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MULTIELEMENT INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS OF MACROALGAE *CYSTOSEIRA* USED AS BIOMONITOR OF THE BLACK SEA COASTAL WATERS POLLUTION IN SEVASTOPOL REGION

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In Bulgaria, Turkey, Romania and some parts of Russian coast of the Black Sea macroalgae are already used as biomonitors for determination of 5-7 elements by mean of AAS (**monitoring data and local observations)**

The aim of our work was to determine a wide spectrum of elements, using NAA, to study features of accumulation of macro- and microelements by macroalgae from the coastal waters of south-western Crimea (Sevastopol region) and relate their concentrations with the seasons, ages and different parts of the thalli.

Marine macroalgae

Marine macroalgae, or seaweeds – are lower chlorophyll-containing eukaryotic plants that generally live attached to rock or other hard substrate in coastal areas; lacking true stems, roots and leaves.

Types of marine algae

Green algae

Brown algae

Red algae

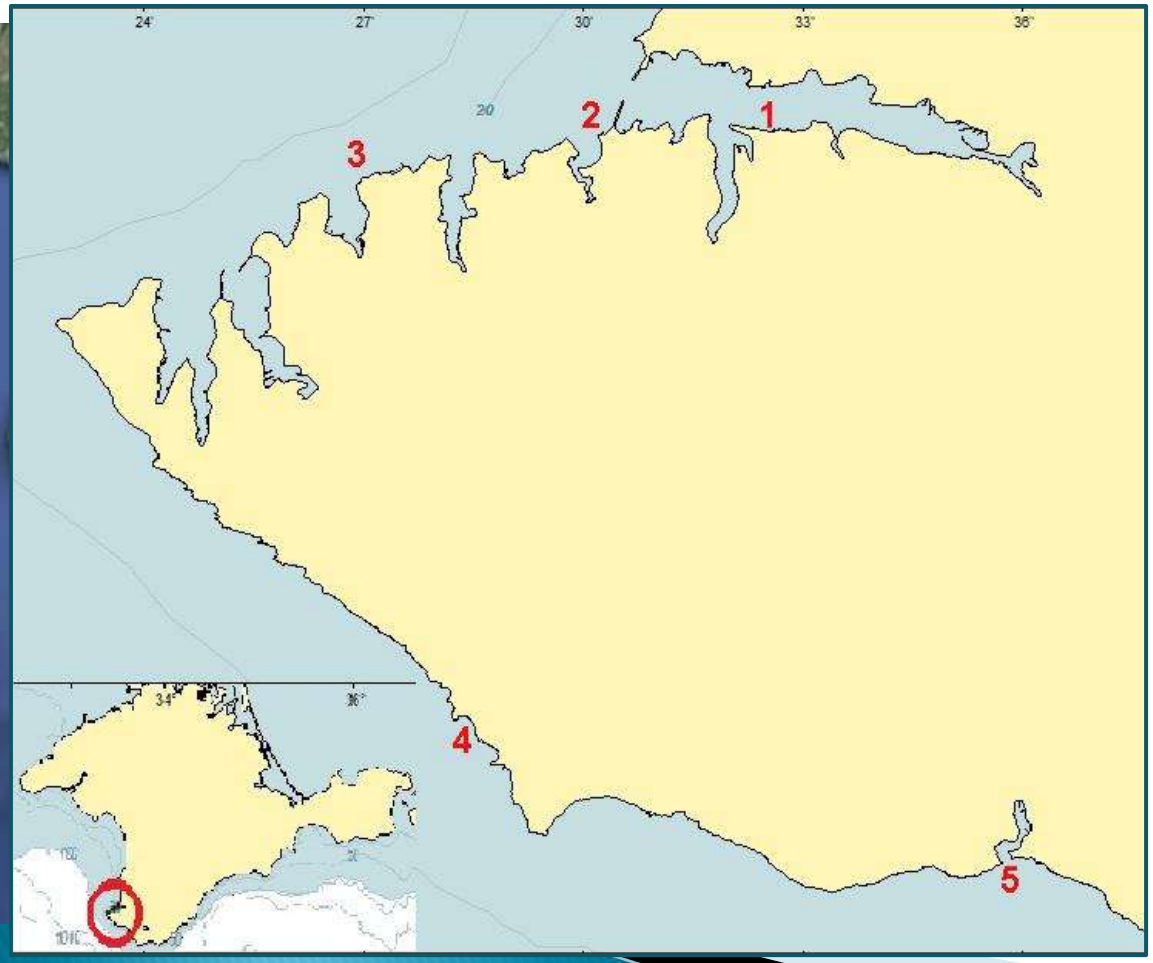
Brown algae – *Cystoseira crinita* and *Cystoseira barbata*

Advantages of macroalgae as biomonitors

- They are proven indicators for analysis and control of dissolved trace elements in the sea, because of their accumulation capacity;
- Dominant species of algae are widely distributed in different environmental conditions;
- They can adapt to environmental changes while retaining their life functions;
- The sampling of macroalgae in the coastal zone does not require sophisticated diving equipment;
- Brown algae are the most preferable ones for monitoring of trace elements pollution in the coastal waters. Due to the presence of alginic acids, they have a higher resistance to heavy metals as compared with red and green algae.

Study area

South-western Crimea
Sevastopol region



Five aquatic sites with different degree of anthropogenic pollution:

1 – Sevastopolskaya bay

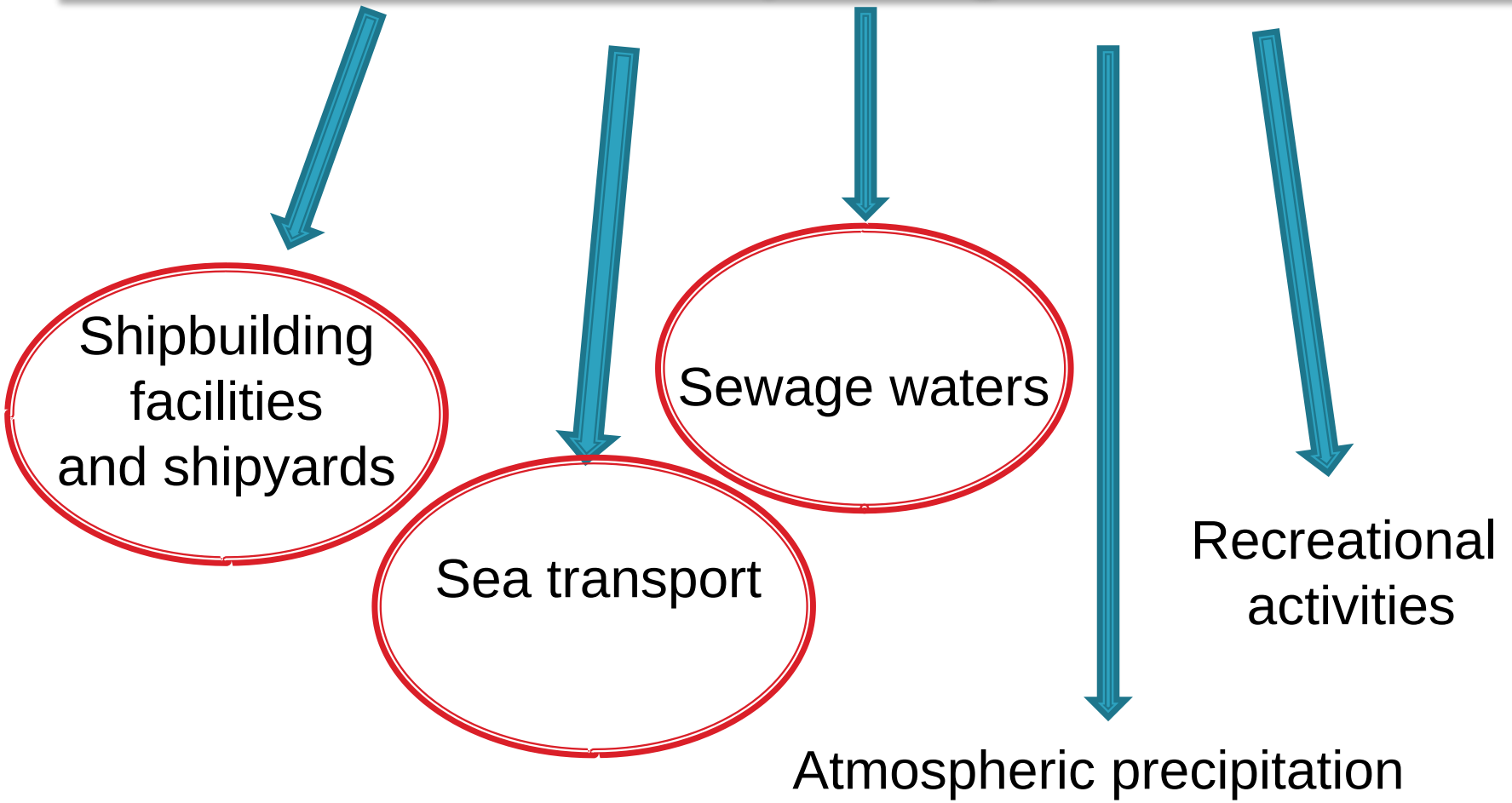
2 - Karantinnaya bay

3 – Kruglaya bay

4 – Coastal aquatic complex near cape Fiolent

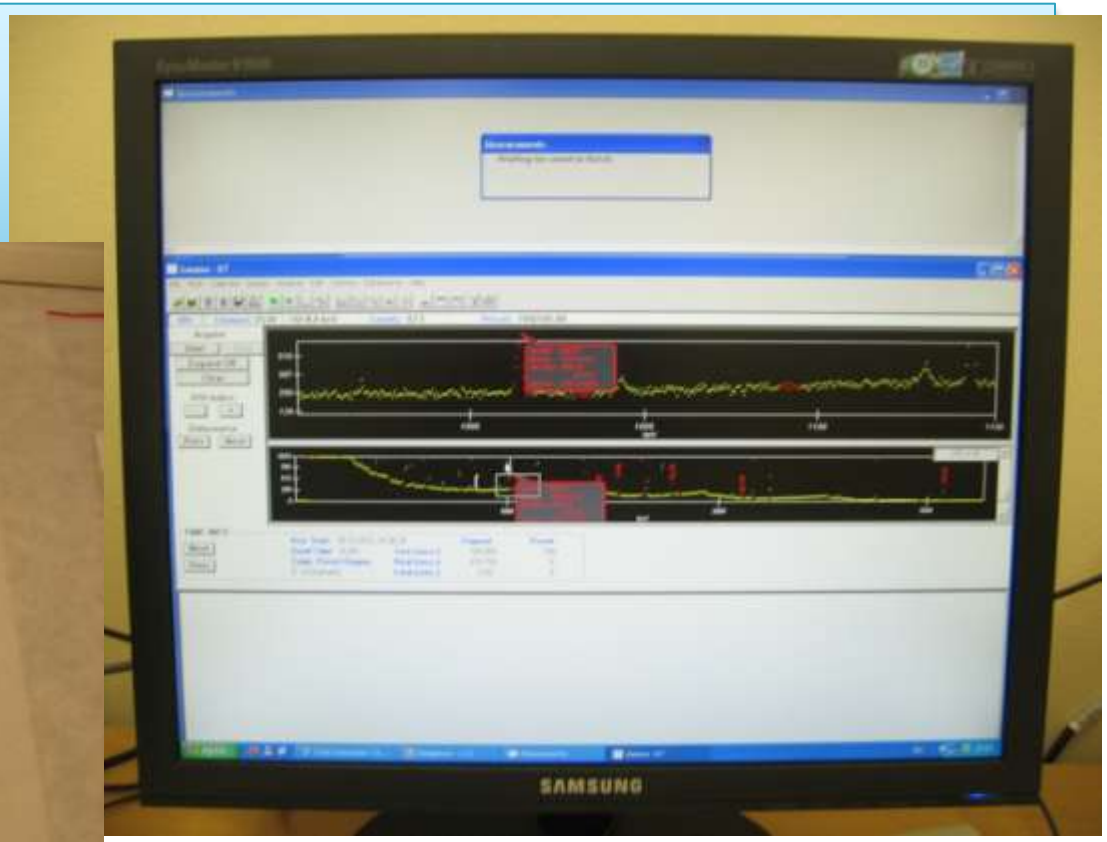
5 – Balaklavskaya bay

Main sources of water pollution in Sevastopol region



Materials and methods

- The macroalgae *Cystoseira barbata* and *Cystoseira crinita* were sampled in spring and summer of 2012 at the depth of 0.5–1 m
- Plants were carefully cleaned from epiphytes and thalli was divided into the stem and branches.
- Samples were dried at room temperature and then brought to a constant weight at 40 C during 24 hours. Further the samples were manually homogenized in an agate mortar.
- A total of 52 samples in the age range from 6 months to 5 years were prepared for analysis.



sotopes samples were irradiated for
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they were re-packed and measured
l of decay, respectively. Measuring
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INAA

- To process gamma spectra and to calculate concentrations of elements the software developed at FLNP JINR was used. The errors in the concentrations determined were in the range of 3-15%
- Quality control was provided by using certified reference materials SRM Rice Flour-1568a, Pine needles-1575a and Apple Leaves-1515, all NIST production, irradiated in the same containers with samples under investigation.
- The total of **26** (Na, Mg, Al, Cl, K, Ca, Sc, V, Mn, Fe, Co, Ni, Zn, As, Br, Rb, Sr, Sb, I, Cs, Ba, Sm, Nd, Ag, Au and U) macro- and microelements were determined

Results

Macro- and microelements content in the Black Sea water (mg/kg), macroalgae *Cystoseira* and corresponding accumulation coefficients

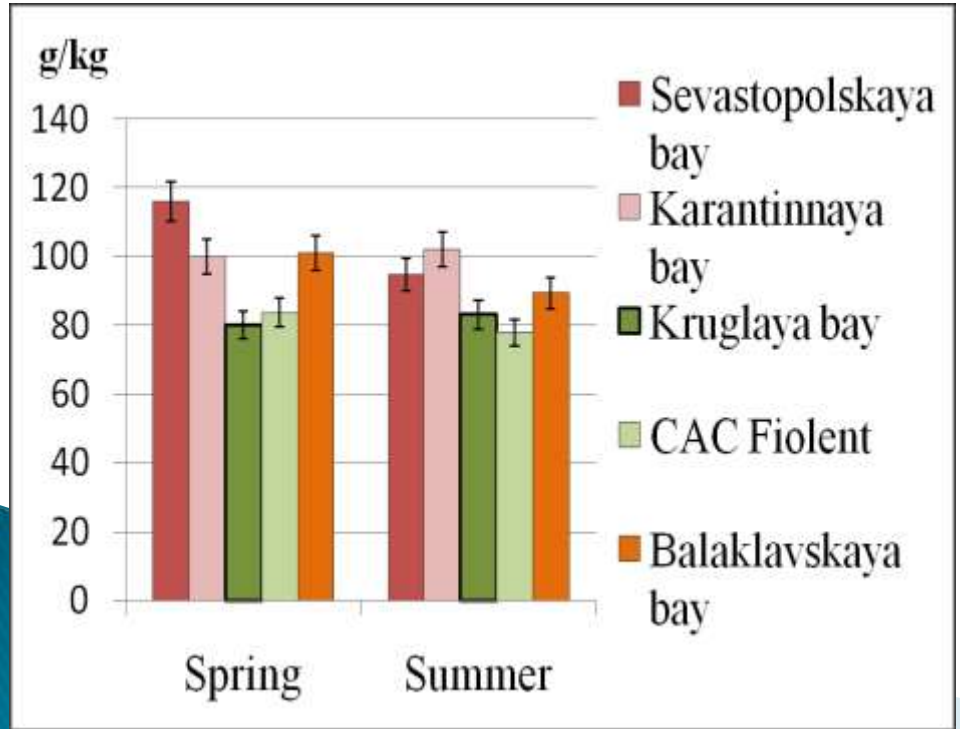
Element	Concentration in the Black Sea	Concentration in macroalgae *Cystoseira*	Accumulation coefficients by macroalgae *Cystoseira*
Al	100×10^{-4}	213	10^4
Sc	$0{,}014 \times 10^{-4}$	0,07	10^4
V	3×10^{-3}	0,8	10^3
Mn	19×10^{-4}	17	10^4
Fe	300×10^{-4}	173	10^4
Co	$0{,}34 \times 10^{-3}$	0,31	10^3
Ni	$1{,}8 \times 10^{-3}$	3,2	10^3
Zn	70×10^{-3}	35	10^3
As	19×10^{-4}	32	10^4
Rb	32×10^{-2}	14	10^2
Sr	1800×10^{-3}	1005	10^3
Ag	$0{,}013 \times 10^{-2}$	0,04	10^2
Sb	$0{,}18 \times 10^{-2}$	0,07	10^2
Cs	$0{,}01 \times 10^{-3}$	0,03	10^3
Ba	47×10^{-4}	44	10^4
U	$0{,}24 \times 10^{-2}$	0,32	10^2

Results

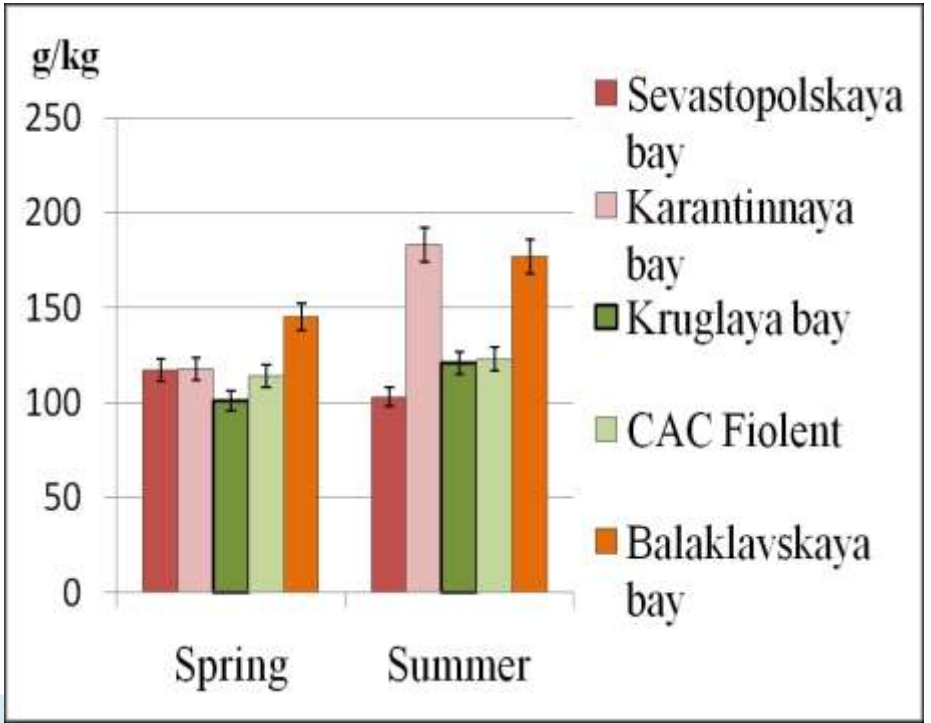
The results showed a tendency to increase concentrations of elements in algae towards more polluted waters

Total concentration of elements (g/kg, dry weight) in stems and branches of *Cystoseira spp.* in spring and summer season 2012 (Sevastopol region)

Stems



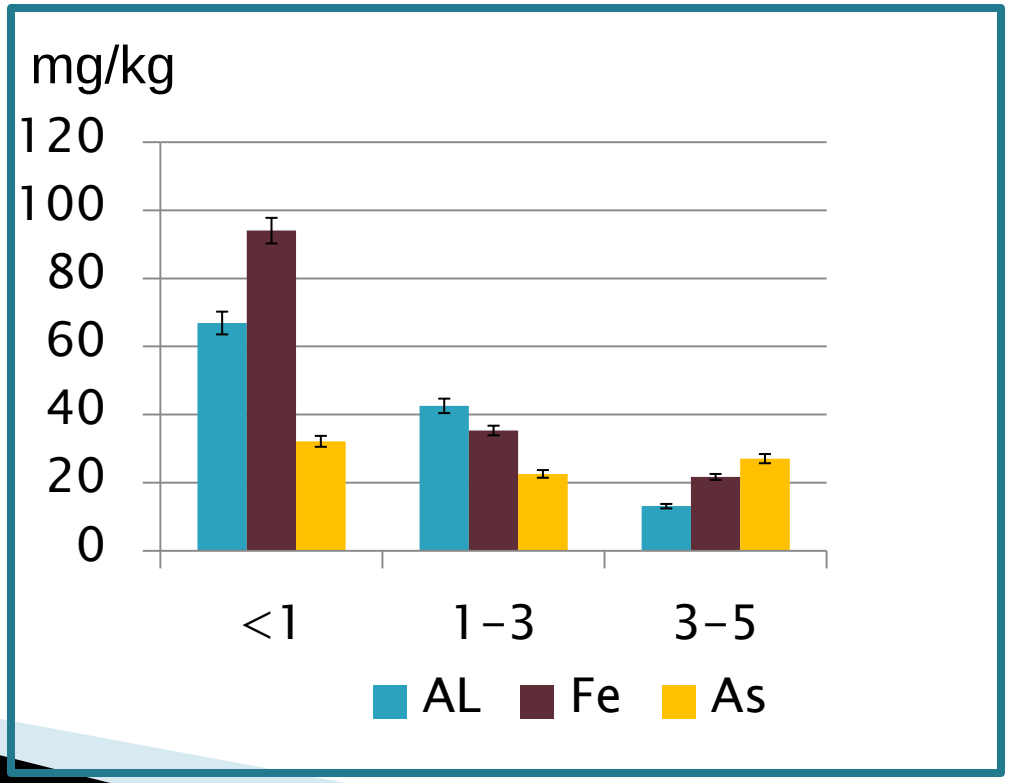
Branches



Results

The highest concentrations of trace elements were found in young plants less than one year old at all stations, regardless of their degree of pollution.

Average concentrations of Al, Fe and As (mg/kg) in *Cystoseira* spp. stems at various ages in summer season 2012 (Sevastopol region)



Factor analysis

Factor 1 – geological origin (Al, K, Sc, V, Fe, Cs)

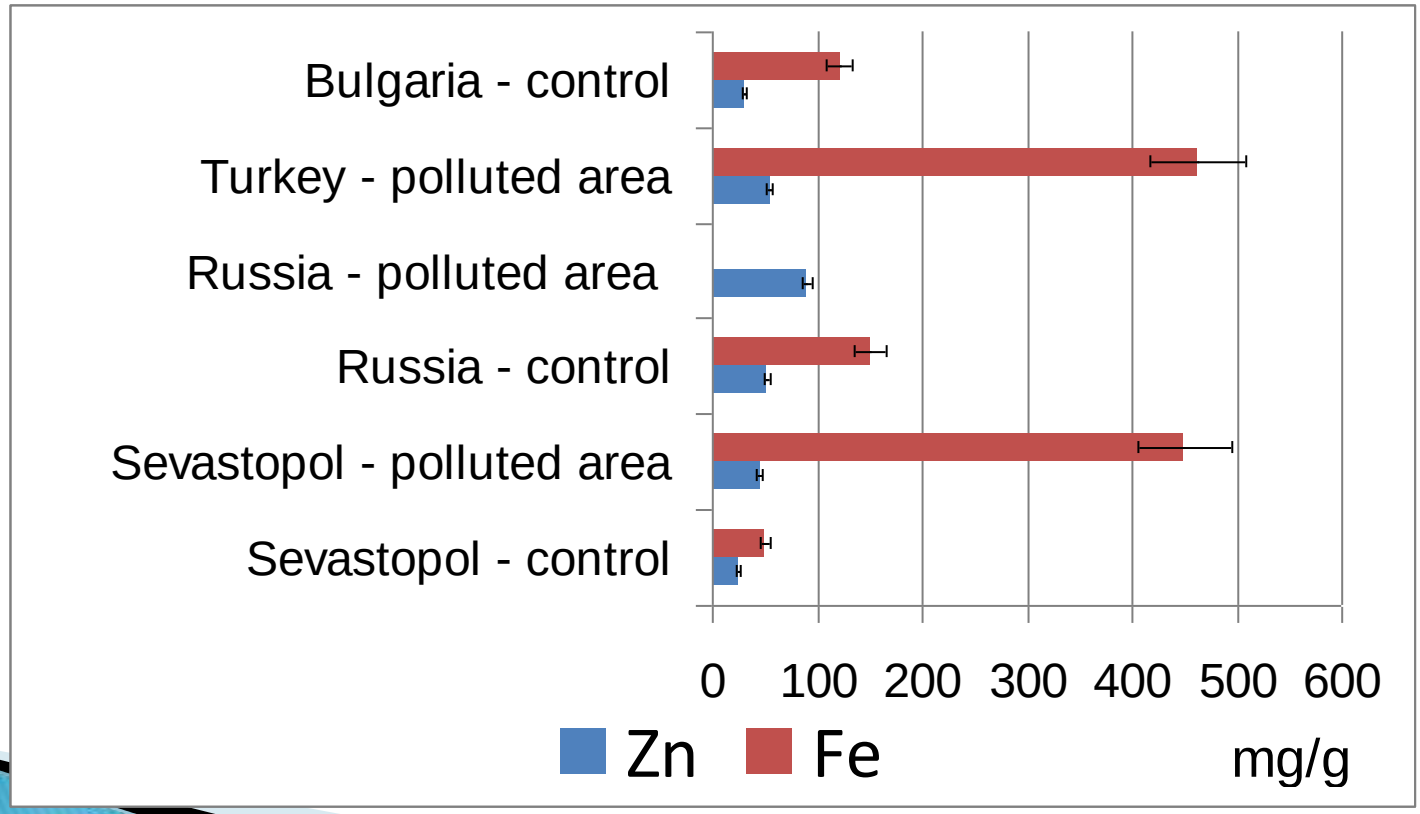
Factor 2 – marine component (Mg, Cl, Br, I;

Ni and As – pollutants)

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Na	0,24	0,42	-0,17	0,50	0,52
Mg	-0,07	0,70	-0,14	0,29	0,40
Al	0,93	-0,01	0,19	0,18	-0,03
Cl	0,45	0,55	0,60	-0,01	0,18
K	0,62	0,19	0,64	0,01	0,22
Sc	0,71	0,25	0,23	-0,01	0,21
V	0,85	-0,05	-0,28	0,01	0,11
Mn	0,26	0,14	-0,02	0,78	-0,11
Fe	0,92	0,03	0,22	0,13	0,07
Ni	0,47	0,68	-0,07	-0,12	-0,11
Co	0,31	0,26	-0,31	0,79	0,03
Zn	0,22	0,09	-0,67	-0,04	-0,46
As	-0,21	0,73	0,05	0,09	0,29
Br	0,28	0,65	0,23	0,43	0,29
Rb	0,49	0,20	0,73	-0,21	0,17
Sr	-0,04	0,17	0,13	-0,06	0,92
Sb	0,31	0,26	-0,18	-0,68	-0,02
I	0,00	0,79	0,19	-0,04	-0,05
Ba	0,37	0,13	0,18	-0,03	0,77
Cs	0,92	0,00	0,14	0,16	-0,05
U	-0,13	-0,03	-0,88	0,02	0,08
Expl.Var	5,47	3,37	3,07	2,35	2,46
Prp.Totl	**0,26**	**0,16**	**0,15**	**0,11**	**0,12**

Cystoseira spp as a biomonitor in others regions of the Black Sea

Concentrations of Fe and Zn in *Cystoseira* spp. from different regions of the Black Sea



Main conclusions

- For the first time for Sevastopol region the peculiarities of 26 (Na, Mg, Al, Cl, K, Ca, Sc, V, Mn, Fe, Co, Ni, Zn, As, Br, Rb, Sr, Sb, I, Cs, Ba, Sm, Nd, Ag, Au and U) macro- and microelements accumulation in the thalli of brown algae *Cystoseira* were studied using INAA
- Average concentrations of macro- and microelements in the thalli of *Cystoseira barbata* and *C. crinita* widely differ and are dependent on ecological conditions
- The results showed a tendency to increase concentrations in the thalli towards more polluted waters.
- The highest concentrations of trace elements were found in young plants less than one year old at all stations, regardless of their degree of pollution

Main conclusions

- The content of trace elements in the stems and branches of the thalli from the same station differed by a factor of 1,5-7;
- In the spring, the greatest concentration of elements in stems was higher than in the summer; the reverse was observed for the branches;
- In the summer season the epiphytic macroalgae are an additional source of elemental sorption from the aquatic environment resulting in raised concentrations in the branches of *Cystoseira barbata* and *C. crinita.*

Main conclusions

- For biomonitoring purposes it is recommended to use stems and branches of the same age that were sampled in the same season.
- The stems of 2-3 year old plants of *Cystoseira barbata* and *C. crinita,* sampled in the summer season, could be the biomonitors of water pollution in the Sevastopol coastal zone.

Thank you for attention!