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Original scientific paper

## Accumulation of trace metals in marine organisms of the southeastern Adriatic coast, Montenegro

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**Abstract:** The concentration and accumulation of trace metals (Co, Ni, As, Cd, Pb and Hg) were measured in seawater, sediments and marine organisms on the coastline of Montenegro. The obtained results of trace metals in sea grass and mussels were compared with those found in the water column and sediment. Sampling was performed in the fall of 2005 at five locations on the Montenegrin coastline, Sveti Stefan, Herceg Novi, Zanjan, Budva and Bar, which present different levels and sources of human impact. The heavy metals analyses of seawater, sediment, *Posidonia oceanica* and *Mytilus galloprovincialis* identified the harbor of Bar as the most Hg-contaminated site, Zanjan as the most As-contaminated and Sveti Stefan as the most Pb-contaminated areas of the Montenegrin coastal area. This study showed that *P. oceanica* may have a greater bioaccumulation capacity than *M. galloprovincialis* for the considered metals, except for As and Hg, and both organisms may reflect contamination in the water column and in the sediment. For the first time, the sea grass *P. oceanica* and *M. galloprovincialis* were employed as metal bioindicators for the southeastern Adriatic. The results of this study could serve as a baseline for future assessments of anthropogenic effects in this marine ecosystem.

**Keywords:** heavy metals; seawater; sediment; marine organisms; biomonitoring; Montenegro.

### INTRODUCTION

The Adriatic Sea is situated between the northeastern Italian coast and the southwestern coasts of Slovenia, Croatia, Montenegro and Albania. It is especially subject to pollution due to its enclosed character. The coastal parts of this Adriatic area receive large amounts of contaminants introduced by domestic, industrial and agricultural activities, directly, *via* rivers, or through atmospheric deposition. The pollution of the Adriatic Sea is more marked along the Italian

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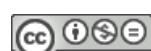


coast, especially of the northern basin, than along the eastern coast.<sup>1</sup> Most of the previous studies considered trace metal concentrations in sediments and mussels from selected coastal areas of the Adriatic, mainly of northern part of the Italian Adriatic coast.<sup>2</sup> Along the eastern Adriatic coast, the effects of coastal pollution were investigated mainly in the Slovenian<sup>3</sup> and Croatian coastal areas<sup>4–7</sup> and some initial investigations in the Montenegrin coastal area.<sup>8,9</sup> Investigation of sediments also included a number of sites in the Albanian coastal area.<sup>10,11</sup>

The chemical analysis of waters does not provide sufficient information on the bioavailability of the metals present in a marine environment.<sup>12</sup> Currently, there is great interest in the use of living organisms as pollution bioindicators in aquatic ecosystems in order to evaluate the quality of a marine environment. A comparison of metal contamination in different aquatic environments is possible by analysis of water,<sup>13</sup> sediment<sup>14</sup> and biota,<sup>15–17</sup> but in most cases, the impact and synergistic effects of trace metals in marine ecosystem are poorly understood.

Sea grasses and mussels are increasingly used as indicators of chemical contamination of coastal regions. The endemic sea grass *Posidonia oceanica* (L.) Delile has been used as a metal bioindicator<sup>17</sup> for the last two decades in the Mediterranean Sea, but in the area of the southeastern Adriatic coast, there is no published data concerning *P. oceanica* as a metal bioindicator. The mussel *Mytilus galloprovincialis* has the ability to accumulate metals from the environment in which lives<sup>18</sup> and their usefulness as sentinel organisms in metal biomonitoring studies is widely recognized. Bivalves are filter feeders and thus obtain elements not only from food and water but also from particulate materials.<sup>19,20</sup> In both organisms, the concentration of heavy metals is largely governed by the biological, chemical, and physical characteristics of the surrounding environment. For example, light and nitrogen availability positively affected the rate of Cd uptake in sea grass, which increased with increasing concentration of nitrate in the growth medium.<sup>21</sup> However, in environments with high nutrient levels, Ni uptake by plants can be inhibited due to complex formation between the nutrients and metal ions.<sup>22</sup>

For the first time, the concentrations of Co, Ni, As, Cd, Pb and Hg have been determined and compared in different marine environmental compartments in the area of the southeastern Adriatic Sea, Montenegro: seawater, sediment, the mussel *M. galloprovincialis* (L) Lamarck, 1819 and the sea grass *P. oceanica* (L) Delile. As there is no quantitative data available on the concentration of these metals in seawater, sediment, mussels and sea grass in this coastal part of the southeastern Adriatic Sea, the results of this study could serve as a baseline for future assessments of anthropogenic effects in this part of the Adriatic Sea.



## EXPERIMENTAL

### *Chemicals and instrumentation*

Ultra pure water ( $18.2 \text{ M}\Omega \text{ cm}$ ) from a Milli-Q system (Millipore, Bedford, MA, USA) was used to prepare all the aqueous solutions. All the employed mineral acids and oxidants ( $\text{HNO}_3$ ,  $\text{H}_2\text{O}_2$  and  $\text{HCl}$ ) were of the highest quality (Suprapure, Merck, Germany). The mineralized samples were analyzed using a cold vapor atomic absorption spectrometer (CV-AAS and F-AAS Perkin-Elmer, AAnalyst 200) and graphite furnace atomic absorption spectrometer (GF-AAS, Perkin-Elmer, 4100ZL, with Zeeman background correction).

### *Sampling locations*

Samples were collected at five selected locations from this Adriatic coastal area: Sveta Stasija and Herceg Novi in the semi-enclosed Boka Kotorska Bay, which is on the UNESCO's World Heritage List, and on the open coastline at Zanjice, Budva and Bar, Fig. 1, situated in the proximity of different geochemical, hydrological and human impacts.



Fig. 1. Sampling locations in the southeastern Adriatic Sea, Montenegro: 1. Sveta Stasija,  
2. Herceg Novi, 3. Zanjice, 4. Budva and 5. Bar.

Boka Kotorska Bay is on the northern coast of Montenegro with a mouth 2.95 km in width and an in-land length of 28.13 km, surrounded by mountains, with 75000 inhabitants living on its coast. Sveta Stasija is located in a small Kotor bay near Kotor, a city where a previous galvanization plant discharged used galvanization baths directly into the sea between 1965 and 1991. Herceg Novi was/is a favored tourist city with marine, shipyard and food industries. The beach Zanjice with hotels and cottages is situated close to the entrance of the Bay. Budva is an urban, tourist and industrial city located in the middle of the Montenegrin coastline with 18000 inhabitants. The Harbor Bar is in the south of the Montenegrin coastal area with 15000 inhabitants. Bar was an important industrial harbor in former Yugoslavia, the largest on the eastern side of the Adriatic, especially for crude oil and oil products traffic, and still is. The problem of pollution in the vicinity of these sites increases in the fall periods because of the summer tourist seasons and increased discharge of wastewater directly into the sea. For this reason, the samples of seawater and sediment, and mussels and sea grass were collected in the fall, at the same time. No mussels were found at the location Budva.

*Sampling method, sample preparation and trace metal analyses*

All the seawater samples, from the surface and the bottom, were collected at the same time as the sediment and the biota samples at all the studied locations. The water samples were analyzed after filtration and acidification with nitric acid ( $\text{pH} \leq 2$ ) for the determination of metals, immediately in the days following sampling. The pre-concentration technique was applied for the analysis of the sea water samples following a solvent extraction technique<sup>23</sup> prior to analysis by GF-AAS (Ni, Co, Cd and Pb), while Hg and As were measured following a CV-AAS procedure<sup>17</sup> using a Perkin-Elmer Hydride System coupled to an atomic absorption spectrometry (AAS). The accuracy of the methods was checked with three calibration standards laboratory prepared from standard solutions of  $1000 \text{ mg L}^{-1}$  (Merck) and a seawater matrix was used for the preparation of the Ni, Co, Cd and Pb standards. These standards were analyzed directly after solvent extraction as mentioned above.

Surface sediments (500 g) were collected in the vicinity of *P. oceanica* meadows. Only the top 5 cm was used for the purpose of this study. The fraction of the sediment smaller than 2 mm was frozen, lyophilized and analyzed by AAS. At the same time and place, about 350 g of fresh *P. oceanica* samples and two liters of seawater from the bottom were collected at a depth of  $7 \pm 1$  m. The *P. oceanica* samples were washed very thoroughly, rinsed with ultra pure water, frozen, lyophilized and reduced to powder, dissolved and analyzed.

The mussels and the seawater samples from the surface were collected in the vicinity of the *P. oceanica* meadows. 25–30 mussels of similar shell length were collected, placed in plastic bags and transported to the laboratory. The mussels were washed and cleaned out, opened raw and the flesh scraped out of the shells, which was then frozen, lyophilized, reduced to powder, dissolved and analyzed.

Preparation of dissolved biota samples (approximately 0.5 g) for trace metal analysis was performed as follows: the powder was digested with a mixture of 7 mL concentrated  $\text{HNO}_3$  (65 % Merck, Suprapur) and 2 mL  $\text{H}_2\text{O}_2$  (30 % Merck, Suprapur). The sediment samples (0.5 g), were digested with 2 mL of  $\text{HNO}_3$  (65 %) and 6 mL HC1 (37 %) in a high microwave digestion system (CEM. Corporation, MDS-2100) for 30 min at 200 °C. The digested samples were diluted with ultra pure water in 25 mL volumetric flasks and then transferred to 100 mL polypropylene bottles until analysis.

To ensure the quality control and accuracy of the applied analytical procedure for the determination of heavy metals in the sediments, mussels and sea grass, certified reference materials, IAEA 158 (Marine sediment), NIST 2976 (Mussel homogenate) and IAEA 140 (Fucus sample), were also digested and analyzed.

All the results of the investigated elements in sediment, sea grass and mussel are expressed in dry weight (dw). To check for contamination, procedural blanks were analyzed after every five samples. The recovery of metals in the standard reference materials was in the range of 82–115 % of the certified total concentrations. This was indicated by results of triplicate measurements for the all samples. No correction was applied to the obtained data.

To evaluate the efficiency of metal bioaccumulation by *M. galloprovincialis* and *P. oceanica*, the bioconcentration factor (BCF) and the biosediment factor (BSAF), defined as the ratio between the metal concentration in the organism and that in the seawater<sup>24</sup> and sediment,<sup>16</sup> respectively, were calculated.

*Statistical analysis*

The certified values and analysis results of the reference materials are given in Table I. The analytical precision, measured as the relative standard deviations for Ni, Co and Hg, were routinely under or around 10 %, but were higher than 10 % for Cd, Pb and As. The average



analytical standard errors observed with the reported certified materials were below 10 % for all investigated elements, except for Ni and As in the sediment samples, and Cd and As in the mussel tissue and *Fucus* samples.

TABLE I. Analysis of certified reference materials: certified values and found values (mean  $\pm$  S.D., mg kg<sup>-1</sup> dw.)

Element	IAEA 158 (marine sediment)		NIST 2976 (mussel tissue)		IAEA 140 ( <i>Fucus</i> sample)	
	Certified	Found	Certified	Found	Certified	Found
Ni	29.4 $\pm$ 4.12	31.0 $\pm$ 0.72	0.93 $\pm$ 0.12	0.91 $\pm$ 0.20	3.79 $\pm$ 0.41	4.10 $\pm$ 0.31
Co	9.0 $\pm$ 1.35	10.1 $\pm$ 1.5	0.61 $\pm$ 0.02	0.70 $\pm$ 0.05	0.83 $\pm$ 0.13	0.95 $\pm$ 0.09
Pb	38.0 $\pm$ 7.7	35.0 $\pm$ 3.9	1.19 $\pm$ 0.18	0.98 $\pm$ 0.23	2.19 $\pm$ 0.28	1.87 $\pm$ 0.11
As	11.4 $\pm$ 1.71	12.6 $\pm$ 0.91	13.3 $\pm$ 1.8	14.7 $\pm$ 2.10	44.3 $\pm$ 2.1	47.10 $\pm$ 3.4
Cd	0.37 $\pm$ 0.09	0.45 $\pm$ 0.05	0.82 $\pm$ 0.16	0.84 $\pm$ 0.18	0.54 $\pm$ 0.04	0.65 $\pm$ 0.03
Hg	0.132 $\pm$ 0.017	0.12 $\pm$ 0.018	0.061 $\pm$ 0.0036	0.053 $\pm$ 0.006	0.038 $\pm$ 0.006	0.037 $\pm$ 0.009

For the metal concentrations in the sediment, differences between the sampling locations were evaluated by the Kruskal–Wallis test. For the metal concentrations in *M. galloprovincialis* and *P. oceanica*, the differences between the organisms and between locations were determined by a two-way analysis of the variance (ANOVA). Correlations between the metal concentrations in *P. oceanica* and *M. galloprovincialis* and in the sediment and water samples were performed by analysis of the Pearson's correlations.

## RESULTS AND DISCUSSION

### Marine water

The measured trace element concentrations are listed in Table II. The Co, Ni, As, Cd, Hg and Pb mean levels are relatively high (up to 10.4. µg L<sup>-1</sup> Co, 7.8 µg L<sup>-1</sup> Ni, 3.1 µg L<sup>-1</sup> As, 8.1 µg L<sup>-1</sup> Cd, 1.56 µg L<sup>-1</sup> Hg and 27.8 µg L<sup>-1</sup> Pb). In the Venice lagoon and southern Adriatic of Italy such a high levels of elements in sea water were also found.<sup>2,3</sup> The concentration of Cd was below the detection limit at the location Budva. The relative standard deviation of replicate analyses of each sample was within 10–30 %.

Following recommended marine water quality criteria for the protection of aquatic life and human health, *i.e.*, the *MAC* values<sup>25</sup> of the investigated metals in surface waters, the Hg concentrations were below the *MAC* value for Hg and the Pb concentrations were above the *MAC* value for Pb in seawater at three locations (Table II). Considering the Montenegrin regulations for the maximum permissible concentrations of hazardous and harmful substances in waste water that may be discharged into surface waters,<sup>26</sup> the concentrations of the investigated elements that may be discharged into the seawater of Montenegro are much higher than the *MAC* values and the values measured in this study. The EU Directive 2008/56/EC in the field of marine environmental policy establishes common principles based on which Member States must draw up their own strategies, in



cooperation with other Member States and third countries, to achieve a good ecological status in the marine waters for which they are responsible.<sup>27</sup>

TABLE II. Total metal concentrations in seawater in  $\mu\text{g L}^{-1}$  (*MAC* – maximum allowable concentration; nv – no value)

Sampling place	Co	Ni	As	Cd	Hg	Pb
Surface						
Sv. Stasija	4.4	5.7	1.4	2.5	1.38	18.0
H. Novi	4.3	3.4	2.5	6.2	1.36	3.9
Zanjice	3.5	4.9	3.1	1.9	1.56	2.09
Budva	–	4.3	2.7	–	0.70	5.75
Bar	4.7	6.9	2.4	7.0	1.01	27.8
Bottom						
Sv. Stasija	3.9	6.4	2.5	2.5	0.92	5.7
H. Novi	10.4	5.9	2.6	6.2	0.98	3.9
Zanjice	4.5	5.0	2.9	3.3	0.40	2.6
Budva	3.9	3.9	2.5	–	0.62	2.9
Bar	4.3	4.3	2.7	8.1	1.28	26.4
<i>MAC</i> <sup>25</sup>	nv	8.2	36.0	8.8	0.94	8.1
Montenegrin Regulation <sup>26</sup>	100	1250	100	10	5.0	500

### Sediment

The highest As and Cd concentrations were recorded in Zanjice, the highest Hg and Co levels in the Harbor Bar, whereas the concentrations of Ni and Pb were the highest in H. Novi and Sveta Stasija ( $p < 0.05$ ; Table III). In Table III, the Interim Marine Sediment Quality Guidelines (*ISQG*) and Probable Effect Level (*PEL*) values are given in dry weight. The *ISQG* and *PEL* values for marine organisms have been adopted by Environment Canada for a range of toxic substances.<sup>28</sup> These guidelines may not be validated for use everywhere; there may be fundamental differences in sediment geochemistry.<sup>28</sup> However, in the absence of any standards, these guidelines can be used as a first approximation in assessing whether organisms are at risk from sediment concentrations of toxic substances. The concentrations of the investigated elements measured in this study were below the *PEL* values in all sediment samples.

TABLE III. Trace metal concentrations in surface sediment (mean  $\pm$  S.D. in  $\text{mg kg}^{-1}$  dw, for  $\text{Hg } \mu\text{g kg}^{-1}$  dw; nv – no value)

Sampling place	Co	Ni	As	Cd	Hg	Pb
Sv. Stasija	3.9 $\pm$ 0.35	18.2 $\pm$ 1.7	4.9 $\pm$ 0.55	0.75 $\pm$ 0.10	24.2 $\pm$ 2.2	7.0 $\pm$ 1.2
H. Novi	9.0 $\pm$ 0.80	32.3 $\pm$ 3.3	3.7 $\pm$ 0.4	0.77 $\pm$ 0.11	28.4 $\pm$ 2.3	3.7 $\pm$ 0.4
Zanjice	6.6 $\pm$ 0.72	16.3 $\pm$ 1.5	19.7 $\pm$ 2.6	0.87 $\pm$ 0.13	9.20 $\pm$ 1.0	3.9 $\pm$ 0.5
Budva	5.2 $\pm$ 0.5	2.7 $\pm$ 0.2	2.6 $\pm$ 0.37	0.063 $\pm$ 0.01	14.0 $\pm$ 1.1	2.6 $\pm$ 0.3
Bar	11.4 $\pm$ 1.1	15.8 $\pm$ 1.2	3.1 $\pm$ 0.4	0.068 $\pm$ 0.01	154.7 $\pm$ 9	5.2 $\pm$ 0.7
<i>ISQG</i> <sup>28</sup>	nv	15.9	7.24	0.7	130	30.2
<i>PEL</i> <sup>28</sup>	nv	42.8	41.6	4.2	700.0	112.0



### *Biotia*

The metal concentrations found in the marine organisms *M. galloprovincialis* and *P. oceanica* from the different locations are presented in Table IV. The maximum allowable concentrations or *MACs*<sup>8</sup> for Ni, As, Hg and Pb in mussels are shown in Table IV. In the all investigated mussel samples, the Cd concentrations were lower than the *MAC* value for Cd and the Hg concentrations were higher than the *MAC* value for Hg. Recommended *MLC* values for the sea grass do not exist in the literature.

TABLE IV. Trace metal concentrations in *M. galloprovincialis* (*Mg*) and *P. oceanica* (*Po*); mean  $\pm$  SD in mg kg<sup>-1</sup> dw; *MAC* – maximum allowable concentration; nv – no value

Sampling place	Co	Ni	As	Cd	Hg	Pb
<i>Mg</i>						
Sv. Stasija	3.92 $\pm$ 0.4	3.35 $\pm$ 0.3	7.35 $\pm$ 1.0	2.15 $\pm$ 0.3	0.95 $\pm$ 0.12	9.10 $\pm$ 1.1
H. Novi	1.10 $\pm$ 0.10	4.7 $\pm$ 0.46	17.8 $\pm$ 2.3	1.50 $\pm$ 0.19	0.35 $\pm$ 0.031	3.50 $\pm$ 0.4
Zanjice	8.98 $\pm$ 0.76	18.9 $\pm$ 1.8	40.8 $\pm$ 5.6	1.70 $\pm$ 0.24	0.59 $\pm$ 0.062	1.77 $\pm$ 0.23
Bar	6.07 $\pm$ 0.6	12.3 $\pm$ 1.2	7.54 $\pm$ 1.1	3.53 $\pm$ 0.47	1.06 $\pm$ 0.130	8.50 $\pm$ 0.9
MAC <sup>8</sup>	nv	3.40	16.0	3.70	0.23	3.20
<i>Po</i>						
Sv. Stasija	4.15 $\pm$ 0.4	24.8 $\pm$ 2.3	3.82 $\pm$ 0.53	2.20 $\pm$ 0.25	0.26 $\pm$ 0.03	10.1 $\pm$ 1.5
H. Novi	3.75 $\pm$ 0.38	22.8 $\pm$ 2.1	2.71 $\pm$ 0.41	2.90 $\pm$ 0.39	0.35 $\pm$ 0.04	8.2 $\pm$ 0.9
Zanjice	4.30 $\pm$ 0.41	31.0 $\pm$ 3.2	7.96 $\pm$ 1.34	2.80 $\pm$ 0.46	0.57 $\pm$ 0.06	3.4 $\pm$ 0.28
Bar	6.50 $\pm$ 0.60	36.7 $\pm$ 3.6	2.50 $\pm$ 0.29	3.50 $\pm$ 0.52	1.37 $\pm$ 0.12	5.1 $\pm$ 0.60
Budva	3.80 $\pm$ 0.39	24.7 $\pm$ 2.5	2.68 $\pm$ 0.38	2.70 $\pm$ 0.44	0.46 $\pm$ 0.04	4.5 $\pm$ 0.5

The *M. galloprovincialis* and *P. oceanica* samples from Zanjice presented the highest As concentrations ( $p < 0.05$ ), whereas from the Harbor Bar, they had the highest Cd and Hg concentrations ( $p < 0.05$ ) and from Sveta Stasija, the highest Pb concentrations ( $p < 0.05$ ; Table IV). The Cd and Hg concentrations in the biota samples from Bar and the Pb concentrations in the Sveta Stasija samples were very similar. The concentrations of Ni were significantly higher in *P. oceanica* than in *M. galloprovincialis*, whereas the As concentrations were significantly higher in *M. galloprovincialis* ( $p < 0.05$ ; Table IV).

### *Bioconcentration and sediment accumulation factors*

The bioconcentration and sediment accumulation factors (*BCF* and *BSAF*) are shown for both species from the same sampling points, Figs. 2 and 3, respectively. The mean values the *BCF* should be multiplied by 10<sup>3</sup> in Fig. 2. The metal which presents the highest mean *BCF* is As and Hg is the metal with the lowest one (Fig. 2), while Cd is the metal which presents the highest mean *BSAF* and Hg is the metal with the lowest one (Fig. 3). *P. oceanica* exhibited higher mean *BCF* and *BSAF* values compared to *M. galloprovincialis*, except for As and Hg (Figs. 2. and 3).



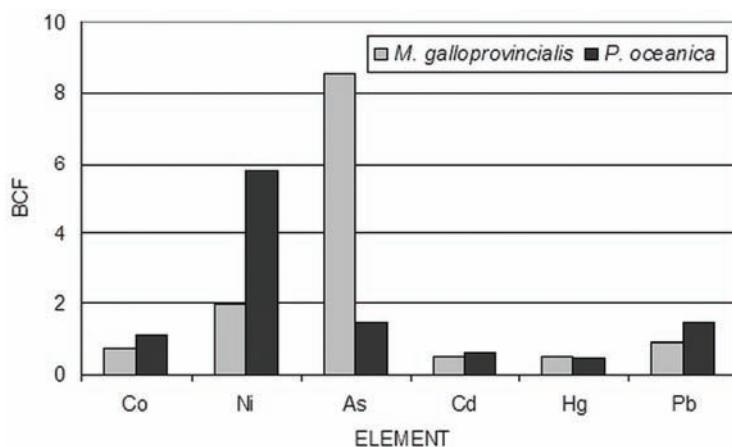


Fig. 2. Mean bioconcentration factor (*BCF*) values in *M. galloprovincialis* and *P. oceanica* (multiplied by  $10^3$ ).

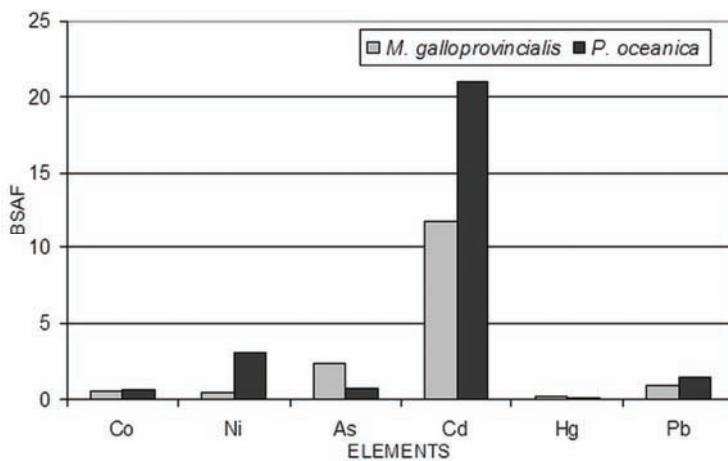


Fig. 3. Mean biosediment accumulation factor (BSAF) values in *M. galloprovincialis* and *P. oceanica*.

#### *Relation between the metal concentrations in P. oceanica and M. galloprovincialis with the metal concentrations in seawater*

There were significant positive correlations for the Cd and Pb concentrations in *M. galloprovincialis* and *P. oceanica*, relative to their concentrations in seawater ( $r_{Cd} = 0.95$ ;  $r_{Pb} = 0.92$ ;  $p < 0.05$ , and  $r_{Cd} = 0.95$ ;  $r_{Pb} = 0.95$ ;  $p < 0.05$ , respectively) and positive relations for the As and Co concentrations ( $r_{As} = 0.62$ ;  $r_{Co} = 0.73$ ;  $p < 0.05$  and  $r_{As} = 0.78$ ;  $r_{Co} = 0.66$ ;  $p < 0.05$ , respectively). Significant relations were found in the case of Ni ( $r_{Ni} = 0.61$ ;  $r_{Ni} = 0.49$ ).

*Relation between the metals concentrations in P. oceanica and M. galloprovincialis with the metal concentrations in the sediments*

There were positive correlations for the As in *P. oceanica* and the Hg concentrations in *M. galloprovincialis* relative to their concentrations in the sediments ( $r_{\text{As}} = 0.52$ ;  $r_{\text{Hg}} = 0.65$ ;  $p < 0.05$ ) and positive relations for the Pb concentrations in *P. oceanica* and *M. galloprovincialis* relative to their concentrations in sediments ( $r_{\text{Pb}} = 0.65$ ;  $r_{\text{Pb}} = 0.52$ ;  $p < 0.05$ ), but non-significant relations were found in the case of the Cd concentrations for both organisms ( $r_{\text{Cd}} = -0.70$ ;  $r_{\text{Cd}} = -0.64$ ;  $p < 0.05$ ), respectively.

The Harbor Bar was previously identified as the most Hg- and Cd-contaminated location based on previous mussels studies<sup>29</sup> and by the investigated compartments, except for Cd in the sediment analysis, for which a maximum value was revealed for Zanjice. The fact that no correlations were found between the Cd concentrations in *M. galloprovincialis* and *P. oceanica* and in the sediment, but very high correlations were found between the Cd concentrations in the investigated biota and seawater indicate that the Cd in *P. oceanica*<sup>5,15,30</sup> and *M. galloprovincialis*<sup>6,31</sup> tissues reflect the Cd in the water column. Cd accumulation in *M. galloprovincialis* and *P. oceanica* seems to be a function of the Cd concentration in seawater, which was also found in the present study.

The Harbor Bar was identified as the most Hg-contaminated location according to the results obtained for all the investigated compartments, especially the surface sediment. This result is probably related to the effluents from the storage of crude oil and oil products, transoceanic ships and tankers traffic, as well as untreated urban and industrial effluents. In this study, a positive correlation was found between the Hg concentrations ( $r_{\text{Hg}} = 0.65$ ) in *M. galloprovincialis* and in the sediment but a non-significant relation with the concentration in seawater ( $r_{\text{Hg}} = 0.01$ ). This result could be related to the presence of a high level of Hg from sediment in the suspended particulate matter and of high levels of the particulate matter in the water column.<sup>19</sup> Metals in mussels can correlate with metal levels in sediments, although mussels are not in direct contact with the sediment, which is resuspended and wafted to them by wave action.<sup>32</sup>

Sveta Stasija was identified as the most Pb-contaminated location according to the results obtained for all the investigated compartments, except the bottom seawater. Seawater had maximum Pb values in the Harbor Bar. The extreme Pb contamination in the vicinity of Sveta Stasija could be associated with an anthropogenic impact due to the proximity of Kotor, a city with a harbor, chemical industry, food industry and the geographical location of Sveta Stasija, *i.e.*, there is a low hydrological influx to the small Kotor Bay.

The identification of Sveta Stasija as the most Pb-contaminated site was previously explained by the fact that the bed of the small Kotor bay is clay<sup>33</sup> and a trace element such as Pb is preferentially associated with clay mineral particles,<sup>34</sup>

which form more or less soluble organic matter particles, indicating that the evidenced Pb originated primarily from human activities.<sup>7</sup> Significant correlations between the concentrations Pb in the organisms and Pb in the surrounding water were obtained. The positive correlations found between the Pb concentrations in *P. oceanica* and *M. galloprovincialis* and in the water would suggest that Pb in the tissues of the organisms primarily reflects the Pb in the water.<sup>16,17</sup> Therefore, in the case of *P. oceanica*, this leads to the hypothesis of preferential Pb uptake from the water column.<sup>16</sup> However, the positive correlation found for Pb related to the sediment, and previously in this study for Hg related to the water in this sea grass suggests that there could be some other uptakes and distributions routes for these two elements, not only by leaves and for Pb also by the root system,<sup>5</sup> and *vice versa*, leaves for Hg.<sup>35</sup> The maximum Pb level in sediment found in Sv. Stasić is related to the highest Pb level in *M. galloprovincialis* at this location. Pb in *M. galloprovincialis* is absorbed bound to particulate material and in a water-soluble form.<sup>36</sup>

Zanjice was identified as the most As-contaminated location by the results of all the investigated compartments. Arsenic was homogeneously distributed along the Montenegrin coast in the sediment except at the location Zanjice. This could be due to natural leaching of terrestrial soils and sediments or increases in the As concentration when the sediment content changed,<sup>37</sup> which in Zanjice could be attributable to the transport of metals by waves from the open sea and by the branch of the Mediterranean current coming from the southeastern side of the Adriatic<sup>38</sup> entering into the Bay, or on leaving, carrying wastes from the Bay. For the other locations, the low As concentrations in the sediment may be explained by the lack of low contaminant inputs and the low leaching of natural arsenic. In this study, the concentrations of As in *M. galloprovincialis* were higher than those in the sediment were, but slightly less in *P. oceanica* than in the sediment (Tables III and IV). Positive correlations were found between the As levels in these organisms and the As levels in the sediment and water. Generally, the arsenic levels in these organisms generally reflect the total arsenic in the sediment.<sup>39</sup> Langston<sup>39</sup> supports the view that particulate arsenic is the most important source of the metal accumulated in bivalves, although some absorption from solution cannot be disregarded, which is in agreement with the results obtained in the present study. The lower relationship between As in *P. oceanica* and in water/sediment, compared to mussels, may be explained by other factors such as phosphate competition related to As<sup>39</sup> or that As is mostly immobilized as a form not available to plants.<sup>40</sup>

The *M. galloprovincialis* from Zanjice, located at the entrance of the Bay, had greater contents of As, Ni and Co than *M. galloprovincialis* from the Bay. This could be attributable to the hydrological influence mentioned above in the case of this location.<sup>19,20</sup>

The Ni concentrations in the biomonitored organisms in this study were similar to those reported in the literature.<sup>2,15,17</sup> Positive correlations between the Ni concentrations in the organisms and those in seawater/sediment were not evidenced. This is possibly due to the background Ni levels<sup>15</sup> in the organisms. In the case of the Co concentrations, the positive correlations found between the Co concentrations in *P. oceanica* and *M. galloprovincialis* with those in seawater indicate that Co in these organisms mainly came from the water, which is contrary to the assertions of Lafabrie.<sup>16,17</sup>

#### CONCLUSIONS

The data obtained in the present investigation showed that the sea grass *P. oceanica* and the mussel *M. galloprovincialis* could be used as organisms for the biomonitoring of heavy metals pollution in the marine environment of the southeastern Adriatic Sea. These data showed that the accumulation ratios of the six studied metals in the sea grass and in the mussel differed. From the determined *BCF* and *BSAF* values calculated for the two different marine species investigated in this study, *P. oceanica* was found to be a stronger accumulator for Cd, Pb, Ni and Co, and *M. galloprovincialis* for As and Hg. *P. oceanica* was a stronger Cd accumulator from the surrounding water and *M. galloprovincialis* had a higher capacity to accumulate As, mostly from particles. The Hg accumulation by both the investigated organisms was the lowest of the investigated metals.

However, it must be born in mind that the actual uptake mechanisms of heavy metals by the studied organisms are probably rather complex because their exposure to trace elements is not limited to soluble metals in the aquatic medium. Metal uptake from sediment particles and food, in the case of the mussels, and from sediments (through the roots), in the case of the sea grass, cannot be ignored.

The results of this first study provide a valuable baseline for further monitoring of the marine ecosystem of the southeastern Adriatic Sea.

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ИЗВОД

АКУМУЛАЦИЈА ТРАГОВА МЕТАЛА У МОРСКИМ ОРГАНИЗМИМА  
ЈУГОИСТОЧНЕ ЈАДРАНСКЕ ОБАЛЕ

ДАНИЈЕЛА ЈОКСИМОВИЋ<sup>1</sup> И СЛАВКА СТАНКОВИЋ<sup>2</sup>

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Концентрација и акумулација трагова метала (Co, Ni, As, Cd, Pb и Hg) одређивана је у седименту, морским организмима и морској води дуж Црногорске обале. Добијени резултати трагова метала у морској трави *Posidonia oceanica* и школјкама *Mytilus galloprovincialis* били су анализирани у односу на исте елементе добијене у морској води и седиментима.



Узорковање је вршено у јесен 2005. године на пет локација, Света Стасија, Херцег Нови, Жањице, Будва и Бар, које су под утицајем различитих загађивача изазваних човековом активношћу. Анализом трагова метала у морској води, седиментима и испитиваним морским организмима у приобалном делу Црногорског приморја утврђено је да је лука Бар првенствено загађена живом, Жањице арсеном, а Света Стасија оловом. Такође је утврђено да морска трава *P. oceanica* има већи капацитет биоакумулације у односу на школјку *M. gallo-provincialis* за Co, Ni, Cd и Pb, али не и за As и Hg. Први пут у овом раду морска трава *P. oceanica* и школјка *M. galloprovincialis* коришћене су као биоиндикатори трагова метала у морској води и седименту Црногорског приморја. Такође резултати овог рада могу бити коришћени као основа за процену будућих антропогених утицаја на испитивани екосистем.

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