Neutron Activation Analysis for Ecological State Assessment of Coastal Ecosystems of the Black Sea

Pavel Nekhoroshkov, Alexandra Kravtsova, Marina Frontasyeva, Octavian Duliu, Alexander Kamnev, Nikita Yushin, Inga Zinicovscaia

- Frank Laboratory of Neutron Physics of Joint Institute for Nuclear Research, Dubna
- Kovalevsky Institute of Marine Biological Research, Sevastopol
- Biological and Soil Science Faculties of Moscow State University, Moscow
JINR PRIZES
2016

Applied Physics Research


“Neutron activation analysis for ecological state assessment of coastal ecosystems of the Black Sea”. 


Plan

- General principles of development of coastal ecosystems
- Material and Methods: Neutron Activation Analysis
- Material and Methods: sampling
- Results: Substrates (Soils, BS, Water)
- Results: Objects (Aquatic Plants, Macrophytes, Phytoplankton)
Aim and tasks

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

- Selection of model zones
- Determination (checking) of organisms-biomonitors
- Estimation of the levels of accumulation of elemental groups in these organisms by different zones
- The comparative analysis of data with reference values

Natural reserves

Recreational zones

Industrial regions
Neutron Activation Analysis
for assessment of elemental accumulation in coastal zones

- Macrophytes
- Sediments and soils
- Aquatic vegetation
- Phytoplankton
Neutron Activation Analysis

- Elemental contents of macroalgae, phytoplankton and aquatic plants were determined by means of neutron activation analysis performed at the reactor IBR-2 of the Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, Dubna.

- 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.

Elements, with the highest concentrations:

**Macroalgae:** Cl, Br, Sr

**Phytoplankton:** Al, Ca, Cl

**Aquatic plants:** Al, Mn, Fe
Model zones and Sampling

The Black Sea

- Beaches with sands
- Shingly shore
- macroalgae
- phytoplankton
- aquatic plants/soils and bottom sediments
The Anapa Bay

The Black Sea

Coastal transect: from dump to beach

- **Aquatic plants:** cane *Phragmites australis*, sedge *Carex canescens*
- **Macroalgae:** *Cladophora sericea*
- **Bottom sediments and soils**

**Anapa model**

recreational coastal zone
Soil or BS milieu (substrate) in coastal zone

Enrichment of elements (concentrations/upper continental crust) at the polluted station (7) and station on the beach (2c):

- Se, Br and I: feature of accumulation of marine elements in coastal area
- As, Mo and Sb: anthropogenic origin, pesticides, oil refining
<table>
<thead>
<tr>
<th>Element</th>
<th>Original data ($n=40$)</th>
<th>Russia</th>
<th>Germany</th>
<th>Netherlands</th>
<th>USA</th>
<th>Finland</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>min</td>
<td>max</td>
<td>median</td>
<td>(Kolesnikov et al., 2012)</td>
<td>(Mynbayeva et al., 2013)</td>
<td></td>
</tr>
<tr>
<td>V</td>
<td>10</td>
<td>150</td>
<td>30</td>
<td>150</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cr</td>
<td>6</td>
<td>105</td>
<td>30</td>
<td>90</td>
<td>100</td>
<td>250</td>
</tr>
<tr>
<td>Mn</td>
<td>150</td>
<td>900</td>
<td>370</td>
<td>1500</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Co</td>
<td>1.6</td>
<td>24</td>
<td>4</td>
<td>-</td>
<td>50</td>
<td>50</td>
</tr>
<tr>
<td>Ni</td>
<td>3</td>
<td>80</td>
<td>12</td>
<td>85</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Zn</td>
<td>6</td>
<td>270</td>
<td>50</td>
<td>100</td>
<td>300</td>
<td>500</td>
</tr>
<tr>
<td>As</td>
<td>3</td>
<td>36.8</td>
<td>7</td>
<td>2</td>
<td>50</td>
<td>30</td>
</tr>
<tr>
<td>Se</td>
<td>0.06</td>
<td>2.31</td>
<td>0.25</td>
<td>-</td>
<td>10</td>
<td>-</td>
</tr>
<tr>
<td>Mo</td>
<td>0.2</td>
<td>15.7</td>
<td>1.1</td>
<td>-</td>
<td>10</td>
<td>40</td>
</tr>
<tr>
<td>Sb</td>
<td>0.1</td>
<td>2.1</td>
<td>0.6</td>
<td>4.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ba</td>
<td>150</td>
<td>690</td>
<td>250</td>
<td>-</td>
<td>-</td>
<td>400</td>
</tr>
</tbody>
</table>
Aquatic vegetation: accumulation features

Traits of the two types of biomonitors:
Cane – root-biomonitor,
Sedge – leaf-biomonitor
Special “biochemical signature” of aquatic vegetation in recreational coastal zone

Phragmites australis

RP – reference plant by B. Markert (1992)
Special “biochemical signature” of aquatic vegetation in recreational coastal zone

Carex canescens

RP – reference plant by B. Markert (1992)
Special “biochemical signature” of aquatic vegetation in recreational coastal zone

*Cladophora sericea* (whole plant)

RP – reference plant by B. Markert (1992)
Macroalgae

Macroalgae – marine plants without roots

Fig. 1. Al, Fe and As in Cystoseira crinita “stems” at various ages
From Kravtsova et al., 2014
Anthropogenic effects in coastal zones based on biomonitoring of macroalgae

Biological accumulation of Al, Sc, V, Mn, Fe, Zn, Se
Peculiarities of elemental accumulation in phytoplankton

Vanadium (V)

- Related to pollution in the bays (waste water, oil)
- Related to terrigenous flows in shallow water areas
Maximal values in different coastal organisms of elements based on our data (in comparison with substrate)

<table>
<thead>
<tr>
<th>Aquatic plants</th>
<th>Cl, V, Fe, Co, As, Se, Br, Sr, I</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phytoplankton</td>
<td>V, Cr, Mn, Br, Mo, I, Sb</td>
</tr>
<tr>
<td>Macroalgae</td>
<td>V, Mn, Fe, Zn, As, Sr, Se</td>
</tr>
<tr>
<td><strong>Important elements</strong></td>
<td>V, Cr, Fe, Mn, Co, Ni, As, Se, Cu, Zn, Mo, Sr, I,</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Terrigenous</th>
<th>Biologically important</th>
<th>Anthropogenic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al, K, Ca, Sc, Ti, Rb, Sr, Zr, Cs, Th, U</td>
<td>Co, Cr, Cu, Zn, Mn, Fe, Se, Mo, I</td>
<td>V, Co, Ni, Cu, Zn, As, Sr, Sb</td>
</tr>
</tbody>
</table>
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.
- Roots and leaves of Phragmites australis are good accumulators of Na, Ti, and Br and, in contrast, contain lower levels of Zn, Rb, and Ba than in RP. In Carex canescens 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 TE in Cystoseira spp. 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 TE 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 could be analyzed.
Acknowledgement

- To our chemists Inga Zinicovscaia and Nikita Yushin for preparing the samples
- To our colleague Octavian Dului for help with analysis of data
- To our colleagues from Moscow State University for sampling and information
- To all which were involved in this cycle of works
To you for your attention!
Spatial variability of elemental contents in coastal organisms (biota)

- Elemental Flows
  - Along coast
  - Storms and upwellings
  - River flows
  - Atmospheric deposition
- Terrigenous particles
- Transition zones

Shore – Transitional zone – buffer water area
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

<table>
<thead>
<tr>
<th>Elements</th>
<th>Soils in Anapa region &lt;br&gt; ((n=40))</th>
<th>Soils in the Southern part of Russia(^1)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Max</td>
<td>Median</td>
</tr>
<tr>
<td>V</td>
<td>150</td>
<td>30</td>
</tr>
<tr>
<td>Cr</td>
<td>105</td>
<td>30</td>
</tr>
<tr>
<td>Mn</td>
<td>900</td>
<td>370</td>
</tr>
<tr>
<td>Co</td>
<td>24</td>
<td>4</td>
</tr>
<tr>
<td>Ni</td>
<td>80</td>
<td>12</td>
</tr>
<tr>
<td>Zn</td>
<td>270</td>
<td>50</td>
</tr>
<tr>
<td>As</td>
<td>36.8</td>
<td>7.1</td>
</tr>
<tr>
<td>Se</td>
<td>2.31</td>
<td>0.25</td>
</tr>
<tr>
<td>Sr</td>
<td>840</td>
<td>510</td>
</tr>
<tr>
<td>Mo</td>
<td>15.7</td>
<td>1.1</td>
</tr>
<tr>
<td>Sb</td>
<td>2.1</td>
<td>0.6</td>
</tr>
<tr>
<td>Ba</td>
<td>690</td>
<td>250</td>
</tr>
</tbody>
</table>

\(^1\) Elements in soil according to (Kolesnikov et al., 2012)
Special traits of halogens accumulation in aquatic plants
Peculiarities of elemental accumulation in phytoplankton

Zinc (Zn)

- Related to local source of pollution (nonferrous metallurgy, foundry, pesticides and herbicides)
- Related to deep water convection and resuspend of bottom sediments in the mouth area