ASSESSMENT OF CHANGES IN THE MINERAL COMPOSITION OF THE BROWN ALGA *CYSTOSEIRA BARBATA* (TURN.) C.AG., COLLECTED ALONG THE COAST OF ANAPA

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Introduction

The study of the biology and ecology of marine benthic microalgae due to their importance to the world's oceans as one of the major primary producers of the shelf zone, where their products are comparable to the products of temperate forests. Moulded macrophytes coastal thickets are, on the one hand, and spawning habitat for fish and invertebrates, and on the other - a natural barrier to anthropogenic pollution coming from coastal runoff. Currently, one of the most important areas of research of macroalgae is to assess their contribution to the exchange of biogeochemical ocean.

Objects and methods

Fig. 1. Field sampling (Anapa district)

Object of this research are representatives of one of dominant trade views of the Black Sea - *Cystoseira barbata* (Turn.) C. Ag. *Cystoseira barbata* (Stachouse) of C. Agardh – large (to 1 m of height) the attached sea brown alga living on a solid substratum: stony terraces, boulders, stones. Absorbs all difficult differentiated surface of a thallus. The root system is absent.

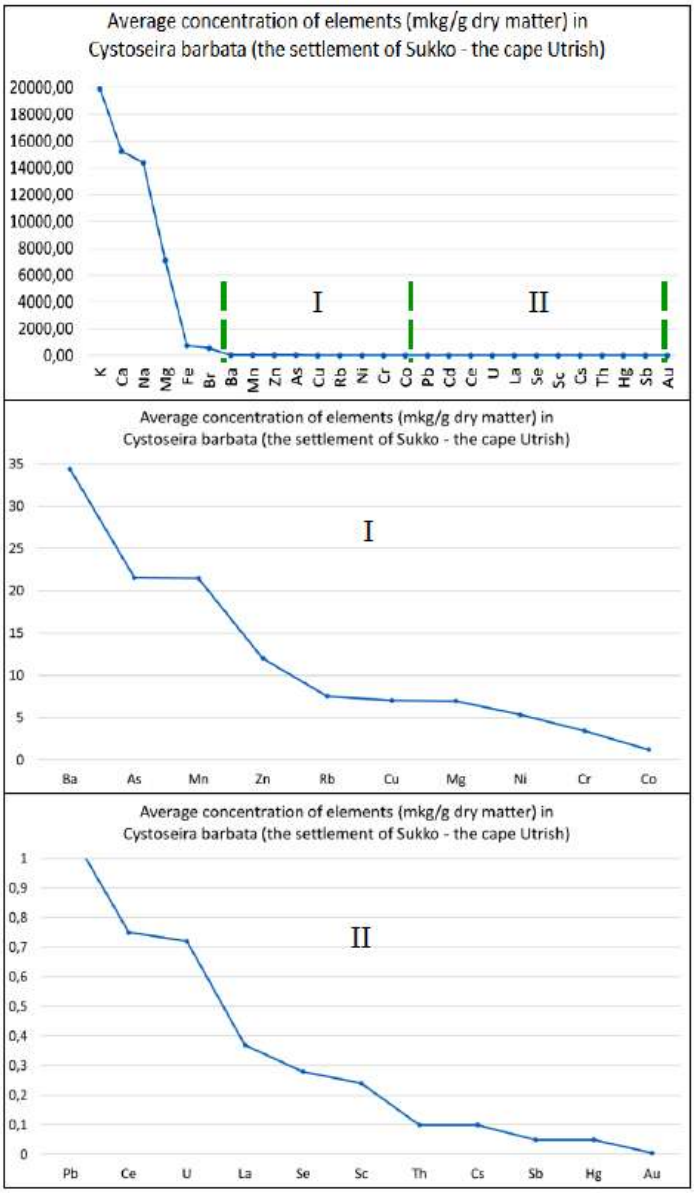
Collecting material was carried out in 1980 - 2015 on various shallow sites of the Black Sea. As model sites from 2001 to 2015 served the sites around Anapa which are settling down from the settlement of Sukko to the cape Utrish. The algae were collected at depths of 0,5; 2; 4; 6 and 8 meters (fig. 1).

Determination of content of Na, Rb, Cs, Ba, Sc, La, Ce, Th, U, Au, Cr, Fe, Co, Zn, Hg, As, Se, Sb, Br in thalli

Cystoseira barbata were determined by neutron activation, and K, Mg, Ca, Mn, Cu, Ni, Cd, Pb by atomic absorption and x-ray fluorescence analysis.

Results and its discussion

Figure 2 shows the long-term (over 20 years), these changes of mineral composition *Cystoseira barbata* (Bunkova et al, 2014; Kamnev et al, 2014). Only such long-term data allow relatively correctly judge the actual concentration opportunities *Cystoseira barbata* (Stachouse) C. Agardh.



As a result, our research has received several patterns of different chemical elements in the thallus of the brown alga *Cystoseira barbata*, collected in the waters of the river to the Sukko – the cape Utrish. Within chemical group we analyzed alkali metals (Na, K, Rb), alkaline earth metals (Mg, Ca, Ba), and IV group metals of the B subgroup (Pb), and V group B subgroups (Sb) of the periodic table.

Figure 2 shows that the mineral elements in their average content in thallus *cystoseira barbata* can be arranged in the following descending order: K> Ca> Br> Na> Fe> Mg> Ba> As> Mn> Zn> Ni> Rb> Cu> Cr> Co> Pb> U> Ce> La> Se> Sc> Cs> Sb> Th> Hg> Au.

As can be seen, the content of the same mineral elements in the algae contemporaneous depending on various factors can vary from 2 to 99 times (depending on the item). The reason for such fluctuations may be changing as the concentration of a particular

Fig. 2. Average concentration of elements in Cystoseira barbata.

element in the mineral water and the complex environmental factors environment, affecting the accumulation of this element of the vegetable organism and the physiological condition of the macrophytes.

The ratio of the maximum and minimum macronutrients concentrations, such as the Na, K, Mg, Ca in thallus *Cystoseira barbata* can vary from 2 (Mg) 5 (K) times, and trace elements - 22 (Zn) and 99 (Fe) times. Similar fluctuations are also characteristic of physiologically "unimportant" items. These results, on the one hand, to some extent, show absorption physiological selectivity of chemical elements *Cystoseira barbata* and confirm the presence of physiological regulatory mechanisms of accumulation of nutrients. Perhaps this is due to the fact that the availability of these elements in different geological epochs changed and, accordingly, the physiological mechanisms of accumulation are different ranges. On the other hand, these results indicate the existence of a particular pool is able to accumulate these elements. In the case of Cystoseira - a storage pool such minerals may be alginic acid and fucoidan forming intercellular spaces and cell walls, and excessive penetration of the delay elements in the cell concentration.

These results, summarizing long-term observations, may indicate the potential need algae in certain elements, as well as the carrying capacity of the cell walls C. barbata in relation to the accumulation of the individual elements.

Seasonal variations

The study changes depending on the mineral composition of C. barbata on the degree of contamination of the habitat and its depth has been found that in general, the content of the majority of these elements in the thallus in the river above the removal area - "conditionally dirty" stations. This is most clearly seen at a depth of 2 m, which is probably due to the immediate removal of the various elements of the drain of the river, and the higher the metabolic activity of the algae in shallow water. An exception is the concentration of non-metals arsenic and selenium contents of which are higher value-added station. It is possible that this is due to local pollution by these elements of the "value-added" station.

On the "value-added" the station the mineral elements are also generally higher in the algae at a depth of 2 m. The exception to both stations is Ba, Sb and Br.

At a depth of about 4 meters of both stations, metal concentrations in thallus vary slightly. Nevertheless, a number of active elements is stored at this depth. Thus, in place of the river removal have high concentrations of bromine, the content of which is almost 1,4 times higher than that at a depth of 2 m the same station and 2-4 times higher than 4 m and 2 m, respectively "value-added" station. Furthermore, at a depth of 4 m "conditionally dirty" stations are the highest concentrations of uranium and gold.

As for the "heavy" metals, some of the general laws fall Pb, whose concentration decreases with depth, but the maximum on the "value-added" station, and Mn, m. To. Its concentration is also higher on the "value-added" station. It can be concluded that to "conditionally dirty" river station takeaway clearly affects the accumulation of minerals, and in the value-added station may have some local flooded contaminants (As, Se, Pb, Mn).

Seasonal variations

To study the content of mineral elements in the daylight saving time following contact was chosen mineral elements: Fe, Mn, Cu, Zn, Pb, Cd. When harvesting season, summer or winter (within a limited time period), the picture is somewhat different (even if the collection was carried out at several stations, several depths, located a few kilometers from each other). Especially clearly this is manifested in the analysis of changes in the content of macro and micro elements (fig.3).

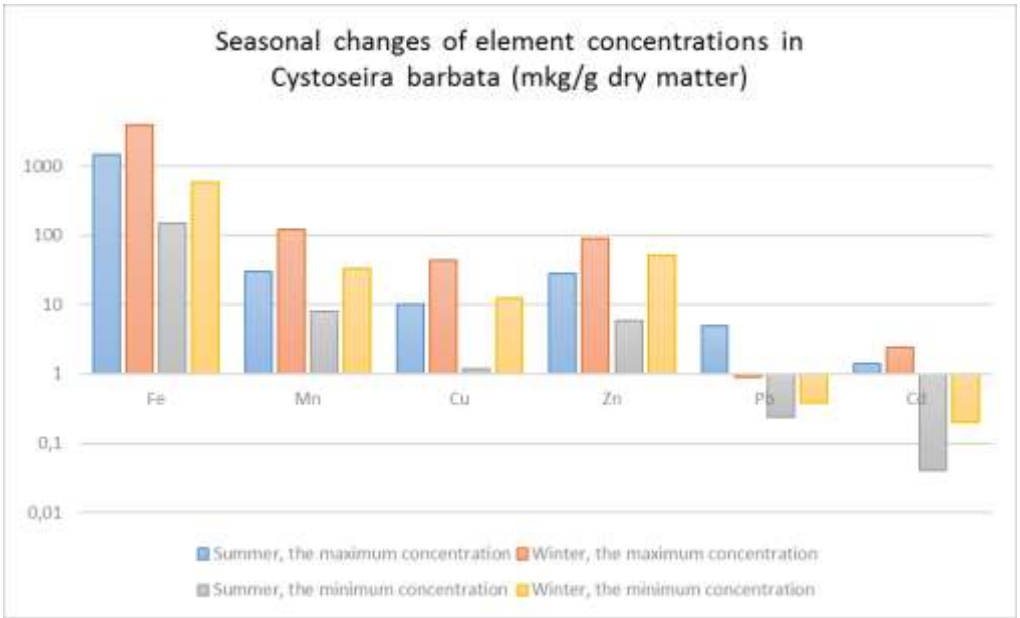


Fig. 3. Seasonal changes of element concentrations in Cystoseira barbata.

The ratio of the maximum and minimum contents of macronutrients (Na, K, Mg, Ca) in the algal thallus varies 1,5 – 4,3 times, trace elements (Fe, Mn, Zn, Cu) – 3,8 – 9,9 times, heavy "physiologically insignificant" heavy metals in the 20,8 – 34,6 times.

The results clearly demonstrate the selectivity of the physiological absorption of chemical elements macroalgae and confirm the presence of the physiological regulatory mechanisms of accumulation of biogenic elements.

The difference in concentrations in the winter, namely an increase in 2-3 times, probably due to a change in the length growth rate, growth prevailing in thickness, and accordingly, changes in the structure and functioning of the cell walls. Reducing Pb content,

probably due to its level of change in the environment. Reducing Pb content, probably due to its level of change in the environment.

Age-related changes

Defined contribution is age-related changes in the accumulation of elements of different ages algae and their parts. In order to study the dependence of change in the content of mineral elements of the age part thallus contact 8 elements (Ca, Na, K, Mg, Fe, Mn, Zn, Cu). In age-related changes are most clearly traced to the copper, magnesium,sodium, potassium, iron and manganese (fig.4, fig. 5, fig. 6, fig.7, fig. 8, fig. 9).

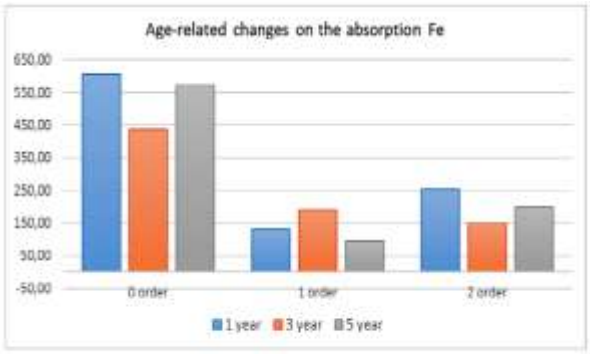


Fig. 4. Age-related changes on the absorption Fe (mkg/g dry matter).

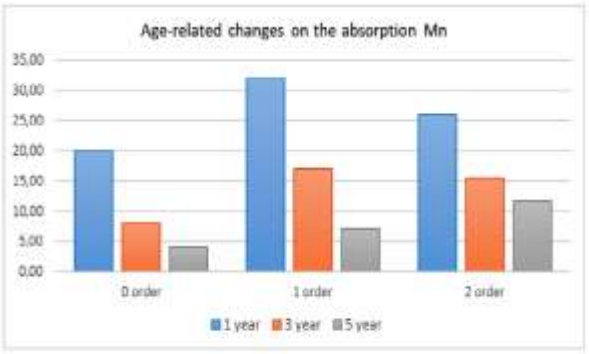


Fig. 5. Age-related changes on the absorption Mn (mkg/g dry matter).

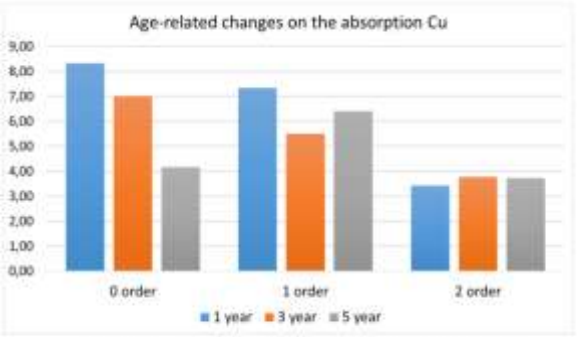


Fig. 6. Age-related changes on the absorption Cu (mkg/g dry matter).

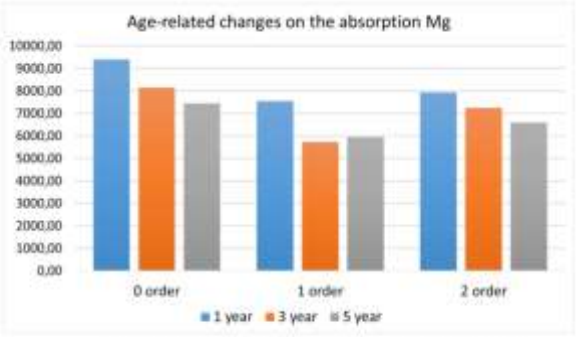


Fig 7. Age-related changes on the absorption Mg (mkg/g dry matter).

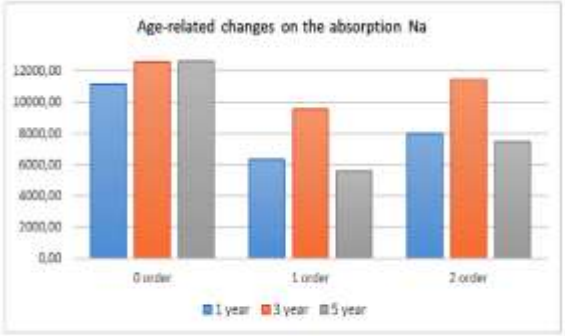


Fig. 8. Age-related changes on the absorption Na (mkg/g dry matter).

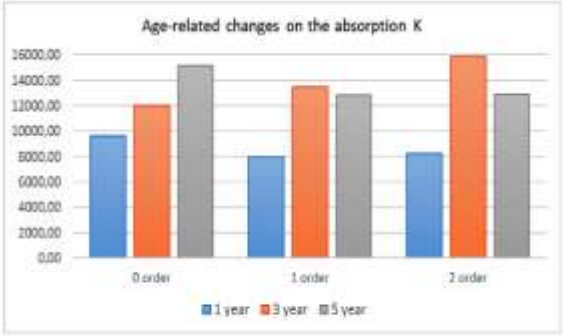


Fig. 9. Age-related changes on the absorption K (mkg/g dry matter).

According to our research stations clear age-related changes can be traced, and the minimum content of the elements characteristic of the axis 0 of the order, and the maximum - for axis II and higher orders.

Coefficients of concentration and biological absorption

One of the most important areas in biogeochemistry is the concept of biogeochemical provinces, based on the separation of which is the specificity of the behavior of certain elements within the areas associated with excess or deficiency of elements in the environment. Therefore, the establishment of the content in relation to a particular standard element is one of the most important techniques in biogeochemistry (Perelman, Kasimov, 1999; Bogatyrev, 2008).

There are approaches integral consideration of the content of the most important macro- and microelements data. These approaches include the construction of geochemical spectra of the elements. With their construction are guided by the following procedure. Usually, on the x-axis successively placed elements according to their serial number. The ordinate axis represents the ratio of the content of each element in the investigated object to the average content in the earth's crust, or lithosphere (Clarke). Then the indices greater than 1 indicate concentration of the element is smaller - about the dispersion (Bogatyrev, 2008).

When man-made pollution of the environment is not only a dangerous excess of MPC members (maximum permissible concentration), but also changes in the relations of elements to each other, and this should be taken into account when carrying out this kind of work. Clarke values set by AP were used to calculate the concentration factor Vinogradov (Vinogradov, 1962). By geochemical spectra presented above clearly shows that the resulting study data show the graphic elements of the same type of behavior accumulated in macrophytes collected in one region (fig. 10, fig. 11).

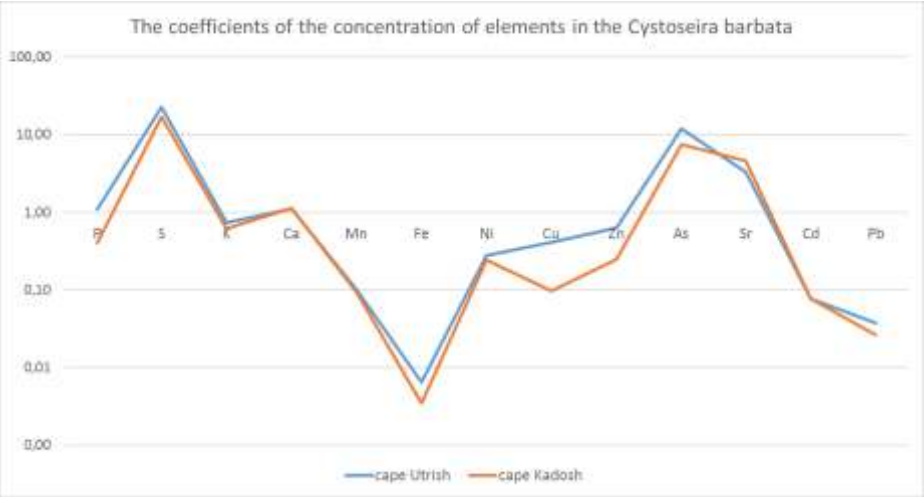


Fig. 10. The coefficients of the concentration of elements in the Cystoseira barbata.

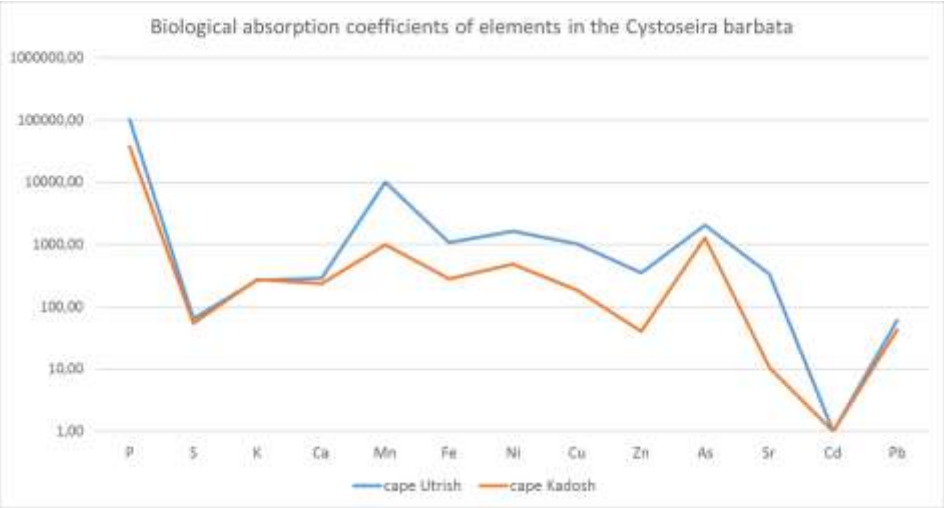


Fig. 11. The biological absorption coefficients of Cystoseira barbata.

Conclusions

1. The availability of these elements to different geological ages varied and accordingly accumulation physiological mechanisms have different ranges. Over the past 100 years, the situation with the availability of many nutrients change, and anthropogenic pollution has led to the fact that some elements of the power plant inaccessible (Cu, Zn, Fe, Co) steel contaminants, which are classified as "heavy toxic metals." Experimental study of the accumulation of some elements of the algae leads to the assumption that a number of elements not found the upper accumulation physiological range, which can lead to a variety of toxic effects on algae.
2. The study changes depending on the mineral composition of C. barbata on the degree of contamination of the habitat and its depth has been found that in general, the content of the majority of these elements in the thallus in the river above the removal area - "conditionally dirty" stations.
3. Seasonal changes of mineral element concentrations in the axes of various orders in the winter becomes less pronounced, which is likely to be associated with reduced metabolism.
4. According to our research stations clear age-related changes can be traced, and the minimum content of the elements characteristic of the axis 0 of the order, and the maximum - for axis II and higher orders.
5. By geochemical spectra clearly it shows that the resulting study data show the graphic elements of the same type of behavior accumulated in macrophytes collected in one region.
6. Only long-term data, including various stations and depth allow relatively correctly judge the real possibilities of uneven concentration of brown algae *Cystoseira barbata.*

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