

UDC (594.133:591.05)(262.5+262.54)

THE ELEMENT CONTENTS IN SOFT TISSUES AND SHELLS OF THE BIVALVE ANADARA KAGOSHIMENSIS (TOKUNAGA, 1906) FROM THE BLACK SEA AND SEA OF AZOV

[©] 2024 L. Kapranova, J. Dikareva, S. Kapranov, and V. Ryabushko

A. O. Kovalevsky Institute of Biology of the Southern Seas of RAS, Sevastopol, Russian Federation E-mail: *lar_sa1980@mail.ru*

Received by the Editor 15.01.2024; after reviewing 13.03.2024; accepted for publication 27.08.2024; published online 09.09.2024.

In the ecosystems of the Black Sea and Sea of Azov, the invasive bivalve mollusc Anadara kagoshimensis is a poorly studied species. This clam is a valuable object in fishery and mariculture. Currently, there is little information about the element contents in soft tissues and shells of the mollusc living in these two seas. The aim of this work is comparative analysis of the elemental composition of A. kagoshimensis from the Black Sea and Sea of Azov. The elemental analysis was carried out using inductively coupled plasma mass spectrometry. The study presents data on the elemental contents in soft tissues and shells of this clam from the two seas. Noticeable differences in contents of elements were found between the sampling areas. These elements include: K, Rb, Cs, Ca, and Ba from the s-element family; the p-elements AI, Ga, Ge, P, As, Bi, and Br; the d-block elements Zn, V, Nb, Ta, Mo, Fe, Ir, and Au; and the f-block elements Pr and Nd. The elemental composition of A. kagoshimensis is determined not only by the composition of seawater, which contains mainly s-elements, but also by mollusc adaptation processes in which p- and d-elements are predominantly involved. In soft tissues of the clam from the Black Sea, concentrations of K, Rb, and Cs are significantly higher than in tissues of A. kagoshimensis from the Sea of Azov, while the concentration of K is one (the Sea of Azov) to two orders of magnitude (the Black Sea) higher in soft tissues than in shells. In shells of the clam inhabiting the Black Sea, Ca content is significantly higher, and these shells are stronger. Against the high calcium content, relatively low phosphorus content is noted in samples of soft tissues and shells from both seas. In soft tissues of A. kagoshimensis from the Black Sea, the contents of P, Al, Ga, Bi, and some heavy metals (Pb and Cd) are significantly higher. The contents of toxic elements in the mollusc from both seas do not exceed the maximum permissible levels. Zn and Mo are accumulated in soft tissues, and Fe is more concentrated in shells. In soft tissues of A. kagoshimensis from the Sea of Azov, Zn content is higher than in this clam from the Black Sea. Rare earth elements (Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb) are more concentrated in soft tissues of the mollusc from both seas than in shells, with Pr and Nd contents in specimens from the Sea of Azov being significantly higher than in those from the Black Sea. Anadara is capable of concentrating elements depending on their contents in the environment; therefore, the element accumulation in individuals of the same species is primarily a function of the biotope conditions.

Keywords: Anadara kagoshimensis, chemical element concentrations, mass spectrometry, Black Sea, Sea of Azov

In the Black Sea and the Sea of Azov, the bivalve *Anadara kagoshimensis* (Tokunaga, 1906) is an invasive and poorly studied species. Due to favorable feeding conditions, high growth rate of anadara is registered [Sahin et al., 2006]. This clam is valuable as a fishing and mariculture target. Specifically, in Thailand, its production reaches 80 million tons *per* year [Suwanjarat et al., 2009].

The content of chemical elements in molluscs is known to be determined by their taxonomic affiliation and genetics [Wala et al., 2016]. The concentration of chemical elements in soft tissues and shells is also dependent on a complex of factors: temperature, salinity, water quality, level of water pollution, *etc.* [Moniruzzaman et al., 2021], with salinity being considered as one of the main environmental parameters altering the functional state of animals [Deaton, 2009]. For example, the concentration of rare earth elements in seawater depends on depth [Elderfield, 1988], and the data on Ce and Eu content indicate the saturation of the marine environment with oxygen and nutrients [Kasper-Zubillaga et al., 2010; Webb, Kamber, 2002]. In soft tissues of mussels sampled in Sevastopol Bay, the concentration of most of the elements considered (54 out of 72) depended on the sampling area [Kapranov et al., 2023].

Levels of chemical elements in molluscs reflect their habitat conditions in different biotopes. The chemical composition of soft tissues characterizes the short-term state of the environment, while the content of chemical elements in shells indicates conditions of the entire life cycle of these hydrobionts [Ravera et al., 2007]. Therefore, when monitoring the metal pollution in the water environment, studying shells of bivalves has methodological advantages compared to the analysis of tissues [Pourang et al., 2014]. At the same time, shells act as accumulators for some metals [Richardson et al., 2001]. Various elements, including heavy metals, can be concentrated in soft tissues and shells of molluscs, and this allows using them as bioindicators of environmental pollution [Hossen et al., 2014]. For example, studies of the content of chemical elements in soft tissues of Anadara spp. from the coast of Vietnam showed the following features: As, Sr, Mo, Sn, and Pb contents in clams from the central coastal zone were higher than in clams from other water areas studied, which differences are due to different anthropogenic load [Tu et al., 2011]. Trace element concentrations were within the safe levels for human consumption. Agriculture and fishing are known to result in heavy metals entering the marine environment and affecting the biota [Wijaya et al., 2019]. To date, there is little information on the accumulation of chemical elements in a bivalve A. kagoshimensis inhabiting the Black Sea and the Sea of Azov. The aim of this work is to carry out a comparative analysis of concentrations of chemical elements in soft tissues and shells of anadara from these seas.

MATERIAL AND METHODS

The object of research is a bivalve *A. kagoshimensis* from the Black Sea and Sea of Azov (Fig. 1) sampled during the period of its relative sexual maturation resting, when the cellular composition of the gonads does not undergo any changes [Suwanjarat, 1999]. In our work, one hundred mollusc individuals from each sea were used, with the weight (17.6 ± 1.9) g and the shell length (30.5 ± 1.0) mm. In the Black Sea, clams were sampled by divers from the collectors of the marine farm in Karantinnaya Bay, Sevastopol $(44^{\circ}61'83.46''N, 33^{\circ}50'33.80''E)$, in October 2022. The sampling depth was 2–3 m, the water temperature was +8 °C, and the salinity was $18\%_0$. In the Sea of Azov, live molluscs were sampled immediately after the storm in Tatarskaya Bay $(45^{\circ}26'51''N, 35^{\circ}50'46''E)$ in October 2022. The sea water temperature was +15 °C, and the salinity was $14.83\%_0$. After the mechanical cleaning of clam shells from fouling, they were washed in clean seawater taken from the sampling site. Tissues lining both shells were excised with a plastic scalpel and blotted with filter paper. Soft tissues and shells were dried at +105 °C.

Quantitative elemental analysis was carried out using an inductively coupled plasma mass spectrometer PlasmaQuant MS Elite (Analytik Jena, Germany) with parameters indicated in the paper [Kapranov et al., 2021]. All laboratory vessels were kept for 24 h in a 2% solution of purified nitric acid and rinsed with deionized water. Pre-dried biological samples were mineralized in PTFE tubes by digesting in purified 65% nitric acid and then diluted with deionized water so that the dilution was in the range of 1,000–2,000 mg·L⁻¹ (on dry weight basis). Calibration curves were plotted using solutions of a multielement standard IV-ICPMS-71A-D (Inorganic Ventures, the USA, 10 mg·L⁻¹). Samples of the certified reference material (0.1 g) were digested in extra pure nitric acid and diluted with deionized water according to the procedure described above. Coefficients of determination of linear regressions for all calibration plots were no lower than 0.998. The error of quantitative determination in the semi-quantitative analysis of ICP-MS is < 50% [Chen et al., 2008; Krzciuk, 2016]. Two-factor analysis of variance was performed using the PRIMER 6.1.16 and PERMANOVA+ 1.0.6 software.



Fig. 1. Map of the study area with sampling stations

RESULTS AND DISCUSSION

Differences in the content of chemical elements in anadara from the Black Sea and Sea of Azov are statistically significant (Table 1). These elements include: K, Rb, Cs, Ca, and Ba from the s-element family; the p-elements Al, Ga, Ge, P, As, Bi, and Br; the d-elements Zn, V, Nb, Ta, Mo, Fe, Ir, and Au; and the f-elements Pr and Nd. The differences are due not only to the composition of seawater which contains chiefly the s-elements, but also to physiological and biochemical characteristics of the molluscs. The p- and d-elements with atomic numbers 24 to 33 are known to be involved in the functioning of cells of marine organisms as minor constituents of proteins, carbohydrates, lipids, and enzymes [Takarina et al., 2013]. Changes in the chemical composition of clams are likely to result from the effect of the combination of internal and external factors [Osibona et al., 2009]. Sedentary living and filter feeding require relatively small energy costs. Apparently, these molluscs have only two processes related to a significant expenditure of energy: reproduction and linear growth. Therefore, during spawning and growing, the concentration of elements in anadara soft tissues and shells can increase.

Table 1. Elemental concentration in *Anadara kagoshimensis* soft tissues and shells ($\mu g \cdot k g_{dw}^{-1}$). The differences are significant (p < 0.05; n = 10): *, between soft tissues and shells of the mollusc from both the Black Sea and Sea of Azov; A or B, between soft tissues and shells of *A. kagoshimensis* from either the Sea of Azov (A), or the Black Sea (B); T, between soft tissues of the clam from the Black Sea and Sea of Azov; S, between shells of *A. kagoshimensis* from the Black Sea and Sea of Azov

$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$							
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	hells						
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	s-elements						
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	4 ± 9						
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	8 ± 7						
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	3 ± 273,410						
$\begin{array}{c} {\rm Ca}^{*{\rm TS}} & 8,311,674 \pm 5,209,732 & 186,445,736 \pm 21,517,954 & 25,067,443 \pm 14,688,981 & 114,796,476,476,47876 & 114,796,476,47876 & 114,796,47876 & 114,796,47876 & 114,796,47876 & 114,796,47876 & 114,796,47876 & 114,796,47876 & 114,796,47876 & 114,796,47876 & 114,796,47876 & 114,796,47876 & 114,796,47876 & 117,496,455,074 & 560,11776,48376 & 117,79276 & 4,834 & 4,786 \pm 2,288 & 7,37876 & 117,767 \pm 4,834 & 4,786 \pm 2,288 & 7,37876 & 117,7381 \pm 2,132 & 6,626 \pm 2,093 & 11,754 \pm 2,206 & 448756 & 321,109 \pm 113,933 & 44,931 \pm 21,499 & 24,078766 & 321,109 \pm 113,933 & 44,931 \pm 21,499 & 24,078766 & 321,109 \pm 113,933 & 44,931 \pm 21,499 & 24,078766 & 321,109 \pm 113,933 & 44,931 \pm 21,499 & 24,078766 & 321,109 \pm 113,933 & 44,931 \pm 21,499 & 24,078766 & 321,109 \pm 113,933 & 44,931 \pm 21,499 & 24,078766 & 321,109 \pm 113,933 & 44,931 \pm 21,499 & 24,078766 & 321,109 \pm 113,933 & 44,931 \pm 21,499 & 24,078766 & 321,109 \pm 113,933 & 44,931 \pm 21,499 & 24,07877777777777777777777777777777777777$	2 ± 15,355						
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	-5 ± 24,088						
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	9 ± 7,733,846						
$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	67 ± 24						
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	6 ± 51,275						
p-elements B^{*TS} 14,713 ± 2,1326,626 ± 2,09311,754 ± 2,2064 Al^{*TS} 173,714 ± 69,956321,109 ± 113,93344,931 ± 21,49924,0 Si^{*S} 177,381 ± 38,679298,780 ± 197,663208,800 ± 54,02030,77 P^{*TS} 4,845,357 ± 301,948245,141 ± 72,7863,777,277 ± 510,62355,80 Ga^{*TS} 179 ± 2459 ± 25351 ± 6156 Ge^{*TS} 499 ± 1511,143 ± 275807 ± 30950 As^{*TS} 15,756 ± 2,5431,583 ± 2308,936 ± 1,5052,77 Se^{*} 5,035 ± 1,7291,425 ± 9545,738 ± 1,12566 Br^{*TS} 356,136 ± 126,346176,248 ± 51,213218,655 ± 44,94023,77 In^{BT} 3 ± 2.91.2 ± 0.80.7 ± 0.60 Sh^{AS} 53 ± 2557 ± 4241 ± 10777 TI^{BT} 9 ± 610 ± 642 ± 19777 I^{BTS} 31,028 ± 5,27655,587 ± 17,31310,552 ± 6,0017,77 I^{BT} 9 ± 32 ± 13 ± 2776 ± 213650 ± 408 Bi^{*TS} 101 ± 80100 ± 735 ± 310 Bi^{*TS} 1005 ± 374945 ± 396409 ± 809 Ti^{AS} 3,843 ± 1,2664,885 ± 2,442500 ± 2002,00	.6 ± 2.5						
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	'5 ± 3,547						
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	p-elements						
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	-8 ± 363						
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	'6 ± 7,625						
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	6 ± 29,529						
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	07 ± 10,943						
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	4 ± 17						
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	08 ± 261						
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	6 ± 130						
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	32 ± 488						
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	6 ± 7,763						
$\begin{array}{c c c c c c c c c c c c c c c c c c c $.8 ± 0.5						
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	9 ± 5						
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	2 ± 6						
$\begin{array}{c c c c c c c c c c c c c c c c c c c $	23 ± 7						
Pb*TS 1,526 ± 682 776 ± 213 650 ± 408 d Bi*TS 101 ± 80 100 ± 73 5 ± 3 1 d -elements	28 ± 1,904						
Bi*TS 101 ± 80 100 ± 73 5 ± 3 100 ± 73 d-elements Sc ^{ATS} $1,056 \pm 374$ 945 ± 396 409 ± 80 G Ti ^{AS} $3,843 \pm 1,266$ $4,885 \pm 2,442$ 500 ± 200 $2,00$	2 ± 1.8						
d-elements Sc ^{ATS} 1,056 ± 374 945 ± 396 409 ± 80 Ti ^{AS} 3,843 ± 1,266 4,885 ± 2,442 500 ± 200 2,00	64 ± 39						
ScATS $1,056 \pm 374$ 945 ± 396 409 ± 80 TiAS $3,843 \pm 1,266$ $4,885 \pm 2,442$ 500 ± 200 $2,00$	$.3 \pm 1.1$						
Ti ^{AS} $3,843 \pm 1,266$ $4,885 \pm 2,442$ 500 ± 200 $2,00$							
	6 ± 54						
X/*TS 2 422 + 1 522 1 (24 + 500 4 227 + 010 1 5	00 ± 400						
	0 ± 407						
	5 ± 97						
	3 ± 17,129						
	8 ± 2,329,125						
	3 ± 137						
	1 ± 2,079						
	4 ± 5,599						
Zn^{*TS} 115,934 ± 59,9028,268 ± 8,851181,026 ± 57,6021,1	1 ± 649						

Continued on the next page...

Element –	Black Sea		Sea of Azov	
	Soft tissues	Shells	Soft tissues	Shells
Y ^{BT}	$1,549 \pm 1,212$	215 ± 81	608 ± 144	144 ± 48
Zr ^{TS}	312 ± 140	345 ± 155	107 ± 48	56 ± 25
Nb*TS	9 ± 3	25 ± 19	6 ± 3	3 ± 2
Mo*TS	$2,239 \pm 1,645$	$1,008 \pm 704$	971 ± 285	55 ± 35
Ru ^{BS}	1 ± 0.5	8 ± 3	2.2 ± 1.7	3 ± 2
Rh ^{*S}	28 ± 8	163 ± 42	43 ± 14	134 ± 11
Pd ^{*T}	191 ± 57	$1,193 \pm 379$	596 ± 107	$1,058 \pm 100$
Ag	780 ± 448	588 ± 252	815 ± 243	569 ± 465
Cd*T	$15,290 \pm 10,450$	192 ± 114	$6,183 \pm 2,524$	147 ± 59
La ^B	$1,076 \pm 1,002$	284 ± 113	759 ± 187	231 ± 153
Hf ^{AT}	7 ± 3	4 ± 2	12 ± 9	2 ± 1.5
Ta ^{*TS}	1 ± 0.5	0.3 ± 0.2	5 ± 4	0.6 ± 0.4
W ^{AS}	152 ± 134	73 ± 31	64 ± 17	7 ± 4
Re ^{AT}	0.6 ± 0.3	0.6 ± 0.3	1.3 ± 0.5	0.3 ± 0.2
Os ^{AT}	2 ± 1.5	1.6 ± 1.2	20 ± 14	1.9 ± 0.5
Ir ^{*TS}	0.2 ± 0.1	0.3 ± 0.04	1.2 ± 1.1	0.2 ± 0.1
Pt ^A	3 ± 2	3 ± 2	5.4 ± 5.3	1.1 ± 0.8
Au*TS	15 ± 3	21 ± 6	172 ± 86	2 ± 1
Hg*	160 ± 90	20 ± 11	193 ± 59	11 ± 6
L. L		f-elements	, ,	
Ce ^{*T}	736 ± 490	184 ± 76	$1,100 \pm 293$	473 ± 308
Pr ^{*TS}	85 ± 66	22 ± 8	158 ± 39	52 ± 34
Nd ^{*TS}	384 ± 239	89 ± 32	662 ± 142	200 ± 121
Sm ^{*T}	65 ± 46	19 ± 7	126 ± 31	32 ± 21
Eu ^A	27 ± 15	16 ± 5	32 ± 13	15 ± 9
Gd*T	84 ± 63	19 ± 6	160 ± 45	38 ± 24
Tb ^{*T}	13 ± 9	3 ± 1	21 ± 9	4 ± 3
Dy*	61 ± 45	15 ± 5	88 ± 22	15 ± 11
Ho [*]	11 ± 8	3 ± 1	9 ± 3	2 ± 1
Er*	33 ± 23	8 ± 3	44 ± 14	7 ± 6
Tm ^{BT}	5 ± 3	1 ± 0.5	1.2 ± 1.1	0.7 ± 0.6
Yb*T	19 ± 12	6 ± 2	29 ± 10	7 ± 5
Lu ^{BT}	4 ± 3	1 ± 0.4	1 ± 0.9	1 ± 0.7
Th	90 ± 68	84 ± 60	45 ± 35	91 ± 82
U*T	51 ± 16	75 ± 25	122 ± 18	72 ± 17

The **s-elements** are distributed differently in *A. kagoshimensis* (Table 1). Noticeable differences in concentrations of K, Ca, Ba, Rb, and Cs were recorded between soft tissues and shells of the clams from both the Black Sea and Sea of Azov. The content of K, Rb, and Cs in tissues of the molluscs from the Black Sea is significantly higher than in individuals from the Sea of Azov, which is mediated by the level of dissolved nutrients in these water areas. In the Black Sea, there is a special type of coastal currents: upwelling. In the areas of upwelling, higher biological productivity is observed due to the remobilization of nutrients from the bottom to surface waters. Most likely, Rb and Cs replace K in its compounds. K plays a key role in the formation of the membrane potential of cells; therefore, K concentration is one (the Sea of Azov) or two (the Black Sea) orders of magnitude higher in anadara

soft tissues than in its shells. In addition, K can affect the thickness of the mollusc shells, and K deficiency leads to a decrease in the thickness of shells [Elegbede et al., 2023]. Thus, shells of the clams from the Black Sea are stronger. This fact should be taken into account when processing soft tissues and shells to produce food supplements, animal feed, mineral fertilizers, *etc.*

A relatively high content of Ca, Na, Mg, and Sr was recorded in *A. kagoshimensis* shells from the Black Sea and Sea of Azov. These are the elements whose compounds make up mollusc shells. Ca content in shells of the clams from the Black Sea is significantly higher than that for the hydrobionts from the Sea of Azov. The higher the Ca content, the stronger the mollusc shell [Dickson, 2013]. Na₂CO₃ and other Na compounds possess binding and moisturizing properties, regulate pH, and provide the shell layers with the ability to stick together and form a compact structure. In our study, against high calcium content in *A. kagoshimensis* soft tissues and shells, relatively low phosphorus concentration was recorded, just as it was established for *Anadara senilis* from Guinea [Elegbede et al., 2023].

The concentration of Li in shells of the anadara from the Sea of Azov is an order of magnitude lower than in shells of the hydrobiont from the Black Sea. Li enters natural springs from sediments; its content in underground waters is consistent with its concentration in sedimentary rocks through which they circulate [von Strandmann, 2020].

Significant differences were revealed between the content of the **p-elements** in *A. kagoshimensis* soft tissues (Table 1). The concentration of P in soft tissues of the Black Sea clams sampled from hanging cages on the mussel-and-oyster farm is higher than that in individuals from the Sea of Azov, and it may evidence for a more intensive metabolism in hydrobionts inhabiting the Black Sea. Anadara grows faster in the water column than in bottom settlements [Acarli et al., 2012]. Al is capable of forming insoluble compounds with P [Haynes, Mokolobate, 2001]; accordingly, Al concentration is significantly higher in soft tissues of the Black Sea clams. Aluminum is considered a toxic element [Toxicological Profile for Lead, 2020].

In soft tissues of *A. kagoshimensis* from the Black Sea, Ga and Bi concentrations are higher than the values for the molluscs from the Sea of Azov. As the occurrence of Ga in water is related to the anthropogenic load, it does not play a noticeable biological role in the life of hydrobionts. The higher content of Bi in soft tissues of the Black Sea clams is likely to result from the higher salinity of the Black Sea water.

Concentrations of P, S, Cl, Pb, Al, Ge, Br, B, Si, Sn, I, Bi, and Sb in shells of anadara from the Black Sea are significantly higher than those for the individuals from the Sea of Azov (Table 1). Probably, shells can concentrate elements in dependence on their content in biotopes, which fact indicates the variability of the elemental composition in both soft tissues and shells of *A. kagoshimensis*.

This species can serve as a bioindicator of environmental pollution with heavy metals. Pb and Cd concentrations significantly differ in soft tissues and shells of clams from the Black Sea and Sea of Azov (Table 1). In general, the content of toxic elements in water from both seas is below the maximum permissible levels established by the requirements of Technical Regulation of the Customs Union 021/2011 [2011]: Pb, 10.0; Cd, 2.0; and Hg, 0.2 mg·kg⁻¹. The main sources of Pb in the marine environment are stormwater runoff from inland areas and wastewater inflow from land [El-Sorogy, Youssef, 2015; El-Sorogy et al., 2012; Peters et al., 1997]. High concentrations of heavy metals Pb, Cd, and Hg pose a threat to molluscs [Dabwan, Taufiq, 2016; Isroni, Maulida, 2022].

Concentrations of such **d-elements** as Zn and Mo are higher in *A. kagoshimensis* soft tissues, while Fe content is higher in its shells (Table 1). Iron is important for the metabolism of molluscs [El-Sorogy et al., 2013]. Fe is evenly concentrated in the outer organic layer of the shell, the periosteum,

and is uniformly distributed across the aragonite layers [Duncan et al., 2009] with accumulation in the periostracum. The concentration of Zn is higher in soft tissues of the clams from the Sea of Azov than from the Black Sea. Zinc is required for the activity of 90 enzymes involved in animal metabolism and is an essential trace element for all living organisms [Astuti et al., 2022]. Zn concentration in hydrobionts is higher than in terrestrial organisms. Zn is concentrated in tissues of hydrobionts in the form of insoluble inclusions or bound with macromolecules [Pourang et al., 2014].

Currently, there is little information about the content of rare earth elements in the marine environment, their accumulation in living organisms, and their effect on the biota. Differences in concentrations of rare earth elements (Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, and Yb) between the molluscs from the Black Sea and the Sea of Azov are obvious (Table 1). On average, their content is higher in *A. kagoshimensis* soft tissues than in its shells. Only Pr and Nd concentrations in tissues and shells differ significantly, as well as the content in the anadara tissues and shells from the Black Sea of Azov. Pr and Nd concentrations in the clams from the Sea of Azov are higher. Like many other rare earth metals, Pr and Nd do not play a key biological role in living organisms. Their occurrence may be related to different anthropogenic load on the water areas studied. Molluscs of the genus *Anadara* are filter feeders; therefore, the concentration of rare earth elements, as a rule, is higher in soft tissues than in shells. These elements can enter the body of clams with bacteria. Bacteria are shown to be able to accumulate metals and, accordingly, affect their transfer in water column [Beveridge, Doyle, 1989].

Conclusion. Concentrations of chemical elements in soft tissues and shells of molluscs depend primarily on environmental conditions. At the same time, the differences in the content are determined not only by the composition of seawater which includes mainly s-elements, but also by physiological processes of mollusc adaptation, since most of the statistically significant differences in this work were revealed among p- and d-elements. It is p- and d-elements that are involved in the functioning of cells of organisms as minor components of proteins, carbohydrates, lipids, and enzymes. Molluscs consume macro elements and trace elements from water and accumulate them in tissues and shells adapting to conditions of their habitat, including salinity. The element contents in *Anadara kagoshimensis* soft tissues and shells are not constant, and the role of certain elements in physiological processes can increase depending on the physiological state of animals. Not all elements accumulated in soft tissues and shells are essential. The process of their accumulation is closely related to the anthropogenic load on the water area.

The work was carried out with the financial support of Russian Science Foundation, grant No. 23-24-00494 (https://rscf.ru/project/23-24-00494/).

Acknowledgements. The authors express their gratitude to S. Shchurov and PhD V. Timofeev (IBSS) for their help in mollusc sampling. ICP-MS analysis was performed at "Spectrometry and Chromatography" core facility (IBSS).

REFERENCES

- TR TS 021/2011. Tekhnicheskii reglament Tamozhennogo soyuza o bezopasnosti pishchevoi produktsii. Moscow : Gosstandart Rossii, 2011, 242 p. (in Russ.)
- 2. Acarli S., Lok A., Yigitkurt S. Growth and survival of *Anadara inaequivalvis* (Bruguiere, 1789) in Sufa Lagoon, Izmir, Turkey. *Israeli Journal*

of Aquaculture – Bamidgeh, 2012, vol. 64, art. no. 691 (7 p.). https://doi.org/10.46989/001c.20623

 Astuti P., Putra M. N. P., Shiddiq M. F. A., Yuneldi R. F., Airin C. M., Sarmin S. The potency of *Anadara nodifera* shell as natural testosterone booster for male canary (Seriunus canaria). HAYATI Journal of Biosciences, 2022, vol. 29, no. 1, pp. 107–113. https://doi.org/10.4308/hjb.29.1.107-113

- 4. Beveridge T. J., Doyle R. J. *Metal Ions and Bacteria.* New York : John Wiley & Sons, 1989, 461 p.
- Chen H., Dabek-Zlotorzynska E., Rasmussen P. E., Hassan N., Lanouette M. Evaluation of semiquantitative analysis mode in ICP-MS. *Talanta*, 2008, vol. 74, iss. 5, pp. 1547–1555. https://doi.org/10.1016/j.talanta.2007.09.037
- Dabwan A. H., Taufiq M. Bivalves as bioindicators for heavy metals detection in Kuala Kemaman, Terengganu, Malaysia. *Indian Journal of Science* and *Technology*, 2016, vol. 9, iss. 9, pp. 1–6. https://doi.org/10.17485/ijst/ 2016/v9i9/88708
- Deaton L. E. Osmotic and ionic regulation in molluscs. In: Osmotic and Ionic Regulation. Cells and Animals / D. H. Evans (Ed.). Boca Raton ; London ; New York : CRC Press, 2009, chap. 4, pp. 107–134. https://doi.org/10.1201/9780849380525
- Dickson U. J. Mineral composition of shells of some animals found in the Niger Delta region of Nigeria. *African Journal of Food Science Research*, 2013, vol. 2, iss. 6, pp. 7–13.
- Duncan E., Mutvei H., Göransson P., Mörth C.-M., Schöne B. R., Whitehouse M. J., Elfman M., Baden S. P. Using ocean quahog (*Arctica islandica*) shells to reconstruct palaeoenvironment in Öresund, Kattegat and Skagerrak, Sweden. *International Journal of Earth Sciences*, 2009, vol. 98, iss. 1, pp. 3–17. https://doi.org/10.1007/s00531-008-0348-6
- Elderfield H. The oceanic chemistry of the rareearth elements. *Philosophical Transactions* of the Royal Society A: Mathematical, Physical and Engineering Sciences, 1988, vol. 325, iss. 1583, pp. 105–126. https://doi.org/10.1098/ rsta.1988.0046
- Elegbede I., Lawal-Are A., Favour O., Jolaosho T., Goussanou A. Chemical compositions of bivalves shells: *Anadara senilis*, *Crassostrea gasar*, and *Mytilus edulis* and their potential for a sustainable circular economy. *Discover Applied Sciences*, 2023, vol. 5, iss. 1, art. no. 44 (12 p.). https://doi.org/10.1007/s42452-022-05267-7
- 12. El-Sorogy A., El Kammar A., Ziko A., Aly M.,

Nour H. Gastropod shells as pollution indicators, Red Sea coast, Egypt. *Journal of African Earth Sciences*, 2013, vol. 87, pp. 93–99. https://doi.org/10.1016/j.jafrearsci.2013.08.004

- El-Sorogy A. S., Mohamed M. A., Nour H. E. Heavy metals contamination of the Quaternary coral reefs, Red Sea coast, Egypt. *Environmental Earth Sciences*, 2012, vol. 67, iss. 3, pp. 777–785. https://doi.org/10.1007/s12665-012-1535-0
- El-Sorogy A. S., Youssef M. Assessment of heavy metal contamination in intertidal gastropod and bivalve shells from central Arabian Gulf coastline, Saudi Arabia. *Journal* of *African Earth Sciences*, 2015, vol. 111, pp. 41–53. https://doi.org/10.1016/j.jafrearsci.2015.07.012
- 15. Haynes R., Mokolobate M. Amelioration of Al toxicity and P deficiency in acid soils by additions of organic residues: A critical review of the phenomenon and the mechanisms involved. *Nutrient Cycling in Agroecosystems*, 2001, vol. 59, iss. 1, pp. 47–63. https://doi.org/10.1023/A:1009823600950
- 16. Hossen F. M., Hamdan S., Rahman R. M. Cadmium and lead in blood cockle (Anadara granosa) from Asajaya, Sarawak, Malaysia. The *Scientific* World Journal, 2014, vol. 2014, art. no. 924360 (4 p.). https://doi.org/10.1155/2014/924360
- Isroni W., Maulida N. Accumulation of heavy metals Pb and Hg in feather shells (*Anadara antiquata*) in Lekok coastal waters, Pasuruan Regency. *IOP Conference Series: Earth and Environmental Science*, 2022, vol. 1036, art. no. 012091 (4 p.). https://doi.org/10.1088/1755-1315/1036/ 1/012091
- Kapranov S. V., Karavantseva N. V., Bobko N. I., Ryabushko V. I., Kapranova L. L. Sex- and sexual maturation-related aspects of the element accumulation in soft tissues of the bivalve *Mytilus galloprovincialis* Lam. collected off coasts of Sevastopol (southwestern Crimea, Black Sea). *Environmental Science and Pollution Research*, 2021, vol. 28, iss. 17, pp. 21553–21576. https://doi.org/10.1007/s11356-020-12024-z
- Kapranov S. V., Kozintsev A. F., Bobko N. I., Ryabushko V. I. Elements in soft tissues of the young Mediterranean mussel *Mytilus galloprovincialis* Lam. 1819 collected in Sevastopol

Bay (Crimea, Black Sea): Effects of age, sex, location, and principal morphometric parameters. *Animals*, 2023, vol. 13, iss. 12, art. no. 1950 (22 p.). https://doi.org/10.3390/ani13121950

- Kasper-Zubillaga J. J., Rosales-Hoz L., Bernal J. P. Rare earth elements in corals from the Isla de Sacrificios Reef, Veracruz, Mexico. *Geochemistry*, 2010, vol. 70, iss. 1, pp. 55–60. https://doi.org/10.1016/j.chemer.2009.09.001
- Krzciuk K. Intelligent analysis of samples by semiquantitative inductively coupled plasma-mass spectrometry (ICP-MS) technique: A review. *Critical Reviews in Analytical Chemistry*, 2016, vol. 46, iss. 4, pp. 284–290. https://doi.org/10.1080/ 10408347.2015.1053106
- 22. Moniruzzaman M., Lee S., Park Y., Min T. S., Bai S. C. Evaluation of dietary selenium, vitamin C and E as the multi-antioxidants on the methylmercury intoxicated mice based on mercury bioaccumulation, antioxidant enzyme activity, lipid peroxidation and mitochondrial oxidative stress. *Chemosphere*, 2021, vol. 273, art. no. 129673 (10 p.). https://doi.org/10.1016/ j.chemosphere.2021.129673
- Osibona A. O., Kusemiju K., Akande G. R. Proximate composition and fatty acids profile of the African catfish *Clarias gariepinus*. *ActaSATECH Journal of Life and Physical Sciences*, 2009, vol. 3, iss. 1, pp. 89–94.
- Peters E. C., Gassman N. J., Firman J. C., Richmond R. H., Power E. A. Ecotoxicology of tropical marine ecosystems. *Environmental Toxicology and Chemistry*, 1997, vol. 16, iss. 1, pp. 12–40. https://doi.org/10.1002/etc.5620160103
- 25. Pourang N., Richardson C. A., Chenery S. R. N., Nasrollahzedeh H. Assessment of trace elements in the shell layers and soft tissues of the pearl oyster *Pinctada radiata* using multivariate analyses: A potential proxy for temporal and spatial variations of trace elements. *Environmental Monitoring and Assessment*, 2014, vol. 186, iss. 4, pp. 2465–2485. https://doi.org/10.1007/s10661-013-3553-0
- 26. Ravera O., Beone G. M., Trincherini P. R., Riccardi N. Seasonal variations in metal content of two Unio pictorum mancus (Mollusca. Unionidae) populations from two lakes of different trophic state. Journal

of Limnology, 2007, vol. 66, no. 1, pp. 28–39. https://doi.org/10.4081/jlimnol.2007.28

- Richardson C. A., Chenery S. R. N., Cook J. M. Assessing the history of trace metal (Cu, Zn, Pb) contamination in the North Sea through laser ablation ICP-MS of horse mussel *Modiolus modiolus* shells. *Marine Ecology Progress Series*, 2001, vol. 211, pp. 157–167. https://doi.org/10.3354/meps211157
- Sahin C., Düzgüneş I. E., Okumuş I. Seasonal variations in condition index and gonadal development of the introduced blood cockle *Anadara inaequivalvis* (Bruguiere, 1789) in the southeastern Black Sea coast. *Turkish Journal of Fisheries and Aquatic Sciences*, 2006, vol. 6, no. 2, pp. 155–163.
- Suwanjarat J. Ultrastructure of the spermatogenesis of the cockle *Anadara granosa* L. (Bivalvia: Arcidae). *Helgoland Marine Research*, 1999, vol. 53, pp. 85–91. https://doi.org/10.1007/PL00012143
- Suwanjarat J., Pituksalee C., Thongchai S. Reproductive cycle of *Anadara granosa* at Pattani Bay and its relationship with metal concentrations in the sediments. *Songklanakarin Journal of Science and Technology*, 2009, vol. 31, no. 5, pp. 471–479.
- 31. Takarina N. D., Bengen D. G., Sanusi H. S., Riani E. Geochemical fractionation of copper (Cu), lead (Pb), and zinc (Zn) in sediment and their correlations with concentrations in bivalve mollusc *Anadara indica* from coastal area of Banten Province, Indonesia. *International Journal of Marine Science*, 2013, vol. 3, no. 30, pp. 238–243.
- 32. *Toxicological Profile for Lead* / US Department of Health and Human Services. Public Health Service, Agency for Toxic Substances and Disease Registry. Washington, DC : US Department of Health and Human Services, 2020, 530 p.
- 33. Tu N. P. C., Ha N. N., Agusa T., Ikemoto T., Tuyen B. C., Tanabe S., Takeuchi I. Trace elements in *Anadara* spp. (Mollusca: Bivalva) collected along the coast of Vietnam, with emphasis on regional differences and human health risk assessment. *Fisheries Science*, 2011, vol. 77, iss. 6, pp. 1033–1043. https://doi.org/10.1007/s12562-011-0410-3
- 34. von Strandmann P. A. E. P., Kasemann S. A., Wimpenny J. B. Lithium and lithium isotopes

in Earth's surface cycles. *Elements*, 2020, vol. 16, no. 4, pp. 253–258. https://doi.org/ 10.2138/gselements.16.4.253

- 35. Wala C., Hart A. I., Babatunde B. B., Zabbey N. Assessment of human health risk from heavy metal loads in freshwater clam, *Ergeria radiata*, from the Nun River, Niger Delta, Nigeria. *Journal of Environment and Earth Science*, 2016, vol. 6, no. 9, pp. 10–20.
- 36. Webb G. E., Kamber B. S. Rare earth elements in Holocene reefal microbialites:

A new shallow seawater proxy. *Geochimica et Cosmochimica Acta*, 2002, vol. 64, iss. 9, pp. 1557–1565. https://doi.org/10.1016/S0016-7037(99)00400-7

37. Wijaya W. A., Yulianto B., Setyati W. A. Study of the impact of heavy metal (Cd, Pb and Hg) contamination in Wedung waters, Demak on *Anadara granosa* (Linnaeus, 1758). *International Journal of Applied Environmental Sciences*, 2019, vol. 14, no. 5, pp. 461–473.

СОДЕРЖАНИЕ ХИМИЧЕСКИХ ЭЛЕМЕНТОВ В ТКАНЯХ И РАКОВИНАХ ДВУСТВОРЧАТОГО МОЛЛЮСКА *ANADARA KAGOSHIMENSIS* (ТОКИNAGA, 1906) ИЗ ЧЁРНОГО И АЗОВСКОГО МОРЕЙ

Л. Л. Капранова, Ю. Д. Дикарева, С. В. Капранов, В. И. Рябушко

ФГБУН ФИЦ «Институт биологии южных морей имени А. О. Ковалевского РАН»,

Севастополь, Российская Федерация

E-mail: lar_sa1980@mail.ru

В Чёрном и Азовском морях двустворчатый моллюск Anadara kagoshimensis является инвазивным и малоизученным видом. Моллюски — ценный объект промысла и марикультуры. В настоящее время мало сведений об особенностях содержания элементов в тканях и раковинах анадары, обитающей в этих морях. Цель данной работы — провести сравнительный анализ элементного состава тканей и раковин A. kagoshimensis Чёрного и Азовского морей. Элементный анализ проводили с помощью масс-спектрометра с индуктивно-связанной плазмой. В работе приведены данные о концентрациях элементов в тканях и раковинах анадары из двух морей. Обнаружены значимые различия концентраций следующих элементов в анадаре из Чёрного и Азовского морей: K, Rb, Cs, Ca и Ba из семейства s-элементов; Al, Ga, Ge, P, As, Bi и Br из числа р-элементов; Zn, V, Nb, Ta, Mo, Fe, Ir и Au из семейства d-элементов; Pr и Nd из числа f-элементов. Содержание элементов в тканях и раковинах A. kagoshimensis обусловлено не только составом морской воды, куда входят в основном s-элементы, но и адаптационными процессами в моллюсках, в которых преимущественно участвуют р- и d-элементы. В тканях анадары из Чёрного моря концентрации K, Rb и Cs достоверно выше, чем в тканях особей из Азовского моря, при этом концентрация К на один (Азовское море) или два порядка (Чёрное море) выше в тканях, чем в раковинах. В раковинах A. kagoshimensis из Чёрного моря содержание Са достоверно выше. Раковины анадары из Чёрного моря прочнее. На фоне высокого содержания кальция в образцах тканей и раковин A. kagoshimensis из обоих морей зарегистрировано относительно низкое содержание фосфора. В тканях анадары из Чёрного моря концентрация P, Al, Ga и Bi, а также тяжёлых металлов (Pb и Cd) достоверно выше. Содержание токсичных элементов в анадаре из обоих морей не превышает предельно допустимых концентраций. Содержание Zn и Мо выше в тканях, Fe — в раковинах. В тканях A. kagoshimensis из Азовского моря концентрация Zn выше, чем в тканях особей из Чёрного моря. Концентрации редкоземельных элементов (Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Но, Er, Tm и Yb) выше в тканях анадары из обоих морей, чем в раковинах. В A. kagoshimensis из Азовского моря концентрации Pr и Nd значимо выше, чем в моллюске из Чёрного моря. Анадара способна концентрировать элементы в зависимости от их содержания в среде, поэтому концентрация элементов в моллюсках, принадлежащих к одному виду, в первую очередь зависит от биотопа.

Ключевые слова: двустворчатый моллюск *Anadara kagoshimensis*, концентрация химических элементов, масс-спектрометрия, Чёрное море, Азовское море