



Assessment of the Content of Cr, Cu, Fe, Mn and Ni in Water and Algae from the Region of Makarska Riviera in Croatia

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1. Introduction

Trace metals play a key role in the functioning of oceanic and sea ecosystems. Many of them, like manganese and iron are elements indispensable for the growth of living organisms, however, other physiological roles have not been found yet. Trace elements are particularly significant for ecosystems of saline reservoirs thanks to a low concentration found in oceanic and sea water (Aparicio-Gonzalez et al. 2012, Kováčik et al. 2018). The content of trace elements in sea water is several or several hundred times lower compared to their concentration in fresh water. Additionally, bio-assimilability of these elements in sea environment is lower than in fresh water. These conditions cause that sea organisms as a result of evolution have developed an ability to intensify collection of trace elements to satisfy a physiological demand for them (Titilawoa et al. 2018). These abilities of sea organisms induce a threat, both for them as well as for organisms from higher levels of a trophic chain mainly in the regions of the increased anthropopressure. The shallow coastal zones or estuaries with a greater amount of nutrients and favourable thermal conditions are especially exposed to the increased content of trace elements (Li et al. 2018). In such zones there are particularly good conditions for development of sea organisms living in water and outside it. In coastal regions and estuarine areas, a high variability of their reaction and oxygen content in water is observed (Jureczko et al. 2018). Bio-accumulation is an ability to collect elements or chemical compounds by living organisms (Goher et al. 2016). Assessment of the quality of the environment very often is made based on the bio-indication method, because it helps to determine not only

the level of pollution in biotic elements of the ecosystem but also their impact on living organisms from subsequent levels of the trophic chain (Niemiec & Wiśniowska-Kielian 2015, Niemiec et al. 2018). Methods with the use of algae are the most often used for assessment of marine environmental pollution (Brito et al. 2012, Szelaż-Sikora et al. 2016). The main issue related to these organisms is selection of a suitable species, development of which will not be inhibited by such factors as water temperature, flow speed or salinity. There are some algae which have great abilities for accumulation of elements (Sikora et al. 2018), but they are sensitive to salinity which limits their use in monitoring tests (Sinaei et al. 2018). It is of particular meaning in the zones of strong mixing of river water with sea water on the areas of great seasonal fluctuation of river water flow. The use of algae as a material for research is an incredibly significant practical aspect since ca. 6 million tons of these organisms annually is used in the food industry. Moreover, even their greater use for production of medicines, cosmetics and fodder is observed (Naser 2013, Wang et al. 2017). A high content of protein with a favourable composition of amino acids decide about exceptional value of algae. Moreover, algae have anti-septic properties. Macro-algae have a great ability to accumulate potassium thus, their use as a fertiliser or fodder constitutes an unconventional source of this element. *Cystoseira* and *Ulva* algae are the most popular organisms that live in the sea and estuary bottoms since they are resistant to the above-mentioned factors. Therefore, they meet all criteria for bio-indicators. Due to a strong root system they may collect elements related to bottom deposits (Horta-Puga et al. 2013). Moreover, algae form a living and reproductive environment for water organisms and constitute their food and buffer the waving intensity.

The objective of the paper was assessment of Cr, Cu, Fe, Mn and Ni in water and algae collected in the region of Makarska Riviera.

2. Material and methods

The paper assesses the content of five elements in water and algae collected from the Adriatic Sea in the region of Makarska Riviera. Water and algae samples were collected in August 2016 from nine sampling points located in: Makarska, Podgora, Baska Voda, Split ul. Jana Pawła II, Storbeč, Podstrana, Omiš, Mimice, Dvernik (Figure 1). Water samples were collected from the surface layer (depth of 0-120 cm).

Samples of algae *Cystoseira barbata* and *Ulva rigida* were collected in the same points. The collected species of algae are popular on the investigated area. Water after collection was preserved by adding nitric acid (V) in the amount of 2 cm³ per each 100 cm³ of water sample, then samples were transported to a laboratory while algae were cleaned in distilled water, dried and homogenised. Five laboratory samples of water and algae were collected from the sampling

point. Laboratory samples of algae were mineralised in the closed microwave system by Anton Paar Multivawe 3000. An analytical portion was 0.5 g per dry mass. Material was solubilised in the mixture of HNO₃ and H₂O₂ in the proportion of 5:1, v/v. The content of chromium, copper, iron, manganese and nickel in water and solubilised algae samples were determined using the optical emission spectrometry technique by Perkin Elmer Optima 7600 DV. Certified reference material EA-V-10 was used for the control of correctness of analysis of the investigated elements. Results of analysis of the referential material and a value of recovery estimated based on analyses made in 4 iterations were presented in Table 1.

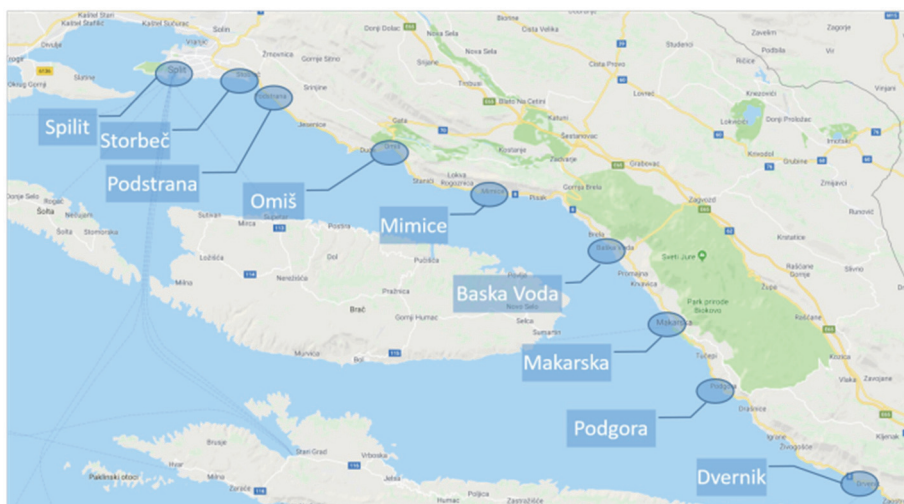


Fig. 1. Location of sampling points

Table 1. Parameters of the applied analytical method

Element	Length of waves	Limit of determination	Content in the referential material	Measured content	Coefficient of recovery
	(nm)	(mg·dm ⁻³)	(mg·kg ⁻¹)	(mg·kg ⁻¹)	(%)
Cr	267.707	0.0071	6.5	6.412	98.6
Cu	327.393	0.0097	9.4	9.125	97.1
Fe	238.204	0.0046	185	201.2	108.8
Mn	257.608	0.0014	47	48.56	103.3
Ni	231.604	0.015	4	3.856	96.4

3. Results of research and discussion

The highest content of chromium in *Cystoseira barbata* algae biomass was found in plants collected in Mimice point at the level of $3.417 \text{ mg}\cdot\text{kg}^{-1}$ and the lowest in Podstrana ($1.367 \text{ mg}\cdot\text{kg}^{-1}$) (Table 2). In case of *Ulva rigida* algae - the chromium content ranged from 7.570 to $13.26 \text{ mg}\cdot\text{kg}^{-1}$ with the highest amount in Baska Voda and the lowest in samples collected in Podgora (Table 3). A lower concentration of this element in *Ulva* in comparison to its amount in *Cystoseira* by 50% was reported. The content of chromium in both species of algae does not pose any risk to environment. The content of chromium in various species of algae collected from Aegean Sea in coastal regions of Turkey was slightly higher than the ones obtained in own research (Akcali & Kucuksezgin 2011). Those authors concluded higher concentration of this element in *Cystoseira barbata* compared to its amount in *Ulva rigida*. Brito et al. (2012) provide approximately two times higher values of chromium in biomass of various species of algae from the area in Brazil under high anthropopressure, while accumulation of this element in algae collected in the Turkish coastal zone of the Black Sea was comparable to the ones obtained in own research. Caliceti et al. (2002) provide an average chromium content in *Cystoseira barbata* at the level of ca. $\text{mg}\cdot\text{kg}^{-1}$ in algae from Venice Lagune collected from the regions with varied intensity of anthropopressure. Strezov and Nonova (2009) provide chromium content in both algae collected from the Bulgarian coastal zone of the Black Sea at a similar level as the ones reported in this study in the points of the lowest accumulation of this element.

The concentration of copper in the investigated algae *Ulva rigida* range of 4.236 to $8.367 \text{ mg}\cdot\text{kg}^{-1}$ with the average content $5.622 \text{ mg}\cdot\text{kg}^{-1}$ (Table 3). The highest copper content in *Cystoseira* algae was observed in the sampling point located in Baska Voda and the lowest in Podstrana (Table 2). In case of *Ulva rigida* the highest amount of copper was observed in the sample collected in Storbec, while the lowest in algae from Podgora. Akcali and Kucuksezgin (2011) observed in the studies in the Aegean Sea that the copper content in *Cystoseira* algae was $0.269 \text{ mg}\cdot\text{kg}^{-1}$. On the other hand, Strezov and Nonova (2009) reported the copper content in *Ulva rigida* at the level from 2.2 to $10.9 \text{ mg}\cdot\text{kg}^{-1}$.

The iron content in *Cystoseira barbata* algae in own research was within $48.28 \text{ mg}\cdot\text{kg}^{-1}$ and $225.1 \text{ mg}\cdot\text{kg}^{-1}$ and in *Ulva rigida* algae from 201.9 to $412.9 \text{ mg}\cdot\text{kg}^{-1}$ (Table 3). A relatively low content of iron was reported in algae collected in Omiš. The content of this element in *Ulva rigida* algae was almost threefold higher compared to *Cystoseira barbata*. Strezov and Nonova (2009) state that the average iron content in both species collected in the Bulgarian coastal zone ca. $450 \text{ mg}\cdot\text{kg}^{-1}$, but these authors did not find any differences of this element in both algae species. Wallenstein et al. (2009) provide much lower,

(< 50 mg·kg⁻¹) iron content in *Cystoseira humilis* from regions of a varied intensity of anthropopressure. The manganese content in *Cystoseira barbata* ranges from 20.62 mg·kg⁻¹ to 66.53 mg·kg⁻¹ (Table. 2), while in *Ulva rigida* from 44.15 mg·kg⁻¹ to 197.5 mg·kg⁻¹ (Table 3). Results of own research show a higher manganese content in *Ulva* algae biomass than in *Cystoseira* biomass. The highest amount of this element was determined in algae collected in Mimice, Dwernik and Omiš. In the remaining samples, the content of this element was similar and within 44.15 to 63.38 mg·kg⁻¹. Brito et al. (2012) in various algae species from the region in Brazil under an elevated level of anthropopressure, provide the content of this element from 10 to almost 500 mg·kg⁻¹. Wallenstein et al. (2009) reported much lower content of manganese from 4 to 5 mg·kg⁻¹ in *Cystoseira humilis* from Azores.

Table 2. Content of elements in biomass of *Cystoseira barbata* algae

Sample collection point	Cr	Cu	Fe	Mn	Ni
Unit	(mg·kg ⁻¹)				
Makarska	1.433a*	5.683b	141.5c	59.28bc	3.662c
Podgora	1.660a	3.967a	84.26b	20.62a	2.253b
Baska voda	2.236ab	6.236c	225.1d	33.35a	2.967bc
Split ul. Jana Pawła II	3.333c	5.333b	104.2b	51.78b	3.617c
Storbeč	3.033c	5.167b	64.25ab	43.25ab	2.417b
Podstrana	1.367a	3.560a	50.98a	33.58a	1.633a
Omiš	3.258c	3.836a	48.28a	63.23bc	3.948c
Mimice	3.417c	4.817ab	123.9c	61.78bc	3.567c
Dwernik	3.257c	5.456b	156.2	66.53c	3.586c
Average	2.555	4.895	111.0	48.16	3.072
Standard deviation	0.876	0.920	57.72a	16.21	0.799

*Letters at values in particular locations stand for statistically significant differences at p = 0.05

The nickel content in *Cystoseira barbata* algae was within 1.633 to 13.26 mg·kg⁻¹ (Table 2). The highest amount of this element was reported in samples collected in Mimice, Dwernik and Omiš, and the lowest in Podstrana and Podgora. The content of nickel in *Ulva rigida* was within 2,493 to 5,617 mg·kg⁻¹, with the average of 4,021 mg·kg⁻¹ (Table 3). The results obtained in own research concerning the nickel content in algae in majority of case are not high and similar to

the content of this element in algae from the areas with a low coefficient of anthropopressure. Brito et al. (2012) provide the nickel content that is several times higher in algae of various species from the region in Brazil with a prominent level of anthropopressure. Caliceti et al. (2002) reported the average content of this element from Venice Lagune at the level of $1.8 \text{ mg}\cdot\text{kg}^{-1}$, at slight differences of concentration in algae collected in the region with a varied intensity of anthropopressure. Wallenstein et al. (2009) provide much lower, ca. $1 \text{ mg}\cdot\text{kg}^{-1}$, nickel content in *Cystoseira humilis* from the region of Azores from stations under a varied intensity of anthropopressure. In Chlorophyta (green algae) collected in the contaminated region of the coastal zone of Saudi Arabia, the concentration of this element was within 25 to $44 \text{ mg}\cdot\text{kg}^{-1}$ (Naser 2013). On the other hand, Rodriguez-Figueroa et al. (2009) provide the maximum content of nickel in algae from the Gulf of Mexico in the region with the impact of the copper mine at the level of $28 \text{ mg}\cdot\text{kg}^{-1}$. The nickel content in *Ulva rigida* collected from San Jorge in Argentina was within 0.9 - ca. $4 \text{ mg}\cdot\text{kg}^{-1}$ (Perez et al. 2007).

Water samples collected from particular sampling points were variable with regard to the concentration of the investigated elements. The biggest number of the tested elements was in water collected in Split and Dwernik, and the lowest in Podgora and Podstrana (Table 4). In case of majority of samples, water was enriched in chromium, copper, iron, and nickel (Bonnand et al. 2013, Akcali & Kucuksezgin 2011).

Sea algae are much related to trace elements (Niemiec et al. 2015). Due to the specificity of physiological processes, they can collect massive amounts even in the conditions of their small concentrations in a biotype (Chakraborty et al. 2014).

The results of the research show that the highest value of the bio-accumulation ratio was in case of manganese both in case of *Cystoseira barbata* and *Ulva rigida* (Figure 2 and 3).

The chromium bio-accumulation coefficient in organisms used in the research was at a level of 1102 to 2527 respectively for the sampling points Makarska and Mimice (Figure 2). The chromium bio-accumulation factor in *Ulva rigida* algae was within 6626-11984 (Figure 3). Literature data show similar values of chromium bio-accumulation coefficient in macro-algae from various regions of the world. Akcali and Kucuksezgin (2011) claim that the value of the chromium bio-accumulation coefficient in algae from the Aegean Sea were from several to several thousand.

Table 3. Content of elements in the biomass of *Ulva rigida* algae

Samples collection points	Cr	Cu	Fe	Mn	Ni
Unit	(mg·kg ⁻¹)				
Makarska	8.957a*	4.967ab	348.6c	62.28ab	4.657b
Podgora	7.570a	4.236a	266.6b	51.24a	2.235a
Baska Voda	13.26b	6.159bc	299.6bc	56.56ab	3.867b
Split ul. Jana Pawła II	11.27b	5.657b	353.2c	63.38ab	4.425b
Storbeč	10.10ab	8.367d	412.9d	155.8cd	3.667ab
Podstrana	8.550a	6.685c	261.2b	44.15a	2.493a
Omiš	11.20b	4.438a	403.7d	75.33b	4.375b
Mimice	13.18b	4.667a	201.9a	197.5d	5.617c
Dvernik	12.26b	5.423b	245.7ab	132.5c	4.856b
Average	10.70	5.622	310.4	93.19	4.021
Standard deviation	2.047	1.307	73.24	54.78	1.096

*Letters at values in particular locations stand for statistically significant differences at $p = 0.05$

Table 4. Content of elements in water

Samples collection points	Cr	Cu	Fe	Mn	Ni
Unit	(µg·dm ⁻³)				
Makarska	1.300b*	12.00b	132.0ab	13.00cd	2.400b
Podgora	0.900a	8.000a	120.0a	5.000a	1.800ab
Baska Voda	1.400b	15.00bc	144.0b	9.000b	2.500b
Split ul. Jana Pawła II	1.700c	21.00d	162.0c	8.000b	3.100c
Storbec	1.200ab	17.00c	139.0b	11.00c	1.800ab
Podstrana	1.000a	12.00b	112.0a	9.000b	1.200a
Omiš	1.500b	11.00b	144.0b	12.00c	1.300a
Mimice	1.100a	13.00b	115.0a	9.000b	1.400ab
Dvernik	1.300b	18.00c	135.0ab	14.00d	2.600b
Average	1.267	14.11	133.3	10.00	2.011
Standard deviation	0.250	4.014	16.48	2.784	0.666

*Letters at values locations stand for statistically significant differences at $p = 0.05$

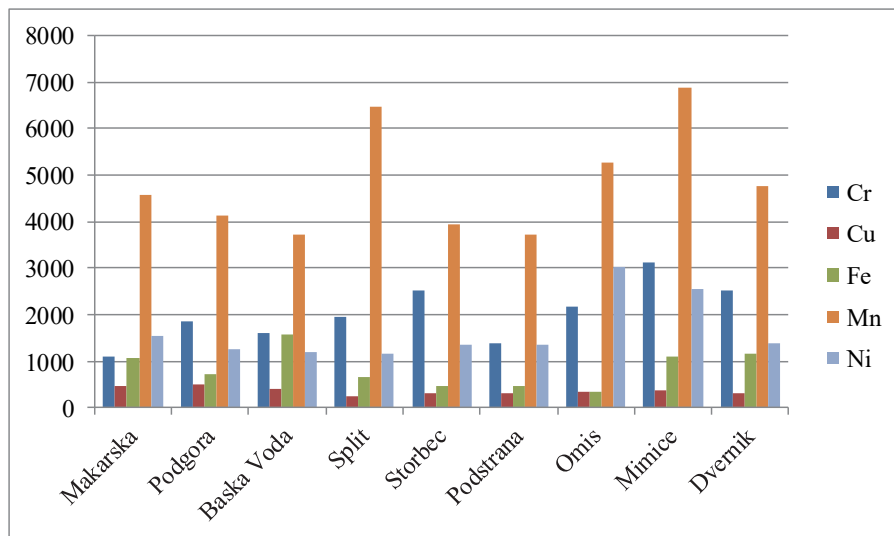


Fig. 2. Bio-accumulation coefficient in *Cystoseira barbata* algae

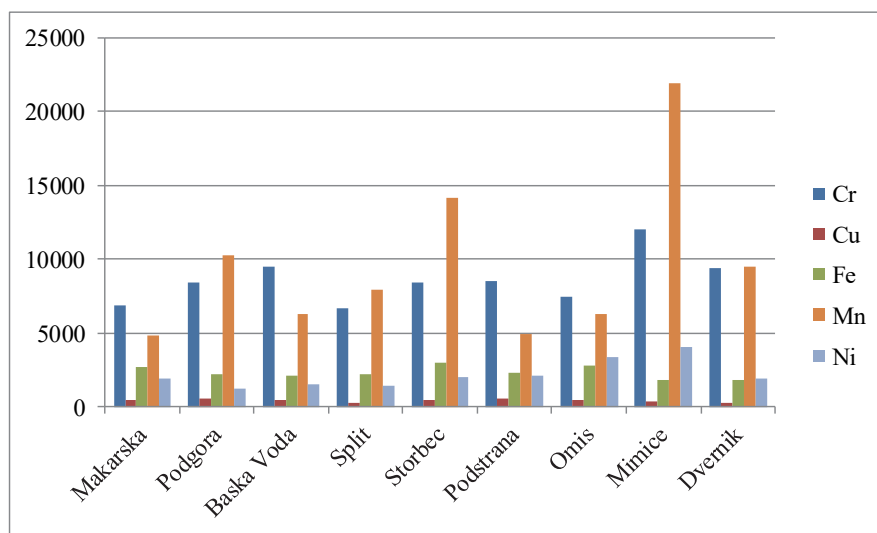


Fig. 3. Bio-accumulation factor in *Ulva rigida* algae

The copper bio-accumulation coefficient in *Cystoseira barbata* ranged from 253 to 495 respectively in Split and Podgora, while *Ulva rigida* algae these values were respectively 269 and 528 (Figure 2 and 3). The average value of the iron bio-accumulation coefficient was 1574. In *Cystoseira barbata* algae, the bio-accumulation coefficient of this element was threefold lower than in *Ulva rigida* algae tissues. The lowest value of iron coefficient in case of both algae was in Mimice and its highest values were in the samples of *Cystoseira barbata* collected in Baska Voda and *Ulva rigida* collected in Storbec. Results of the research show big differences of the investigated parameters in studied area. Melville and Pulkownik (2007) concluded a noticeably big variability of the iron content in algae at a low diversity of concentration of this element in water for various estuaries. It resulted from differences in bio-availability of the analysed element in test stations which mainly result from water properties. The bio-accumulation coefficient of iron in various regions of the Aegean Sea were from 4000 to 9000 (Akcali & Kucuksezgin 2011). The bio-accumulation coefficient of manganese was at the level of 3705 to 21941 respectively for Baska Voda and Mimice. The stated values of the manganese bio-accumulation coefficient were high which is related mainly to a low content of this element in water. Sanders et al. (2012) say that the analysed coefficient for manganese in algae present in few estuaries in the Western Australia was ca. 50. The last analysed element is nickel for which the bio-accumulation coefficient was within 329.3-857.1 for Mimice and Split. Melville and Pulkownik (2007) provide values of the nickel bio-accumulation coefficient in various species of algae collected in the estuaries of the western Australia at a similar level for the one stated in own research.

In case of nickel, a slightly higher value of the bio-accumulation coefficient was found in *Ulva rigida* compared to *Cystoseira barbata*. The average values for those algae were respectively 2168 and 1644. According to the data presented by Strezow and Nonova (2009), values of these coefficients in algae from the Bulgarian coastal zone of the Black Sea are like the ones presented in this paper.

4. Conclusions

1. The content of the investigated elements in water collected from particular sampling points show anthropogenic enrichment.
2. Higher concentrations of the investigated elements in water collected in Split compared to samples from other places were determined.
3. The content of all investigated elements in *Cystoseira barbata* and *Ulva rigida* algae from the region of Makarska Riviera are characteristic for non-contaminated regions.

4. Algae collected in Split region which is under increased anthropopressure, generally did not show up higher amounts of the investigated elements compared to the samples from the regions located far from urban centres.
5. The content of the investigated elements in water decreased in the order Fe>Cu>Mn>Ni>Cr. In the biomass of *Cystoseira barbata* algae in the order Fe>Mn>Cu>Ni>Cr and in *Ulva rigida* Fe>Mn>Cr>Cu>Ni.
6. Bigger differences of the content of the investigated elements in the biomass of algae were determined when compared to their concentration in water from particular sampling points.

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Abstract

The aim of this paper was to assess the content of Cr, Cu, Fe, Mn and Ni in water and in algae collected in the region of the Makarska Riviera. The samples of water and algae were collected in August 2016 from nine sampling points: Makarska, Podgora, Baska Voda, Split ul. Jana Pawła II, Storbeč, Podstrana, Omiš, Mimice, Dvernik. The concentrations of the elements in the water and in the digested algae samples were determined using the ICP-OES method. The study results indicate anthropogenic enrichment of all studied elements in water, with the exception of manganese. Higher contents of studied elements in water collected in Split were found. The concentrations of elements in algae do not indicate pollution of the natural environment and are characteristic of non-contaminated areas. The content of the studied elements in the water decreased in the order Fe>Cu>Mn>Ni>Cr in *Cystoseira barbata* algae decreased in the order Fe>Cu>Mn>Ni>Cr and in *Ulva rigida* in the order Fe>Mn>Cr>Cu>Ni.

Keywords:

macroalgae, bio-accumulation, trace elements, Adriatic Sea

Ocena zawartości Cr, Cu, Fe, Mn i Ni w wodzie i algach z regionu Riwieri Makarskiej w Chorwacji

Streszczenie

Celem pracy była ocena zawartości Cr, Cu, Fe, Mn i Ni w wodzie i glonach pobranych w rejonie Riwieri Makarskiej. Próbkę wody oraz glonów pobrano w sierpniu 2016 roku z dziewięciu punktów badawczych: Makarska, Podgora, Baska Voda, Split ul. Jana Pawła II, Storbeč, Podstrana, Omiš, Mimice, Dvernik. Zawartość pierwiastków w wodzie oraz roztworzonych próbkach glonów oznaczono metodą spektrometrii emisyjnej, w aparacie Optima 7600 DV firmy Perkin Elmer. Wyniki przeprowadzonych badań wskazują na antropogeniczne wzbogacenie wody we wszystkie badane pierwiastki

z wyjątkiem manganu. Stwierdzono większe zawartości badanych pierwiastków w wodzie pobranej w Splicie w porównaniu do próbek z innych miejsc. Zawartości pierwiastków w glonach nie wskazują na zagrożenie na środowiska naturalnego i są charakterystyczne dla obszarów niezanieczyszczonych. Zawartość badanych pierwiastków w wodzie malała w kolejności Fe>Cu>Mn>Ni>Cr. W biomasie glonów z rodzaju *Cystoseira barbata* w kolejności Fe>Mn>Cu>Ni>Cr, zaś w glonach *Ulva rigida* Fe>Mn>Cr>Cu>Ni.

Słowa kluczowe:

makroglony, bioakumulacja, pierwiastki śladowe, Morze Adriatyckie