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METAL POLLUTION DETERMINED BY POLLUTION INDICES FOR SEA GRASS *P. OCEANICA* AND SURFACE SEDIMENTS

Slavka Stanković[1,*], Mihajlo Jović[2], Marija L. Mihajlović[3], Danijela Joksimović[4] and Bojan Tanaskovski[1]

[1] *TMF, Department of Analytical Chemistry, University of Belgrade,* Belgrade, Serbia
[2] *Vinca Institute of Nuclear Sciences, University of Belgrade,* Belgrade, Serbia
[3] *Institute for Technology of Nuclear and Other Mineral Raw Materials,* Fransa Deperea 86, Belgrade, Serbia
[4] *IBM, University of Podgorica,* Dobrota bb, Kotor, Montenegro

[*]Corresponding author: slavka@tmf.bg.ac.rs

Abstract - Concentrations of Fe, Mn, Cu, Zn, Pb, Ni, Co, As, Co, and Hg in the sea grass *Posidonia oceanica* and surface sediment samples were determined. Together with *P. oceanica*, surface sediment samples were collected at eight locations in the major demographic, tourist and port areas along the Montenegrin coast to assess metal pollution. The metal pollution index (MPI) and metal enrichment factor (EF) were calculated and used to evaluate the impact of heavy metals in the surface sediment on *P. oceanica*. The sediment MPI and EF values were lower than these values in *P. oceanica* at the same locations. Since the surface sediment contained lower mean concentrations of Zn, Ni, Pb, Cd and Hg, than the sea grass *P. oceanic*, we concluded that the sea grass absorbed some metals from the seawater column.

Key words: heavy metals; *P. oceanica*; surface sediment*;* metal pollution index; enrichment factor

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INTRODUCTION

Trace elements are serious pollutants of the marine environment because of their toxicity and persistence, their difficult biodegradability and tendency to concentrate in aquatic organisms (Lafabrie et al., 2007; Conti et al., 2010). Much attention has been paid to the use of marine organisms as bioindicators for trace-metal pollution in marine waters (Luy et al., 2012, Markovic et. al., 2012). The sea grass *Posidonia oceanica* (L.) Delile has been studied as a bioindicator of microelement contamination in various parts of the world, especially on the Mediterranean coast (Lafabrie et al., 2007; Conti et al., 2010; Richir et al., 2010; Luy et al., 2012). They form dense populations that frame the so-called *Posidonia* meadows. Meadows of *P. oceanica* have a crucial role in the ecology of the Mediterranean and most occur in shallow and sheltered coastal waters anchored in sand or mud bottoms. *P. oceanica* may absorb trace elements directly from the water column or/and from interstitial water in sediments (Lafabrie et al., 2007); it has a high capacity to accumulate trace elements and concentrating pollutants occurring in the environment (Di Leo et. al., 2013). Many microelements were found in trace amounts in seawater, but often at elevated levels in seagrass (Morillo et al., 2005). Sea grasses are increasingly used as indicators of chem-

ical contaminations of coastal regions (Conti et al., 2010; Di Leo et. al., 2013).

In the last decade, human and industrial activities in the coastal area of the southeastern Adriatic have increased and resulted in different types of pollutants, including trace elements. Investigations of the southeastern Adriatic marine environment have intensified in the last decade and included a number of sites from the southeastern Adriatic region, such as the Albanian and Montenegrin coastal areas (Çelo et al., 1999; Çullaj et. al., 2000 Rivaro et al., 2004 Rivaro et al., 2011; Jovic et al., 2011a,b; Joksimovic et al., 2011; Markovic et al., 2012); however, no papers were found on trace-metal distribution in surface sediments of Montenegro or their impact from sediments on the bioaccumulation in *P. oceanica* along the eastern Adriatic Sea. Hence, the main objectives of the presented research were: (1) to determine element concentrations (Fe, Mn, Ni, Zn, Cu, Co, Pb, As, Cd and Hg) and to evaluate the status of contamination level in surface sediment and *P. oceanica*; (2) to estimate concentration impact of the elements in sediments and in the sea grass *P. oceanica* by their related correlation coefficients (r), and (3) to compare the obtained results with results from other Mediterranean parts to assess the degree of pollution in the studied area.

MATERIALS AND METHODS

Samples of surface sediment and *P. oceanica* were collected at eight selected locations in the Montenegrin coastal area: Sveta Stasija, Kukuljina and Herceg Novi in the Boka Kotorska Bay, and at locations of the open Montenegrin coastal area: Mamula, Zanjice, Bigova, Budva and Bar (Stankovic et al., 2014), situated in the proximity of different geochemical, hydrological and human impacts.

About 350 g of fresh *P. oceanica* samples were collected at a depth of 7±1 m. The *P. oceanica* samples were washed, rinsed with ultrapure water, frozen, lyophilized and reduced to powder, dissolved and analyzed. A preparation of dissolved *P. oceanica* samples (approximately 0.5 g) for trace-metal analysis was performed as follows: the powder was digested with a mixture of 7 ml concentrated HNO_3 (65% Merck, Suprapur) and 2 ml H_2O_2 (30% Merck, Suprapur).

At the same time, 500 g of surface sediment was collected in the vicinity of the *P. oceanica* meadows. Only the top 5 cm of sediment was used for this study. Sediment samples were freeze-dried in the laboratory and stored for further analysis. A representative portion of the sample (about 20 g) was used for grain size analysis using the standard dry sieving and sedimentation techniques (Badr et al., 2009). For trace-elements analysis, a portion of each sediment layer was homogenously mixed and the dried fraction of the sediment smaller than 2 mm was dissolved and analyzed by atomic absorption spectroscopy (AAS). The sediment samples (0.5 g) were digested with 2 ml of HNO_3 (65%) and 6 ml HCl (37%) in a High Microwave Digestion System (CEM. CORPORATION, MDS-2100), for 30 min at 200°C. Three digested samples of sediments and *P. oceanica* from each location were diluted with ultrapure water in 25 ml volumetric flasks and then transferred to 100 ml polypropylene bottles until analysis. Ultrapure water from a Milli-Q system (Millipore, Bedford, MA, USA) was used to prepare all solutions. Mineral acids and oxidants (HNO_3, H_2O_2 and HCl) were of the highest quality (Suprapure, Merck, Darmstadt, Germany). Hg and As were measured following a form of CV AAS procedure using a Perkin-Elmer Hydride System coupled to an atomic absorption spectrometer. The accuracy of measurements was tested with Reference Material IAEA 158 (Marine sediment) and IAEA 140 (*Fucus* Sample). The results were in agreement with certified values, showing good repeatability, maximum ±10% (Table I).

The metal pollution index (MPI) defined by Usero et al. (1997) was used to compare the total metal content in the sediment and *P. oceanica*. It is obtained with the following equation: $MPI = (Cf_1 \times Cf_2 \ldots Cf_n)^{1/n}$ where Cf_n is the concentration of the metal *n* in the sample. To determine the anthropogenic and natural impact on the concentration of investigated elements in the tested samples, the concentration of each element in the samples was compared to the

Table 1. Analysis of certified reference materials IAEA 158 (Marine sediment) and IAEA 140 (*Fucus* Sample): certified values and found values (mean ± S.D.).

Elements	IAEA 158 (Marine sediment)		IAEA 140 (*Fucus* Sample)	
	Certified	Found	Certified	Found
	(mg kg^{-1} dw)		(mg kg^{-1} dw)	
Ni	29.4 ± 4.12	31.0 ± 0.72	3.79 ± 0.41	4.10 ± 0.31
Co	9.0 ± 1.35	10.1 ± 1.5	0.83 ± 0.13	0.95 ± 0.09
Pb	38.0 ± 7.7	35.0 ± 3.9	2.19 ± 0.28	1.87 ± 0.11
As	11.4 ± 1.71	12.6 ± 0.91	44.3 ± 2.1	47.10 ±3.4
Cd	0.37 ± 0.09	0.45 ± 0.05	0.54 ± 0.04	0.65 ± 0.03
Hg	0.132 ± 0.018	0.12 ± 0.018	0.038±0.006	0.037 ± 0.01
Fe*	25.8 ± 2.58	25.1 ± 2.0	2.19 ± 0.36	2.11 ± 0.20
Mn	350 ± 3.8	345 ± 9.0	56.1 ± 2.4	56.9 ± 1.7
Zn	138 ± 13.2	135 ± 7.5	47.3 ±2.0	46.5 ± 1.4
Cu	47.9 ± 5.27	49 ± 3.0	5.05 ± 0.28	4.8 ± 0.30

baseline metal levels. The background shale metal values were as follows: Hg 0.30, Cd 0.30, As 13, Co 19, Pb 20, Cu 45, Ni 68, Zn 95, Mn 850, and Fe 47200 mg/kg, (Rivaro et al., 2011).

The EF is generally defined as the observed metal concentration to Al concentration ratio in the sample divided by the background metal/Al concentrations ratio. Geochemical normalization of the heavy metals data to a conservative element such as Al or Fe is commonly employed in order to identify anomalous metal concentrations (Esen et al., 2010). Al concentrations in the samples were not measured in this study. Fe in sediments is mainly from natural weathering processes and has been broadly used to normalize metal concentrations in order to reduce particle grain-size influence, (Esen et al., 2010). Several authors have successfully used Fe to normalize heavy metal contaminants in sediment (Çelo et. al., 1999; Esen et al., 2010), but not in seagrass. Therefore, Fe was used to calculate the EF value in the sediment and seagrass samples by the equation: $EF = (C_{metal}/C_{Fe})_{sample} / (C_{metal}/C_{Fe})_{background}$. Correlations between the average concentrations of investigated elements in the surface sediment, *P. oceanica* and sediment-*P. oceanica* were performed by analysis of the Pearson correlations in MS Excel.

RESULTS AND DISCUSSION

Sediment

Several studies have reported that the composition of sediment particles plays a significant role in the deposition of pollutants during sedimentation process (Esen et al., 2010; Tavakoly Sany et al., 2011). The composition of the grain size in surface sediments was determined by the percentage of sand (0.063-2 mm) and silt/clay (<0.063 mm) (Fig. 1). Based on the tests performed on sediment samples, the sediment is generally sandy on the Montenegrin coast. The sand content was between 82.2-96.5% and the clay and silt content was between 3.5-17.8% (Fig. 1). The surface sandy sediments into the Bay at locations Kukuljina and Sveta Stasija had the highest content of clay and silt, 9.34+8.37% and 12.15+1.85%, respectively (Fig. 1). Outside the Bay, 10.6 % of clay was in the sandy sediment of Zanjice. The sediment at location Budva had the highest content of sand (96.5%). These deposits are in accordance with hydrographic conditions of the Montenegrin coastal area.

In the surface sediment of the Montenegrin coast, the dominant elements were Fe, and then Mn: Fe was present with about 80-95%, Mn with about

Table 2. Trace metal concentrations in surface sediments with minimum, maximum and mean concentrations (mg/kg dw), MPI and EF values.

Location	Fe	Mn	Zn	Ni	Pb	Cu	Co	As	Cd	Hg	MPI*
Sv.Stasija	9263 ± 268	209 ±19	25.1 ±2.2	18.2 ± 1.7	7.0 ± 1.2	6.6 ±0.5	3.9 ±0.3	4.9 ±0.5	0.75 ± 0.1	0.024 ± 0.002	10.4
Kukuljina	11711 ±396	326 ±28	45.2 ±5.3	74.5 ± 3.2	9.6 ±1.3	14.4 ±1.3	10.2 ±1.0	5.2 ±0.5	0.54 ±0.05	0.098 ± 0.004	18.2
H. Novi	6090 ±221	772 ±64	23.8 ±1.9	32.3 ±3.3	3.7 ±0.4	11.9 ±0.9	9.0 ±0.8	3.7 ±0.4	0.77 ±0.11	0.028 ± 0.002	12.6
Mamula	1591 ±140	282 ±24	7.8 ±0.9	12.8 ±1.1	5.1 ±0.5	4.7 ±0.4	5.0 ±0.4	4.6 ±0.6	0.42 ±0.05	0.029 ± 0.003	7.0
Zanjice	10507 ±363	497 ±44	19.8 ±1.9	16.3 ±1.5	3.9 ±0.5	7.7 ±0.7	6.6 ±0.7	19.7 ±2.6	0.87 ±0.13	0.009 ±0.0001	11.8
Bigova	714 ±61	184 ±18	4.0 ±0.5	10.5 ±0.8	1.3 ±0.1	5.6 ±0.4	13.9 ±1.2	3.5 ±0.5	0.30 ±0.03	0.029 ± 0.003	8.2
Budva	1243 ±124	132 ±12	5.1 ±0.6	2.7 ± 0.2	2.6 ±0.3	3.2 ±0.3	5.2 ±0.5	2.6 ±0.4	0.06 ±0.01	0.014 ± 0.001	3.4
Bar	6216 ±238	657 ±56	22.4 ±2.0	15.8 ±1.2	5.2 ±0.5	14.7 ±1.2	11.4 ±1.1	3.1 ±0.5	0.07 ±0.01	0.155 ± 0.009	11.6
EF$^{**}_{mean}$	1	3.6	1.6	2.7	1.9	1.5	3.4	3.6	12.5	1.3	
Min	714	132	4.0	2.7	1.3	3.2	3.9	2.6	0.06	0.009	3.4
Max	11711	772	45.2	74.5	9.6	14.7	13.9	19.7	0.87	0.155	18.2
Mean	5917	382	19.2	22.9	4.8	8.6	8.2	5.9	0.47	0.048	10.4

*MPI – metal pollution index; **EF – Metal enrichment factor

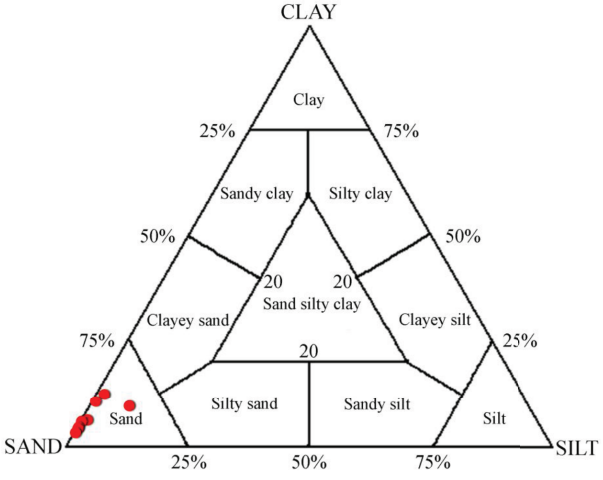

Fig. 1. Sediment type classification by Shepard's ternary diagram (Shepard, 1954).

3-18%, with respect to the remaining elements in the tested surface sediment samples. All the other elements together were present in less than 1%-3 %, depending on the location (Table 2). Ranges and average metal concentrations in the surface sediment shown in Table 2 were in the following order: [Fe]>[Mn]>>[Ni]>[Zn]>[Cu]>[Co]>[As]>[Pb]>[Cd]>[Hg]. Fe and Mn are the most abundant metals in marine environments where their sources are land-based and their abundances show regional variations (Dolenc et al., 1998). Depending on the sediment composition, the concentrations of connected microelements in sediment samples were different. Since clay minerals carry more Fe than sand grains, this element is principally associated with silt-clay fraction (Dolenc et al., 1998), while Rubio et al. (2000) have found the highest concentrations of Mn in a sand fraction. That was the case at locations Herceg Novi and Bar, with the highest Mn concentrations, 772 and 657 mg/kg, respectively, and with low percentages of silt and clay. This phenomenon is most probably attributable to Mn oxide coatings on the sand grains, (Shrader et al., 1977).

The metal pollution index (MPI) was calculated for all sites and is shown in Table 2. The location with

Table 3. Trace metal concentrations in *P. oceanica* (mg/kg dw) with minimum, maximum and mean concentrations (mg/kg dw), MPI and EF values.

Location	Fe	Mn	Zn	Ni	Pb	Cu	Co	As	Cd	Hg	MPI*
	1332	211	110	25	10.1	8.1	4.1	3.8	2.2	0.92	
Sv. Stasija											17.0
	±77	±21	±8.3	±2.3	±1.5	±0.53	±0.4	±0.43	±0.25	±0.25	
	1700	104	82	33	10.5	6.8	4.0	7.5	2.6	0.40	
Kukuljina											16.0
	±101	± 9.4	±5.3	±3.4	±2.0	±0.44	±0.3	±0.5	±0.35	±0.35	
	825	120	49	23	8.2	6.2	3.7	2.7	2.9	0.98	
H. Novi											13.2
	±69	±10.5	±3.5	±2.1	± 0.9	±0.37	±0.4	±0.60	±0.39	±0.1	
	750	134	45	32	6.2	5.9	4.3	1.2	3.9	0.40	
Mamula											11.5
	±51	± 11	±2.5	±3.0	±0.56	±0.30	±0.4	±0.30	±0.43	±0.03	
	1075	118	42	31	3.4	7.5	4.3		2.8	0.68	
Zanjice								8.0 ±1.34			13.6
	±109	±10.2	±2.3	±3.2	±0.3	±0.63	±0.4		±0.46	±0.46	
	540	137	44	39	6.9	5.3		2.0	2.8	0.54	
Bigova							4.1 ±0.4				11.9
	±37	± 14	±3.3	±4.1	± 0.7	±0.43		±0.31	±0.41	±0.41	
	725	106	35	25	4.5	5.7	3.8	2.7	2.7	0.62	
Budva											11.1
	±49	±9.5	±3.1	±2.5	± 0.5	±0.5	± 0.4	± 0.3	± 0.4	± 0.4	
	550	385	93	37	5.1	8.9	6.5	2.5	3.5	1.28	
Bar											17.3
	±46	±31	±6.1	±3.6	±0.63	±0.75	±0.60	±0.29	±0.52	±0.52	
EF^{**}_{mean}	6	9.7	30	23	17.4	7.6	11.7	14.7	487	118	
Min	540	104	35	23	3.4	5.3	3.7	1.2	2.2	0.4	11.1
Max	1700	385	110	39	10.5	8.9	6.5	8.0	3.9	1.3	17.3
Mean	937	164	57	31	6.9	6.8	4.4	3.8	2.9	0.7	14.6

* MPI – metal pollution index; **EF – Metal enrichment factor

95% of sand in surface sediments, or higher, had an MPI lower than 10. For example, surface sediments at locations such as Budva, Mamula and Bigova had 96.5, 95.5 and 95.4 % of sand, and their MPIs were 3.4, 7.0 and 8.2, respectively. The highest MPI value was that of the Kukuljina surface sediment in the Bay, 18.2, at the site with highest percentage of clay and with the highest content of trace elements in the surface sediment (Table 2), while in the coastal open-sea area MPIs were highest at locations Bar and Zanjice, with about 90% of sand in sediments: MPIs were 11.6 and 11.8, respectively. Budva is in the open coastal area with the highest concentrations of sand in the surface sediment and lowest MPI value, 3.4.

Heavy metal concentrations tend to increase and are associated with fine-grained sediment (Tavakoly Sany et al., 2011). This was the case in the surface sediment from the location Kukuljina. The surface sediment at here had the highest clay percentage (12.15%) and very fine sand (67.9%) and at the same time the highest content of Fe, Zn, Ni, Cu,

and Pb in the sediment (Table 2), as was expected with regard to the sediment composition. Clay has relatively high trace-metal content due to a greater active surface area on which metals can be adsorbed (Dolenc et al., 1998). A wide variety of other factors such as hydrogeology, vicinity of anthropogenic input, or the different amount of organic matter, can affect trace-metal concentrations, their distribution and thus the difference between MPI values. Comparing these MPIs with MPIs from other Mediterranean areas (Rodríguez-Barroso et al., 2010; Uluturhan, 2010), the surface sediment in the coastal area of Montenegro was one of the least contaminated by trace elements.

In comparing concentrations of the analyzed elements in the surface sediment from the Montenegrin coastline with literature data, the obtained values were close to, or even smaller, than their concentrations in surface sediments of the other Mediterranean areas, (Çelo et al., 1999; Çullaj et al., 2000; Rivaro et al., 2004; Yilmaz, 2006; Ščančar et al., 2007; Ünlü et al., 2008; Rivaro et al., 2011).

Seagrass

Metal concentrations in *P. oceanica* collected at the different locations are presented in Table 3. The dominant elements in *P. oceanica* were Fe, and then Mn, as in the surface sediments. Fe was present with about 80% and Mn 12-15 %, while all the other elements together presented less than 8%, depending on the location. In *P. oceanica*, the highest Fe concentrations were at locations Kukuljina and Sveta Stasija, 1 700 and 1 332 mg/kg, respectively. Considerably less Fe concentration was in the seagrass samples from the open-sea costal area at locations Mamula, Bigova, Budva and Bar (540-750 mg/kg dw). This was obviously impacted by sediment kind and hydrology at these locations. Ranges and mean elements concentrations in the *P. oceanica* samples were in the following order: [Fe]>[Mn]>>[Zn]>[Ni]>[Pb]>[Cu]>[Co]>[As]>[Cd]>[Hg].

The metal pollution index (MPI) was calculated for the *P. oceanica* to compare the total metal content in the grass at different stations (Table 3). The highest MPI was obtained for the grass from location Bar (17.3), followed by location Sveta Stasija (17.0) and Kukuljina (16.0). Obviously, the sediment granulometric composition and its metal pollution impacted the highest MPIs at the location Kukuljina for seagrass and surface sediment. The lowest MPI value for *P. oceanica* was obtained at location Budva (11.1), like the MPI for the surface sediment (3.4) at this location. The minimum, maximum and mean values of MPIs in the *P. oceanica* were higher than in surface sediments (Tables 2 and 3). A large difference observed between MPI values for the sediment and *P. oceanica* sampled from the same locations (Sveta Stasija, Budva and Bar) can be explained by higher water column pollution by trace elements at these locations, by their higher absorption from the water column than from sediments, impacted by temperature, pH, and light (Fritioff and Greger, 2006). Based on MPIs for sediment and seagrass, it can be concluded that Budva was the least polluted location.

The mean concentrations of Fe, Mn, Cu, Co and As were higher in the sediment, but Zn, Ni, Pb, Cd and Hg were higher in *P. oceanica* (Tables 2 and 3). The uptake of Zn, Ni, Pb, Cd and Hg seems to occur mainly through the water column. The mean concentration of As in *P. oceanica* was less than in the sediment, 3.8 and 5.9 mg/kg, respectively. The highest As concentration in *P. oceanica* was in samples at locations with the highest Fe concentrations in the surface sediment. If we exclude the extremely high values of Zn at locations Sveta Stasija, Kukuljina and Bar (Table 3), the Zn concentration was mainly between 35-49.0 mg/kg in the samples of *P. oceanica*. The high Zn concentrations in *P. oceanica* at locations Sveta Stasija, Kukuljina and Bar can be explained by the high concentrations of Zn in seawater and its bioavailability from the sediment at these locations (Fritioff and Greger, 2006). It has already been observed by Fritioff (2005) that the concentrations of Zn and Cd in the seagrass are higher than in sediments. For example, the Cd concentration in the sediment was not particularly high at the sampling site Bar (0.07 mg/kg), but the very high Cd concen-

Table 4. The correlation coefficient of mean elements concentrations in: *a)* the sediment *b) P. oceanica* and *c)* the sediment – *P. oceanic.*

a) Sediment	**Fe**	**Mn**	**Zn**	**Ni**	**Pb**	**Cu**	**Co**	**As**	**Cd**	**Hg**
Fe	1									
Mn	0.34	1								
Zn	**0.89**	0.35	1							
Ni	**0.66**	0.2	**0.89**	1						
Pb	**0.73**	0.03	**0.86**	**0.77**	1					
Cu	**0.61**	**0.71**	**0.79**	**0.69**	**0.54**	1				
Co	*-0.12*	*-0.48*	*-0.09*	*-0.2*	*-0.08*	*-0.22*	*1*			
As	***0.51***	0.18	0.12	-0.01	-0.01	-0.05	-0.46	1		
Cd	**0.59**	0.33	0.44	0.36	0.27	0.13	-0.28	0.48	1	
Hg	**0.65**	0.35	**0.85**	**0.86**	**0.69**	**0.66**	-0.08	-0.11	**0.63**	1
b) P. oceanica	Fe	Mn	Zn	Ni	Pb	Cu	**Co**	**As**	**Cd**	**Hg**
Fe	1									
Mn	-0.32	1								
Zn	0.46	**0.64**	1							
Ni	-0.23	0.34	0.05	1						
Pb	0.14	0.41	0.22	0.24	1					
Cu	0.22	**0.79**	**0.76**	0.06	**0.74**	1				
Co	-0.35	**0.94**	0.45	**0.52**	**0.54**	**0.72**	1			
As	**0.76**	-0.27	0.14	0.00	**0.63**	0.30	-0.15	1		
Cd	-0.61	0.31	-0.29	0.38	0.00	-0.05	0.50	-0.50	1	
Hg	*0.09*	*0.14*	*0.26*	*-0.44*	-0.14	0.17	-0.04	-0.05	-0.51	1
c) Sediment – P.oceanica	**Fe**	**Mn**	**Zn**	**Ni**	**Pb**	**Cu**	**Co**	**As**	**Cd**	**Hg**
Fe	1									
Mn	**0.54**	1								
Zn	-0.21	-0.17	1							
Ni	0.31	0.04	**0.56**	1						
Pb	-0.18	-0.21	**0.68**	0.44	1					
Cu	**0.62**	**0.73**	0.15	**0.54**	0.14					
Co	0.41	0.2	-0.51	-0.3	-0.4	0.11	1			
As	**0.53**	0.22	-0.1	-0.07	0.04	0.06	-0.09	1		
Cd	-0.55	-0.45	**0.75**	0.31	**0.57**	-0.25	-0.73	-0.22	1	
Hg	*-0.35*	*-0.28*	*0.37*	*0.10*	*0.26*	*-0.15*	*-0.42*	*-0.16*	*0.47*	*- 0.25*

tration in the seagrass at this location, 3.5 mg/kg dw, could be due to seawater pollution and its high bioavailability to *P. oceanica*. Seagrass is known to be very efficient in accumulating Cd. For example, light and nitrogen availability positively affected rates of uptake of Fe, Mn, Zn and Cd in *Ulva fasciata*, and it has been demonstrated that uptake of Cd in *Ulva fasciata* increased with increased ambient concentration of nitrate in the growth medium, (Lee and Wang, 2001).

A very high Pb concentration (the average was 6.9 mg/kg dw) was found in the examined seagrass samples, and much higher Pb concentrations were found in the seagrass on the Bay locations: Sveta Stasija, Kukuljina and Herceg Novi (Table 3). *P. oceanica* absorbs Pb from seawater and sediment (Fritioff, 2005; Lafabrie et al., 2007). It is well known that the alkaline pH value makes Pb insoluble and certainly other factors affect the bioavailability of Pb, such as the level of phosphate in seawater (Favero et al., 1996), which can be explained by the increase in activity of bacteria, causing a higher uptake of oxygen and an intensive release of phosphate from sediment to water (Rakočević, 2012).

Enrichment factor in the sediment and P. oceanica

Metal enrichment factor (EF) is a powerful tool for evaluating the anthropogenic impact of trace elements in sediments. To determine the anthropogenic and/or natural impact on the concentration of the investigated elements in the tested samples, the mean concentration of each element was compared with the background level in shale (Rivaro et. al., 2011). Concentrations of elements in sediment samples from Montenegrin coastal area were lower than the background value in shale, and generally lower than the Mediterranean background level given in the literature (Celo et al., 1999), with the exception of Cd (Table 2). Some researches indicated that Cd contamination sources are widely due to the use of agriculture land pesticides and fertilizers (Tavakoly Sany et al., 2011).

The mean metal EFs were counted for the investigated elements in surface sediments and are shown in Table 2. EF values between $0.5 \leq EF \leq 1.5$ suggest that the trace metals may be entirely from crustal materials or natural weathering processes. When EF >1.5, it suggests that a significant portion of trace elements are provided by other sources (Zhang et al., 2007), which means that heavy metals were from anthropogenic sources. Hg, Zn, and Cu had EFs close to 1.5 in the surface sediment (Table 2). In the cases of Cd, As, Mn, Co, Ni, and Pb, the EF results were higher than 1.5 and this indicates metal sources other than natural. When the background levels of Cd, As, Mn, Co, Ni and Pb were considered, the scenario was quite different: all metal concentrations in surface sediments, except Cd, were within or lower than the background levels recorded by Rivaro et al. (2011). Since the EF value for Cd was particularly high (mean value 12.5), it can be concluded that there was an anthropogenic contamination of surface sediments by Cd in the area.

To determine the EFs of the analyzed elements in *P. oceanica*, the same equation was used as was used for the sediment. The mean EFs were calculated with respect to metal averages in shale (Rivaro et al., 2011) and are presented in Table 3. EFs below 10 indicate a crustal origin of the metal, whereas an EF ≥ 10 denotes non-crustal sources, (Hernandez et al., 2003). The EFs for Fe, Cu and Mn were lower than or around 10, indicating their lithogenic source. This was not the case for the rest of the elements: these showed slightly higher (Co and As), higher (Zn > Ni > Pb) and very high (Cd and Hg) EF values, indicating that they were enriched in the seagrass by absorption from the seawater column as well. According to the USEPA regulation (Ligero et al., 2002), sediments with Hg concentrations below 0.3 mg/kg dw are considered as not polluted. This was the case for the analyzed sediments (Table 2), and EFs for Hg show that Hg was not enriched in the sediments, but was enriched in the *P. oceanica* samples, obviously impacted by anthropogenic sources into seawater and absorbed from the water column. The highest EF values were found for Cd in the sediment and in *P. oceanica* (Tables 2 and 3).

The correlation coefficient of element concentrations

The correlation coefficient r values (at $p < 0.05$) related to element concentrations in sediment, *P. oceanica* and sediment-*P. oceanica* are given in Table 4. The $r \geq 0.5$ value is evidence of element synergism, and if r is closer to 1.0, this is the greatest synergetic effect between metal pairs and their absorption in sediment, *P. oceanica*, and biosorption from a sediment to *P. oceanica*. The correlations between Fe and Zn, Ni, Cu, Pb, As, Cd and Hg concentrations, such as between

Cu and Mn, Zn, Ni and Pb, and also Ni with Pb, indicate a geochemical association of these elements and anthropogenic input. The correlation of Fe with with Hg, Pb, and Cd, point to an anthropogenic fraction, as confirmed by EFs (Table 2). It is known that Fe oxy/hydroxides are effective scavengers for heavy metals (Alexsakis, 2008). There was no correlation of Co with other studied metals in the surface sediment and the sediment-*P. oceanica* (Table 4 *a,c*), and most of the accumulated metal was probably derived directly from the water column (Fritioff, 2005). The concentrations of Co were approximately the same in *P. oceanica* samples, except at the location Bar (6.5 mg/kg dw). This lead to the conclusion that the Co in the plant is primarily through absorption from seawater, and thar Co in the marine environment is from the atmosphere (Morel and Price, 2003).

There were no Cd and Hg correlations with the other analyzed elements in *P. oceanica* (Table 4*b*). A significant correlation was found between Cd and Zn concentrations in the plant-sediment relation (0.75) (Table 4*c*). The correlation between Cd in plant and Zn in sediment has also been noticed in the Gulf of Antikyra, Greece, in *C. nodosa* and *P. oceanica* and in other phanerogams in other areas (Malea et al., 1994). The correlations between Cu and Pb concentrations in the sediment and in plant species from the Montenegrin coastal area indicate similar accumulation patterns for both metals in the surface sediment and the sea grass, but not from the sediment to the sea grass (Fitzgerald et al., 2003).

Correlations of the Fe-As pair were observed in the sediment, *P. oceanica* and in the sediment-*P. oceanica*, 0.51, 0.76 and 0.62, respectively (Table 4). Mean As concentrations in *P. oceanica* increased with increased Fe concentrations in the sediment (Tables 2 and 3), supporting the notion that the uptake of As is associated with the uptake of Fe in plant tissues from sediment. In some plants, Fe plaque on roots has been shown to promote the uptake of Fe and associated trace elements, (Foster et al., 2005). Cu correlated positively with Mn in the case of the sediment, sea grass and the surface sediment-*P. oceanica*: 0.71, 0.79, and 0.73, respectively (Table 4*a,b,c*). The strong Cu and Mn associations in *P. oceanica* are expected, since they are micronutrients essential for plant growth. Cu association with Mn in sediment samples suggests that the post depositional processes produced by the organic matter can be responsible, partially or totally, for the enriched Mn concentration observed in surface sediment layers, (Alexsakis, 2008).

Hg correlation with other elements in sediments (Table 4*a*) suggests a preferred association of this element in the sediment, but Hg did not correlate with any other elements in *P. oceanica* and sediment-*P. oceanica* (Table 4*b,c*). This lead us to conclude that Hg in *P. oceanica* is primarily absorbed through seawater, as was confirmed by a very high EF value for Hg in *P.* oceanica (Table 3), and very low EF value for surface sediments (Table 2).

CONCLUSIONS

The surface sediment of the Montenegrin coastal area is mainly sandy. The MPI values for sediment samples depend on the clay percentage in sand and were higher with increased clay percentage, but this was not the case for *P. oceanica*. Higher MPI values in sea grass than in the sediments at the same locations means that the sea grass absorbs some elements from seawater as well. Based on the EF values for Cd in *P. oceanica* and the surface sediment, this element was from anthropogenic sources; on the basis of the EF value for Hg and its correlation coefficients, the plant absorbs Hg from the water column. Concentrations of the analyzed elements in *P. oceanica* and in the surface sediment from the Montenegrin coast are similar to concentrations in other areas of the Mediterranean coast.

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