strong positive correlation noted between Al, K, Fe, and the trace elements mentioned above.

Table 3: The Pearson correlation matrix analysis between major and trace elements (marked correlations are significant at p < 0.05).

	Si	Al	Fe	Mg	Ca	Na	K	Ti	P	Mn	Cr	LOI	Ba	Co	Sr	U	V	Zr	TOT/C	TOT/S	Mo	Cu	Pb	Zn	Ni	As	Cd
Si	1.00																										
Al	0.95	1.00																									
Fe	0.94	0.99	1.00																								
Mg	−0.09	−0.17	−0.21	1.00																							
Ca	−0.84	−0.88	−0.83	0.09	1.00																						
Na	−0.55	−0.48	−0.50	−0.08	0.12	1.00																					
K	0.94	0.98	0.96	−0.24	−0.90	−0.43	1.00																				
Ti	0.98	0.99	0.98	−0.11	−0.86	−0.52	0.96	1.00																			
P	0.07	0.16	0.10	0.02	−0.37	0.22	0.17	0.09	1.00																		
Mn	0.72	0.81	0.80	−0.33	−0.76	−0.24	0.81	0.78	0.38	1.00																	
Cr	0.75	0.72	0.75	−0.22	−0.55	−0.49	0.73	0.74	−0.17	0.52	1.00																
LOI	−0.95	−0.91	−0.93	0.07	0.68	0.68	−0.86	−0.95	0.13	−0.66	−0.77	1.00															
Ba	0.95	0.98	0.98	−0.20	−0.88	−0.49	0.96	0.98	0.15	0.81	0.72	−0.92	1.00														
Co	0.88	0.93	0.94	−0.33	−0.84	−0.36	0.91	0.92	0.22	0.84	0.70	−0.83	0.94	1.00													
Sr	−0.80	−0.83	−0.78	−0.20	0.93	0.16	−0.81	−0.83	−0.31	−0.66	−0.50	0.68	−0.80	−0.74	1.00												
U	0.72	0.72	0.77	−0.39	−0.51	−0.48	0.70	0.73	−0.28	0.43	0.76	−0.77	0.72	0.70	−0.44	1.00											
V	0.82	0.88	0.90	−0.32	−0.73	−0.43	0.84	0.87	−0.06	0.67	0.63	−0.84	0.90	0.87	−0.63	0.83	1.00										
Zr	0.95	0.90	0.90	−0.04	−0.75	−0.58	0.87	0.94	−0.12	0.62	0.76	−0.97	0.92	0.82	−0.74	0.76	0.84	1.00									
TOT/C	−0.91	−0.90	−0.91	0.00	0.73	0.49	−0.83	−0.93	0.02	−0.69	−0.68	0.94	−0.89	−0.85	0.76	−0.64	−0.78	−0.92	1.00								
TOT/S	0.85	0.93	0.95	−0.40	−0.81	−0.32	0.91	0.90	0.10	0.80	0.66	−0.82	0.92	0.94	−0.71	0.77	0.92	0.81	−0.81	1.00							
Mo	0.48	0.50	0.57	−0.60	−0.28	−0.30	0.49	0.50	−0.38	0.27	0.62	−0.56	0.50	0.55	−0.16	0.90	0.69	0.53	−0.43	0.67	1.00						
Cu	0.18	0.29	0.24	0.39	−0.34	−0.05	0.20	0.26	0.45	0.32	−0.05	−0.14	0.26	0.31	−0.45	−0.09	0.17	0.16	−0.30	0.16	−0.35	1.00					
Pb	0.79	0.81	0.76	0.07	−0.74	−0.57	0.81	0.80	0.16	0.58	0.58	−0.74	0.80	0.68	−0.71	0.55	0.71	0.75	−0.65	0.64	0.25	0.40	1.00				
Zn	0.74	0.74	0.69	−0.05	−0.68	−0.57	0.78	0.72	0.26	0.57	0.59	−0.65	0.73	0.63	−0.59	0.50	0.57	0.65	−0.53	0.56	0.21	0.30	0.93	1.00			
Ni	0.90	0.94	0.94	−0.29	−0.76	−0.60	0.94	0.93	0.05	0.75	0.81	−0.90	0.94	0.88	−0.67	0.79	0.85	0.88	−0.81	0.87	0.60	0.14	0.84	0.83	1.00		
As	0.71	0.69	0.73	−0.36	−0.46	−0.63	0.71	0.70	−0.07	0.47	0.73	−0.75	0.70	0.68	−0.33	0.75	0.69	0.71	−0.57	0.68	0.68	−0.15	0.63	0.66	0.83	1.00	
Cd	0.50	0.55	0.49	−0.13	−0.64	−0.14	0.53	0.53	0.37	0.66	0.14	−0.41	0.59	0.60	−0.55	0.26	0.54	0.47	−0.45	0.54	0.06	0.51	0.53	0.50	0.48	0.18	1.00

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The results of PCA are reported in Fig. 5. The first two principal components (PCs) accounted for 64.22% of the total variance in the dataset. The first component explains 48.02% of the total variance and exhibits one group with negative loadings and one with positive loadings. Highly negative loadings reveal an association of major (Si, Fe, Ti, K) and trace elements (Ba, Co, Ni, V, Zr) related to Al, suggesting their common origin (terrigenous aluminosilicates). Another group of trace elements (Cr, U, Mo, Pb, Zn, As, Cd) also has negative but not high loadings, meaning that those elements are partly associated with terrigenous aluminosilicates and also with other sources. In the first component, Ca, Sr, Mg, Loss of Ignition (LOI), and TC are positively loaded due to their inverse geochemical behaviour with respect to aluminosilicates. LOI, TC, Ca, and Sr represent the autochthonous biogenic fraction of the sediment. Mg corresponds with terrigenous carbonates (dolomite), but could also be related to the autochthonous fraction (aragonite and Mg calcite). Negatively loaded Cu and P are probably anthropogenic sources linked to the use of fertilizers and blue vitriol ($CuSO_4x5H_2O$) in the surroundings of Makirina Bay. The second PC represents 16.2% of the total variance. Cd, Pb, and Zn have similar positive loadings, highlighting their common origin. As, Cr, Mo, U, and V show associations with TS. These trace elements are redox-sensitive elements, known to become highly enriched in anoxic sediments (LEGELEUX et al., 1994).

4.3. Assessment of sediment pollution

For PTE (As, Cd, Cu, Pb, Mo, Ni, Zn), EF were calculated (Table 4). As natural background values, the concentrations of PTE in surface sediments of the Central Adriatic were used (Table 2). Calculated EF values for Cd, Ni, and Zn are < 1 and show no enrichment. EF values for As, Cu, and Pb are < 3, indicate minor enrichment, while EF values for Mo indicate minor to moderate enrichment.

EF values for As, Cu, and Pb are higher in the top 5 cm of sediment cores, which could be a result of recent anthropogenic enrichment with the aforementioned PTE. Enrichment of sediments with As and Cu is probably due to anthropogenic activities in the surroundings of the bay, including
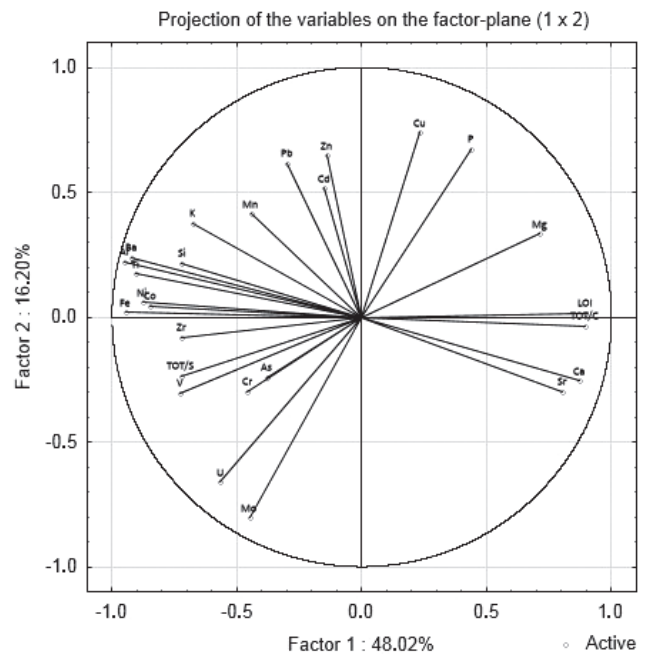

Figure 5: PCA diagram result for overall dataset.

the use of pesticides and fertilizers in agriculture. Pb-enrichment is most likely a consequence of runoff from the Kapela–Tisno road located in the southern part of the bay.

Mo EF values increase with depth of sediment core. Molybdenum is an element that is strongly enriched in highly reducing conditions accompanied by accumulation of organic matter and precipitation of iron sulfide (WEDEPOHL, 1978) and shows the greatest degree of enrichment in reducing sediments relative to crustal values (CRUSIUS et al., 1996).

4.4. Sequential extraction results

In the applied sequential leaching procedure, the labile/residual fractions considered were: water soluble fraction (1), exchangeable fraction (2), oxidizable fraction (3), (easily) reducible fraction (4), and reducible+residual fraction (5).

Table 4: Calculated EF and TF for selected PTE and their concentrations in seagrass *C. nodosa.*

	As	Cd	Cu	Pb	Mo	Ni	Zn
	EF	EF	EF	EF	EF	EF	EF
0–5 cm	1.4	0.7	1.1	2.2	2.4	0.2	0.7
5–10 cm	1.2	0.5	1	2.0	3.1	0.2	0.5
10–15 cm	1.2	0.6	1	1.8	3.1	0.2	0.5
15–20 cm	1.2	0.6	0.9	1.8	3.9	0.2	0.5
20–25 cm	1.2	0.5	0.7	1.7	4.2	0.2	0.5
PTE concentration in C. *nodosa*	1.26	0.13	6.12	1.4	3.1	1.28	17.8
TF range	0.06–0.11	0.36–1.33	0.14–0.32	0.08–0.13	0.09–0.16	0.04–0.07	0.27–0.48
Mean TF	0.09	0.58	0.24	0.1	0.12	0.06	0.38

PTE extracted in the first fraction by H_2O, are relatively labile and thus may be potentially bioavailable to the surrounding ecosystem. This phase contains the water soluble species made up of free ions and ions complexed with soluble organic matter and other constituents (FILGUEIRAS et al., 2002).

The next phase was the exchangeable fraction (2), which includes weakly adsorbed PTE retained on the solid surface by relatively weak electrostatic interaction, PTE that can be released by ion-exchange processes, and PTE that can be coprecipitated with carbonates present in many types of sediments. Changes in the ionic composition which influence adsorption–desorption reactions or lower the pH could cause remobilization of PTE from this fraction (FILGUEIRAS et al., 2002).

The oxidizable fraction (3) corresponds to trace elements bound to organic matter and sulfides. PTE associated with oxidizable phases are assumed to remain in sediments for longer periods, but may be mobilized by decomposition processes. Degradation of organic matter under oxidizing conditions can lead to a release of soluble PTE bound to this component (FILGUEIRAS et al., 2002). The last two fractions, considered in the applied sequential leaching procedure were reducible (4) and reducible + residual fractions (5).

The (easily) reducible fraction (4) is linked to amorphous manganese hydroxides, which are thermodynamically unstable under anoxic conditions. The reducible + residual fraction (5) is linked to amorphous Fe hydroxides (moderately reducible part). The residual fraction includes naturally occurring crystalline Mn hydroxide minerals. PTE in this fraction are retained within their crystal lattices, and thus PTE bound to this component are regarded as stable and are not susceptible to remobilization under normal environmental conditions (FILGUEIRAS et al., 2002, FORGHANI et al., 2009).

Arsenic (As) is mainly bound to the oxidizable (3) and reducible fraction (4) (Fig. 6A). The least mobile was arsenic in the water soluble and exchangeable phase. It has already been reported that in reduced sediments the distribution of arsenic is controlled mainly by sulphides (PRICE & PICHLER, 2005). Arsenic mobility in an anaerobic, sulfur-rich environment is very low and can also be limited by its coprecipitation with secondary sulfide minerals and more generally by clays (REIMANN & DE CARITAT, 1998, PLANT et al., 2003).

The dominant proportion of cadmium (Cd) was found to be associated with the exchangeable fraction (2) (Fig. 6B), meaning that most of the Cd present in the sediments is exchangeable and bound to carbonates. This observation is in agreement with some other studies (BILLON et al., 2002, GHREFAT & YUSUF, 2006, LI et al., 2007, GAO et al., 2010, LIU et al., 2011, ZHANG et al., 2012, LIU et al., 2013). The high content of Cd in the exchangeable fraction could result from the high concentration of Cl⁻ in coastal sediments and the formation of soluble Cd-Cl complexes. This might induce Cd desorption from the sediments (LIU et al., 2011, LI et al., 2007). Cd has no essential biological

function and is highly toxic to plants and animals (GHREFAT & YUSUF, 2006). Although a high mobility and bioavailability of Cd was observed, it could hardly cause a harmful effect on the local environment owing to its low total concentration detected in these sediments.

A significant amount of copper (Cu) is bound to the oxidizable fraction (3) (Fig. 6C). The tendency of Cu to be associated with the oxidizable fraction has been reported in several other studies (LI et al., 2001, NGIAM & LIM, 2001, MORILLO et al., 2004, BURTON et al., 2005). Cu could easily form complexes with organic matter due to the high stability of organic-Cu complexes (JONES & TURKI, 1997, LI et al., 2001, MORILLO et al., 2004, BURTON et al., 2005). Cu is essential for all organisms, but can be toxic at high doses (REIMANN & DE CARITAT, 1998). Under reducing conditions, Cu has very low mobility (REIMANN & DE CARITAT, 1998), but it can be released into the environment under oxidizing conditions.

The highest content of molybdenum (Mo) (Fig. 6D) is associated with the water soluble fraction (1). Molybdenum is essential for all organisms except some bacteria, but is considered toxic in large amounts, causing secondary Cu deficiency (REIMANN & DE CARITAT, 1998, YU et al., 2011). The water soluble form of Mo includes readily soluble molybdates and water soluble organic complexes. The bioavailability of Mo to plants is largely dependent on the sediment pH and is greater under neutral and alkaline conditions than under acidic ones (REIMANN & DE CARITAT, 1998, ADRIANO, 2001).The ready mobility and bioavailability of Mo could be related to neutral–alkaline conditions in the Makirina Bay sediments.

The maximum values of nickel (Ni) (Fig. 6E) were found in the oxidizable (3) fraction. This is in agreement with the results of some other studies (KIRATLI & ERGIN, 1996, PURUSHOTHAMAN et al., 2012). Ni is often bound to organic matter (SAKAN et al., 2011) due to the adsorption of Ni by the formation of ligands in the presence of high organic content (PURUSHOTHAMAN et al., 2012). Ni is toxic to organisms at elevated levels, but trace amounts of this element are required for several biological processes (ADRIANO, 2001).

A large proportion of lead (Pb) was mainly bound to the reducible + residual fraction (5) (Fig. 6F). Similar results were also found in other studies (MORILLO et al., 2004, LI et al., 2007). Fe and Mn hydrous oxides are important scavengers of Pb in sediments (MORILLO et al., 2004, WANG et al., 2010). The proportion of Pb in the last fraction (5) was much higher than that of other PTE in this fraction. The presence of Pb in the exchangeable phase suggest coprecipitation with, or adsorption onto $CaCO_3$ (KIRATLI & ERGIN, 1996). Pb is considered a non-essential and toxic element (ADRIANO, 2001). Its distribution shows an affinity with the oxidizable and exchangeable fraction, but it is also strongly bound to the reducible + residual fraction (5), which reduces its total mobility.

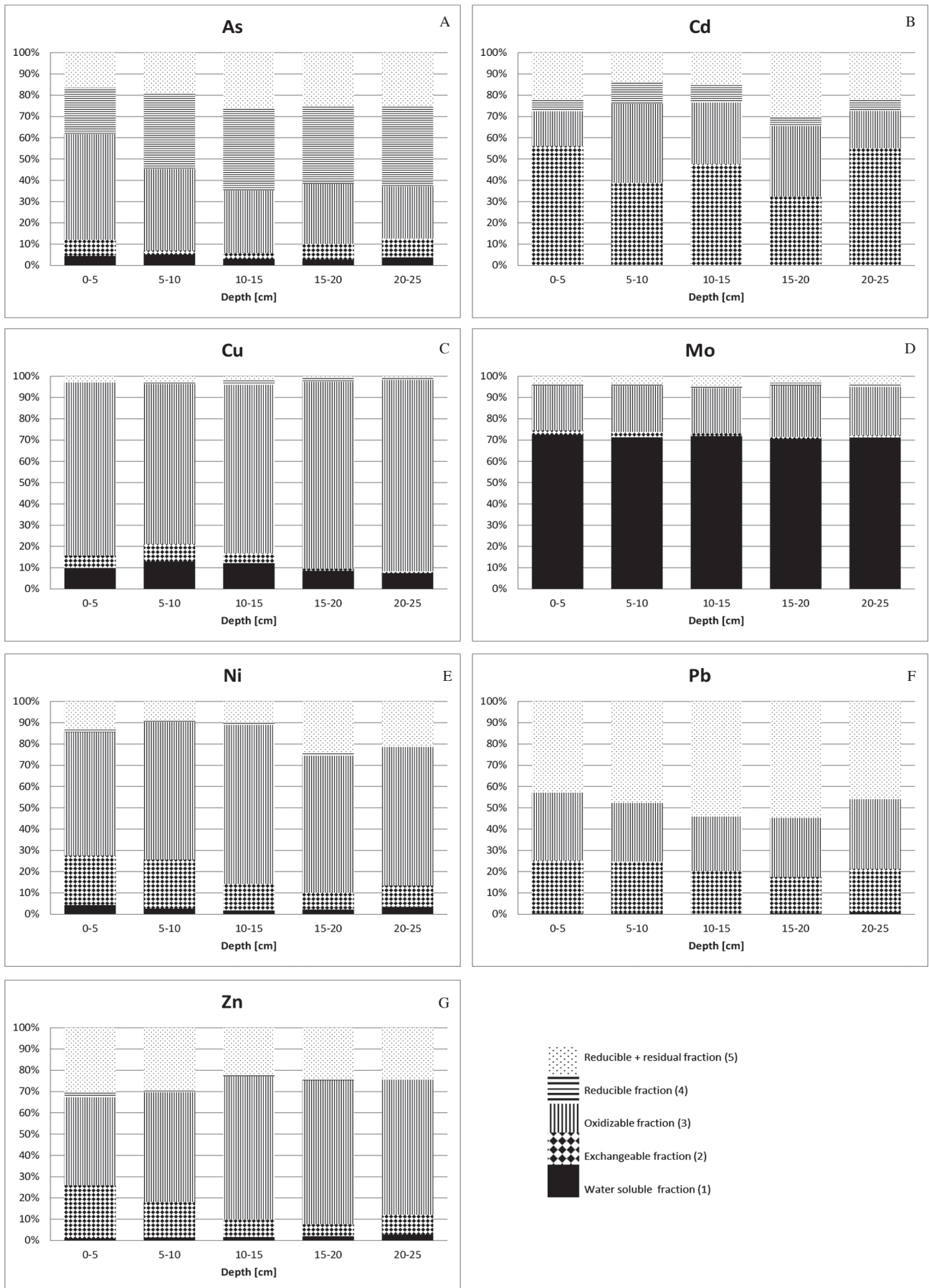The most abundant fraction for zinc (Zn) is the oxidizable fraction (3) (Fig. 6G). Zinc is a micronutrient and chal-

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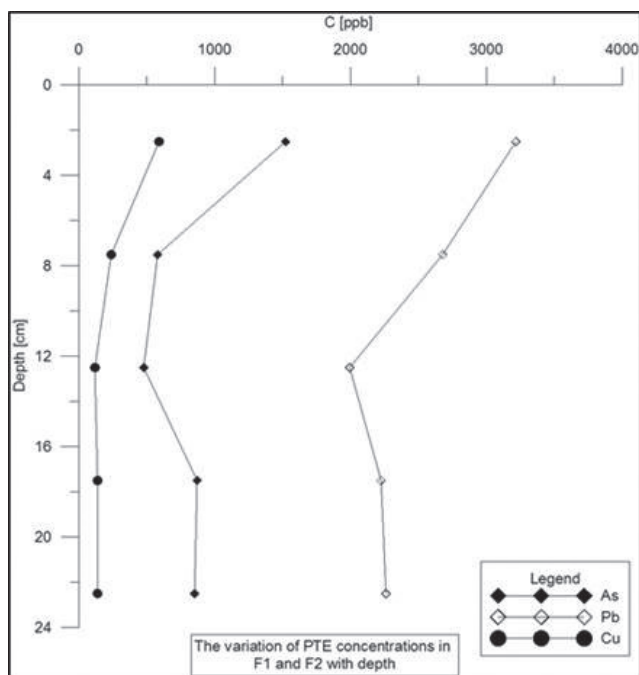
Figure 6: Vertical profiles of PTE partitioning.

Figure 7: The variation of PTEs concentrations in the most mobile fraction (F1 and F2) with depth.

cophilic in nature. In highly anoxic conditions it is associated with carbonate, sulfides, and organic matter and is not affected by the redox conditions (YU et al., 2001, PURUSHOTHAMAN et al., 2012). Organic matter, S, and Zn are closely related in many anoxic sediments (KIRATLI & ERGIN, 1996).

In general, the mobility of PTE in the Makirina Bay sediments decreased in the order Mo > Cd > Pb > Ni > Zn > Cu > As. The results of the sequential leaching procedure reveal that, except for Cd and Mo, PTE in Makirina Bay sediments are not readily mobile or bioavailable since only a small percentage of PTE is extracted in the first two steps. The variation of the speciation of the PTE with depth could provide information about recent enrichment if the concentrations of PTE associated with the more mobile fractions are higher in the upper part of the sediment core (RIBA et al., 2002, FORGHANI et al., 2009). Similarly to EF values (Table 4), the sum of concentrations of As, Cu, and Pb in the first two fractions (Fig. 7) decreases with increasing depth of sediment core, reflecting the fact that the aforementioned PTE have been mainly added to sediments in recent years.

4.5. Transfer factor

Concentrations of As, Cd, Cu, Mo, Ni, Pb, and Zn in the belowground biomass of *C. nodosa*, (the most abundant aquatic plant in the bay), are presented in Table 4. Calculated TF values (Table 4) for selected PTE were in the descending order Cd > Zn > Cu > Ni > Mo > As > Pb. All TF were less than 1, indicating that *C. nodosa* did not effectively transfer selected PTE from the sediment to the root. The TF results more or less confirmed the sequential extraction procedure results, the only exceptions being Cd and Mo, probably as a

consequence of the generally low total Cd concentrations in the Makirina Bay sediments and high anoxic conditions at the sediment–water interface. Mo is predicted to be in the IV oxidation state under anoxic conditions, whereas only the soluble Mo(VI) forms are available for plants (ZIMMER & MENDEL, 1999).

5. CONCLUSION

This paper has examined the basic characteristics (pH, Eh, grain size) of the Makirina Bay sediments, their mineralogical and geochemical composition. The novel contribution of present research is the determination of chemical speciation of several PTE (As, Cd, Cu, Mo, Ni, Pb, Zn) in the Makirina bay sediments, the determination of the PTE content in seagrass (*C. nodosa*) and their TF calculation. The geochemical composition of the Makirina Bay sediments is defined by the mineralogical and granulometric composition of the sediments. The results of the EF and sequential leaching procedure indicate an anthropogenic contribution of As, Cu, and Pb to the sediment due to agricultural activity in the area surrounding the bay (As, Cu) and the vicinity of the main road (Pb). Despite the ready mobility and bioavailability of Cd and Mo, their transfers from sediment to seagrass roots are not effective.

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