NEUTRON ACTIVATION ANALYSIS FOR ECOLOGICAL STATE ASSESSMENT OF COASTAL ECOSYSTEMS OF THE BLACK SEA

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Abstract

The concentration of majority of elements in soils and bottom sediments of chosen model recreational zone are corresponded to values reported for non-polluted zones except the area, which close to city dump. Cl, Br and I, the atmospheric supply from the marine environment is the predominant source for aquatic plants. The root-biomonitor for assessing accumulation of the majority of elements in plants from soils and bottom sediments, and in contrast the good leaf-biomonitor were found and analyzed. Translocation of elements varies depending on the physiological property of elemental uptake and is generally more intense through plant tissues than from sediments to plants. Cu, Zn, Sb, As, Ag, Au accumulated in phytoplankton due to coastal flows from anthropogenic sources.Obtained results could be used in ecological monitoring studies of the coastal zones.

Introduction

The coastal ecosystems with sources of natural runoff evolved from the estuarine areas towards complex shore with beaches, cliffs, wetlands et al. The vegetation and phytoplankton play the key role in elemental flows in these objects.

The aim of this complex study was to determine the ranges of variability of concentrations of different groups of elements in connection with affinity of pollution sources and properties of autotrophic biota in a typical recreational coastal zone.

We were solved several tasks during the study:

- Selection of model coastal zones
- Checking of organisms-biomonitors and choosing
- Determination the elements in different parts of organisms
- Analysis of elemental groups in substrates (soils and bottom sediments)
- Estimation of the levels of accumulation of elemental groups in these organisms by different zones
- The comparative analysis of data with reference values

Material and methods

First of all we were divided the coastal zones into 3 main groups: natural reserves, recreational zones and industrial regions.

In the coastal zone of Anapa city aquatic plants such as cane Phragmites australis, sedge Carex canescens, macroalgae such as Cladophora sericea were analyzed as a biomonitors. As a substrate the bottom sediments and soils from different layers (0, 20, 40 cm) were studied.

For analysis of elemental concentrations the neutron activation analysis performed at the reactor IBR-2 of the Frank Laboratory of Neutron Physics, Joint Institute for Nuclear

Research, Dubna in 2014-2016 were used. The main analytical technique was described in Frontasyeva (2011) with additions based on latest studies of aquatic biota and phytoplankton (Nekhoroshkov et al., 2015, Kravtsova et al., 2014).

Among the aquatic biomonitors we were chosen macrophytes, aquatic vegetation and phytoplankton as different organisms which exist under natural and anthropogenic conditions.

Macroalgae and aquatic plants were dried and prepared by using standards technique which was performed for vegetation. The filters with phytoplankton were divided into two equal portions. The concentrations of elements in filter blanks were taken into account. All samples were packed in plastic bags (to determine the short-lived isotopes) and into aluminum cups (to determine the long-lived isotopes). Quality control was provided by using standard reference materials of different origin: 433, 690CC, 1547, 1572, 1632b, 1633b, 2709, 2710.

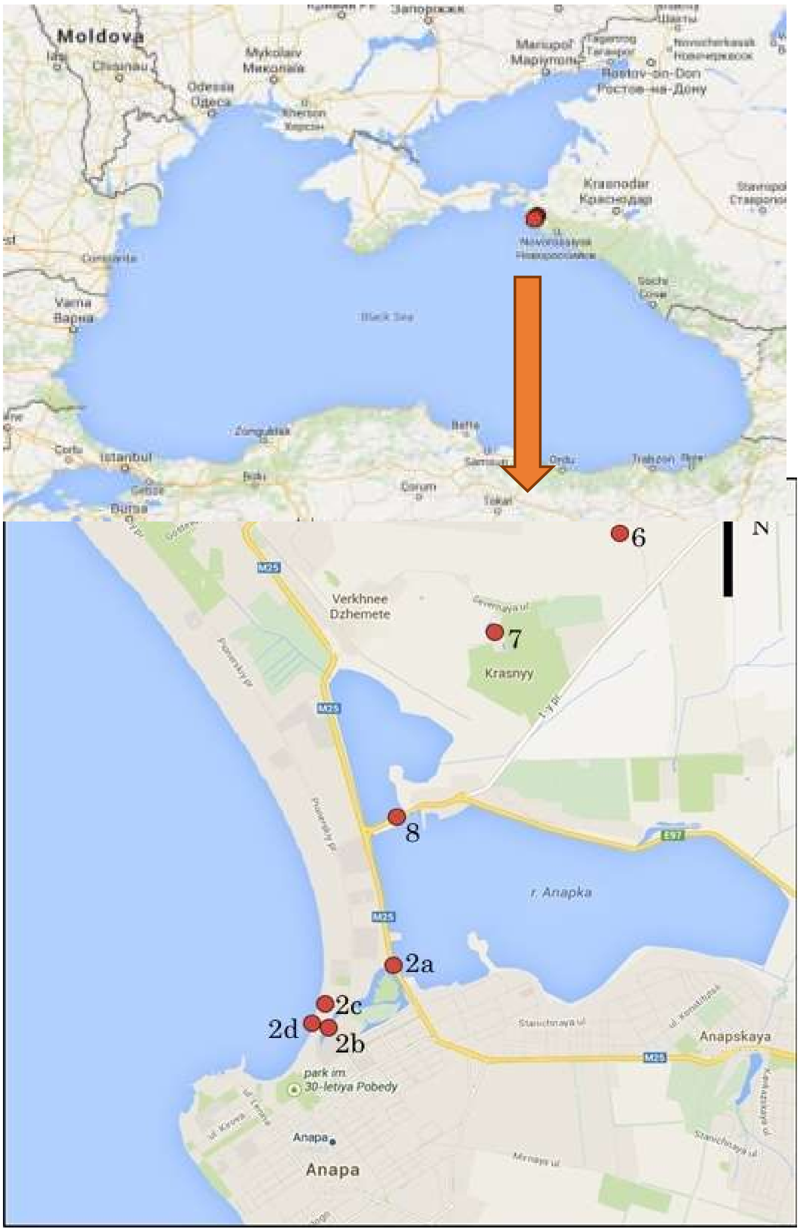

Fig. 1. Sampling sites in coastal zone of Anapa city. Samples of aquatic vegetation, macrophytes, soils, bottom sediments.

The results and discussion

The majority of the results and more detailed discussion were presented in our previous papers (Nekhoroshkov et al., 2015; Kravtsova et al., 2014; Nekhoroshkov et al., 2017).Several references could be find in this sources.

Such elements as Cr, Zn, As and Ba, which contained in soils and sediments and could be translocate and accumulate in aquatic vegetation, had the bigger concentrations than maximum permissible levels established for several developed countries. But these values corresponded to station which situated close to city dump and connected with anthropogenic sources of pollution such as fuel, solid domestic waste combustion and others.

Our data were also compared to results of Kolesnikov et al. (2012) who determined in laboratory conditions the levels of several elements for non-polluted, low polluted and moderate polluted soil from the Southern part of Russia using the integral index of biological state of soil (Table 1). It helps to realize the level of local differences in elemental content of soils from the standard levels for whole region. The maximal concentrations of Cr, Zn, As, Se and Sr in soils of Anapa region that were determined at the stations 6 and 7 (the nearest to city dump) were similar with the values reported for moderate polluted soils.

Table 1. Maximal and median elemental concentrations (μg/g dry weight) in soils from Anapa region (our data) and values for non-polluted and polluted soils from the Southern part of Russia

Elements	**Soils in Anapa region**		**Soils in the Southern part of Russia[1]**		
	Max	**Median**	**Non-polluted**	**Low polluted**	**Moderate polluted**
V	150	30	<200	200-300	300-850
Cr	**105**	30	<70	70-90	90-170
Mn	900	370	<1000	1000-1600	1600-1800
Co	24	4	<18	18-36	36-250
Ni	80	12	<50	50-100	100-700
Zn	**270**	50	<125	125-200	200-850
As	**36.8**	7.1	<17	17-30	30-160
Se	**2.31**	0.25	<0.7	0.7-1.4	1.4-9
Sr	**840**	510	<250	240-450	450-3200
Mo	15.7	1.1	<8	8-400	>400
Sb	2.1	0.6	<5	5-12	12-200
Ba	690	250	<900	900-1500	1500-4000

[1]elements insoil according to (Kolesnikov et al., 2012)

The concentration of elements which relate to moderate polluted range are given in **bold**

The obtained results were compared to the available data for Phragmites, Carex, and Cladophora, reported by other authors (Table 2) to represent the variability of concentrations in different regions. The concentrations of most elements in leaves and roots of *Phragmites australis* sampled in the mountain lake in Italy (Baldantoni et al., 2009) and in the mouth of the longest Sicilian river (Bonanno et al., 2010) are higher compared to our results. The exceptions are Ti, Mn, As, Sb and Ti, V, As, Se, which values in roots and leaves, respectively, are higher in the present study. The values of Co, Zn, Rb, and Th in *Carex pendula* sampled in Germany in botanical garden (Horovitz et al., 1974) are higher than our data; the reverse trend is observed for Sc, Cr, Fe and Cs. The elemental content of *Cladophora* reported by different authors varies in a wide range depending on the sampling region and the species.

Table 2. Elemental content of different species of *Phragmites*, *Carex* and *Cladophora* ($\mu g \cdot g^{-1}$dry weight).

El.	***Phragmitesaustralis***			***Carex pendula***	***Cladophora sp.***	***Cladophoraglomerata***	
	Roots[1]	Roots[2,3]	Leaves[2,3]	Whole plant[4]	Whole plant[5]	Whole plant[6]	Whole plant[7]
Na	–	–	–	–	17100	–	3000
Mg	1550	–	–	–	7800	–	23000
Al	–	3153	389	–	–	–	–
K	17000	–	–	–	24500	–	11000
Ca	–	–	–	–	8500	–	170000
Sc	–	–	–	0.19	–	–	–
Ti	–	<0.05	<0.05	–	–	–	–
V	14.5	9.2	<0.05	–	–	–	–
Cr	3.06	6.97	0.69	0.12	–	–	–
Mn	300	475.8	308	–	470	500	18000
Fe	2990	5561	453	460	2400	10000	2300
Co	–	8.0	0.22	0.03	0.5	–	–
Ni	6.52	9.12	1.69	–	3.1	–	6.3
Zn	54	104	28.4	595	60	200	–
As	–	<0.05	<0.05	–	–	–	5
Se	–	<0.5	<0.5	–	–	–	–
Rb	–	–	–	3.8	–	–	–
Sr	–	48.5	82.3	–	90	–	–
Mo	–	16.8	8.5	–	–	–	–
Sb	–	<0.05	<0.05	–	–	–	–
Cs	–	–	–	0.01	–	–	–
Ba	–	47.3	20.1	–	–	–	–
Th	–	–	–	0.45	–	–	–

1-Baldantoni et al., 2009; 2-Bonanno et al., 2010; 3-Bonanno, 2011; 4-Horovitz et al., 1974; 5-Bojanowski, 1973; 6-Ravera, 2001; 7-Maltsev et al., 2014

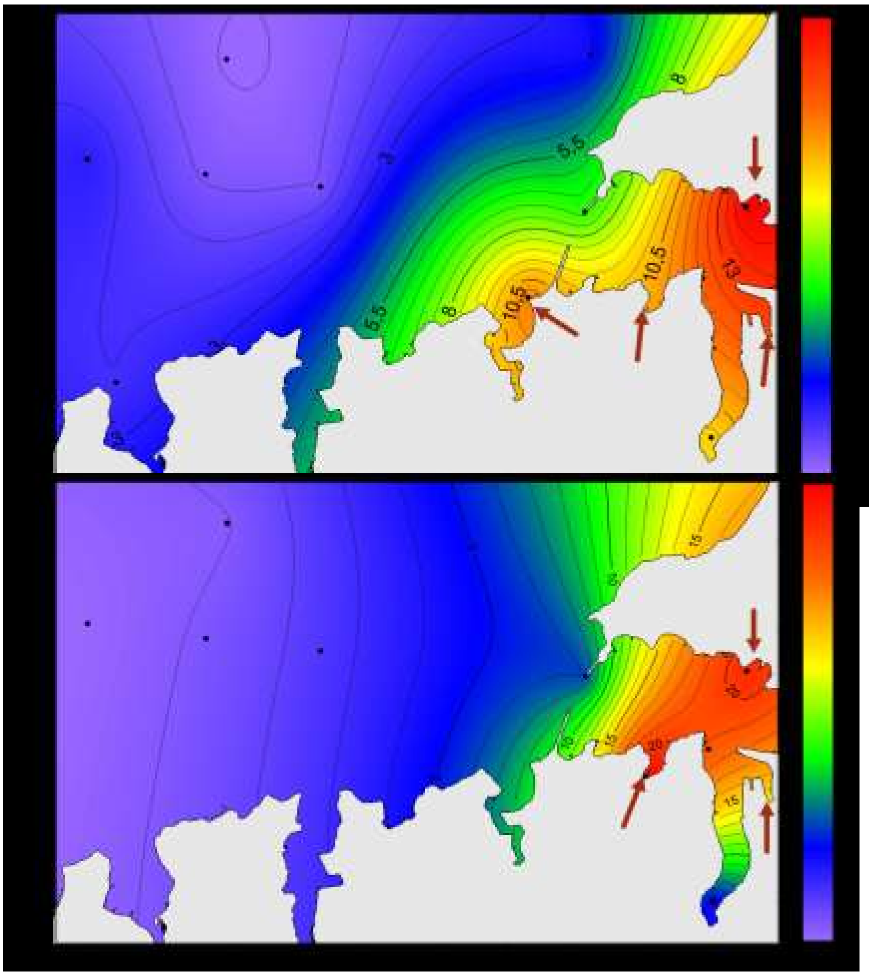

Fig. 2. Concentrations of vanadium (ppm) in phytoplankton samples (>35 μm) in summer and winter period of 2013-2014 from the coastal zone of Sevastopol. Red strings – sources of the coastal runoff and sources of pollution.

The different composition of *Cladophora sericea* and *Phragmites australis* with *Carex canescens* is explainable by different elemental uptake, either mainly by entire surface of plant from water (*Cladophora*) or by roots from sediments (*Phragmites australis* and *Carex canescens*).

The results, which were obtained for the largest phytoplanktonic organisms (>35 μm) in coastal polluted zones, showed that the elements with anthropogenic origin were accumulated in phytoplankton communities high concentrations relate to terrigenous along-coastal flows.

The accumulation of elements (for example vanadium) that could be anthropogenic origin corresponded to sources of terrigenous and anthropogenic flows (Fig. 2, red strings).

Conclusions

Neutron Activation Analysis fits well to assessment of elemental accumulation in organisms from coastal ecosystems. Coastal water objects could be analyzed by using NAA in complex study.

By using NAA we concluded that such elements as Al, Sc, Ti, Zr, REE, Th can be used as markers of terrigenous suspension. The normalizing concentrations in phytoplankton matter reflect the accumulative features of organisms with the higher accuracy excluding the effect of adsorbed mineral particles.

Roots and leaves of *Phragmitesaustralis* are good accumulators of Na, Ti, and Br and, in contrast, contain lower levels of Zn, Rb, and Ba than in RP. In *Carexcanescens* roots and leaves the levels of Na, Ti, As, Th, and U are one order of magnitude higher than in RP. In contrast, Mg, K, Mn, Zn, Rb, Cs, and Ba show lower levels in comparison to RP concentrations.

Cladophora sericea accumulated Cl in small relative amounts in comparison to Br and I. *Phragmites australis* in the major cases selected I and Cl regardless Br. In that sense the *Carex canescens* demonstrated the most flexible ability for accumulation of these halogens.

The environmental levels of the 19 trace elements in *Cystoseiraspp*. From relatively clean waters from marine protected areas, determined in this study, could be used for the further biomonitoring objectives in the Black Sea region.

The revealed peculiarities of elemental accumulation in different morphostructural parts of Cystoseira spp. and the relationship between the concentrations of some trace elements in algae with geological composition of the coast (that is, the type of rocks) improved our knowledge regarding the use of *Cystoseira spp*. as a biomonitor of coastal waters pollution.

Using such organisms as phytoplankton, macroalgae and aquatic vegetation (as basic elements forming primary production) in biomonitoring studies the environmental states of coastal zones and special fingerprints in different regions should be analyzed.

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