



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

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26 slides

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# JINR PRIZES 2016

## ► Applied Physics Research


Il prize: A. Kravtsova, P. Nekhoroshkov, M. Frontasyeva, I. Zinicovscaia, N. Yushin, O. Bunkova, I. Stukolova, A. Yakovlev, A. Kamnev

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

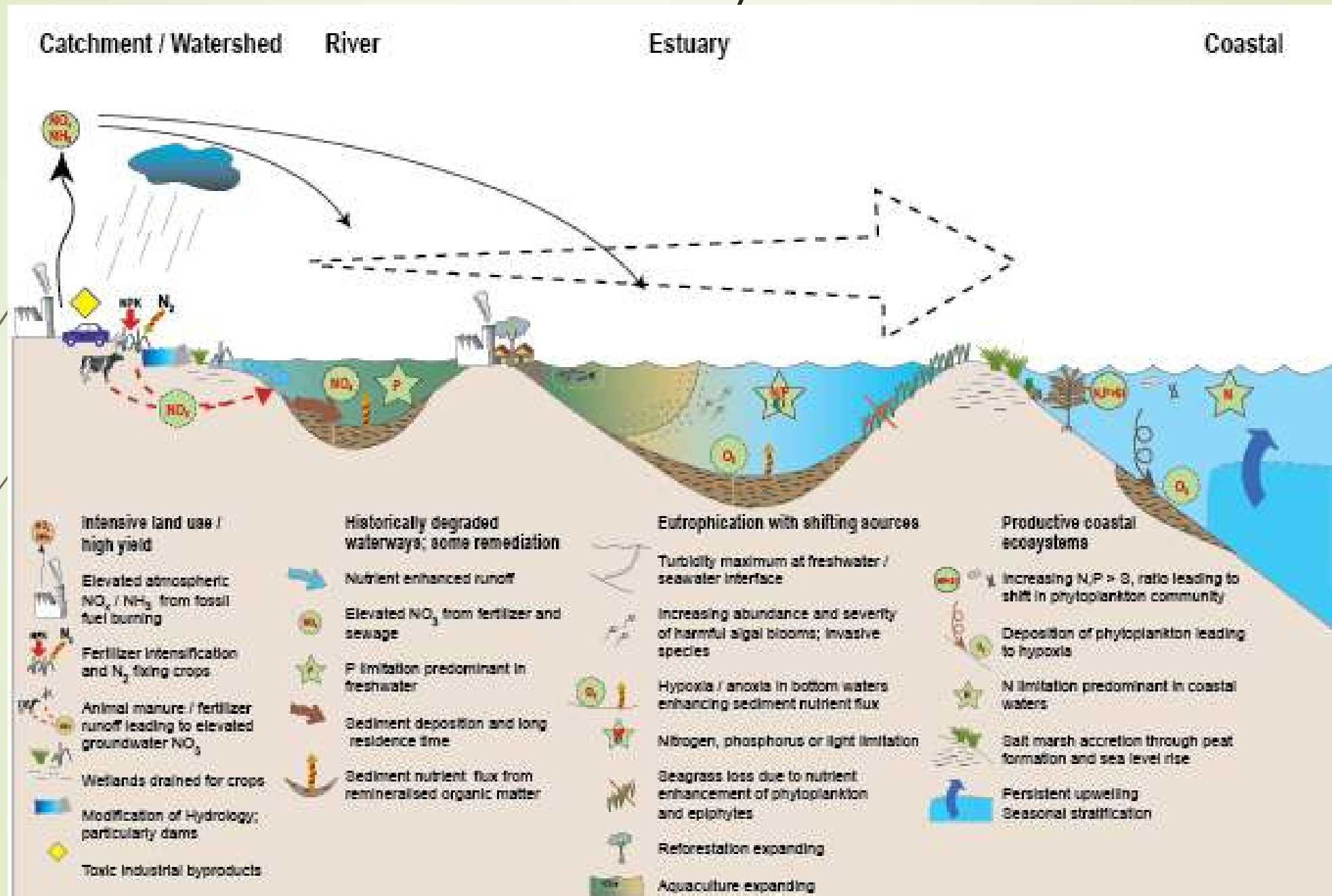
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# Plan

- 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)
- 

# Coastal ecosystems



# 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

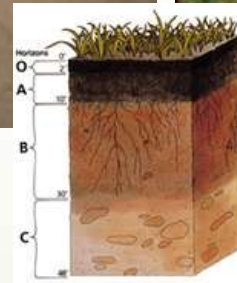
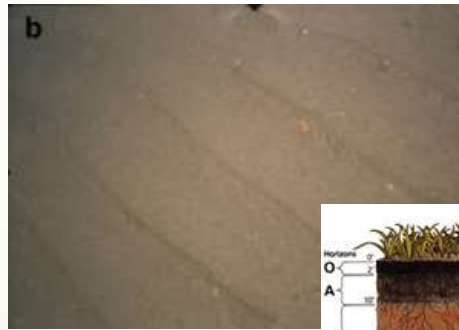
# Neutron Activation Analysis

*for assessment of elemental accumulation in coastal zones*

Macrophytes



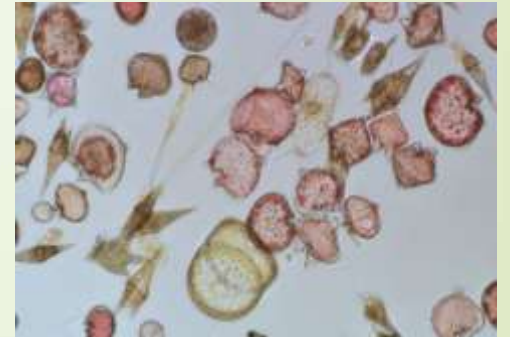
Sediments  
and soils



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

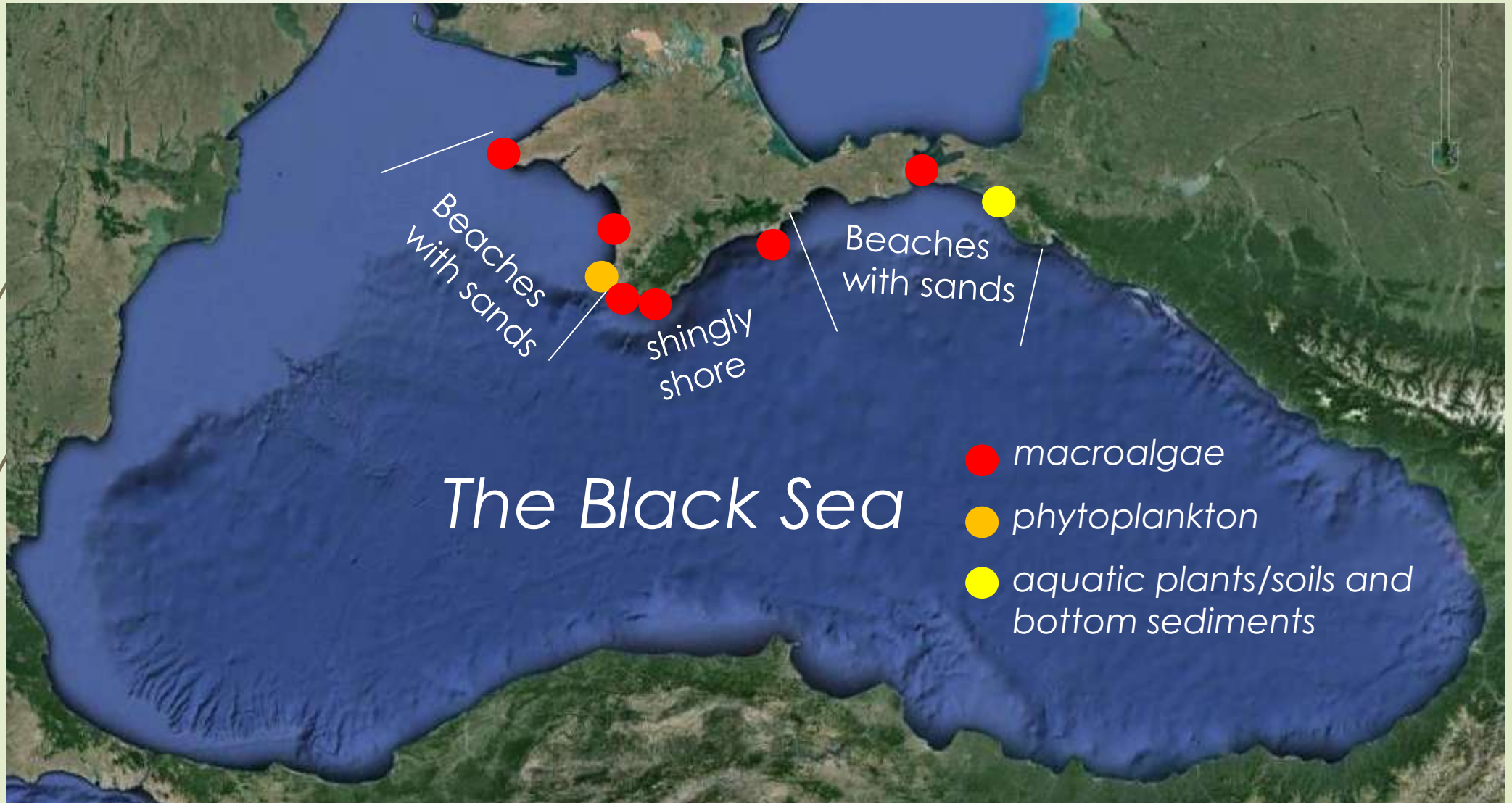
**Macroalgae:**  
Cl, Br, Sr

**Phytoplankton:**  
Al, Ca, Cl

**Aquatic plants:**  
Al, Mn, Fe



# Model zones and Sampling

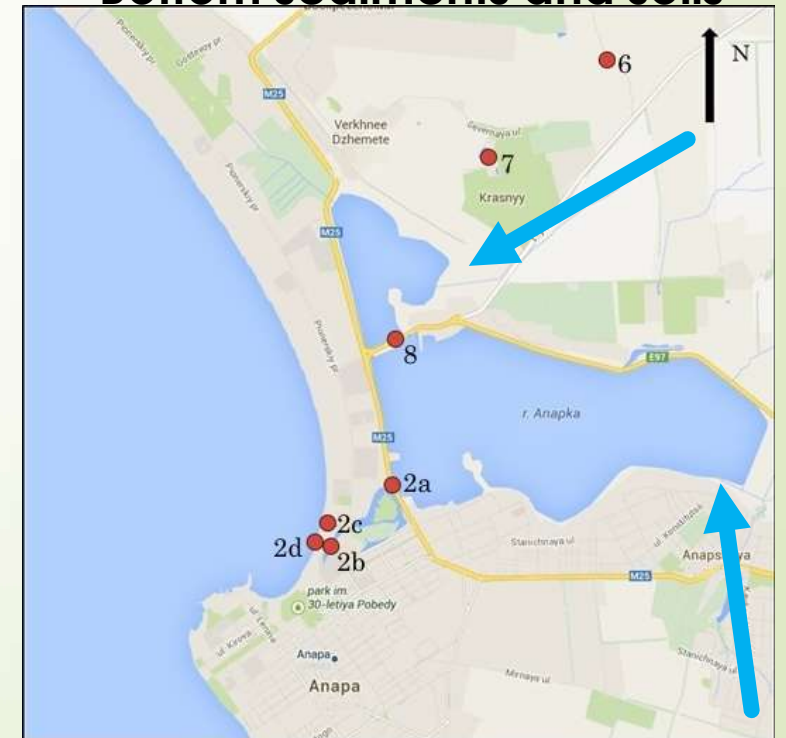


# Anapa model recreational coastal zone

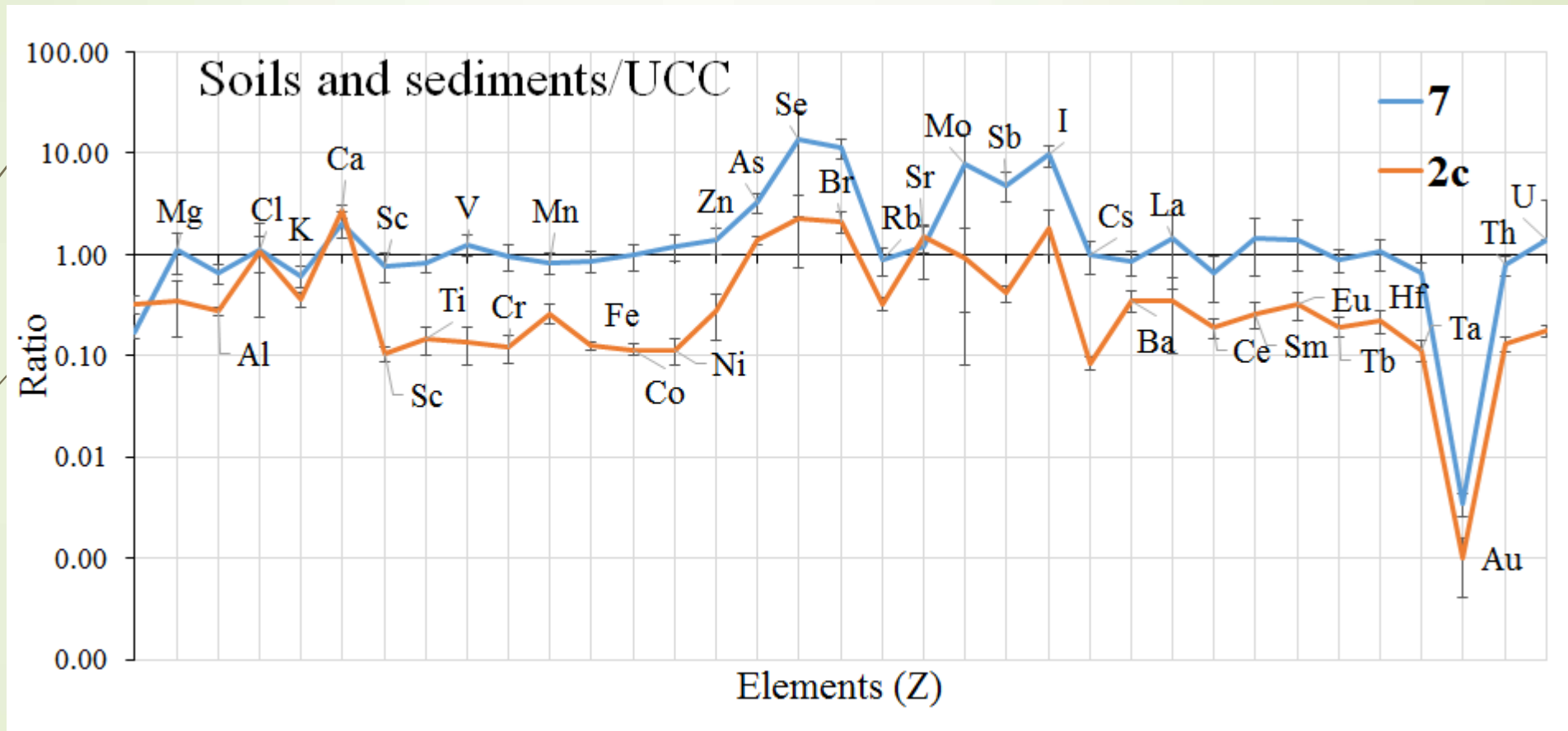


Coastal transect: from dump to beach

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



# Soil or BS milieu (substrate) in coastal zone



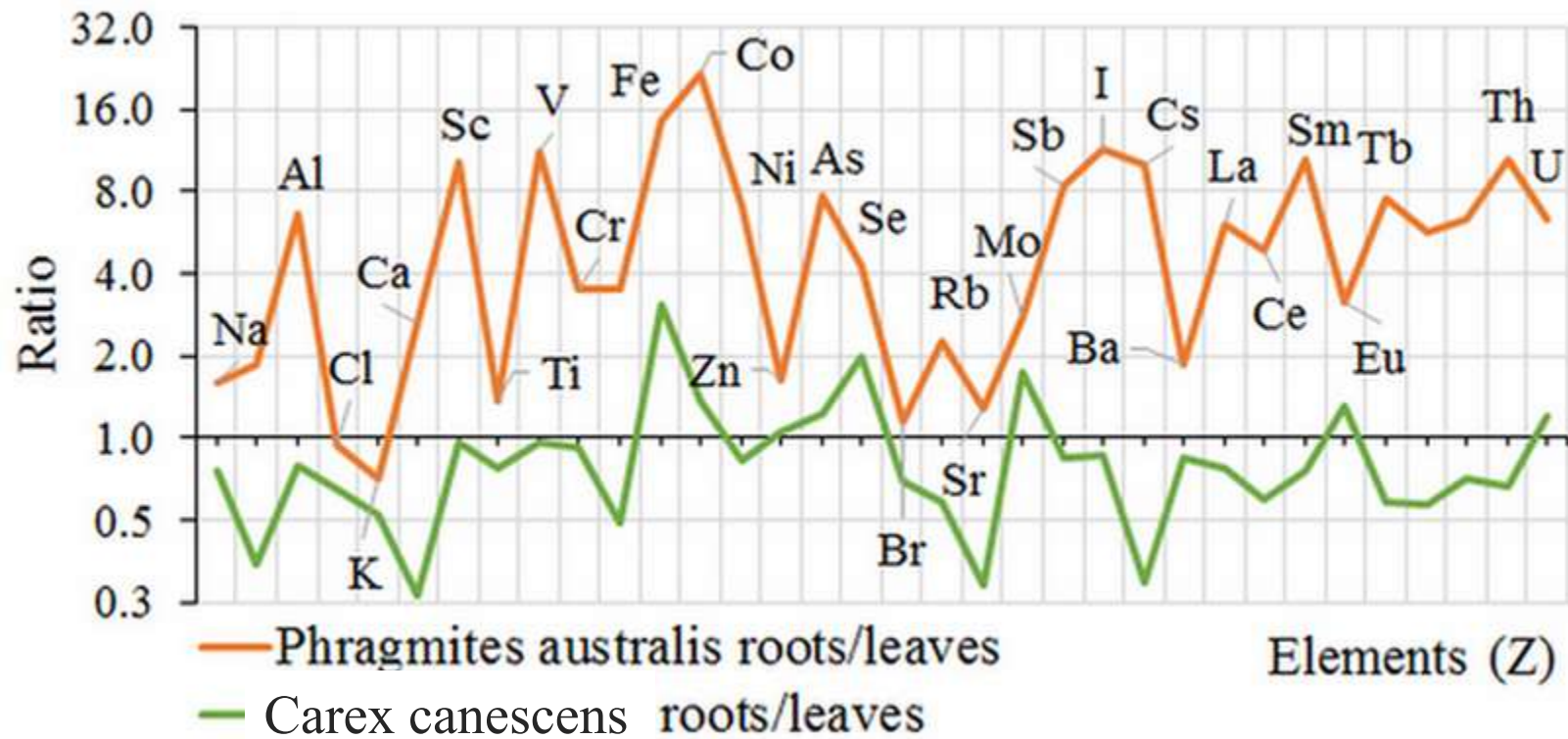
Enrichment of elements (concentrations/upper continental crust) at the polluted station (7) and station on the beach (2c):

- Se, Br and I: feature of accumulation of marine elements in coastal area
- As, Mo and Sb: anthropogenic origin, pesticides, oil refining

**Maximum permissible levels of elements in soils  
established in different countries**

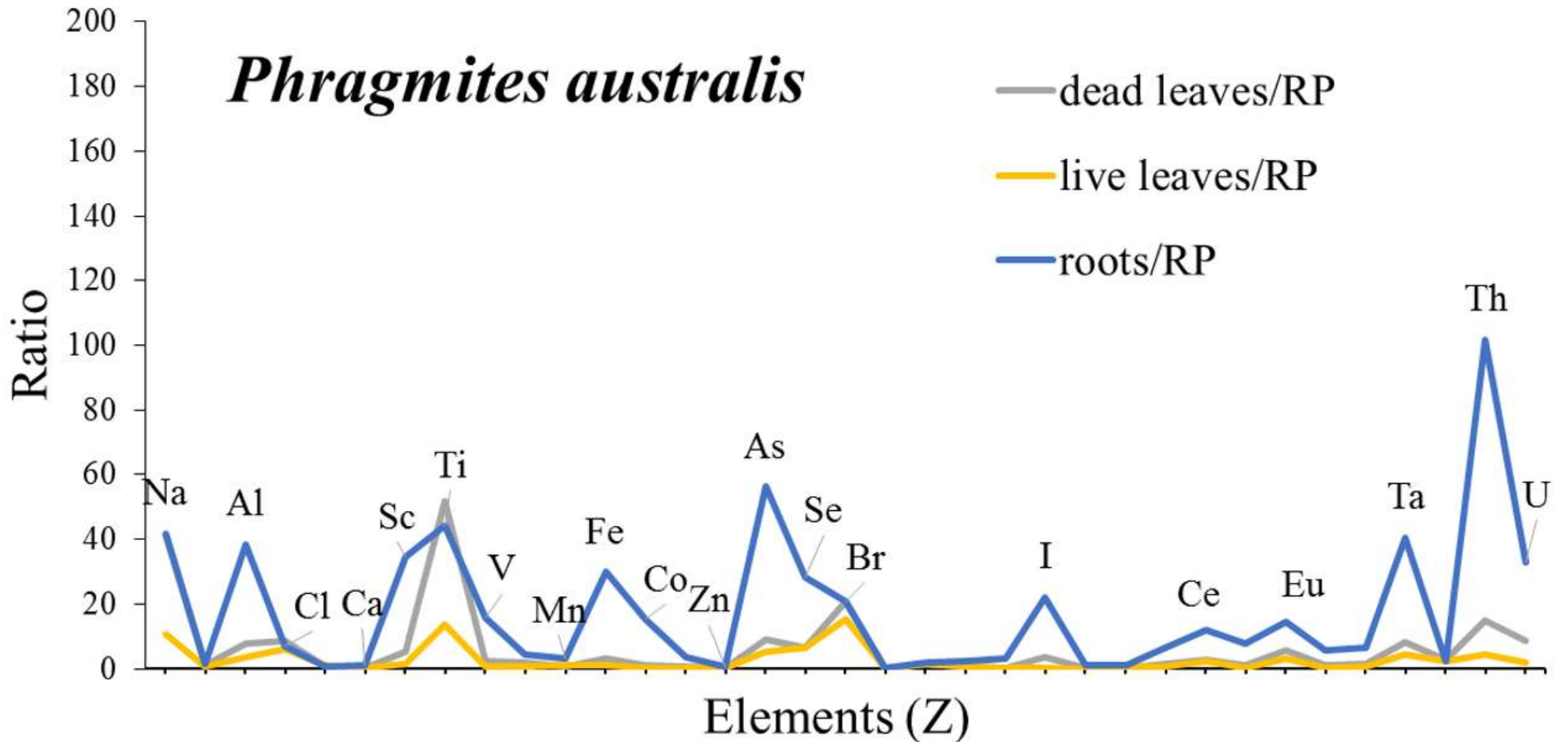
| <b>Element</b> | <b>Original data (<i>n</i>=40)</b> |            |               | <b>Russia</b>                    | <b>Germany</b> | <b>Netherlands</b>              | <b>USA</b> | <b>Finland</b> |
|----------------|------------------------------------|------------|---------------|----------------------------------|----------------|---------------------------------|------------|----------------|
|                | <b>min</b>                         | <b>max</b> | <b>median</b> | <b>(Kolesnikov et al., 2012)</b> |                | <b>(Mynbayeva et al., 2013)</b> |            |                |
| <b>V</b>       | 10                                 | 150        | 30            | 150                              | -              | -                               | -          | 100            |
| <b>Cr</b>      | 6                                  | 105        | 30            | 90                               | 100            | 250                             | 1000       | 100            |
| <b>Mn</b>      | 150                                | 900        | 370           | 1500                             | -              | -                               | -          | -              |
| <b>Co</b>      | 1.6                                | 24         | 4             | -                                | 50             | 50                              | -          | 20             |
| <b>Ni</b>      | 3                                  | 80         | 12            | 85                               | 100            | 100                             | -          | 50             |
| <b>Zn</b>      | 6                                  | 270        | 50            | 100                              | 300            | 500                             | 2500       | 200            |
| <b>As</b>      | 3                                  | 36.8       | 7             | 2                                | 50             | 30                              | 30         | 5              |
| <b>Se</b>      | 0.06                               | 2.31       | 0.25          | -                                | 10             | -                               | -          | -              |
| <b>Mo</b>      | 0.2                                | 15.7       | 1.1           | -                                | 10             | 40                              | -          | -              |
| <b>Sb</b>      | 0.1                                | 2.1        | 0.6           | 4.5                              | -              | -                               | -          | 2              |
| <b>Ba</b>      | 150                                | 690        | 250           | -                                | -              | 400                             | -          | -              |

# Aquatic vegetation: accumulation features



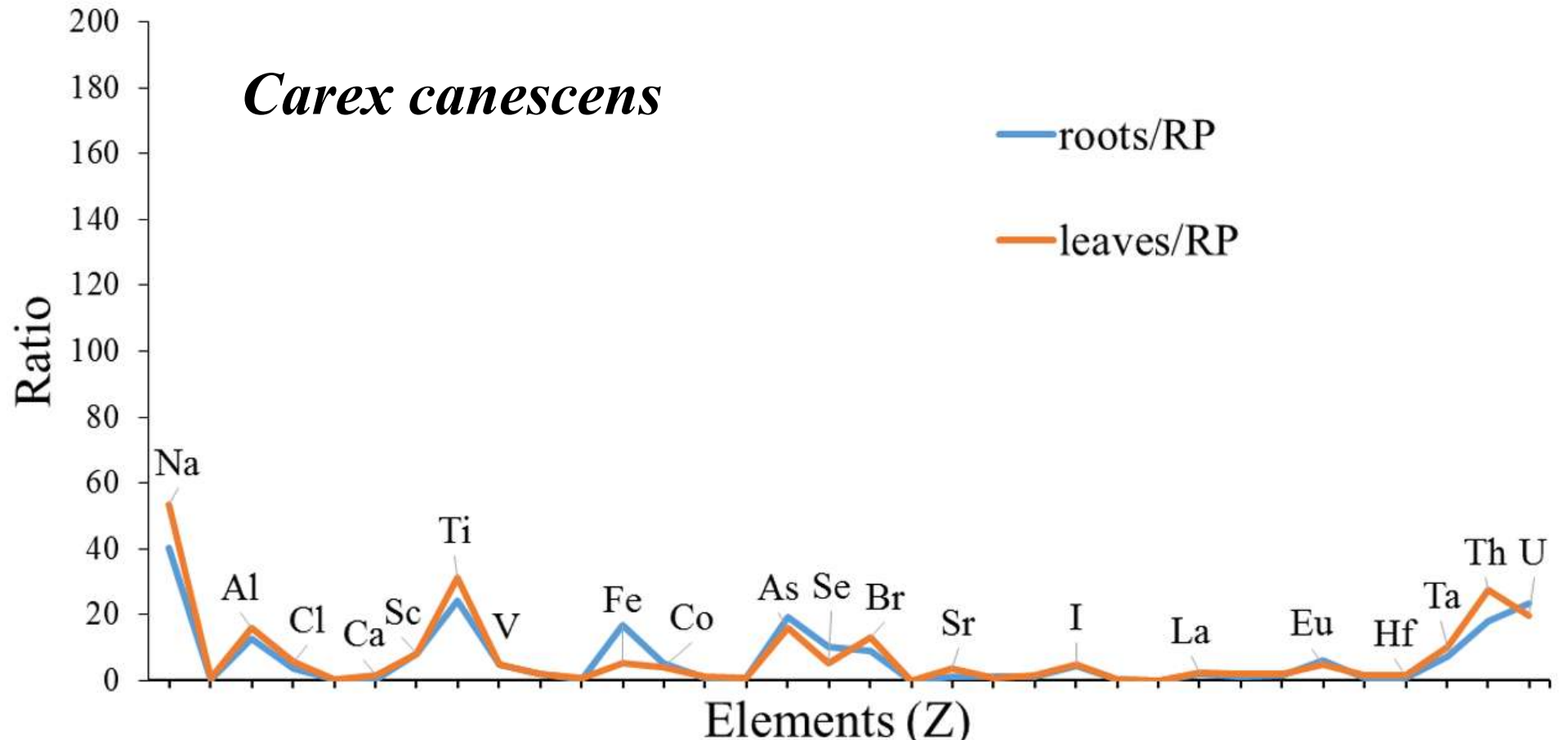
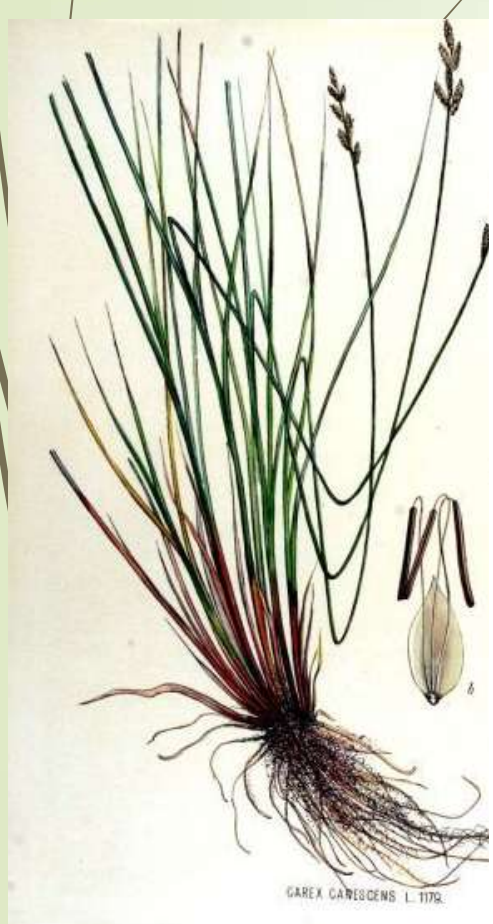
Traits of the two types of biomonitors:  
Cane – root-biomonitor,  
Sedge – leaf-biomonitor

# Special “biochemical signature” of aquatic vegetation in recreational coastal zone



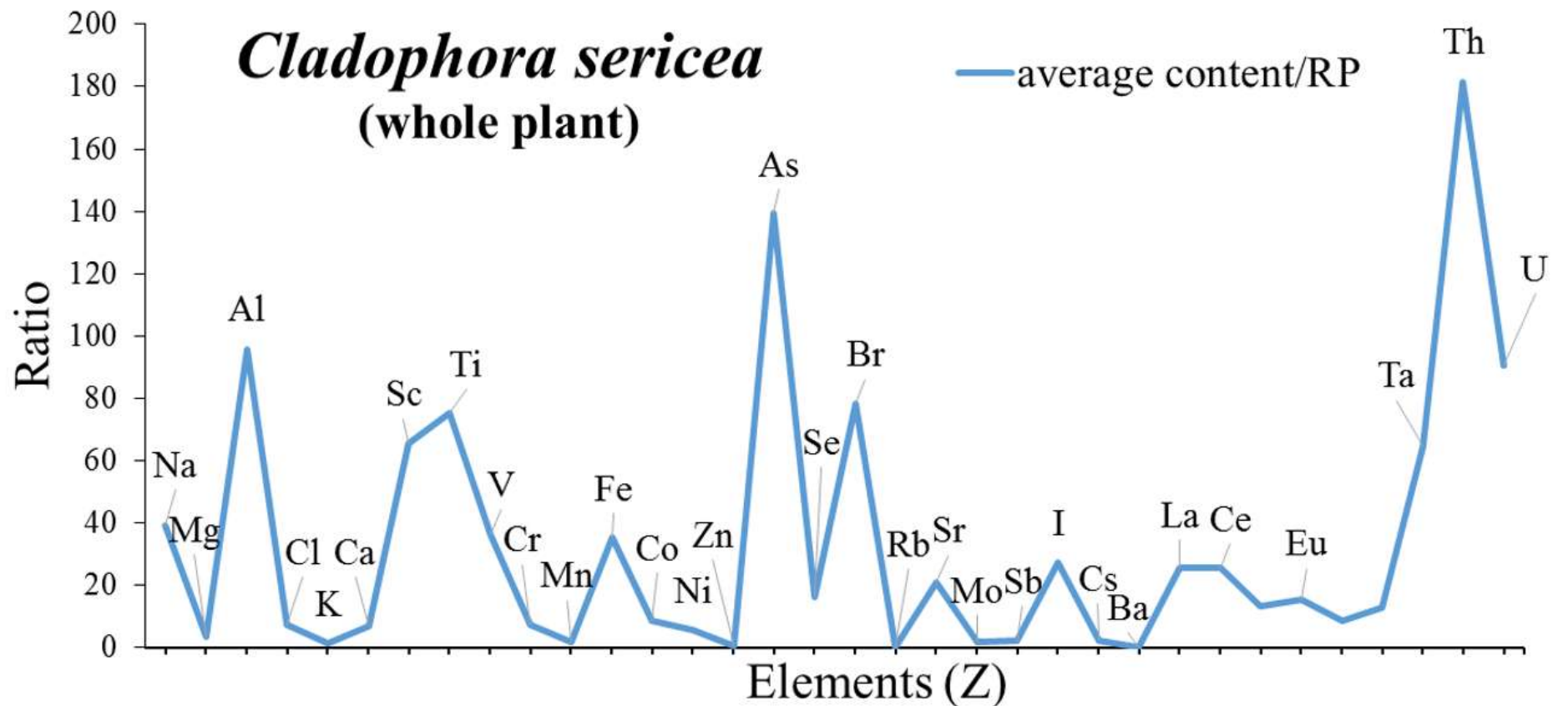
RP – reference plant by B. Markert (1992)

# Special “biochemical signature” of aquatic vegetation in recreational coastal zone



RP – reference plant by B. Markert (1992)

# Special “biochemical signature” of aquatic vegetation in recreational coastal zone



RP – reference plant by B. Markert (1992)



# Macroalgae

Macroalgae – marine plants without roots

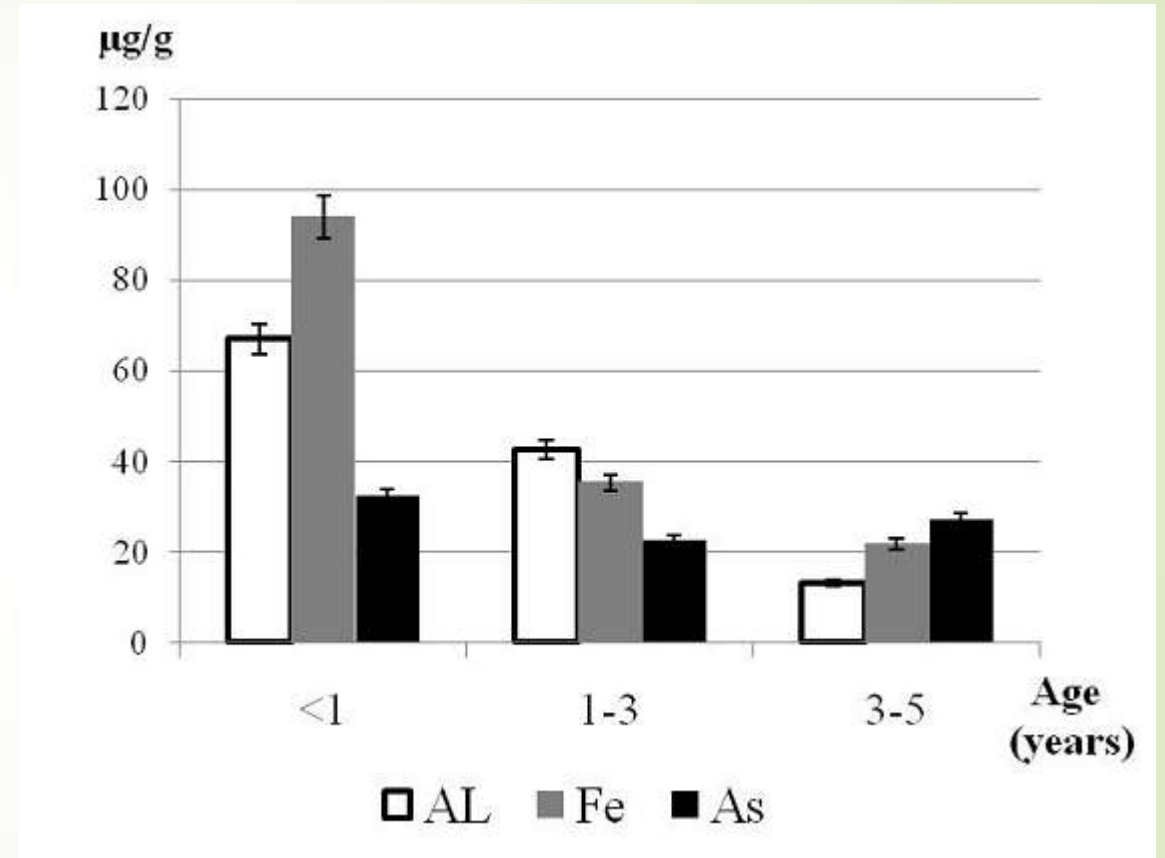
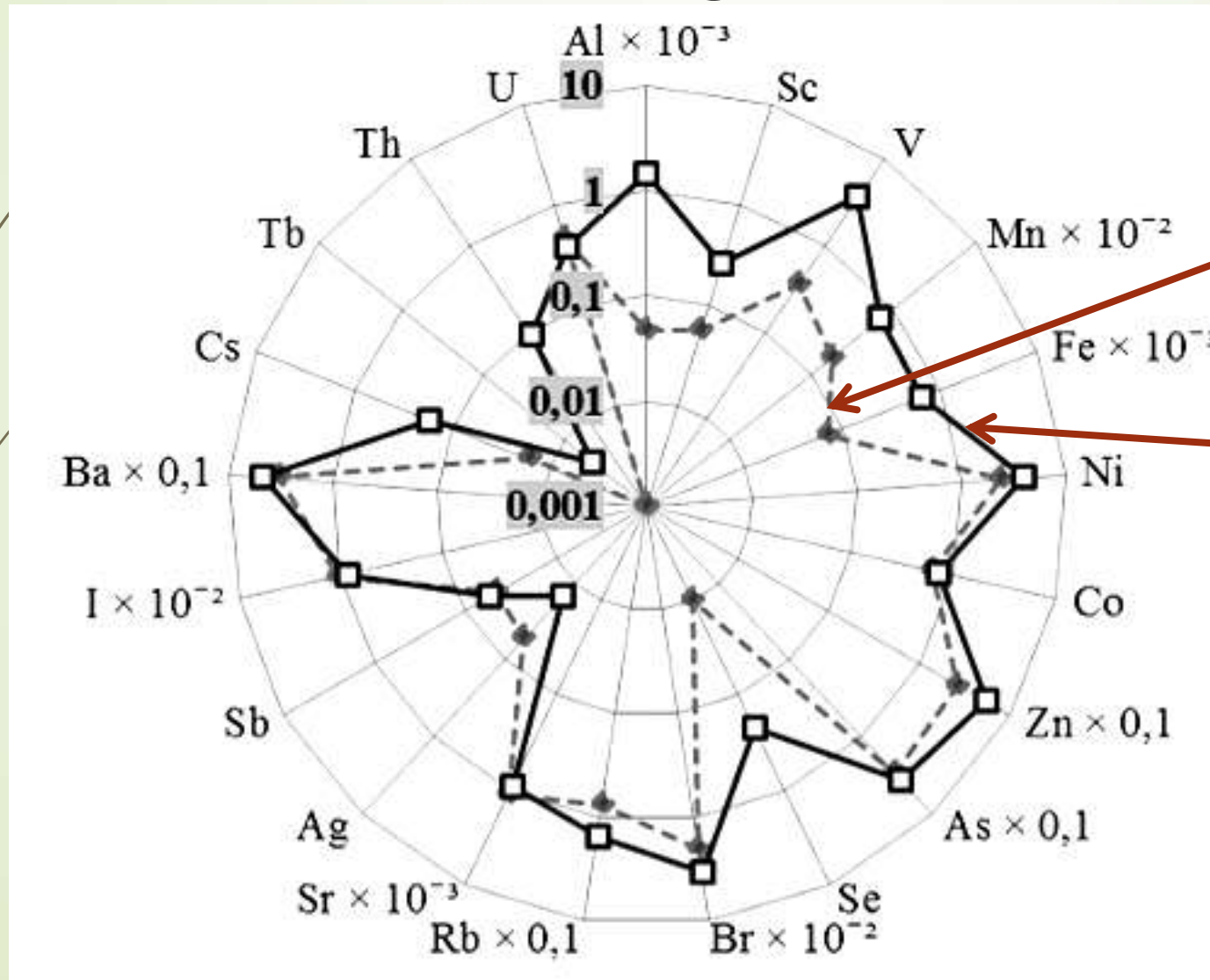


Fig. 1. Al, Fe and As in *Cystoseira crinita* "stems" at various ages

From Kravtsova et al., 2014

# Anthropogenic effects in coastal zones based on biomonitoring of macroalgae



---●--- aquatic natural reserve

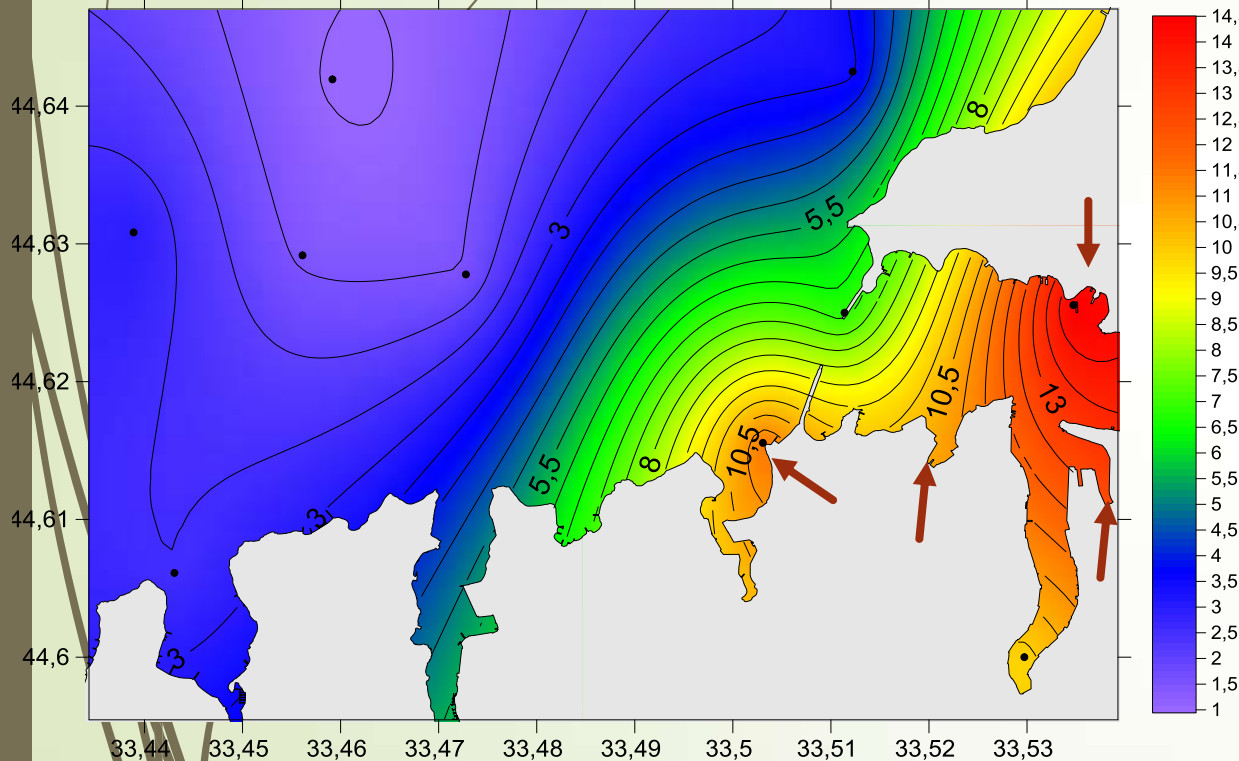
—□— recreational zone (beach)

Biological accumulation of Al, Sc, V, Mn, Fe, Zn, Se

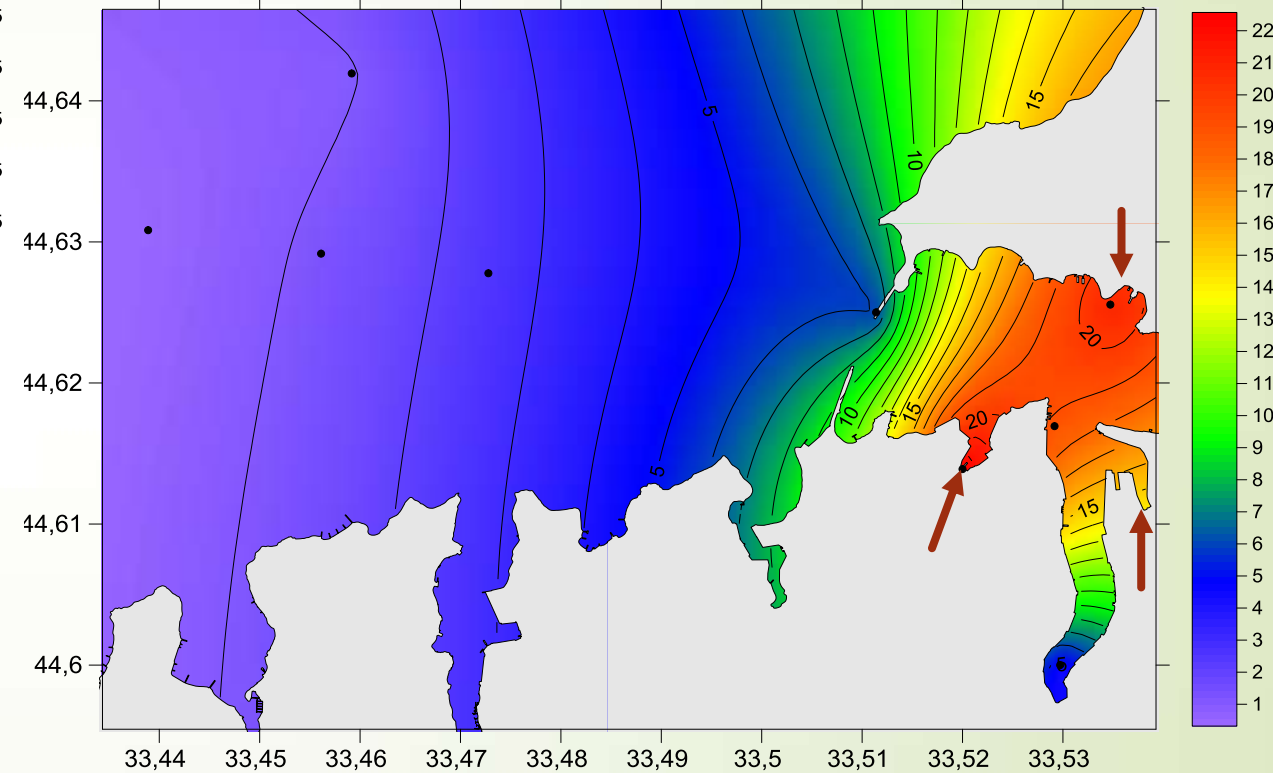
# Peculiarities of elemental accumulation in phytoplankton

## Vanadium (V)

Summer



Winter



- ✓ 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)

|                           |   |
|---------------------------|---|
| Aquatic plants            | Cl, V, Fe, Co, As, Se, Br, Sr, I                  |
| Phytoplankton             | V, Cr, Mn, Br, Mo, I, Sb                          |
| Macroalgae                | V, Mn, Fe, Zn, As, Sr, Se                         |
| <i>Important elements</i> | V, Cr, Fe, Mn, Co, Ni, As, Se, Cu, Zn, Mo, Sr, I, |


| Terrigenous                              | Biologically important            | Anthropogenic                 |
|--|-----------------------------------|-------------------------------|
| Al, K, Ca, Sc, Ti, Rb, Sr, Zr, Cs, Th, U | Co, Cr, Cu, Zn, Mn, Fe, Se, Mo, I | V, Co, Ni, Cu, Zn, As, Sr, Sb |

# 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

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  - 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
- 

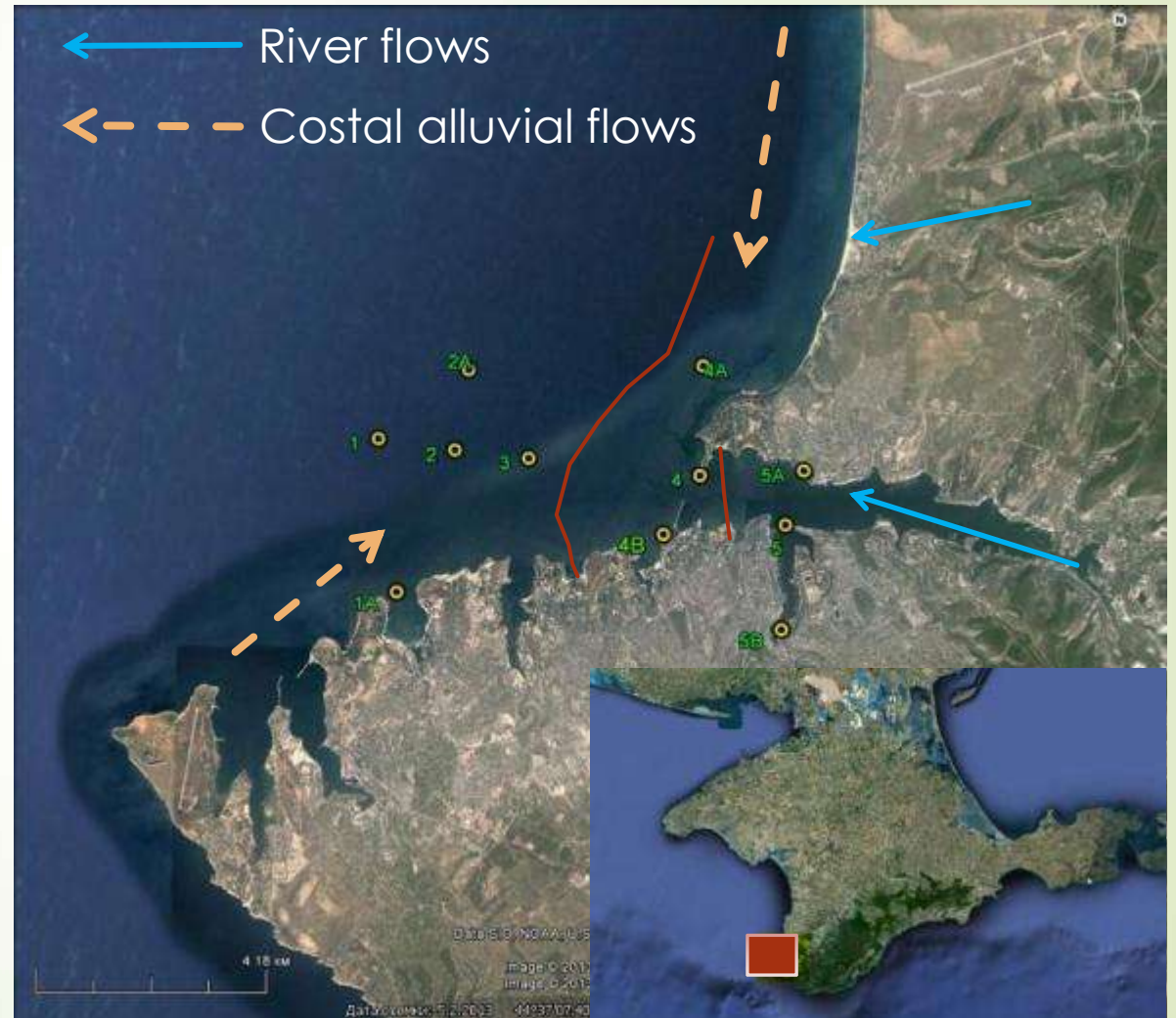
A satellite-style image of the Mediterranean Sea region, showing the sea and surrounding landmasses. A semi-transparent blue overlay covers the entire sea area. The text "To you for your attention!" is centered in white over the sea.

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



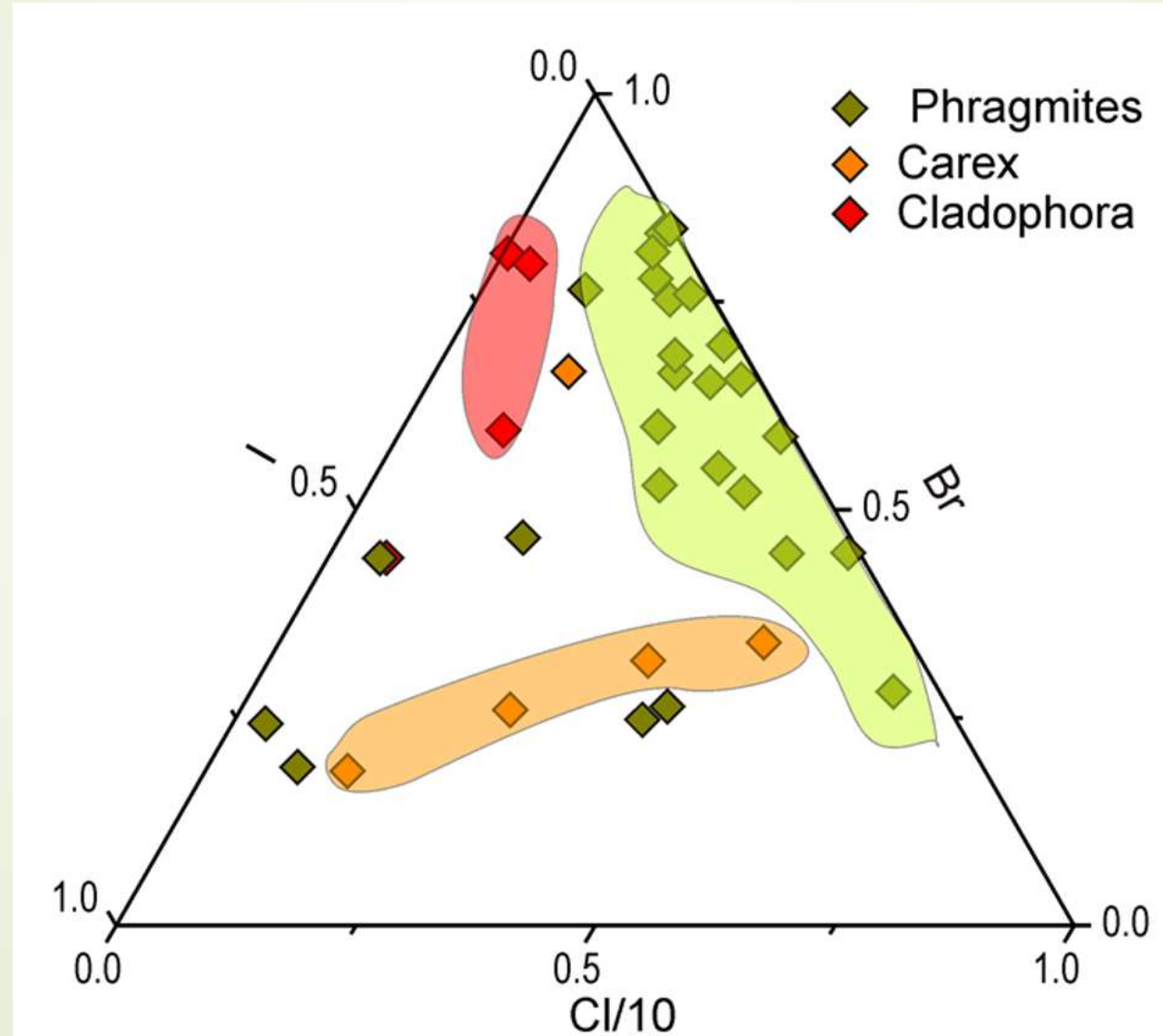


**Maximal and median elemental concentrations ( $\mu\text{g/g}$  dry weight) in soils from Anapa region (our data) and values for non-polluted and polluted soils from the Southern part of Russia**

| Elements  | Soils in Anapa region<br>( <i>n</i> =40) |             | Soils in the Southern part of Russia <sup>1</sup> |              |                   |
|-----------|--|-------------|---|--------------|-------------------|
|           | Max                                      | Median      | Non-polluted                                      | Low polluted | Moderate polluted |
| <b>V</b>  | <b>150</b>                               | 30          | <200  | 200-300      | 300-850           |
| <b>Cr</b> | <b>105</b>                               | <b>30</b>   | <70   | 70-90        | <b>90-170</b>     |
| <b>Mn</b> | <b>900</b>                               | 370         | <1000   | 1000-1600    | 1600-1800         |
| <b>Co</b> | 24                                       | 4           | <18   | 18-36        | 36-250            |
| <b>Ni</b> | 80                                       | 12          | <50   | 50-100       | 100-700           |
| <b>Zn</b> | <b>270</b>                               | <b>50</b>   | <125  | 125-200      | <b>200-850</b>    |
| <b>As</b> | <b>36.8</b>                              | <b>7.1</b>  | <17   | 17-30        | <b>30-160</b>     |
| <b>Se</b> | <b>2.31</b>                              | <b>0.25</b> | <0.7  | 0.7-1.4      | <b>1.4-9</b>      |
| <b>Sr</b> | <b>840</b>                               | <b>510</b>  | <250  | 240-450      | <b>450-3200</b>   |
| <b>Mo</b> | 15.7                                     | 1.1         | <8  | 8-400        | >400              |
| <b>Sb</b> | <b>2.1</b>                               | 0.6         | <5  | 5-12         | 12-200            |
| <b>Ba</b> | 690                                      | 250         | <900  | 900-1500     | 1500-4000         |

<sup>1</sup> elements in soil according to (Kolesnikov et al., 2012)

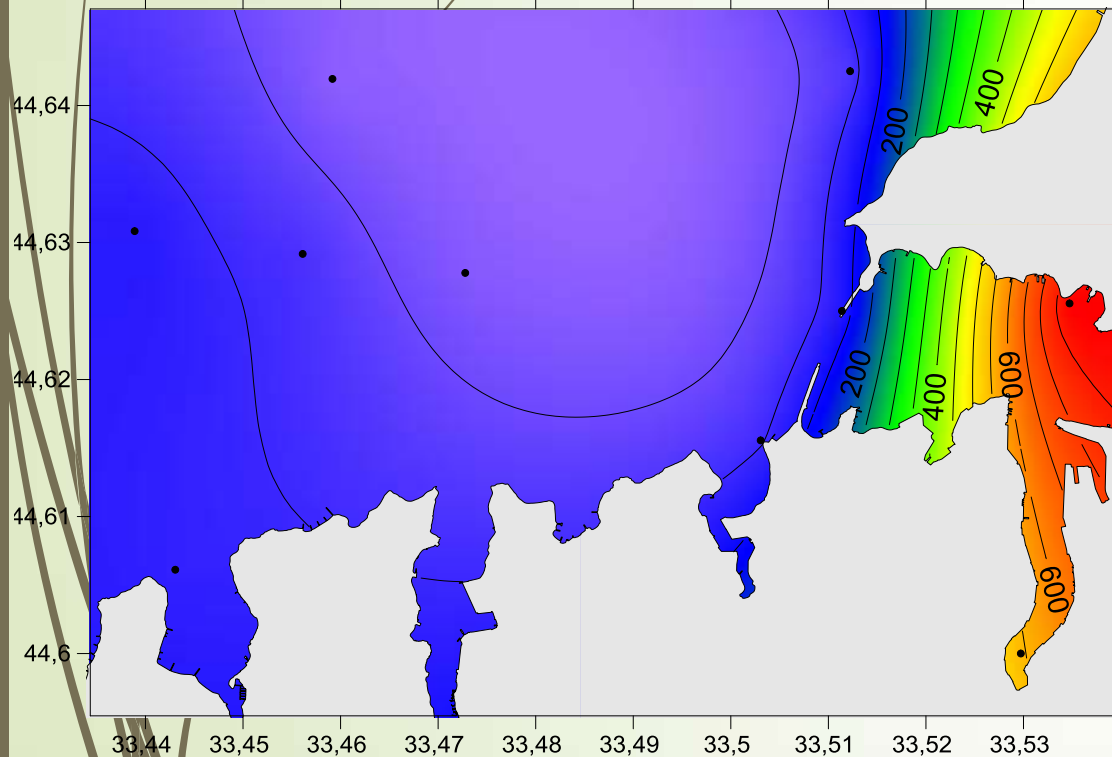
# Special traits of halogens accumulation in aquatic plants



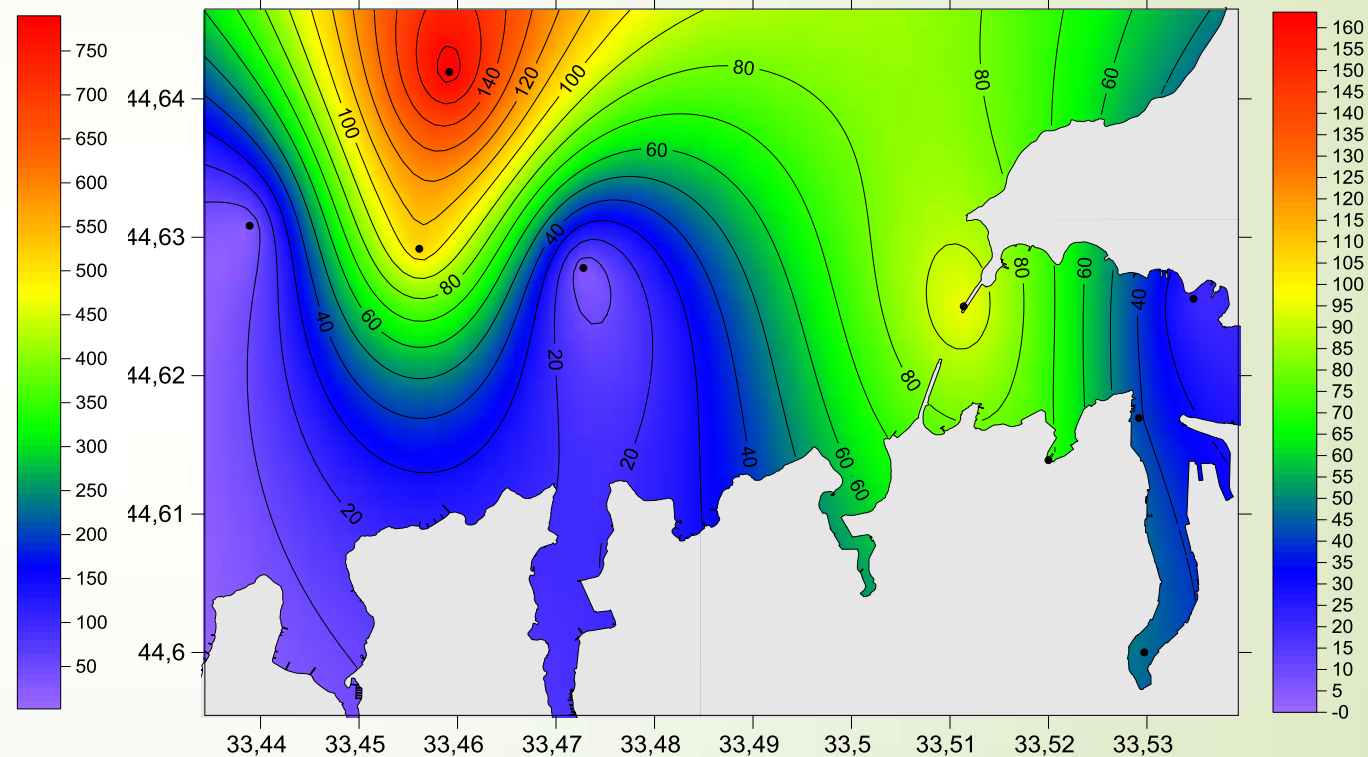
# Peculiarities of elemental accumulation in phytoplankton

## Zinc (Zn)

Summer



Winter



✓ 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