Neutron Activation Analysis in Study of Features of Accumulation of Microelements in Coastal Aquatic Ecosystems

P.S. Nekhoroshkov, A.V. Kravtsova, M.V. Frontasyeva

Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Russian Federation
p.nekhoroshkov@gmail.com

Introduction

Coastal aquatic ecosystems exist under constant anthropogenic pressure nowadays. It includes industrial, agricultural and recreational type of impacts. Any coastal area is a complex of biotic and abiotic objects, which are connected by elemental fluxes in one environmental system. For analysis of ecological state, we should assess the levels of elemental concentrations and ranges of accumulations. After analysis we could create the recommendations for purposes of ecological, industrial and residential management.

Neutron activation analysis (NAA) with the parameters of irradiation at the reactor IBR-2 fits well for accurate determination (at ppm, ppb levels) of 36 elements (Na, Mg, Al, Cl, K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Br, Rb, Sr, Mo, Sb, I, Cs, Ba, La, Ce, Sm, Tb, Yb, Hf, Ta, Au Th and U) in marine organisms and substrate. The quantity of elements is connected with detection limits and minimal presence (at background areas) of element in objects, thus the list of elements can be expanded up to 46. It will be described in the next studies.

The aim of the study was to assess the levels of accumulation of microelements in model coastal aquatic ecosystems at the different component of the environment. Model coastal aquatic ecosystems usually include several types of major organisms on the specific substrates (milieus), which can reflect the major type of the anthropogenic pollution. In the study the phytoplankton, molluscs, seaweeds (macroalgae) were used as biomonitoring organisms on the different shallow water areas. This objects, reflecting the main chemical anthropogenic fluxes in the water area, accumulated major of trace and other microelements, which can be derived from sources of pollution and natural unstudied sources. Besides that the main accumulation processes in the organisms can be different depending on the physiological processes and lifeforms of organisms. For our study, the phytoplankton is a basic member of the trophic chain as well as the seaweeds, which can produce the primary biomass by using the photosynthesis. Then the molluscs as primary filtrators and first stage consuments can reflect the intensity of the elemental fluxes in system of resuspended sediments and primary producers. In addition, the molluscs and seaweeds can accumulate the elements during 1-4 years of lifetimes in comparison with the several days in phytoplankton.

The key task of the study was to evaluate ranges of concentrations of elements corresponded to different marine objects to create the "reference" values for future biomonitoring analysis by using NAA.

Material and Methods

The samples were collected during different projects and studies during 2013, 2015 and 2016 years. To juxtapose the ranges and maximal concentrations among the main organisms from the selected coastal zones we were analyzed 50 samples of phytoplankton, 100 samples of seaweeds (*Cystoseira sp.*) from the Black Sea water areas and 20 samples of soft tissue of molluscs (*Mytilus galloprovincialis*) from the South African coastal model zone (Saldanha Bay). The last one was in good agreement with the reference data for the Black sea molluscs (except the terrigenous elements) (Pantelica et al., 2005). The data was check for reproducibility of the maximal values. The outliers were excluded from the analysis to diminish the influence of the casual cases events. Data for phytoplankton and seaweeds was compared with reference data for plankton (from field studies and from SRMs data) in the previous study (Nekhoroshkov et al., 2014, Kravtsova et al., 2014).

Neutron activation analysis was used as a main technique for determination of contents of microelements in different objects, which were collected in the coastal aquatic ecosystems. The specific parameters of determination are presented in the **Table 1**.

Table 1. Features of elemental determination by using NAA and standard reference materials (SRMs)

Element	Isotope	Gamma line, keV	Half-life	Technique of analysis	Deviation (Certified/ Determined), %	SRM	Organi-zation
Na	^{24}Na	1368.6	14.7 h	2	19.8	2709	NIST
Mg	^{27}Mg	1014.4	9.5 min	1	0.3	1547	NIST
Al	^{28}Al	1779	2.2 min	1	0.2	1632c	NIST
Cl	^{38}Cl	2167.7	37.2 min	1	7.2	1575a	NIST
K	^{42}K	1524.6	12.4 h	2	9.4	2709	NIST
Ca	^{49}Ca	3084.4	8.7 min	1	14.4	1515	NIST
Sc	^{46}Sc	889.2	83.8 d	3	4	1633c	NIST
Ti	^{51}Ti	320	5.8 min	1	7.4	1633b	NIST
V	^{52}V	1434.1	3.8 min	1	1	1633b	NIST
Cr	^{51}Cr	320.1	27.7 d	3	1	1633c	NIST
Mn	^{56}Mn	1810.7	2.6 h	1	0.2	1575a	NIST
Fe	^{59}Fe	1099.2	44.5 d	3	5.3	667	IRMM
Co	^{58}Co	810.8	70.9 d	3	1.8	2709	NIST
Ni	^{60}Co	1332.5	5.2 y	3	3.4	2709	NIST
Cu	^{66}Cu	1039	5.1 min	1	1	2710	NIST
Zn	^{65}Zn	1116	244.0 d	3	3.2	2709	NIST
As	^{76}As	559.1	26.3 h	2	37.4	1633c	NIST
Se	^{75}Se	264.7	119.8 d	3	18.6	1633c	NIST
Br	^{82}Br	776.5	35.3 h	2	0	667	IRMM
Rb	^{86}Rb	1076.6	18.6 d	3	9.3	1633c	NIST
Sr	^{85}Sr	514	64.8 d	3	5.6	2709	NIST
Mo	^{99}Mo	140.5	65.9 h	2	0	2709	NIST
Sb	^{124}Sb	1691	60.2 d	3	7	1633c	NIST
I	^{128}I	442.9	25.0 min	1	22.6	1547	NIST
Cs	^{134}Cs	795.8	2.1 y	3	4.6	1633c	NIST
Ba	^{131}Ba	496.8	11.8 d	2	11.3	1633c	NIST
La	^{140}La	1596.5	40.2h	2	4.8	1633c	NIST

Ce	^{141}Ce	145.4	32.5 d	3	1.4	667	IRMM
Sm	^{153}Sm	103.2	46.8h	2	0.4	667	IRMM
Tb	^{160}Tb	879.4	72.3 d	3	5.1	1633c	NIST
Yb	^{169}Yb	198	32 d	3	3.4	1633c	NIST
Hf	^{181}Hf	482	42.4 d	3	11.7	2709	NIST
Ta	^{182}Ta	1221.4	114.4 d	3	4.9	1633c	NIST
Au	^{198}Au	411.8	2.7 d	2	43	2709	NIST
Th	^{233}Pa	312	27 d	3	0.6	667	IRMM
U	^{239}Np	228.2	2.4 d	2	1	1633c	NIST

1: conventional NAA, measured 15 min after 3 min of irradiation and ~3 min of decay;
2: epithermal NAA, measured 30 min after 4 days of irradiation and ~3 days of decay;
3: epithermal NAA, measured 90 min after 4 days of irradiation and ~22 days of decay.

Deviation (in %) corresponded to differences between certified and determined concentrations at the final stage of the neutron activation analysis. In the case of 0 % (Br, Mo and In) the element was determined by using one standard without comparative analysis between others SRMs. This statement concerns also the elements with high deviation (As, Se, I and Au). The concentrations of such elements were given and used in analysis as indicative forms.

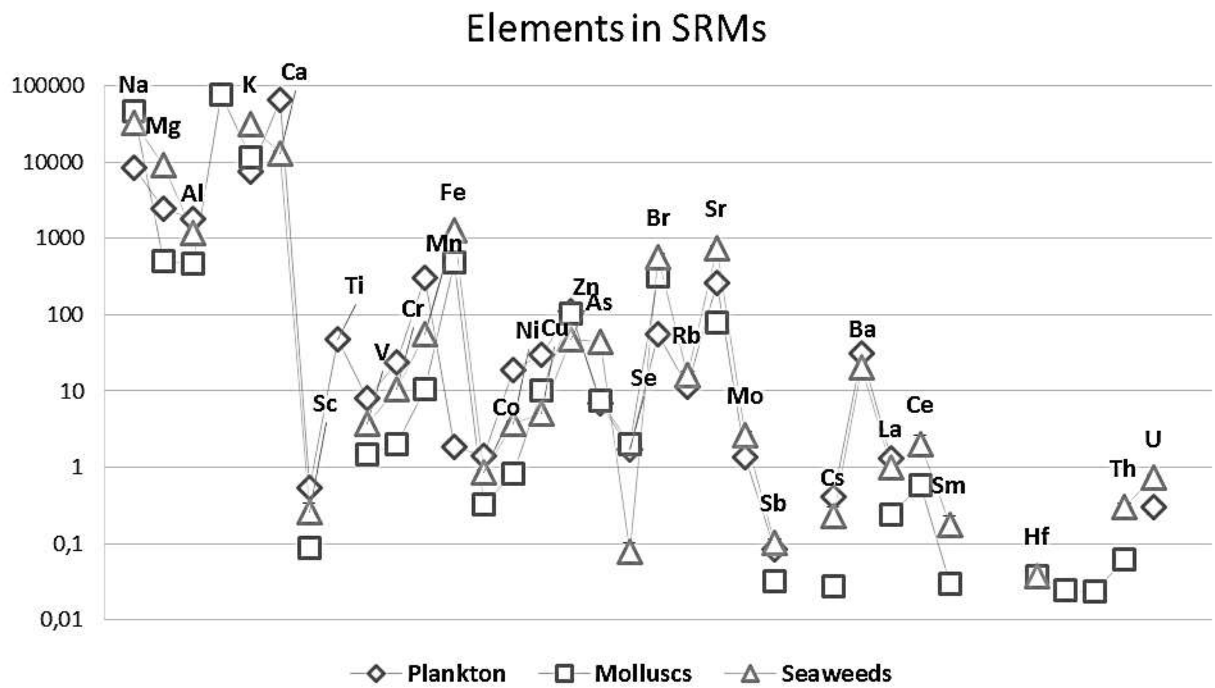

Fig. 1. Certified and indicative concentrations of elements (ppm) in different objects of coastal ecosystems from standard reference materials BCR 414 (plankton >125 um), NIST 2974 (*Mytilus edulis*) and IAEA 140 (*Fucus sp.*).

Results

The concentrations of 36 elements were determined for all kind of samples. For comparison, the same values were analyzed among standard reference materials (**Fig. 1**). Uncertainties (depends on element) for plankton SRM BCR 414 were 1-20 %, molluscs SRM NIST 2974 – 0.1-18.1%, Seaweeds SRM IAEA 140 – 2.1-30.0 %.

Table 2. Maximal concentrations of elements in different kind of objects

Objects	Plankton	Phytoplankton		Molluscs		Seaweeds	
Specification	>115 µm	>35 µm		Mussels		Brown algae	
Element	Reference data[1]			*Mytilus galloprovincialis*		*Cystoseira sp.*	
	Max	Max	%	Max	%	Max	%
Na	64000	4200	1.5	16000	19.8	26600	5.3
Mg	-	2200	2.9	2234	0.3	12100	14
Al	-	13000	0.8	80	0.2	560	32.4
Cl	-	10000	1.8	31500	9.4	73300	17.7
K	17000	3900	1.5	10320	14.4	62000	6.5
Ca	19000	97000	3.2	1470	4	34100	27
Sc	0.45	2.3	30	0.03	7.4	0.2	4.5
Ti	400	870	7.5	-		-	
V	4	23	2.2	1	1	2	24.6
Cr	620	33	1	0.7	1	-	
Mn	80	190	3.2	4.512	0.2	55	31.1
Fe	2460	8600	1	150	5.3	720	1.9
Co	1.5	2.4	1.5	0.2	1.8	0.8	25.6
Ni	6	17	1.2	0.65	3.4	6.08	9.9
Cu	142	200	6.1	9.6	1	-	
Zn	386	280	1	150	3.2	80	20
As	17	4.9	1.3	8	37.4	55	13
Se	0.6	0.4	1.7	4.3	18.6	-	
Br	2000	180	2.1	210	0	370	32.2
Rb	7	22	8.5	4	9.3	22	8.2
Sr	130	120	1.3	30	5.6	1400	3.2
Mo	0.3	4	30	0.6	0	-	
Sb	3.2	1.4	1.8	0.03	7	0.1	10
I	139	50	0.6	7.0	22.6	230	8.2
Cs	0.6	1.4	4.1	0.04	4.6	0.06	50
Ba	47	71	3.8	1	11.3	68	2.2
La	1.2	5	4.8	0.1		-	
Ce	2.6	20	30	0.2		-	
Sm	0.16	0.7	30	-		0.05	40
Tb	0.22	0.12	30	0.004		-	
Yb	0.13	0.4	30	-		-	
Hf	0.11	0.8	30	-		-	
Ta	0.06	0.13	30	0.001		-	
Au	-	0.02	30	0.002	43	0.07	57.1
Th	0.29	2	2.9	0.03	0.6	-	
U		0.5	4.1	0.18	1	0.8	12.5

[1]Reference data of plankton from Leonova et al, 2013.
Underlined values demonstrate the maximal values among objects

Data of concentrations in plankton (in Fig. 1 and in Table 2) were presented for comparison with phytoplankton because the main parameter of such samples is a fraction size, because a lot of different type of plankton organisms can be collected at the same sample.
Maximal concentrations among analyzed standards were distinguished:

- In plankton (SRM BCR 414 fraction >125 um): Al, Ca, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Cs, La.
- In molluscs (SRM NIST 2974 Mytilus edulis): Na, Se
- In seaweeds (SRM IAEA 140 Fucus sp.): Mg, K, Fe, As, Mo, Br, Sr, Sb

The maximal concentrations among different objects of coastal organisms:

- Phytoplankton (>35 um): Al, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Sb, Cs
- Molluscs (*Mytilus galloprovincialis*, soft tissue): Zn, Se
- Seaweeds (*Cystoseira sp.*): Na, Mg, Cl, K, As, Br, Sr, I

Discussions

Almost all elements for each group, which were presented in the high concentrations in SRMs (**Fig. 1**), were corresponded to groups, which were emphasized (**Table 2**). Exception concerning with:

- Fe, Sb in phytoplankton were in higher amounts in real field samples due to additional sources of enrichment
- Zn in molluscs in higher real concentrations can be influenced by hydrological changes in water masses and specificity of hyrgochemical structure of the coastal water in studied zone of the Saldanha Bay
- Na, Cl, I can accumulated in higher amounts due to natural presence in dissolved and suspended particles of salts derived from marine milieu and can deviate around a certified values in a higher or lower side.

Phytoplankton includes small cells which are suspended in a water masses and can adsorb any mineral and organic mollecules. That is the reason why they accumulate a microelements related to mineral (terrigenous) component of the suspended bottom sediments. In addition, the river flows contain the high concentrations of biogenic elements (mainly N, P, Si), which can be attracted feature of water area for develop of community. At the same time they can accumulate the microelements of terrigenous (f. e. Al, Ca, Sc, Ti, …, Cs, La) and anthropogenic origin (depends on the sources: f. e. V, Co, Ni, Cu, Zn) which presented in suspended forms in bottom sediments.

Thus, zooplankton and phytoplankton accumulated in high amounts the elements, which connected and derived from resuspended sediments and other mineral particles from coastal river flows. In the biomonitoring studies, the important task should be analysis of terrigenous component by using specific equations (Nekhoroshkov et al., 2017).

Phytoplankton and zooplankton usually differ by fractions, lifetime, speed of accumulation. Besides that, the plankton in general includes high amounts of mineral suspension and zooplankton organisms. Molluscs feed on phytoplanktonic cells and can adsorb the mineral suspension directly from the water. However, the inner self-cleaning processes during lifetime can regulate the highest concentration of pollutants including such elements as V, Cr, Mn, Fe, Cu, Zn, As, Mo etc.

Key features of groups of macro and microelements in comparison analysis:

- Elements had a terrigenous origin, accumulated at low level in bottom sediments, reached higher values in phytoplankton and seaweeds, molluscs (Al, Ti, Sc, Th, U, REE et al.). To this group can be added such elements as K, Ca, V, Cr, Co, Ni, Rb, Mo, Sb, Cs, Ba, Au), should take into consideration hydrological state
- Elements accumulated to equal levels depending on ratio between suspended and dissolved forms and anthropogenic affects (Cr, Co, Ni, Zn, As, Mo et al.)
- Elements can be accumulated in the higher amounts than presented in this study due to additional intake from sources of pollution (V, Cr, Co, Ni, Cu, Zn, As, Br, Se, Mo, Sb)

Such elemental values can be used as reference for juxtaposing of real field concentrations and in comparison biomonitoring study. Moreover, such values can be recommended as threshold for routine analysis in the verification procedure and identifying the traces of pollution. In the case of source of constant pollution the concentrations of elements in studied organisms should be analyzed by groups to emphasize typical connections.

Conclusions

According to the aim and task the list of microelements were considered. The groups of elements were installed by using comparative analysis: Phytoplankton Al, Ca, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Cs, La. In molluscs: Na, Se. Seaweeds: Mg, Cl, K, As, Br, Sr, I, Fe, Mo. The maximal concentrations of elements, which were given in the study, can be used in the future biomonitoring studies as reference values, such elemental groups should be carefully analyzed separately.

References

1. Pantelica A.I., Salagean M.N., Georgescu I.I. Thirty-year experience in applying neutron activation for analysis of mineral and biological samples from the Romanian sector of the Danube River and the Black Sea. *Ovidius University Annals of Chemistry*. 2005. Vol. **16**, # 1–4, pp. 1–8.
2. Kravtsova, A., Milchakova, N., & Frontasyeva, M. Elemental accumulation in the Black Sea brown algae Cystoseira studied by neutron activation analysis. *Ecological Chemistry and Engineering S*, 2014, **21**(1), pp. 9–23.
3. Kravtsova, Alexandra V., Nataliya A. Milchakova, and Marina V. Frontasyeva. Levels, spatial variation and compartmentalization of trace elements in brown algae Cystoseira from marine protected areas of Crimea (Black Sea). *Marine pollution bulletin.* 2015. Vol. **97**, 1–2, Pp: 548–554.
4. Nekhoroshkov P. S., Kravtsova A. V., Frontasyeva M. V., Tokarev Y. N. Neutron activation analysis and scanning electron microscopy of phytoplankton in the coastal zone of Crimea (the Black Sea). *American Journal of Analytical Chemistry*. 2014. Vol. **5**(5), pp. 323–334.
5. Nekhoroshkov P. S, Frontasyeva M. V., Tokarev Y. N. Variability of concentration of microelements in phytoplankton communities in coastal zone of the Sevastopol city (Crimea) and its features. *Ecology of Urban Areas*. 2017. Vol. **4**. Pp. 37–48.
6. Leonova, G.A., Bobrov, V.A., Bogush, A.A. and Bychinskii, V.A., 2013. Concentration of chemical elements by zooplankton of the White Sea. *Oceanology*, **53**(1), pp.54–70.