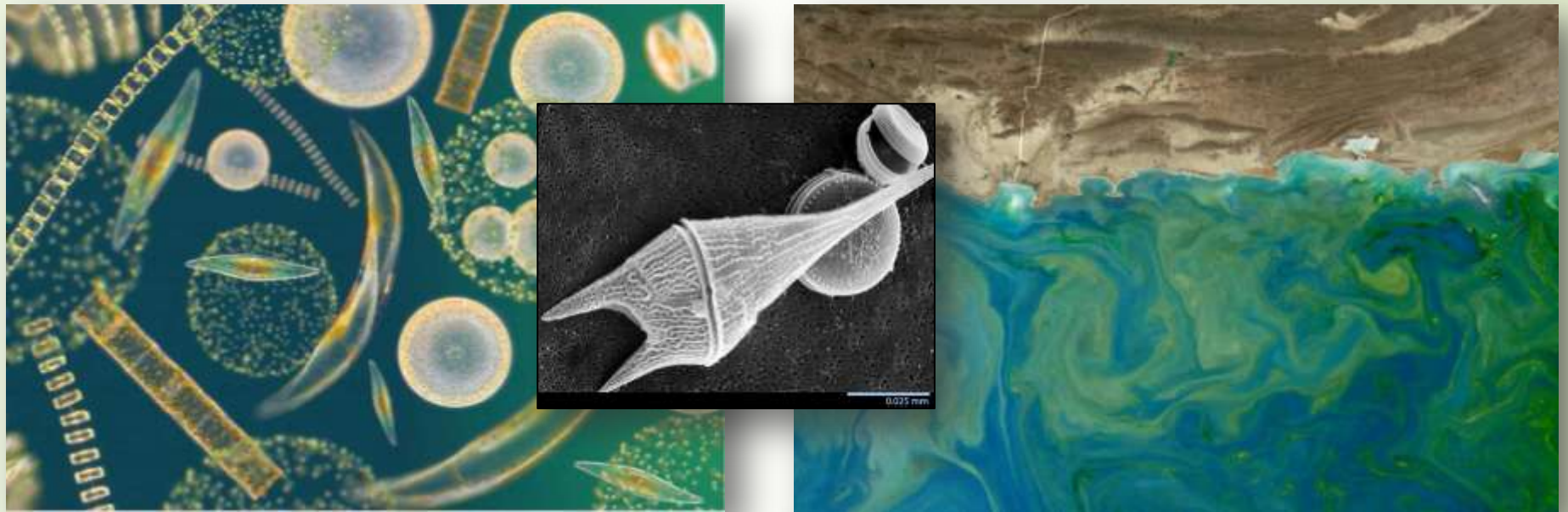




# NEUTRON ACTIVATION ANALYSIS FOR ASSESSMENT OF SEASONAL AND SPATIAL VARIABILITY OF ELEMENTAL CONTENT OF PHYTOPLANKTON



18 slides

P. S. Nekhoroshkov<sup>1,2</sup>, M. V. Frontasyeva<sup>1</sup>, Yu. N. Tokarev<sup>2</sup>

<sup>1</sup>Frank Laboratory of Neutron Physics, JINR, Dubna, Russia

<sup>2</sup>Kovalevsky Institute of the Marine Biological Studies, Sevastopol, Russia

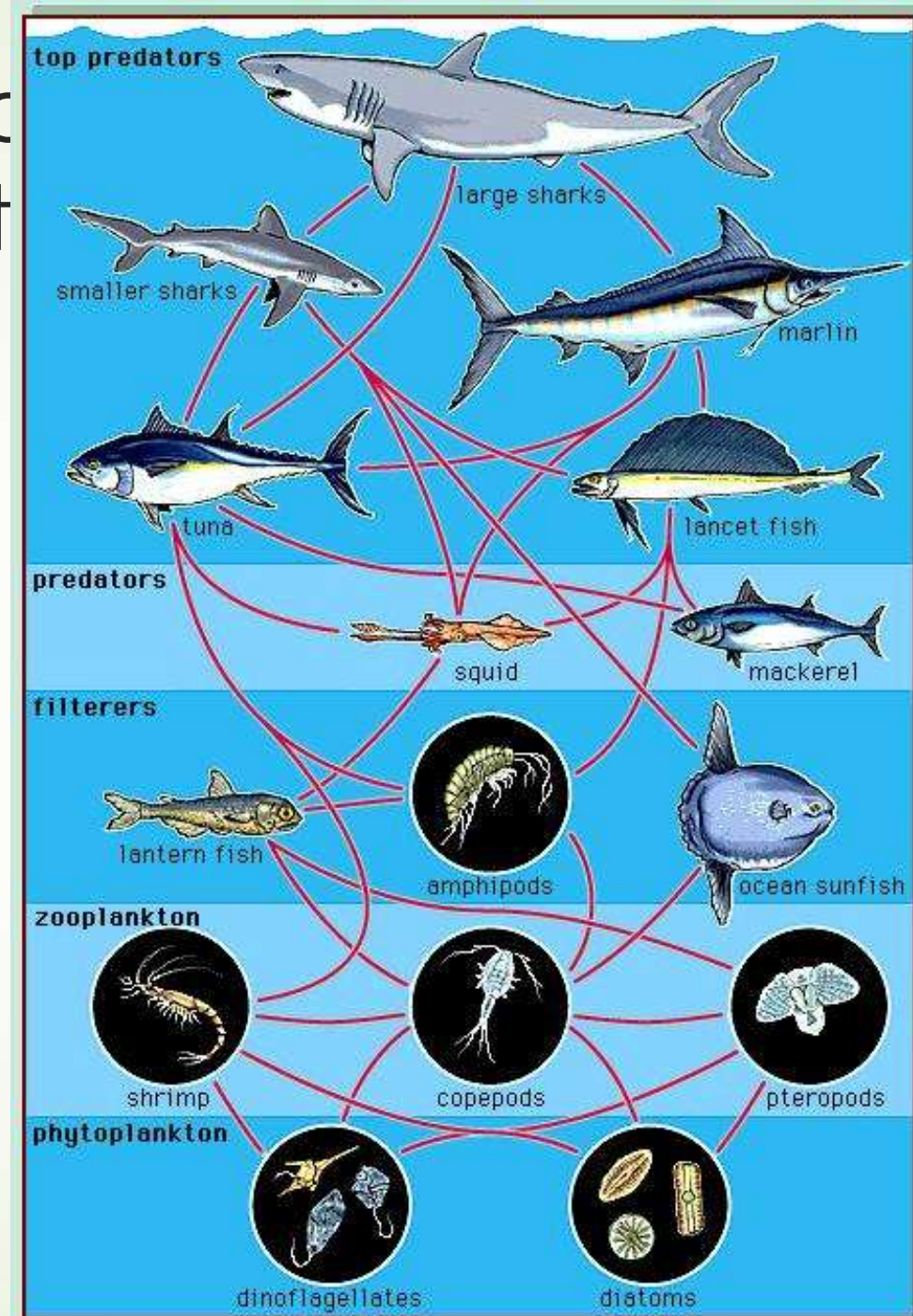
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# Plan

- ▶ Why study of elemental content of phytoplankton is so important for us ?
- ▶ Sampling of phytoplankton
  - stations
  - seasonal variability
- ▶ Preparing for Neutron Activation Analysis:
  - filtration
  - partitioning
  - packaging
- ▶ How much species were in the whole sample?
- ▶ Species structure of dinoflagellates in samples
- ▶ Calculation of elemental concentrations
- ▶ Analysis of obtained data

# Why study of elemental composition of phytoplankton is so important

- Water quality for marine ecosystems, humans
  - Elemental distribution in trophic chains: main level
  - Elemental supply in bottom sediments
  - Sensitive objects for environmental monitoring because of its accumulation properties
- ❖ The main aim is to define the “normal” elemental composition for the studied water area. It helps to solve the problem of identification of the normal physiological and functional state of the whole community of phytoplankton

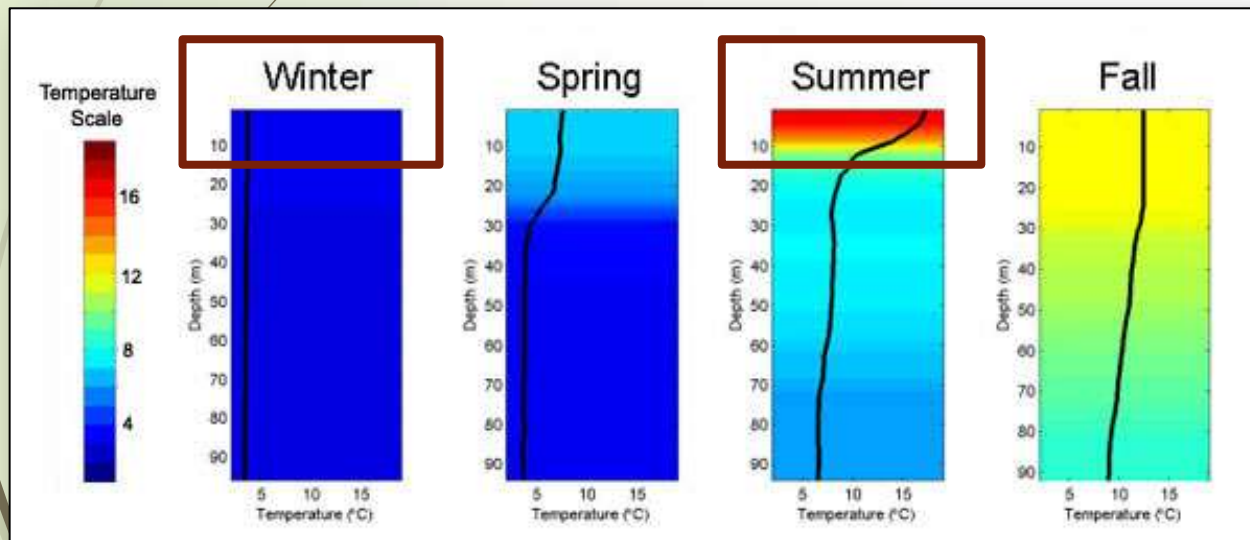




# Sampling of Phytoplankton

Phytoplankton net towing. You should provide:

- vertical and horizontal tows with stable speed
- the same volume of water (column)
- non-working drive of vessel
- necessary place and depth of the station

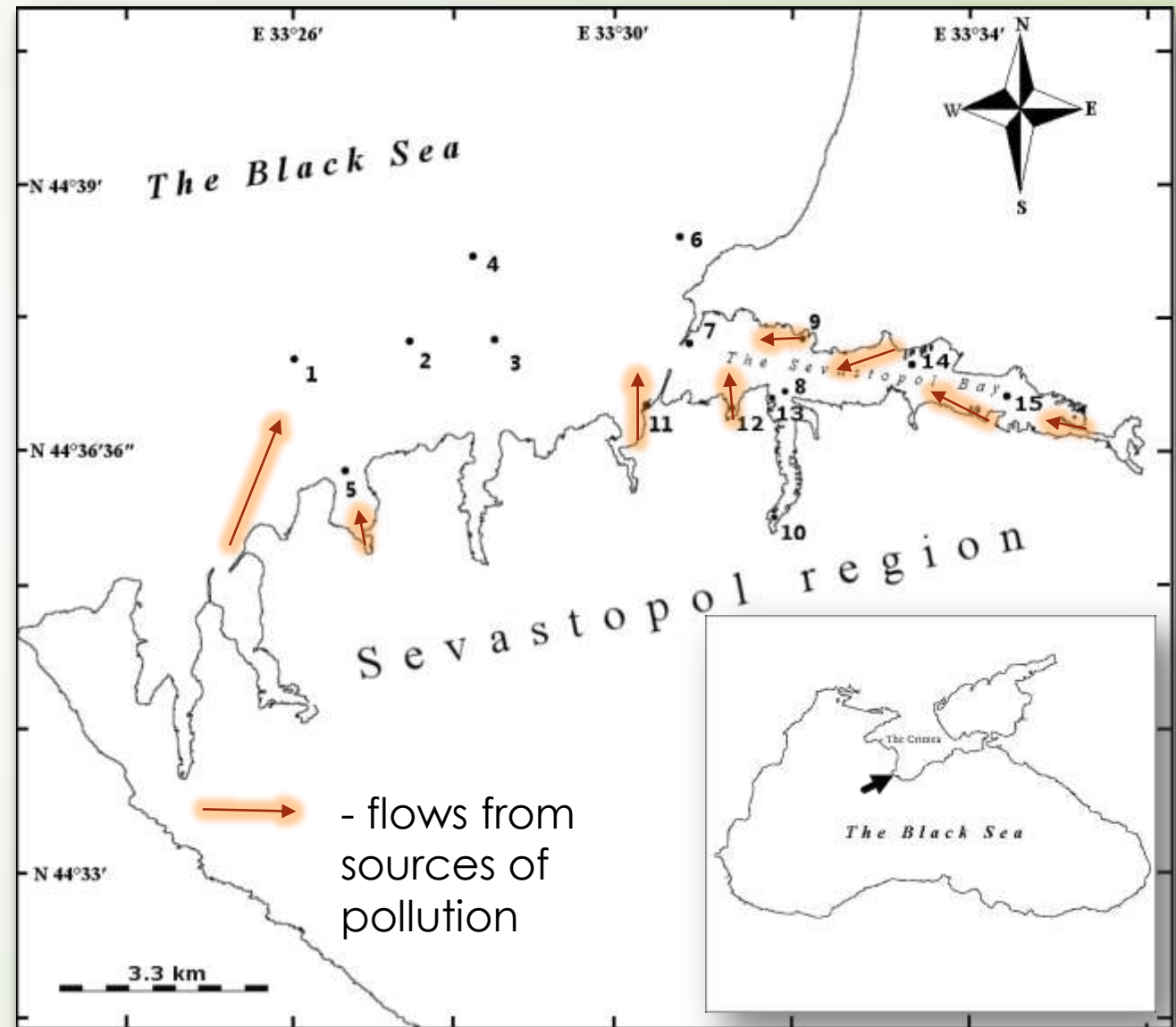


- Periods of opposite hydrochemical structure



# Sampling sites

- ▶ 30 samples in summer of 2013
- ▶ 25 samples in winter of 2014
- ▶ Station #9, 10, 13 – horizontal tows
- ▶ 6 stations inside the Sevastopol bay
- ▶ 4 stations in deep water zone
- ▶ 11 stations in summer and winter



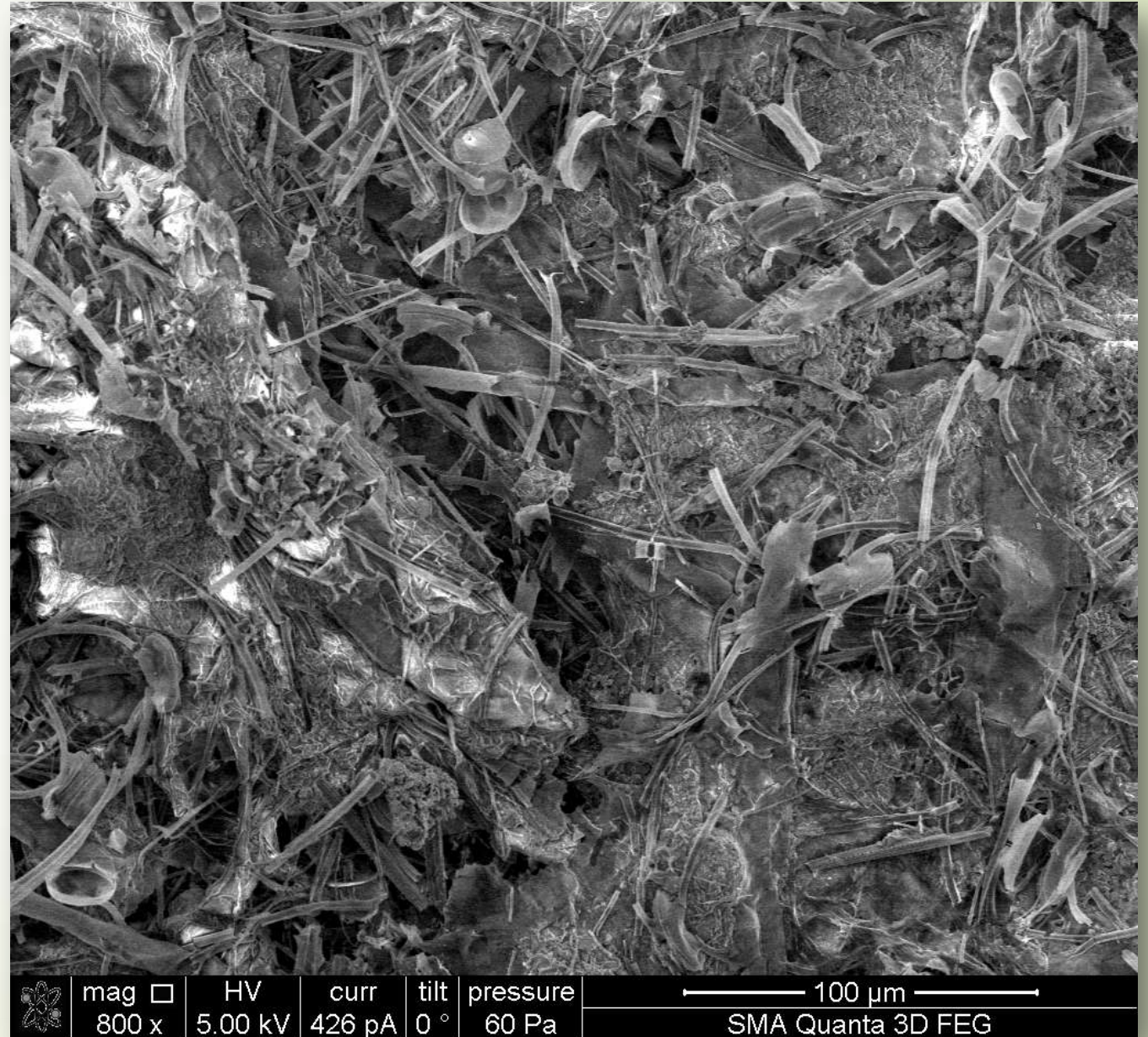


# Preparing to Neutron Activation Analysis

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## Filtration and dividing

- ▶ Vacuum filtration onto Sartorius paper filters with 10  $\mu\text{m}$  size of pore
- ▶ Washing with distillate water (removal a saline particles)
- ▶ Drying 10 days at room conditions



# Neutron Activation Analysis

- ▶ Elemental contents of phytoplankton 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
- ▶ The filters were divided into equal portions, which 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: 433, 690CC, 1547, 1572, 1632b, 1633b, 2709, 2710
- ▶ The errors of the detection of elemental concentrations were in the range of 2-20 %

# The determination of elemental concentrations in the phytoplankton matter

- ▶ 41 elements in the one sample were detected
- ▶ The elemental concentrations in empty filters (cleaned with distillate water) were subtracted from the values of concentrations in the whole samples

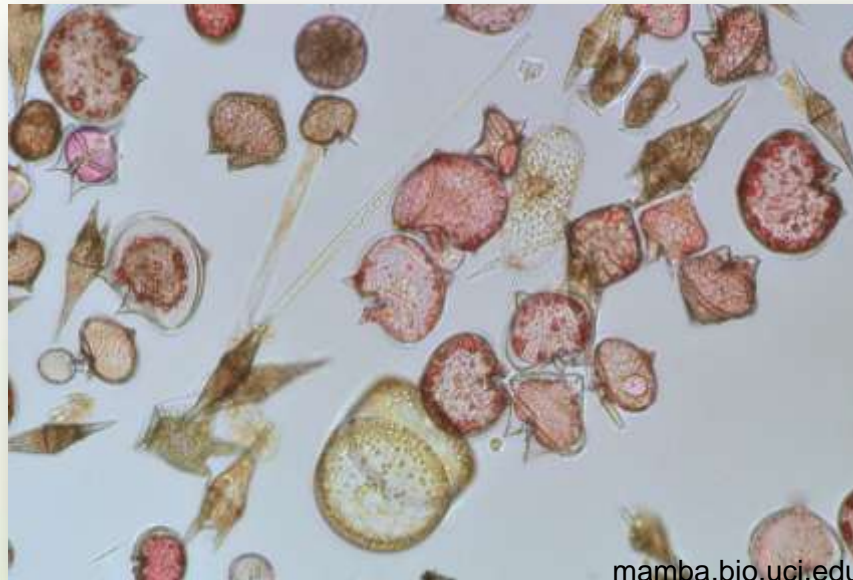
$$C_{element} = C_{calculated} - C_{blank}$$

If the  $C_{element} < 0$ , then this element was considered to not detected



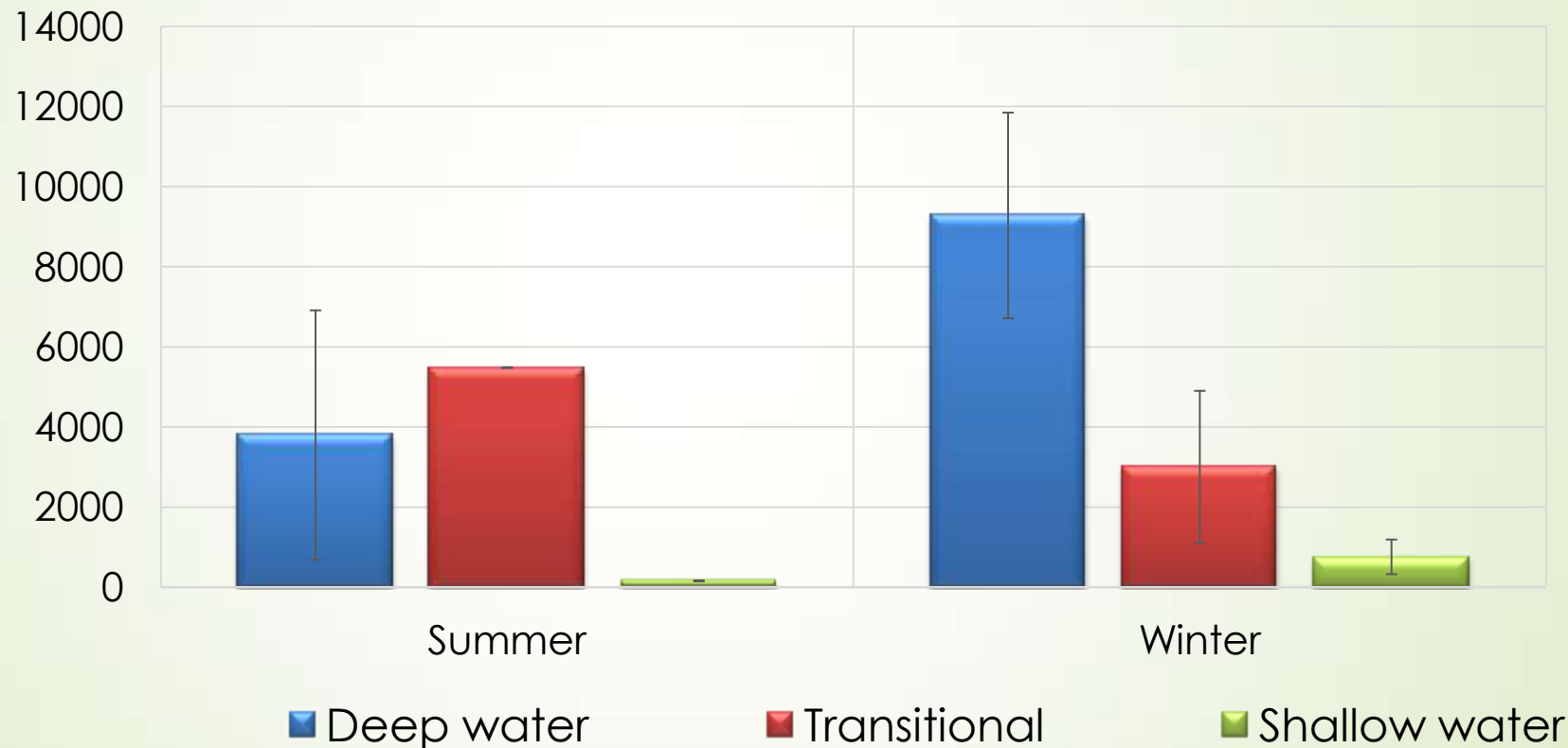
# How much species were in the whole sample?

- ▶ We studied more than 35  $\mu\text{m}$  organisms (mesh size of Nansen net)
- ▶ Minimal amounts of large zooplankton organisms (small diameter of mouth of Nansen net – 35 cm and slow vertical towing)
- ▶ We usually collected phytoplankton from 35 to 200  $\mu\text{m}$  size
- ▶ From 32 species of phytoplankton the most typical species (dinoflagellates) were represented by 5 species (*Neoceratium*, *Protooperidinium*)
- ▶ Abundance of one species is about 12 000 cells in one sample of phytoplankton (1,5 liter)



# Species structure of dinoflagellates in samples

**Average number of cells of *Protoperidinium* and *Neoceratium* in 1 liter of sample for different zones and seasons**

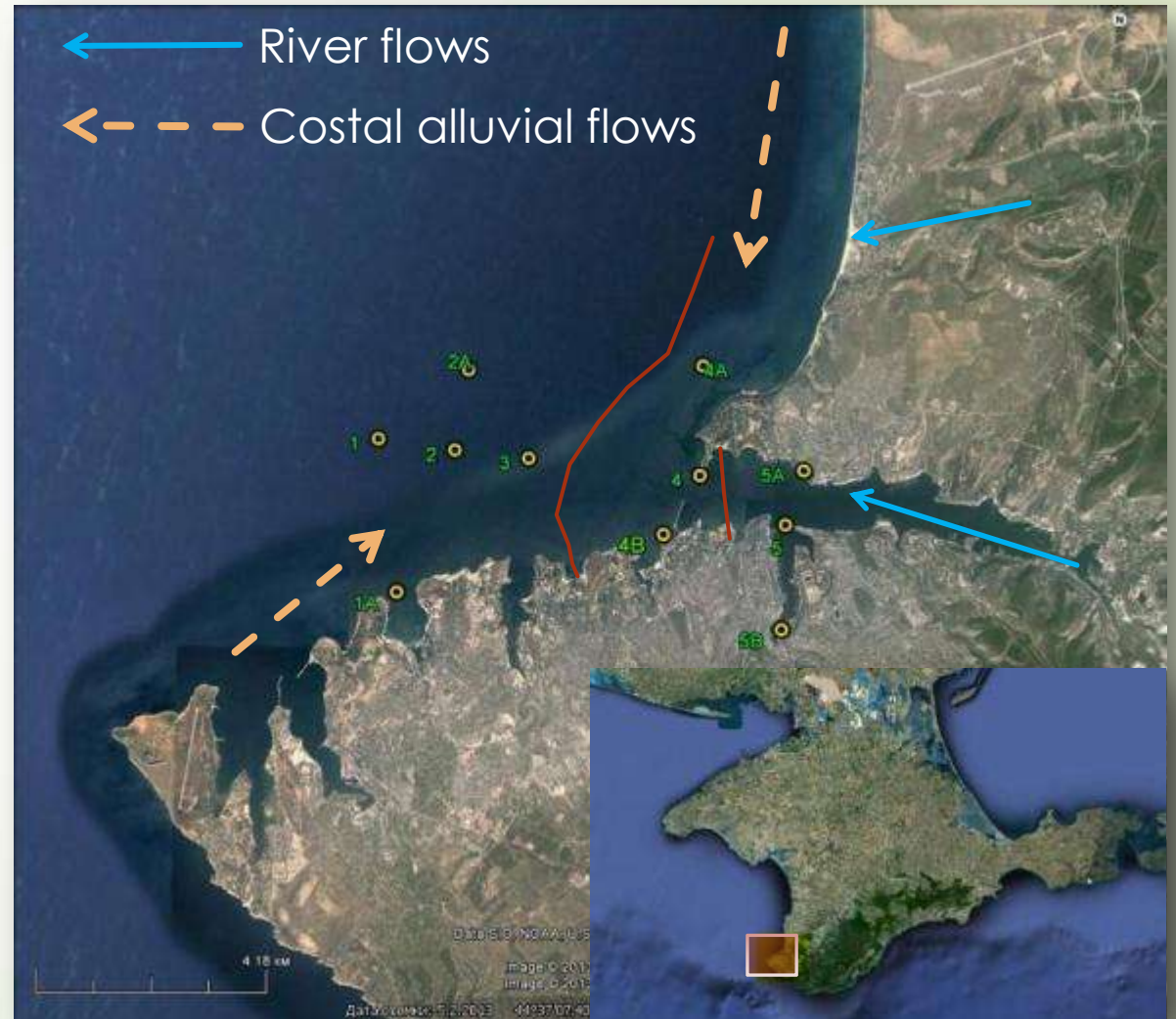


- Spatial variability of the elemental content depended on species structure in water
- Seasonal variability of the elemental content depended on periods of species' growth

# Spatial variability of elemental contents of phytoplankton

- Elemental Flows
- Terrigenous particles
- Transition zones

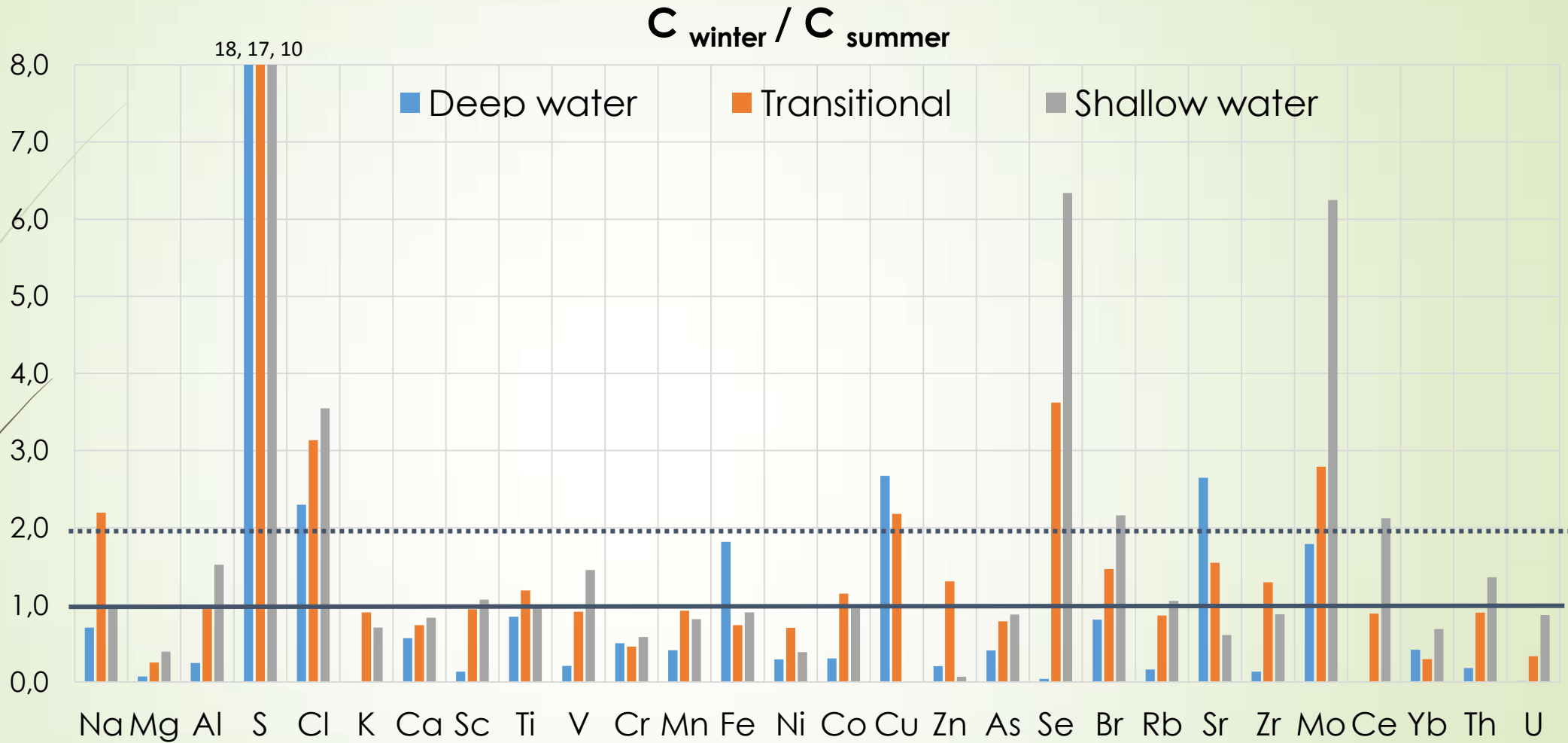
Transitional zone –  
buffer water area





# The comparison of elemental concentrations in different season

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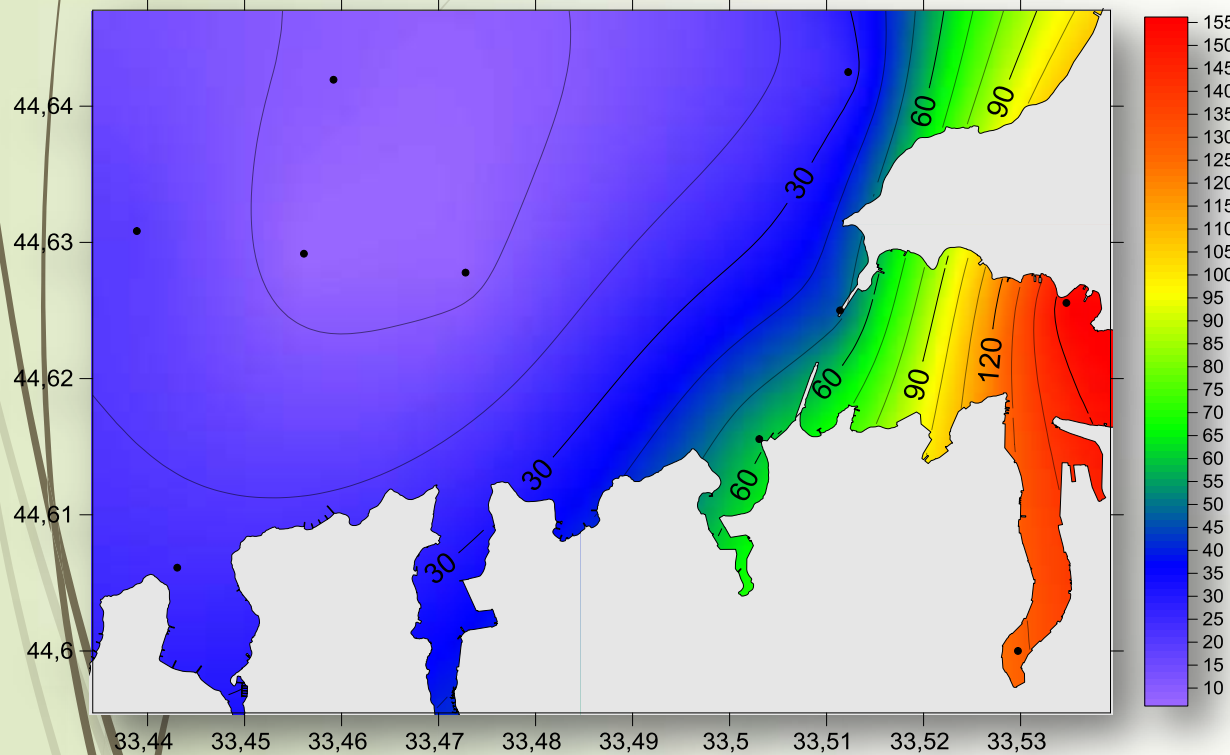
➤ Deep water: S, Cl, Cu, Sr increased more than 2 fold; Mg, Al, K, Sc, V, Cr, Mn, Ni, Co, Zn, As, Se, Rb, Zr, Ag, I, Ba, Cs, La, Ce, Sm, Tb, Tm, Yb, Hf, Ta, W, Au, Th, U decreased more than 2 fold

➤ Trasitional: Na, S, Cl, Cu, Se, Mo, W, Au increased more than 2 fold; Mg, Ag, I, Ba, Sm, Yb, U decreased

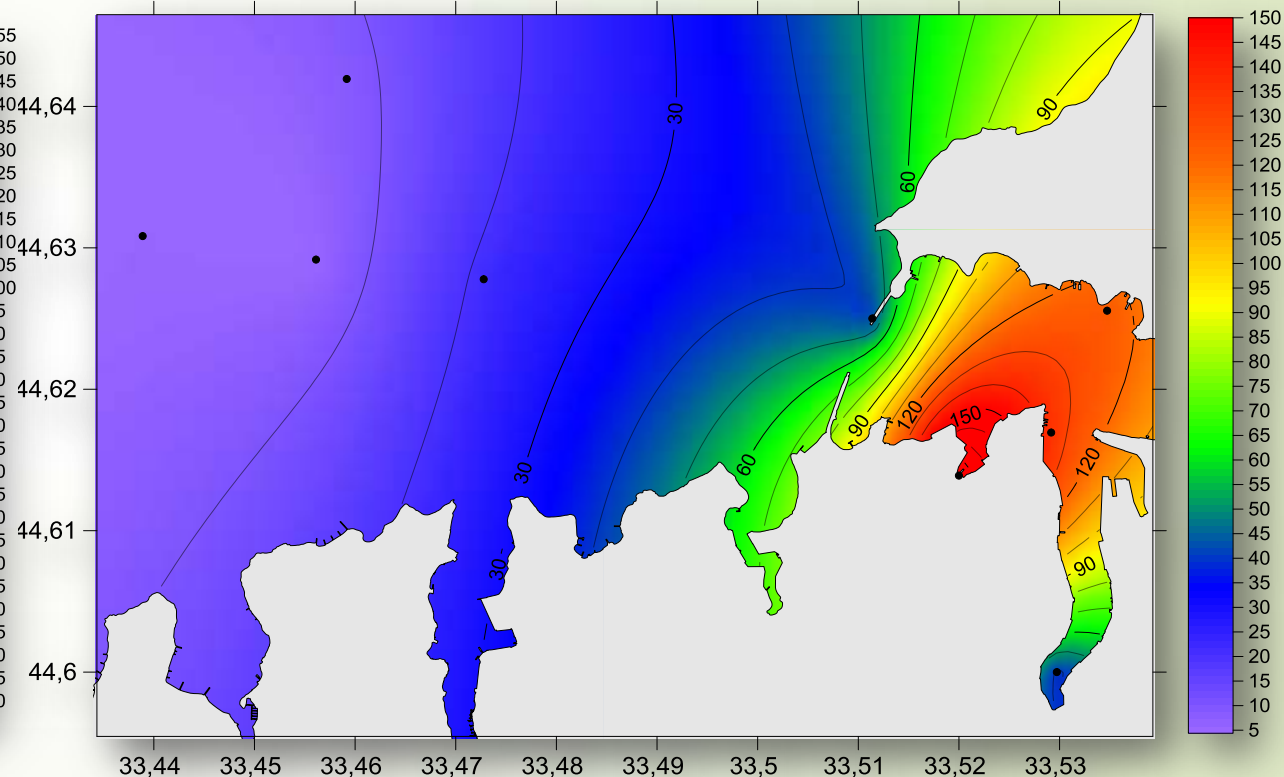
➤ Shallow water: S, Cl, Se, Mo, Ce increased more than 2 fold; Mg, Cu, Ag, Sm decreased

# Manganese – relatively constant

Summer



Winter

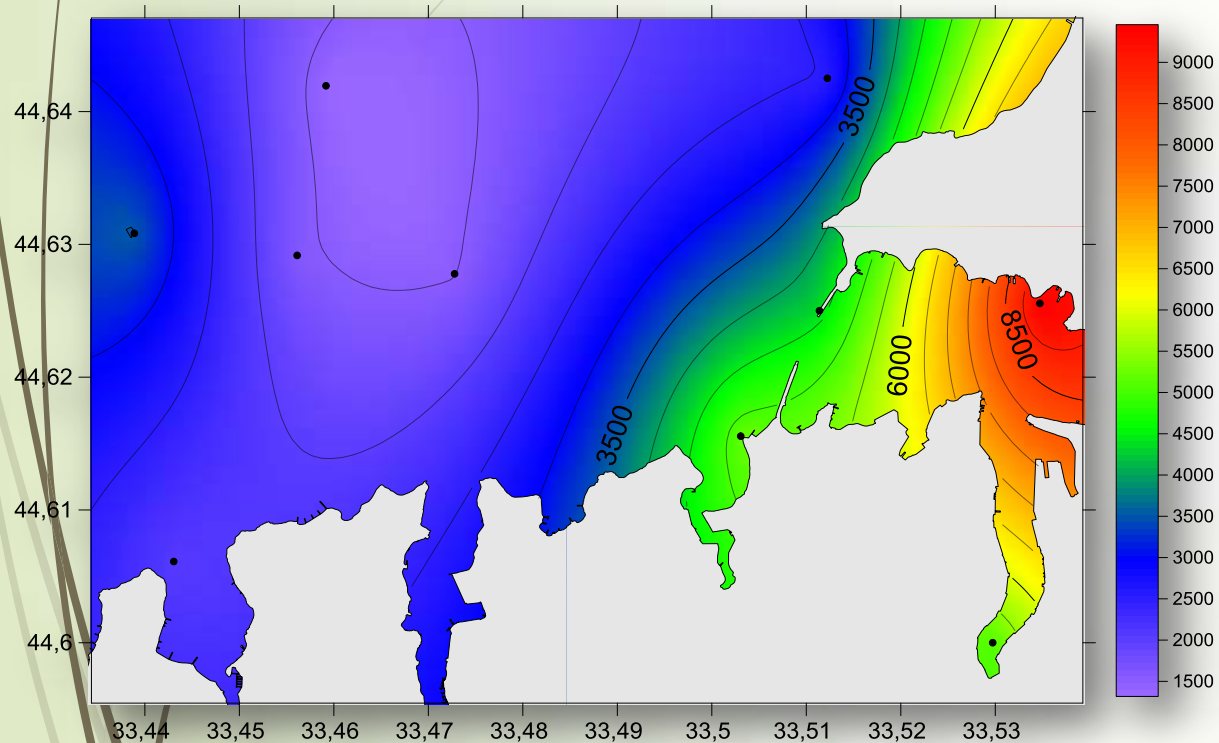


Such as Ca, Ti, V, Cr

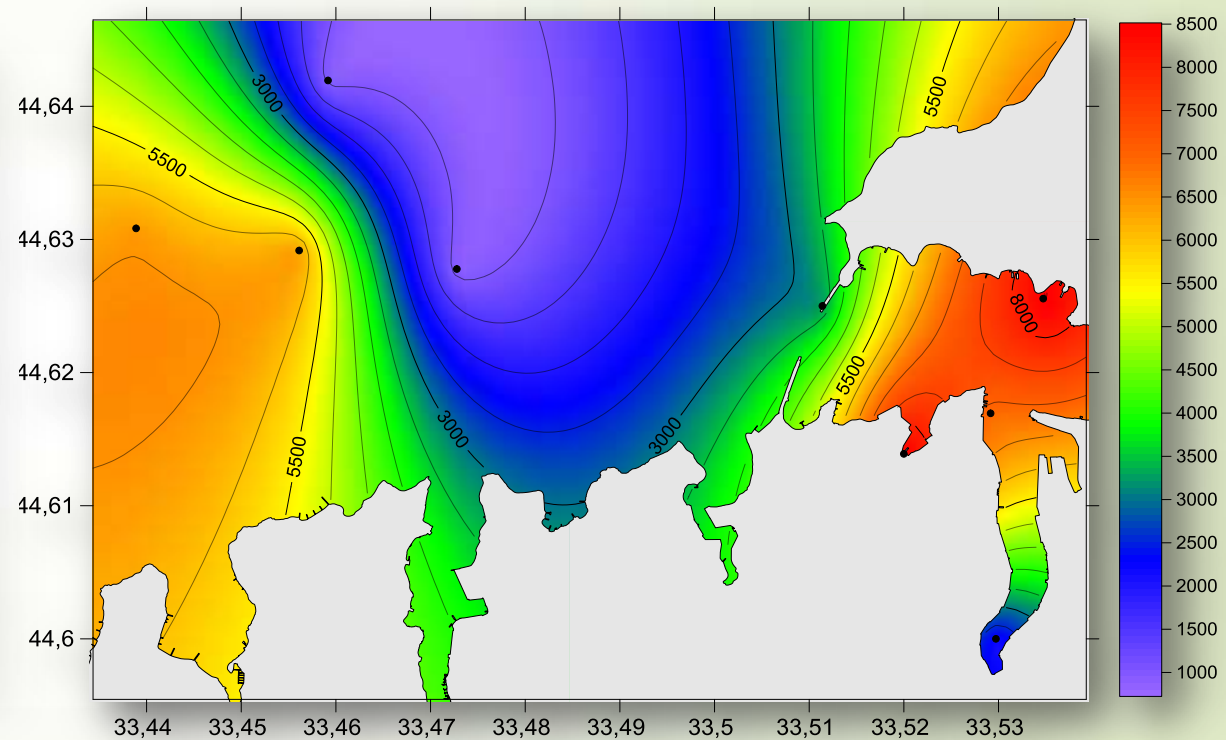
Higher in the biggest bay

# Iron – increased in deep water areas

## Summer



## Winter



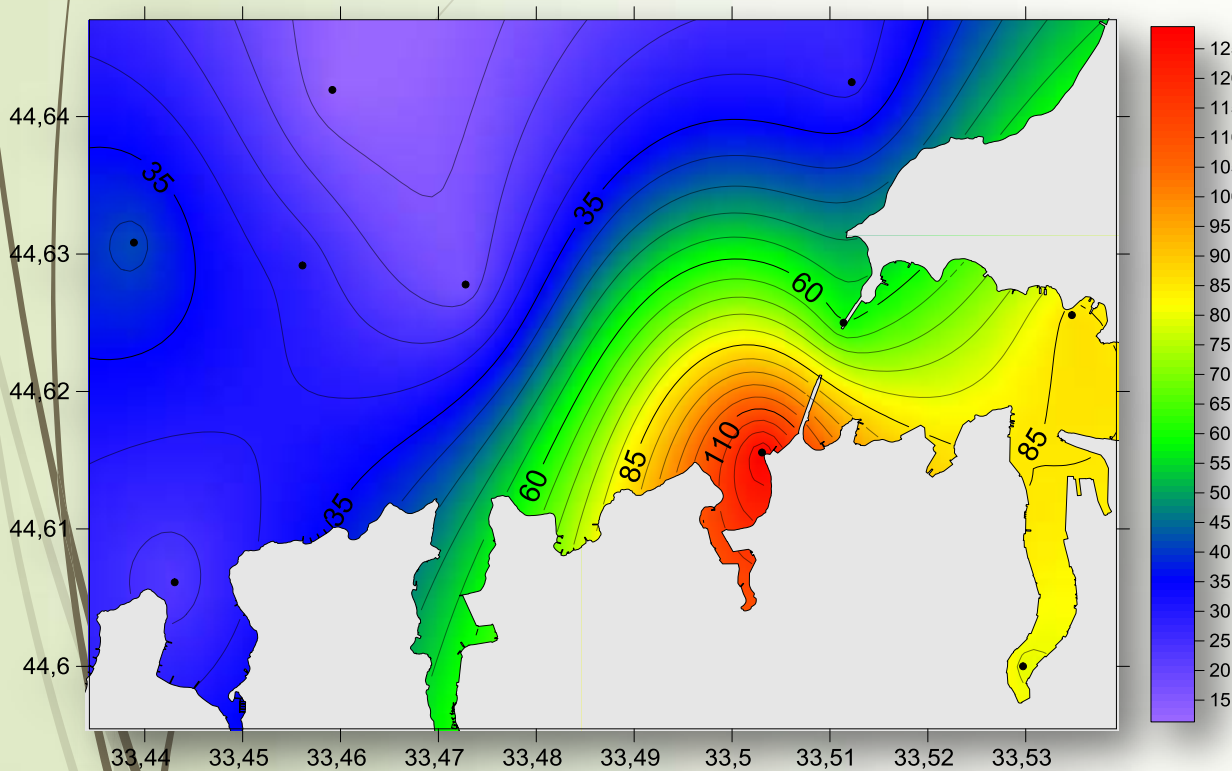
Cl, Cu, Zn, Sr

Influence of west elemental flow  
and winter resuspension of BS

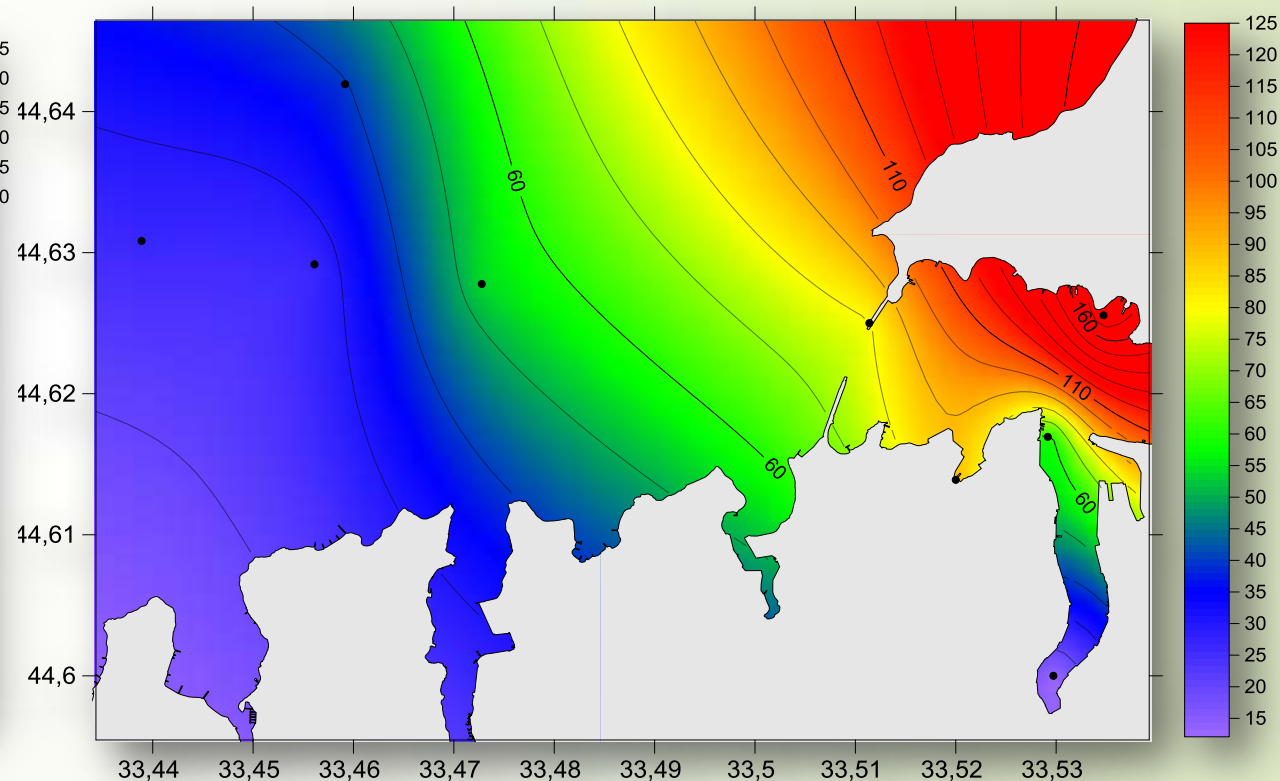


# Bromine – increased in different places

Summer



Winter

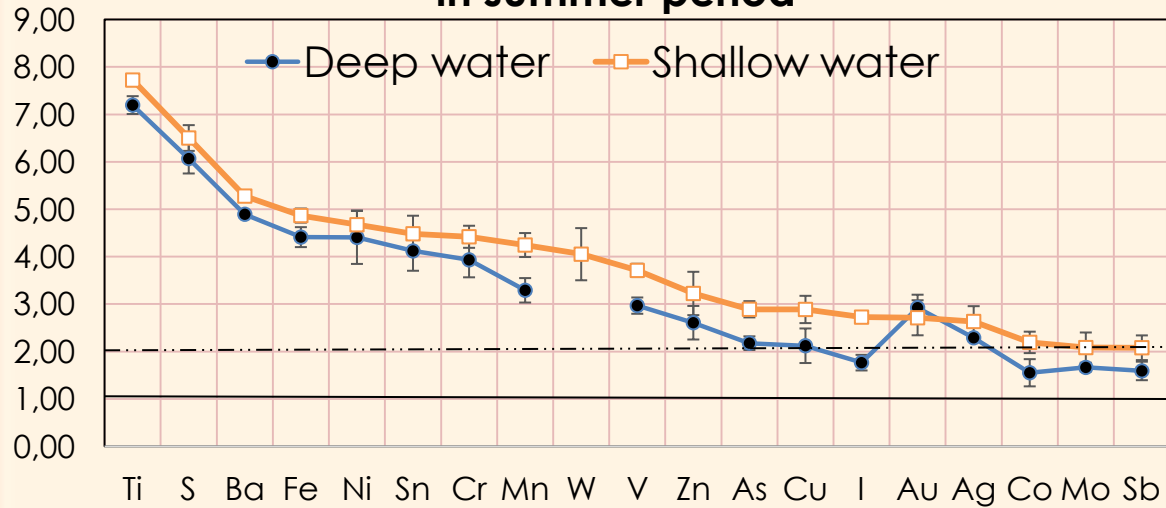


Cu, Se, Mo

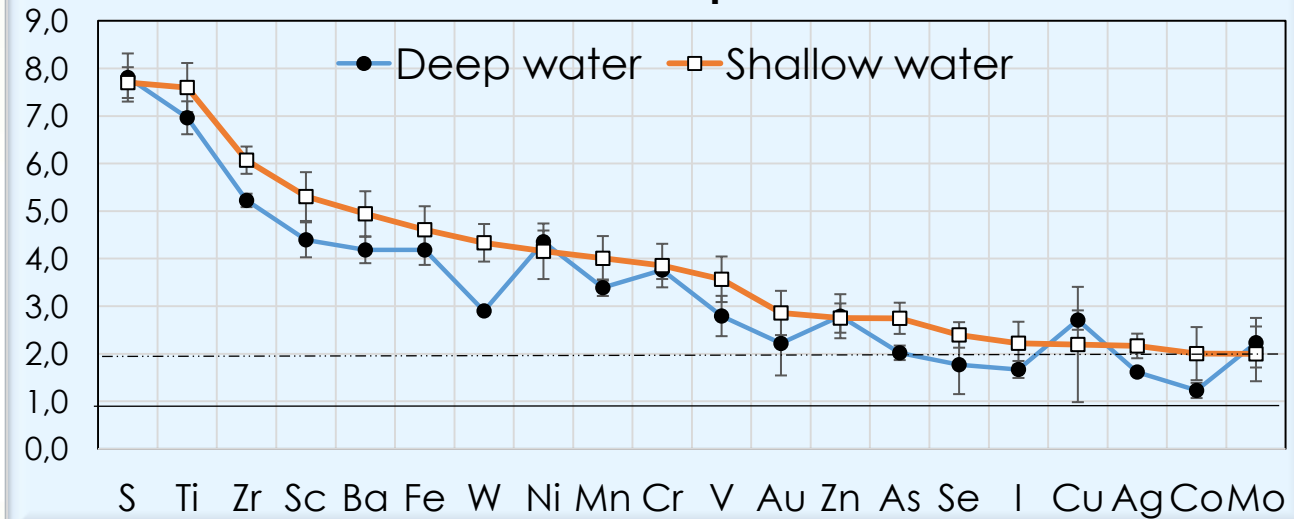
Terrigenous polluted flows in coastal zone

# Seasonal variability of biological accumulation

Coefficients of biological accumulation (Cb) in summer period



Coefficients of biological accumulation (Cb) in winter period



$$C_b = \lg(C_{sample} / C_{water})$$

Summer period:

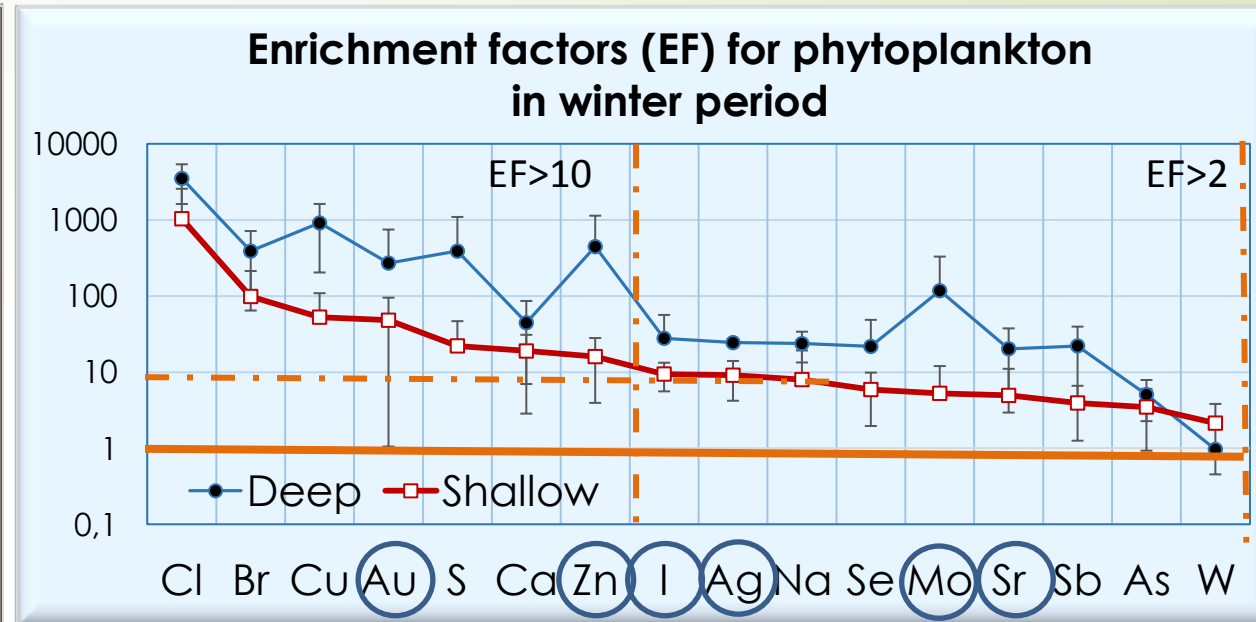
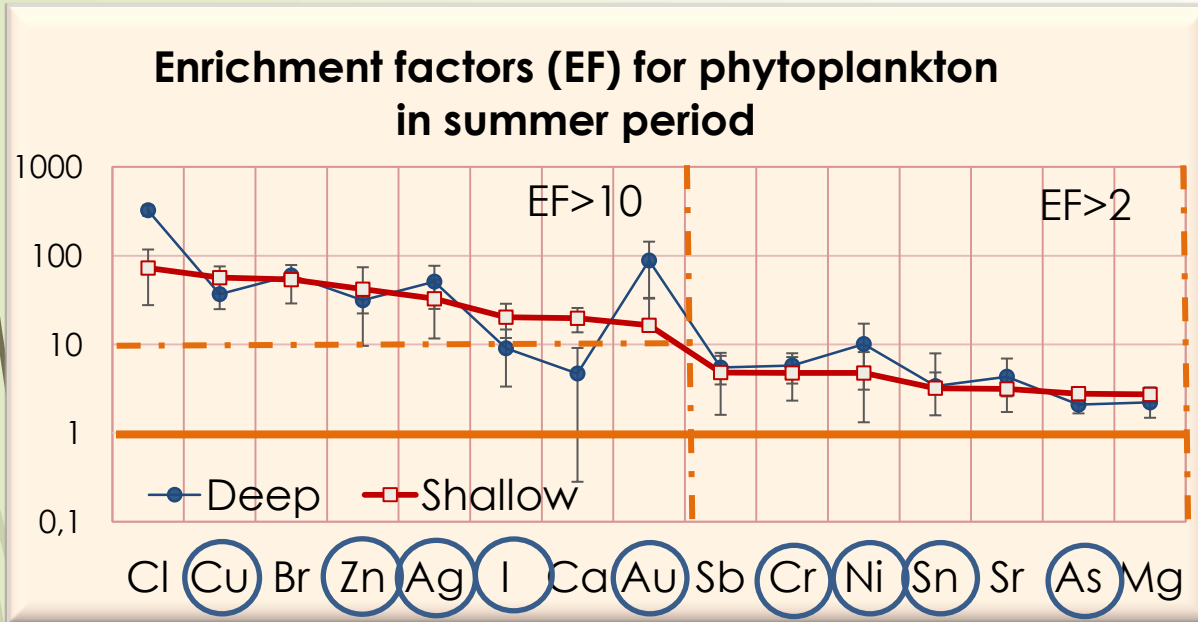
- Cb > 4: Ti > S > Ba > Fe > Ni > Sn > Cr > Mn > W
- Cb > 2: V > Zn > As > Cu > I > Au > Ag > Co > Mo > **Sb** > **U**

Winter period:

- Cb > 4: S > Ti > **Zr** > **Sc** > Ba > Fe > W > Ni > Mn > Cr
- Cb > 2: V > Au > Zn > As > **Se** > I > Cu > Ag > Co > Mo

Seasonal elemental accumulation properties of the phytoplankton: presence of Zr and Sc pointed on increasing amounts of suspended bottom sediments and terrigenous flows in phytoplankton matter

# Seasonal variability of enrichment factors



$$EF = \left( \frac{C_x}{C_{Sc}} \right)_{\text{sample}} / \left( \frac{C_x}{C_{Sc}} \right)_{\text{shale}}$$

Shale – modeled suspension of terrigenous material (Li, 1991)  
Sc – stable element; neutral to biochemical processes

## Summer period:

- EF > 10: Cl > Cu > Br > Zn > Ag > I > Ca > Au
- EF > 2: Sb > Cr > Ni > Sn > Sr > As > Mg

## Winter period:

- EF > 10: Cl > Br > Cu > Au > S > Ca > Zn
- EF > 2: I > Ag > Na > Se > Mo > Sr > Sb > As > W



# Elemental groups

Non-terrigenous elements, which highly accumulated in phytoplankton matter

► In Summer period: Cb>2, EF>10: Cu, Zn, Ag, I, Au;

Cb>2, EF>2: **Cr, Ni, Sn, As**

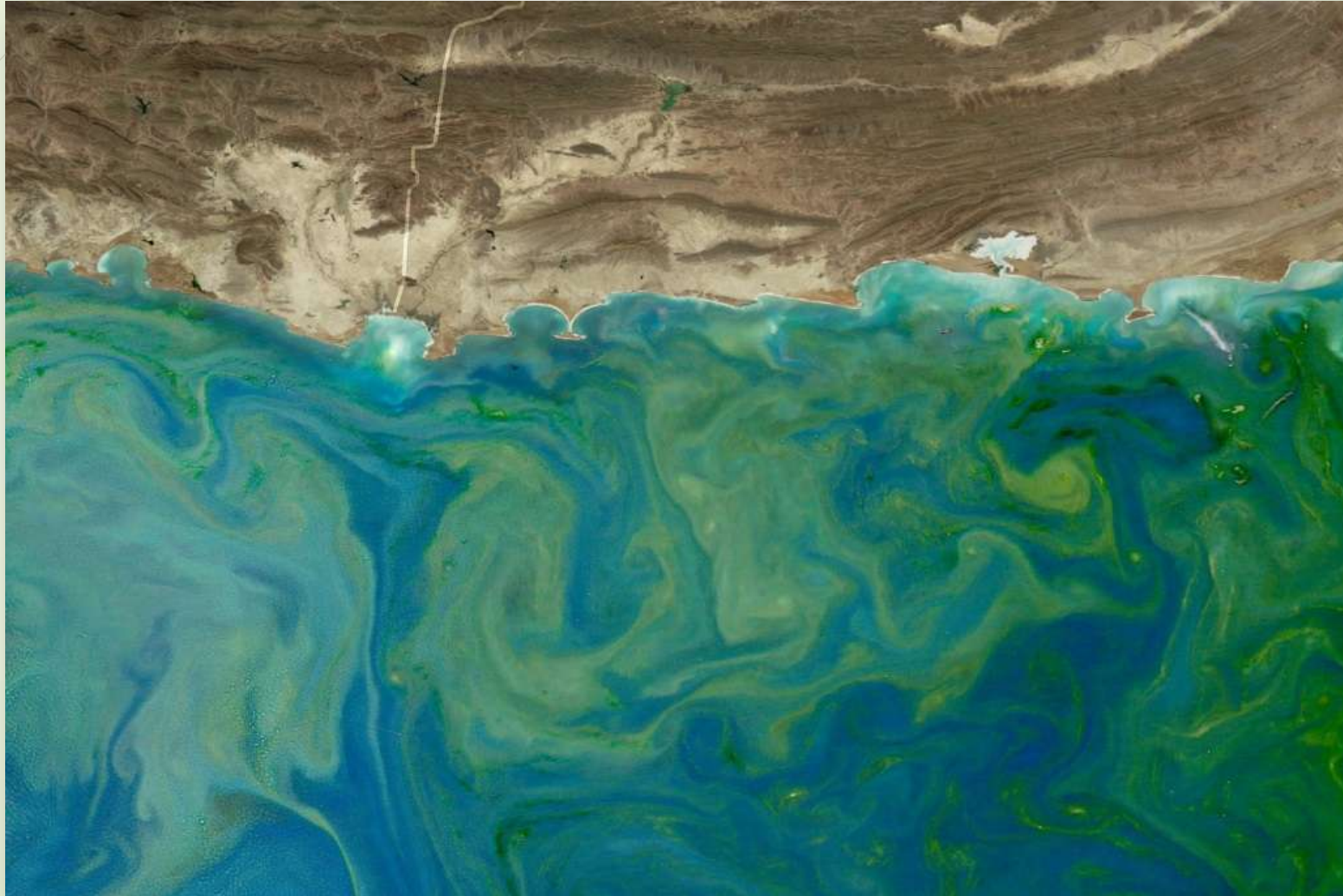
► In Winter period: Cb>2, EF>10: Au, Zn;

Cb>2, EF>2: I, Ag, **Mo, Sr**

# Conclusions

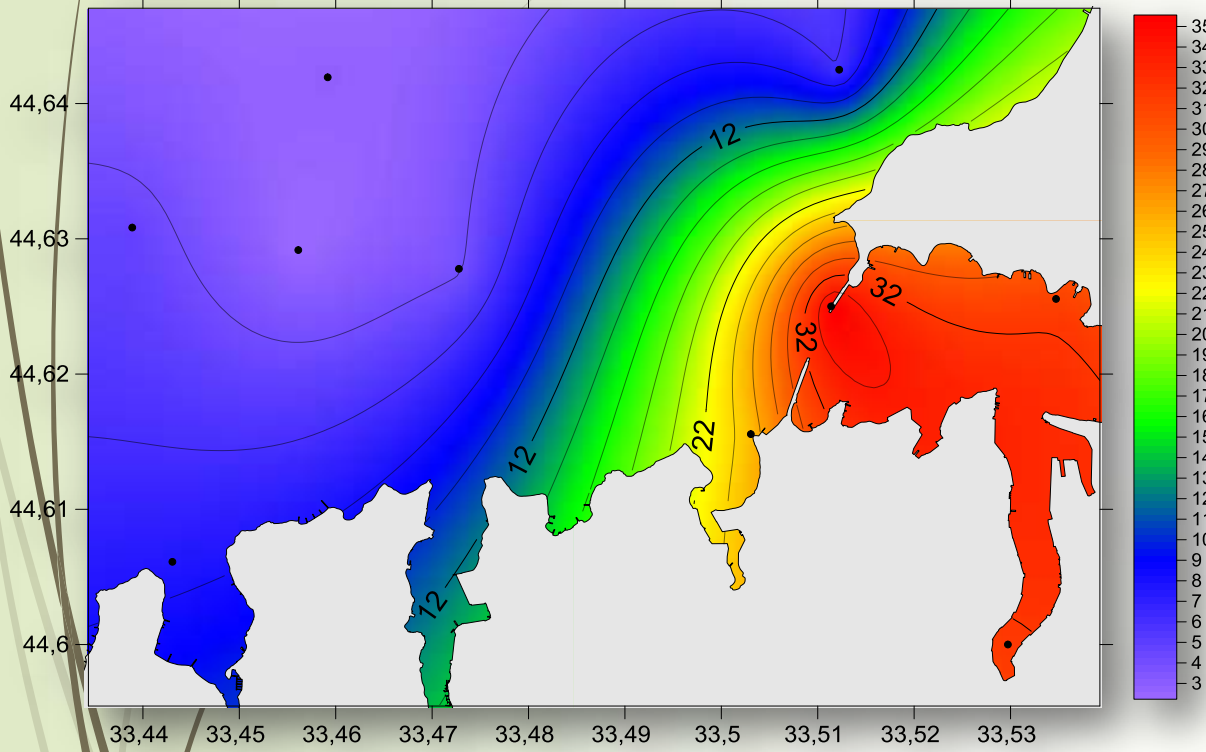
- ▶ Using neutron activation analysis for the first time the seasonal variability of the elemental content of phytoplankton studied in the coastal zone of the Sevastopol;
- ▶ The spatial variability of the phytoplankton contents depended on species structure and accumulation properties of different species in deep water and shallow zones;
- ▶ The seasonal variability of the phytoplankton contents depended on periods of storm activity, increasing of nutrients and changes the typical structure;
- ▶ During the winter and summer the resuspension of bottom sediments in the periods of storm activity led to increasing of concentrations of all elements except Na, S, Cl, Cu, Zn and Br at several stations
- ▶ In the winter season the concentrations of Na, S, Cl, Cu, and Mo increased by several times in comparison with the summer at the majority of stations. It probably connected with changes in hydrochemical structure of water;
- ▶ In winter the Mo and Sr were separated in group with non-terrigenous origin (to Cu, Zn, Ag, I, Au). It was probably associated with anthropogenic pollution flows or unstudied local biogenic factors

Thank for your attention!



# Iodine – increased in closed water areas

Summer



Winter

