CONCENTRATION DATA FOR 30 ELEMENTS IN THE MUSSELS *MYTILUS GALLOPROVINCIALIS*

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PODACI O KONCENTRACIJAMA 30 ELEMENATA U DAGNJAMA *MYTILUS GALLOPROVINCIALIS*

Apstrakt

Priobalni deo jugoistočnog Jadrana prima velike količine zagađujućih materija koje se u morsku sredinu unose putem različitih anropogenih i prirodnih izvora kao što su luke, industrija, turizam, poljoprivredna aktivnost, erozija zemljišta, atmosfersko taloženje, itd. Bokokotrski zaliv je prirodno podeljen na četiri manja zaliva: hercegnovski, tivatski, risanski i kotorski zaliv. Svaki od unutršnjih zaliva ima specifične hidrografske i reljefne karakteristike i u odnosu na otvoreni deo crnogorskog primorja ove vodene površine pokazuju veliku različitost, a samim tim poseduju i specifičan morski život. Bokokotorski zaliv se smatra jednim od glavnih priliva slatke vode južnog Jadrankog mora. Reljefne karakteristike stimulišu razvoj naselja duž obale zaliva i upravo se pogodne poljoprivredne zone i nalaze u neposrednoj blizini velikih naseljenih gradova Kotora, Herceg Novog i Tivta. Poluzatvoren sistem zaliva, slabo strujanje i cirkulacija vode, utiče na veće vreme potrebno da se određene zagađujuće materije prirodnim putem uklone iz samog zaliva.

Dagnja *M. galloprovincialis* je nativna vrsta ove oblasti i ovog zaliva i danas se komercijlno uzgaja i proizvodi, ali i kao nativna vrsta može se naći duž cele obale Bokokotorskog zaliva. Dagnje su veoma važne za ljudsku ishranu i njihovim konzumiranjem u organizam se unose proteini visoke biološke vrednosti, minerali i vitamini. Sa aspekta hranljivosti, školjka je važan izvor hrane bogate bitnim elementima (Ca, Fe, Se, Zn, I, itd.), kao i određenim vitaminima (A, C, B1, B2, B3, B9, B12). Minerali i mikroelementi predstavljaju značajne komponente u ljudskoj ishrani, a njihov nedostatak kao i višak može izazvati ozbiljne zdravstvene probleme. Poznavanje elementarnog sastava dagnji od suštinskog je značaja za procenu dostupnosti hranjivih materija, jer one predstavljaju jeftinu visoko proteinsku hranu sa niskim sadržajem masti i kalorija, ali i sa apekta procene i smanjenja potencijalno negativnih efekata po zdravlje ljudi, jer je ova vrsta plodova mora poznata po sposobnosti da akumulira velike količine prisutnih zagađujućih materija.

Cilj ovog rada je bio da se ispita elementarni sastav mekog tkiva dagnji *M. galloprovincialis* iz Bokokotorskog zaliva, Crna Gora, jugoistočni Jadran. Energetski disperzivnom rendgenskom fluoroscentnom metodom (ED-XRF) analizirani su sledeći elementi: Cl, Si, S, K, P, Ca, Fe, Br, Zn, Mn, Sr, I, As, Cr, Ti, Ce, Ba, Cu, Cs, Rb, Pb, Ni, Th, Sb, Sn, Cd, V, Co, Zr i Hg , na osnovu izmerenih vrednosti, izvršena je procena zastupljenosti makro, mikro, neesencijalnih i toksičnih elemenata u mekom tkivu dagnji.

Ključne reči: Mytilus galloprovincialis; Makro, mikro i elementi u tragovima; ED-XRF; Crna Gora.
Keywords: Mytilus galloprovincialis; Makro, mikro and trace elements; ED-XRF; Montenegro.

INTRODUCTION

Natural weathering and human activities are the sources contributing to element contamination of the marine coastal environment through rivers and atmospheric transport. The Southeastern coastal part of the Adriatic Sea receives large amounts of contaminants which are introduced by marine harbors, domestic, industrial, touristic and agricultural activities, by land erosion and through atmospheric deposition (Jović et al., 2011). The Boka Kotorska Bay is naturally divided into four smaller bays: the Herceg Novi, Tivat, Risan and Kotor bay. They are connected and interact with the open sea through narrow straits and the Bay can be considered as one of the main freshwater inputs into the southern Adriatic Sea. The semi-enclosed systems such as Boka Kotorska Bay, are very sensitive to contamination, and their structure attributes to the longer removal time of the contaminants (Jović and Stanković, 2014).

The mussel *M. galloprovincialis* is a native species for this area. Commercial farming of these mussels dates back 30 years in this area, and today these mussels are cultivated on several farms along the whole coast of Boka Kotorska Bay. In addition to cultivated mussels, wild mussels are widespread throughout the Bay, which are hand-collected for personal consumption (Jović et al., 2012). In the same time mussels are an important and excellent source of proteins, some vitamins and essential elements for humans, but they can potentially be toxic. Mussels are well known to accumulate a wide range of metals in their soft tissues and increasingly frequently are used as an indicator of marine pollution (Jović et al., 2011; Stanković et al., 2011, Stanković and Jović, 2013).

The aim of this work was to investigate the element composition of mussels *M. galloprovincialis* from Southeastern Adriatic by measuring Cl, Si, S, K, P, Ca, Fe, Br, Zn, Mn, Sr, I, As, Cr, Ti, Ce, Ba, Cu, Cs, Rb, Pb, Ni, Th, Sb, Sn, Cd, V, Co, Zr and Hg with the energy dispersive X-ray fluorescence method, and also to identify the contribution of macronutrients, micronutrients, nonessential and toxic elements to the total mussel elemental concentrations.

MATERIALS AND METHODS

Boka Kotorska Bay is located in Montenegro, Adriatic-Mediterranean country. Mussel samples were collected at seven locations: Krašići, Kukuljina, Tivat, Opatovo, Sv Stasija,

Perast and Herceg Novi. At each sampling site about 2 kg of mussels were collected, placed in nylon bags with seawater and transported to the laboratory. The biggest 25–30 mussels, of approximately the same size, were washed and cleaned out, opened raw and the flesh scraped out of the shells, which was then freeze-dried at -40 °C for 48 h, weighed, homogenized and ground to a fine powder. The powdered sample was pressed with a hydraulic press by applying a pressure of 7 t for 20 s. No binder material was applied. The resulting pellets had a diameter of 32 mm and a uniform mass of 400 ± 3 mg. The samples were prepared in this manner, in the form of pressed pellets, for energy dispersive X-ray fluorescence analysis (ED-XRF). In this work a MiniPal 4 ED-XRF spectrometer (PANalytical, Almelo, Netherlands) was used to determine major, minor and trace elements (Cl, Si, S, K, P, Ca, Fe, Br, Zn, Mn, Sr, I, As, Cr, Ti, Ce, Ba, Cu, Cs, Rb, Pb, Ni, Th, Sb, Sn, Cd, V, Co, Zr and Hg) concentrations.

RESULTS AND DISCUSSION

Minerals are inorganic substances present in all body tissues, and their presence is necessary for the maintenance of certain physicochemical processes which are essential to life. Every form of living matter requires minerals for their normal life processes (Soetan et al., 2010). In relation to their concentrations minerals may be classified as macro (major), micro (trace) and ultra trace elements (Stanković et al., 2012). The significance and importance of mineral elements for human and animal nutrition is well clarified in this century, and modern analytical techniques tend to their exact quantification. Element composition of mussels *Mytilus galloprovincialis* from Boka Kotorska Bay was determined by measuring Cl, Si, S, K, P, Ca, Fe, Br, Zn, Mn, Sr, I, As, Cr, Ti, Ce, Ba, Cu, Cs, Rb, Pb, Ni, Th, Sb, Sn, Cd, V, Co, Zr and Hg with the relatively new nondestructive method ED-XRF. Results of the investigated macro, micro and ultra trace elements in the mussels' soft tissue are shown in Table 1.

Table 1. Elements concentrations in the mussels soft tissue (wet weight basis expressed as mg/kg) at seven location in Boka Kotorska Bay, Montenegro

	Sampling locations						
	Krašići	**Kukuljina**	**Tivat**	**Opatovo**	**Sv Stasija**	**Perast**	**H. Novi**
Cl	6402.9	5665.9	7511.8	6454.5	3822.0	3809.5	5399.0
Si	4541.3	4797.4	4648.1	4530.4	4548.3	4520.8	4566.4
S	2155.7	2026.8	2414.4	2041.0	1841.3	1696.0	1904.0
K	1321.6	1398.4	1497.1	1349.3	1270.2	1219.9	1226.3
P	978.7	933.0	1116.6	935.6	1085.1	965.4	885.1
Ca	485.5	468.7	1028.4	373.7	249.8	268.7	825.3
Fe	59.86	179.9	97.75	34.78	22.84	22.84	31.66
Br	63.49	50.52	56.06	67.47	42.04	42.21	65.05
Zn	14.71	22.15	42.04	24.05	14.01	15.92	27.85
Mn	13.84	15.05	16.96	15.57	14.01	14.19	16.78
Sr	9.00	7.44	15.57	6.06	8.48	5.88	7.96
I	7.44	6.75	4.67	7.44	6.06	4.67	7.79
As	5.88	4.15	4.15	4.15	4.50	4.33	4.67
Cr	4.33	4.84	4.33	4.50	4.50	4.33	4.50
Ti	3.63	10.0	0.52	2.60	1.38	0.35	2.25
Ce	2.60	2.60	2.77	2.60	2.25	3.46	2.94
Ba	2.42	2.77	2.25	1.38	1.73	1.90	1.56
Cu	1.52	1.44	2.16	1.45	1.07	1.38	1.38
Cs	1.63	1.57	0.90	1.11	1.28	1.31	1.02
Rb	1.09	1.49	1.07	1.16	0.95	0.88	1.06
Pb	0.66	0.69	1.28	0.80	0.59	0.62	0.69
Ni	0.43	1.04	0.76	0.52	0.36	0.40	0.54
Th	0.381	0.398	0.381	0.450	0.329	0.294	0.502
Sb	0.381	0.398	0.294	0.363	0.415	0.415	0.381
Sn	0.311	0.294	0.450	0.260	0.242	0.706	0.260
Cd	0.242	0.173	0.208	0.277	0.173	0.156	0.190
V	0.104	0.104	0.156	0.087	0.017	0.398	0.069
Co	0.090	0.149	0.140	0.131	0.090	0.045	0.156
Zr	0.190	0.294	0.069	0.035	0.035	0.035	0.035
Hg	0.003	0.016	0.016	0.019	0.043	0.019	0.003

In the investigated mussels the Cl, Si, S, K, P and Ca concentrations are significantly higher than the remaining tested elements, which is understandable since these are macronutrients. These elements have many important roles in the organisms (Soetan et al., 2010). An anthropogenic influence on obtained concentrations is possible and expected since these elements are present in many manufacturing processes and products (Jović et al., 2011). The Cl, K and Ca are dominant elements in seawater, and high concentrations of these elements in mussels are expected. The measured contents of Si in mussels from all sampling locations were in the close range. It is known that Si is the main constituent in marine organisms as a biogenic mineral and in the sediment clay of the Bay bottom (Tanaskovski et al., 2014). Similar distribution of this element in the soft tissue of mussels at all locations primarily indicates its natural origin. Both elements, S and P, are a natural and anthropogenic component of an aquatic environment, but fluctuation of mussels concentrations by locations indicates possible increased anthropogenic influence of these two elements. Fluctuations of individual micronutrients, nonessential and toxic elements concentrations in the investigated mussels from different sampling locations, besides the natural origin of elements, can also indicate the possible increase in anthropogenic input. The specificity of the Bay geo-hydrology can also influence the level and a natural origin of these elements in mussels (Tanaskovski et al., 2014). In relation to the wet matter the mussel soft tissue contained 98.7 % macronutrients, 0.76 % micronutrients and 0.54 % nonessential and toxic elements.

CONCLUSION

Element composition of mussels *Mytilus galloprovincialis* was determined with the relatively new nondestructive method - the energy dispersive X-ray fluorescence. In relation to the wet matter, the mussel soft tissue contained 98.7% macronutrients (Cl, Si, S, K, P and Ca), while the remaining 1.3% refers to all the remaining elements: 0.76% micronutrients (Fe, Zn, Mn, I, Cr, Cu, Ni, V and Co) and 0.54% nonessential and toxic elements (As, Ba, Br, Cd, Ce, Cs, Hg, Pb, Rb, Sb, Sn, Sr, Th, Ti and Zr). Fluctuations of individual elements' concentrations in the investigated mussels' soft tissue from different sampling locations besides the natural origin of elements can also indicate to the possible increase in anthropogenic input. The geo-hydrology impact of investigated area can also influence the level and a natural origin of these elements in mussels.

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