

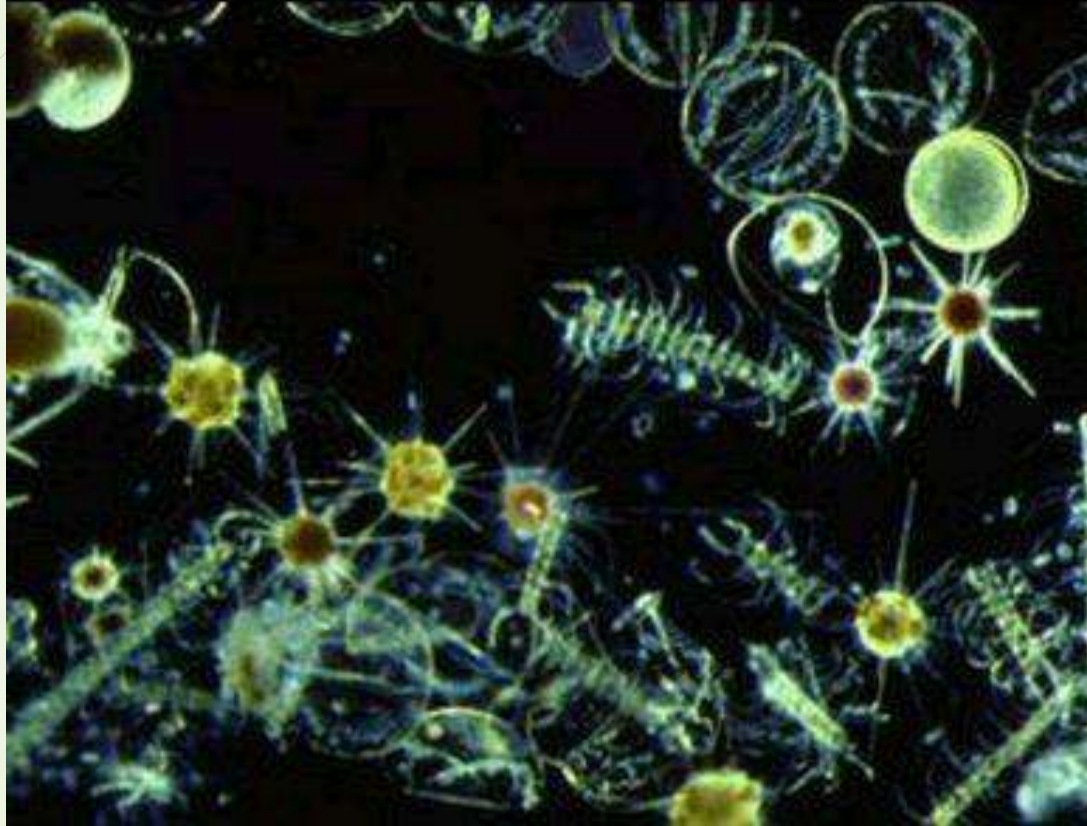
# Neutron activation analysis of the Black sea phytoplankton

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# Phytoplankton is a ...

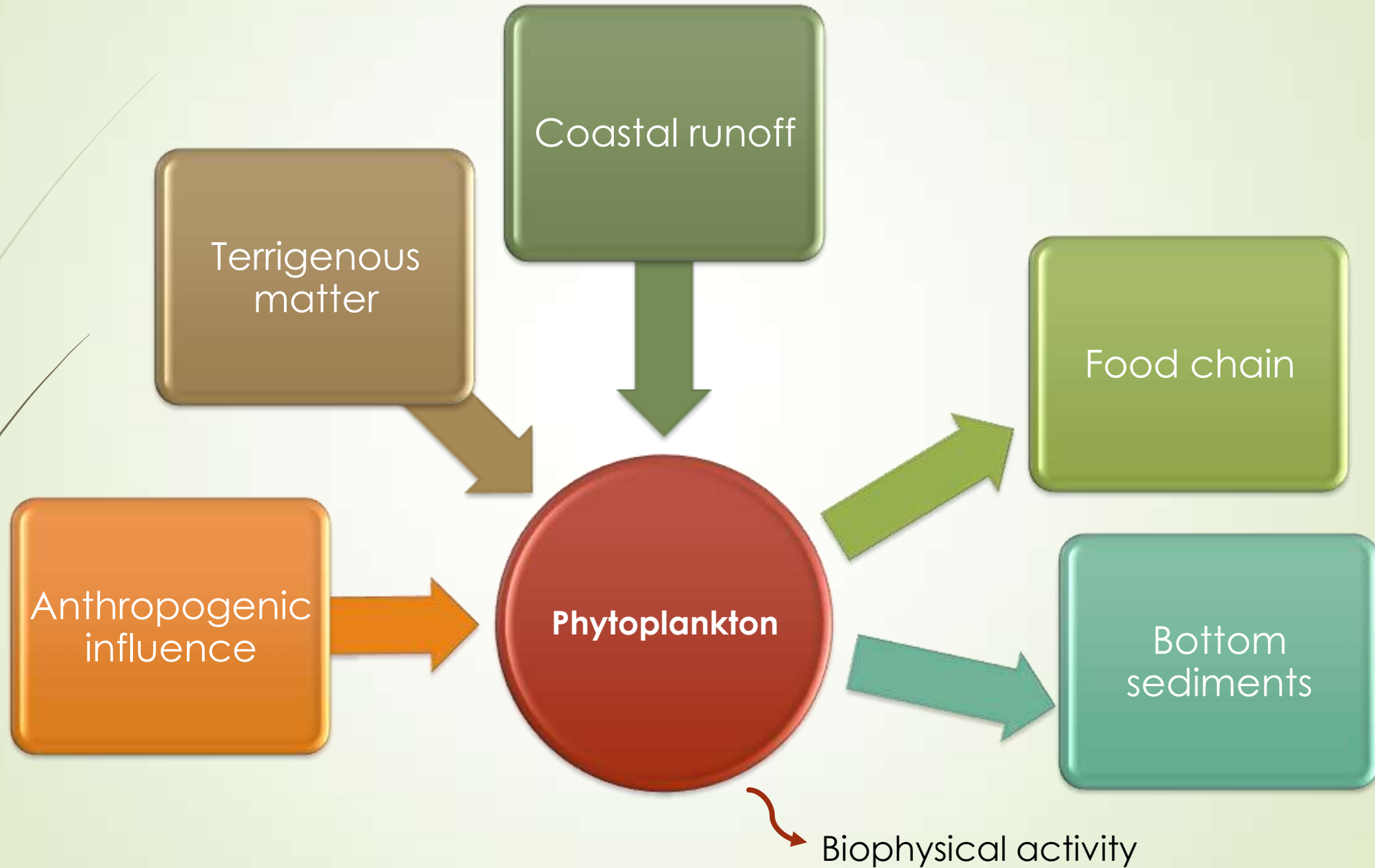


- ❖ Tiny
- ❖ Suspend (can't swim)
- ❖ Produce  $O_2$  like plants
- ❖ It is first eaten by others
- ❖ Its toxic effect may cause death other organisms

- Phytoplankton is a community of small suspended marine organisms, which photosynthesize. It contribute between 50 to 85 percent of the oxygen in the Earth's atmosphere. Size range is about 15 - 400  $\mu m$ . It determines the basic primary productivity of the marine ecosystems. So, it is important for environment and human health.

# Sources of elemental fluxes

2

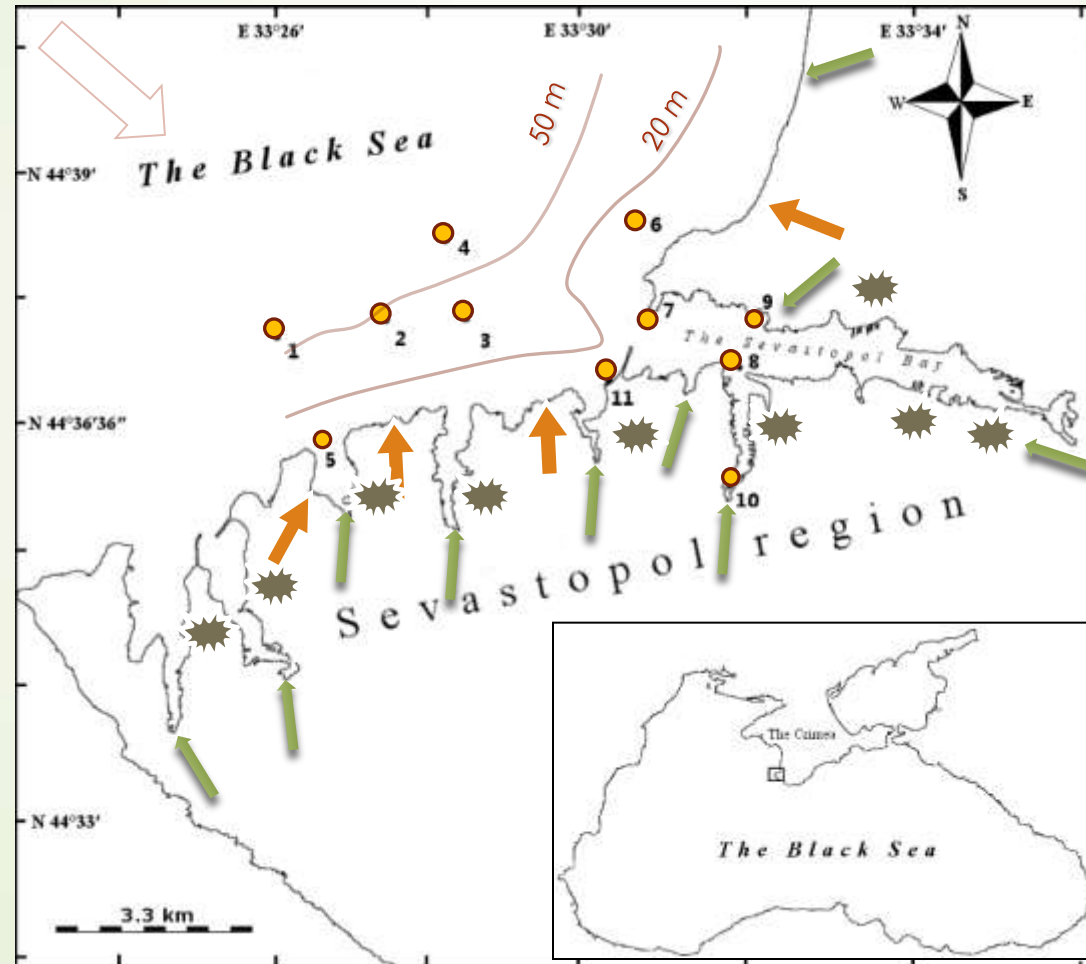


So, the main objective of this study is..

- To analyze functional state of phytoplankton community under the environmental chemical pressure in coastal zone of the Crimea by using neutron activation analysis and assessment of biophysical parameters of its activity
  - ❖ Sampling in period of its active growth in summer 2013 by using Nansen and small Juday net with 35 and 50  $\mu\text{m}$  mesh size
  - ❖ Measurements fluorescence and bioluminescence of living organisms on photometric complex “Svet” and fluorometer “Mega-25”-type
  - ❖ Preparing for NAA: vacuum filtration on 10  $\mu\text{m}$  5 cm paper filters, drying at room temperature and packaging for NAA
  - ❖ NAA on REGATA IBR-2 FLNP JINR: Short lived isotopes, long lived isotopes
  - ❖ Data analysis on program complex, designed in SNAAPI





# Sampling area: the Sevastopol coastal zone



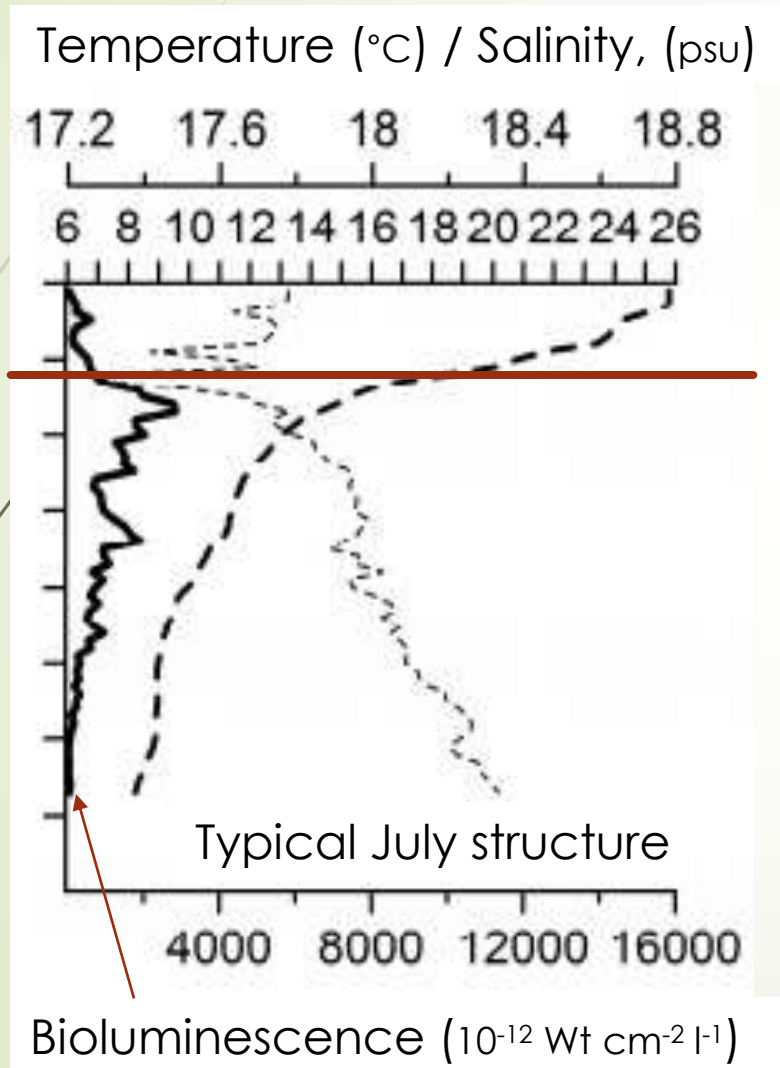
Phytoplankton from 11 stations

## Elemental sources in coastal zone:

-  - coastal and river runoff
-  - recreational zones of sandy and pebble beaches
-  - plants, docks discharge and repair facilities, etc.
- Underwater natural methane source
- Boat traffic, parking
- Cement coast protecting and metal structures
-  - Wind and wave activity of the sea water masses

• Sampling sites

# Environment conditions: hydrological structure



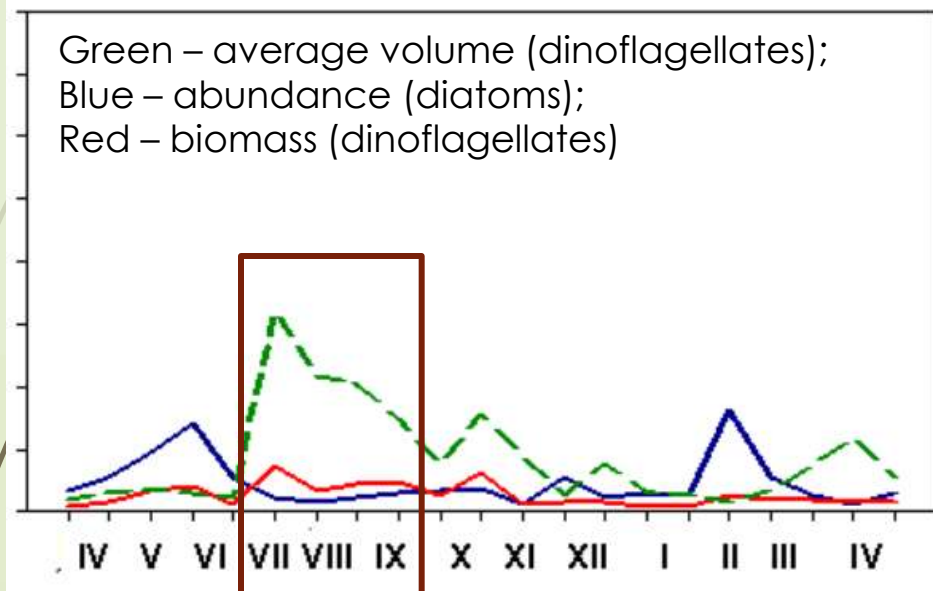
- Light
- Temperature
- Salinity
- Flowing activity (currents, waves and upwelling)
- Nutrients (N, P, O, Si) and microelements (Fe, Mn etc.)



- Transparency (on disk Secchi data)
- Biodiversity, taxonomic and size distribution
- Abundance and growth ratios of phytoplankton
- Functional state of phytoplankton community

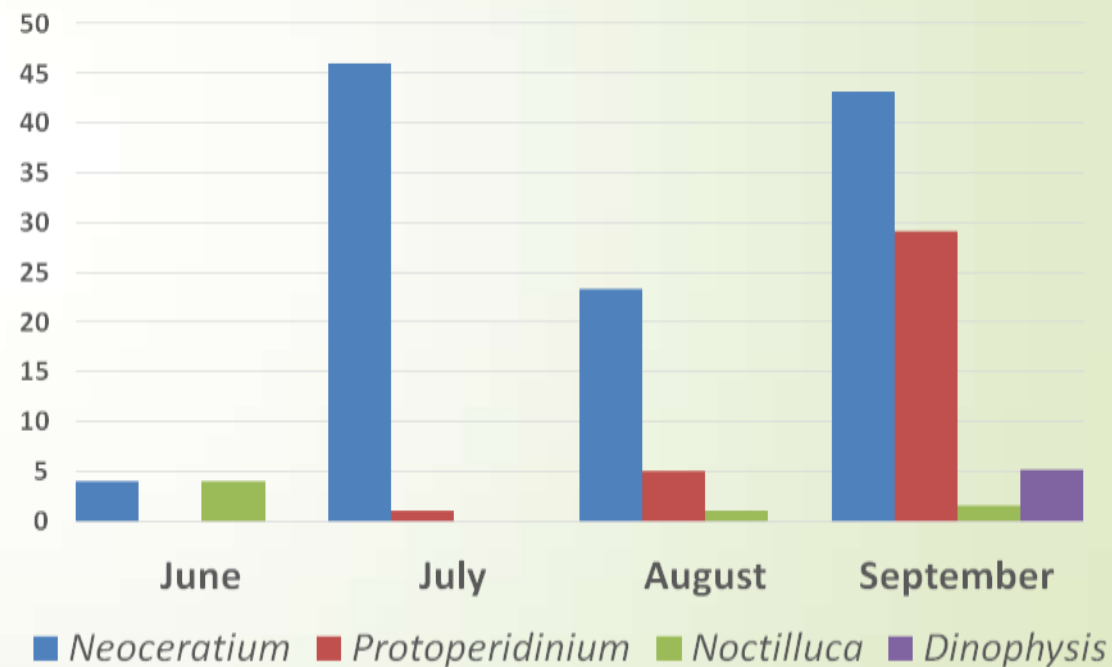
# Phytoplankton in coastal zone of the Sevastopol Bay

Seasonal variability  
of phytoplankton parameters



Eremeev et al., 2012

Average abundance of dinoflagellates  
species in 25 ml aliquot of net sample

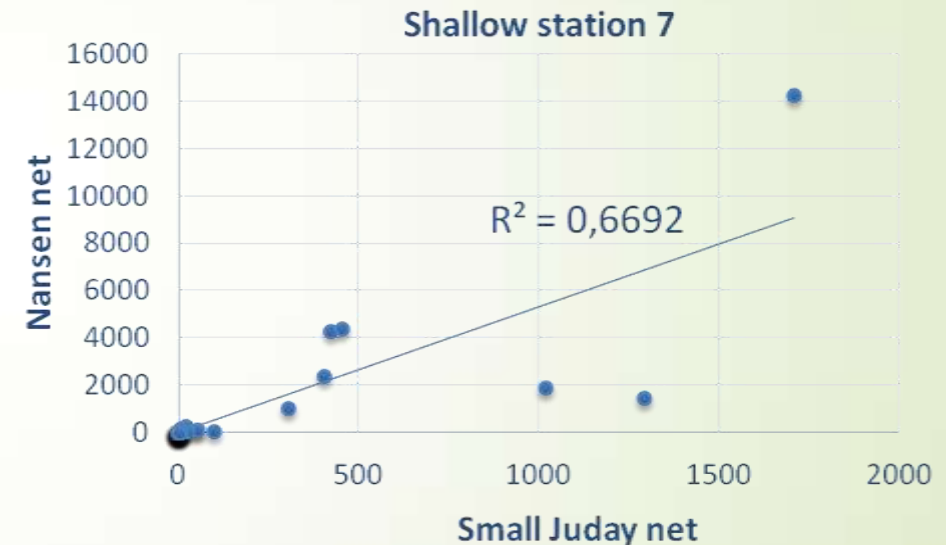
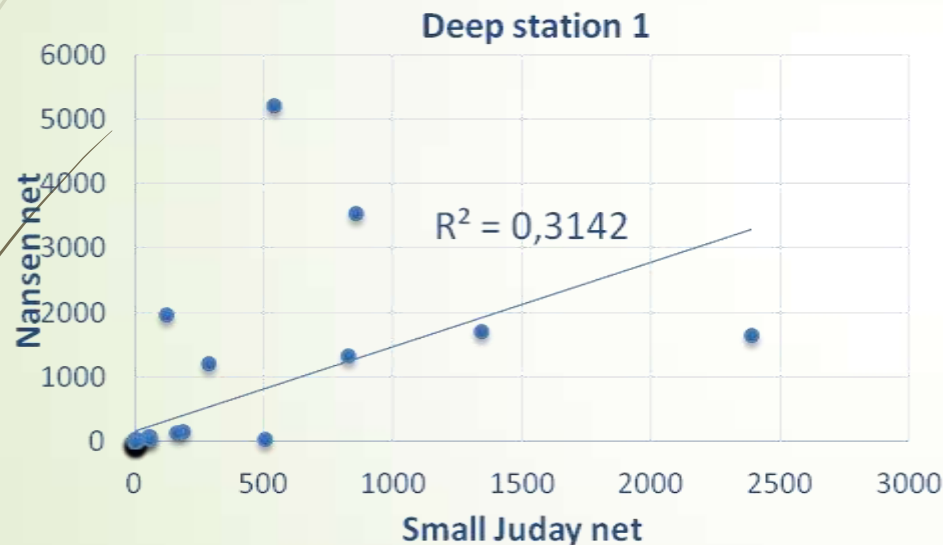


Original data

# Phytoplankton fractions comparison

Concentrations of all elements (46) by INAA

Small **Juday** net (50  $\mu\text{m}$  and 10 cm mouth) vs **Nansen** net (35  $\mu\text{m}$ , 35 cm diameter mouth)

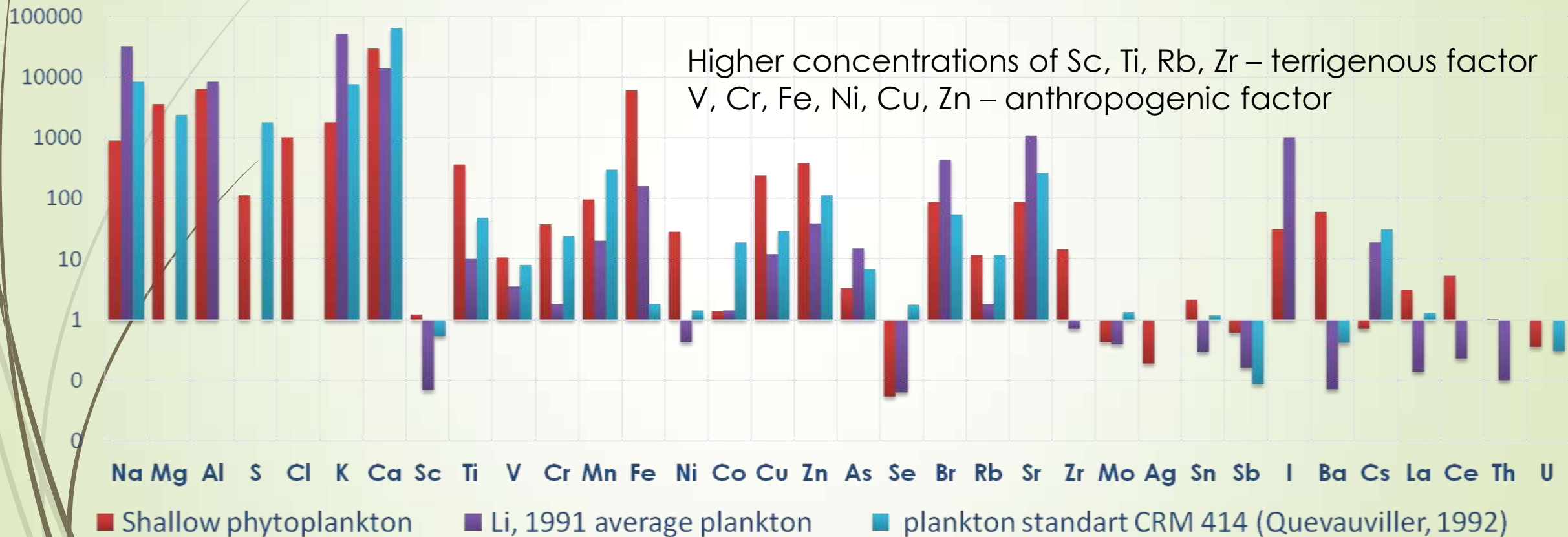


Phytoplankton in shallow coastal areas has minimal amounts of fractions (there is just a several typical species in high abundance) than in deep water zone



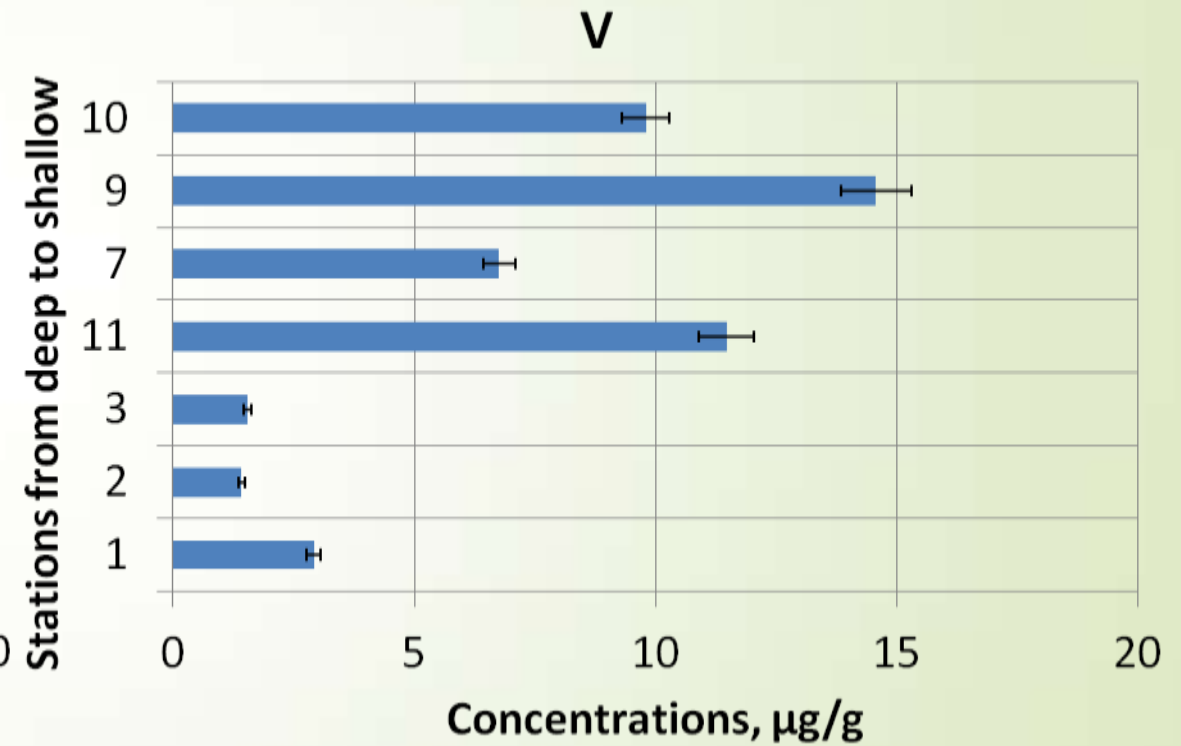
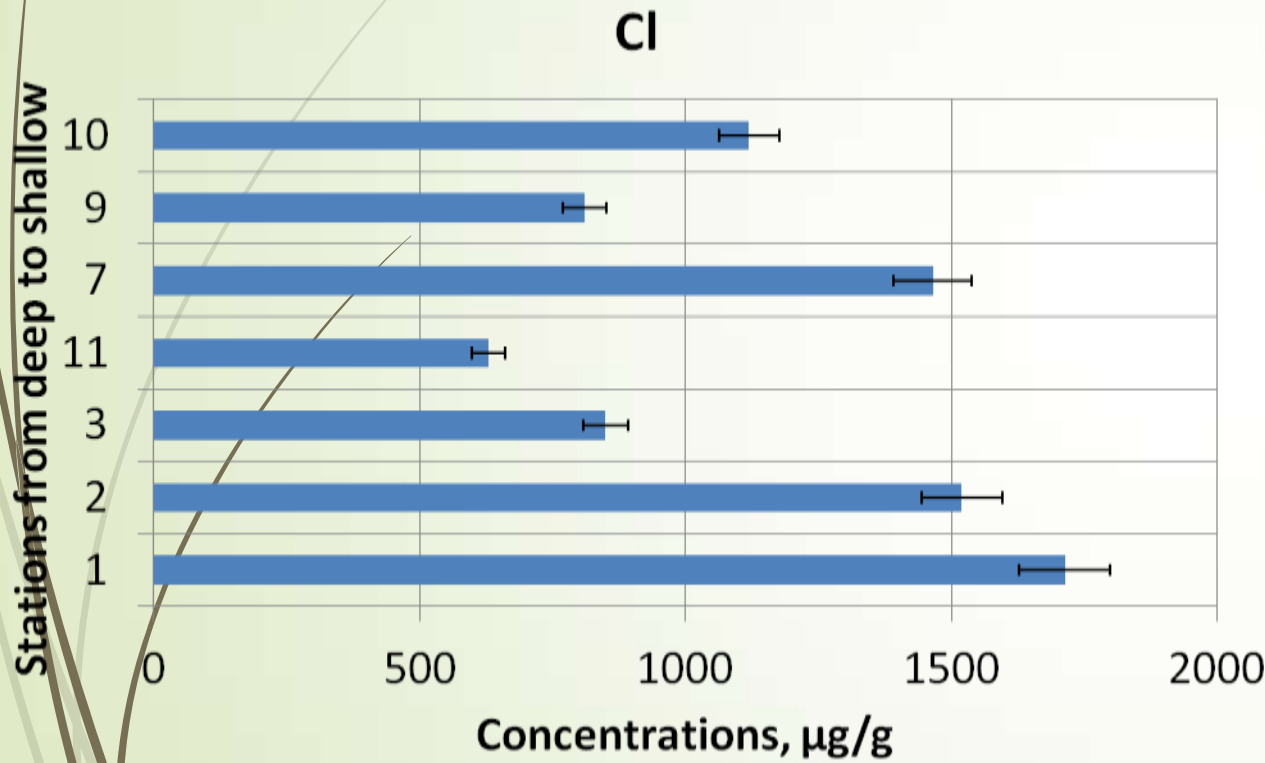
# Elements in phytoplankton

## Reference elemental concentrations in plankton



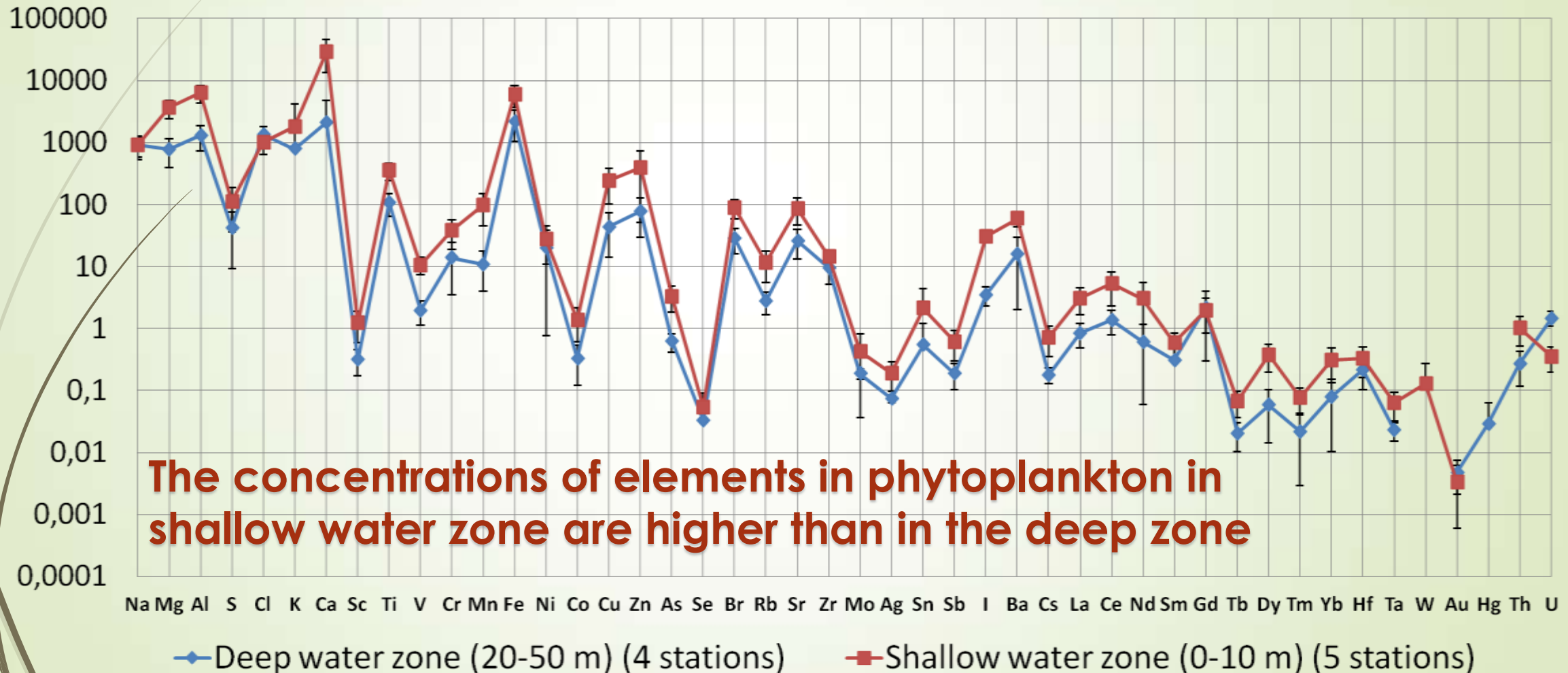
35 µm mesh size – large microphytoplankton

# Typical structure of elemental distribution



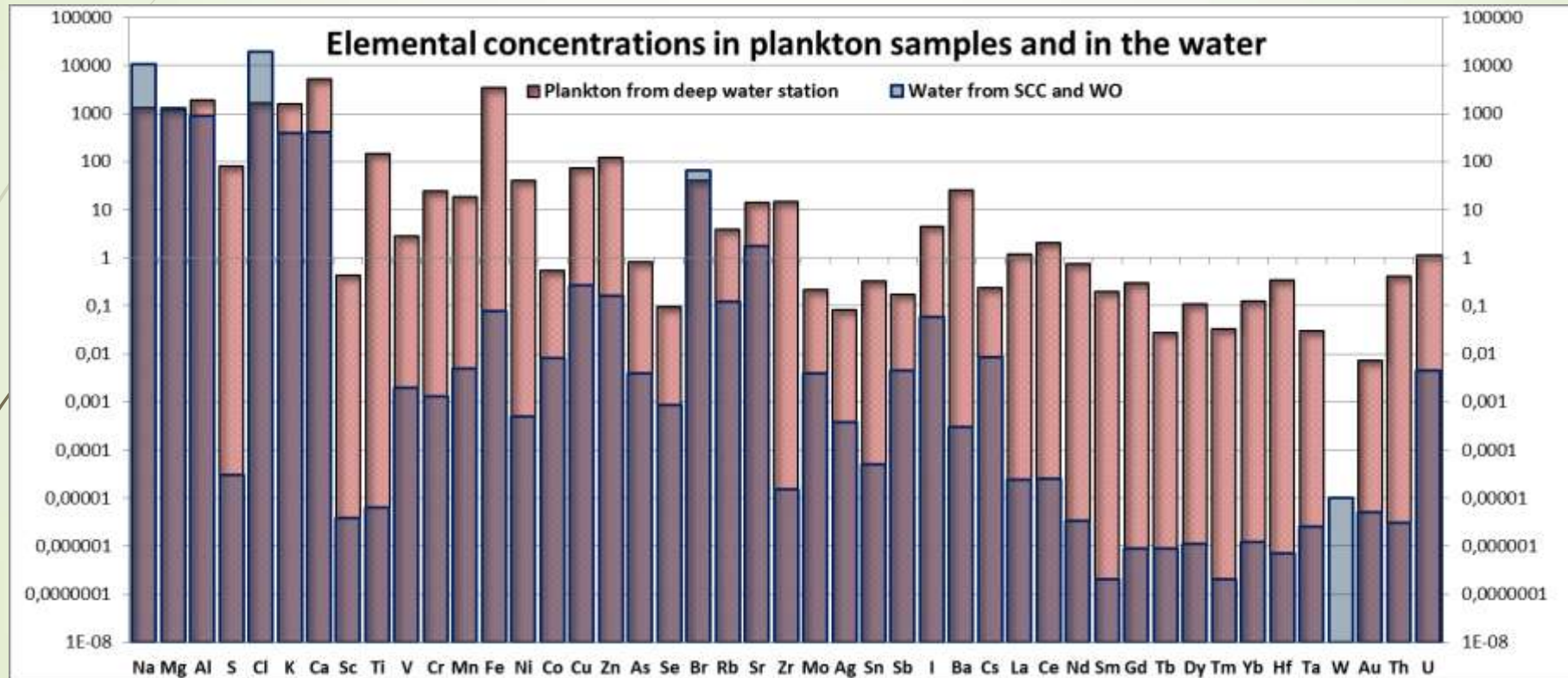
# Elemental concentration for different zones

## Average elemental concentrations in phytoplankton



# Where are from this all elements?

Surrounding sea water



**Red columns** - original data (plankton from deep water station (background station))

**Blue columns** - water from Ryabinin, 2003 and Nozaki, 1997.

# May be it was from terrigenous matter?

- Therefore the concentrations of the most elements must be relatively equal in phytoplankton and in average terrigenous matter

- ❖ *Average shale* – modeling terrigenous mixture matter

- ❖ *Element/Sc* ratio reflect the “pure” concentrations without a terrigenous matter (on Sc concentrations levels)

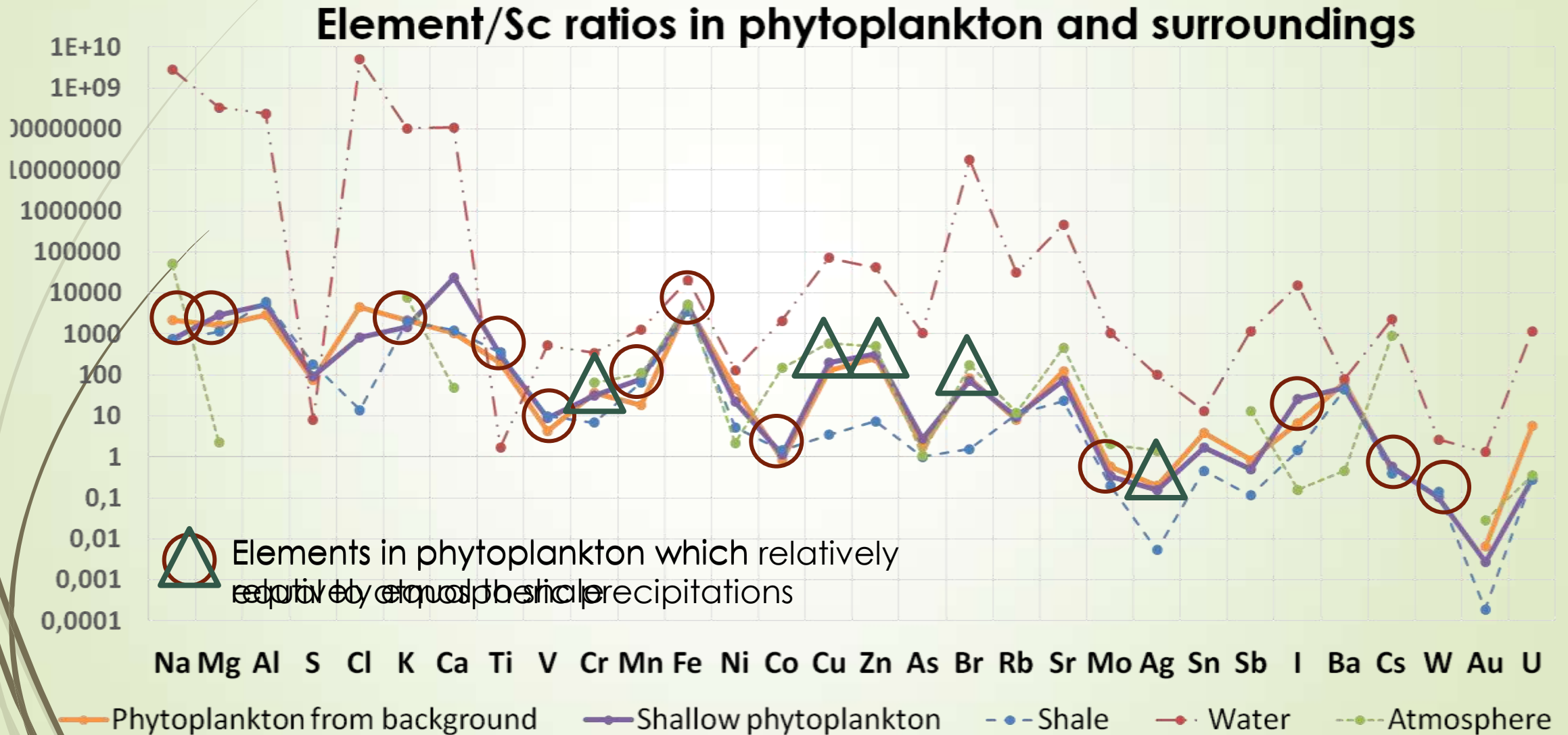
- ❖ *Enrichment factors*  $EF = \frac{\left(\frac{C_x}{C_{Sc}}\right)_{sample}}{\left(\frac{C_x}{C_{Sc}}\right)_{shale}}$ ,

reflect relations to terrigenous matter (*average shale*)



# Where are from this elements?

## Sources of elemental fluxes



# Elements/Sc ratios

## Relatively equal:

- To shale: Na, Mg, K, Ti, V, Mn, Fe, Co, Mo, I, Cs, W and Zr, REE, Th
- To atmosphere: Cr, Cu, Zn, Br, Ag
- Between shale-atmosphere: Ca, As, Rb, Sr, Mo, Ag, Sb, Au, U (sh)
- Between shale-water: Ni, Sn, Ba

### **Data:**

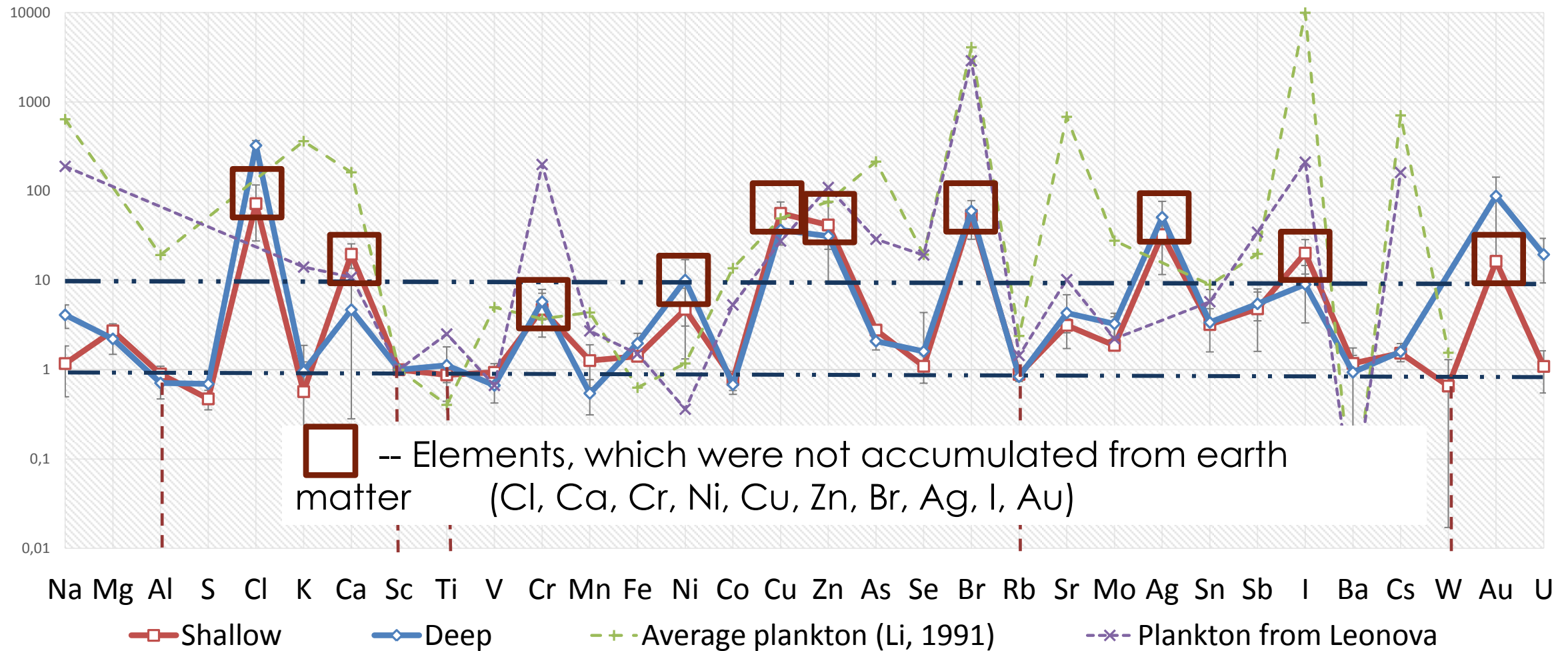
Shale – Li, 1991

Atmosphere – Ryabinin et al., 2011

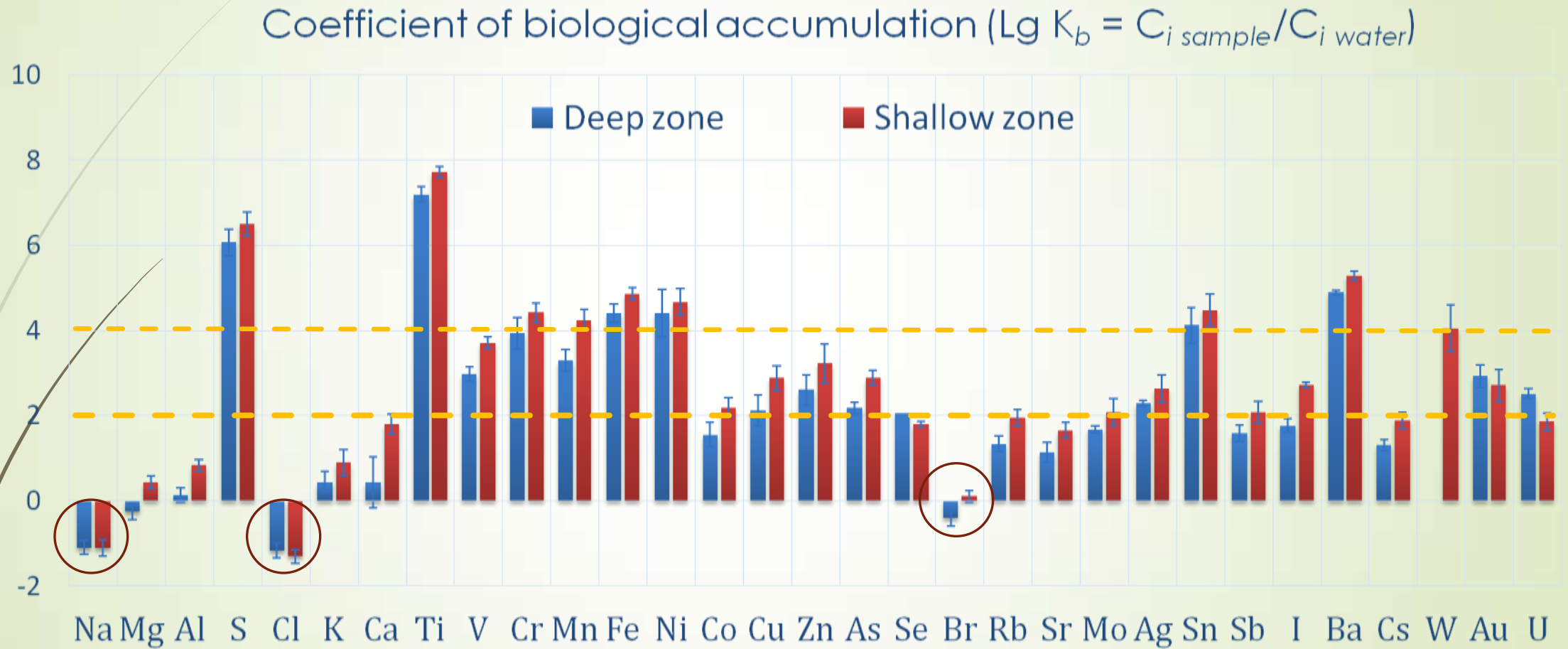
Water - Ryabinin et al., 2011, Nozaki, 1997

# Enrichment factors

EF for phytoplankton from different zones



# Elemental accumulation in phytoplankton



# Biological accumulation of elements by phytoplankton

- $K_b > 6$ : S, Ti
- $K_b > 4$ : **Cr**, Mn, Fe, **Ni**, Sn, Ba, W
- $K_b > 2$ : V, Co, **Cu**, **Zn**, As, Se, Rb, Mo, **Ag**, Sb, **I**, Cs, **Au**, U
- $K_b < 0$ : Na, Cl, Br

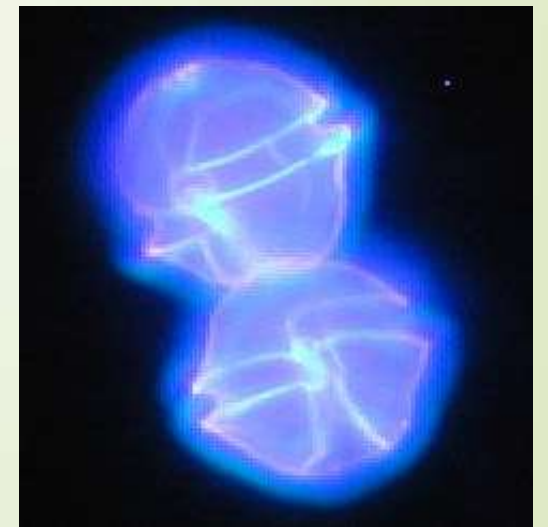
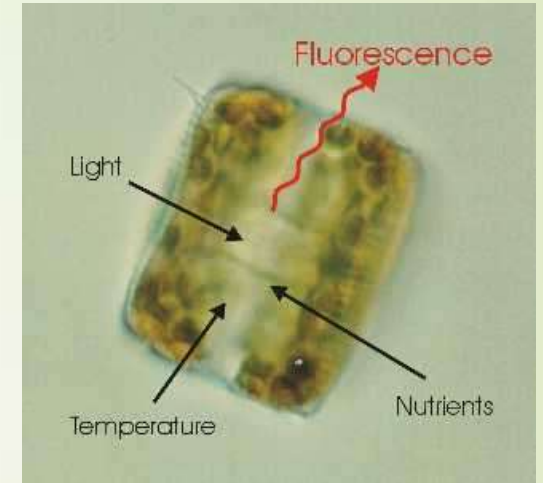
After all we have:  
Cr, Cu, Zn, Ag, I, Au  
+ Ni, Mo, Sb, Sn

❖ Elements with  $K_b > 2$  and more were concentrated by phytoplankton in greater degree than others

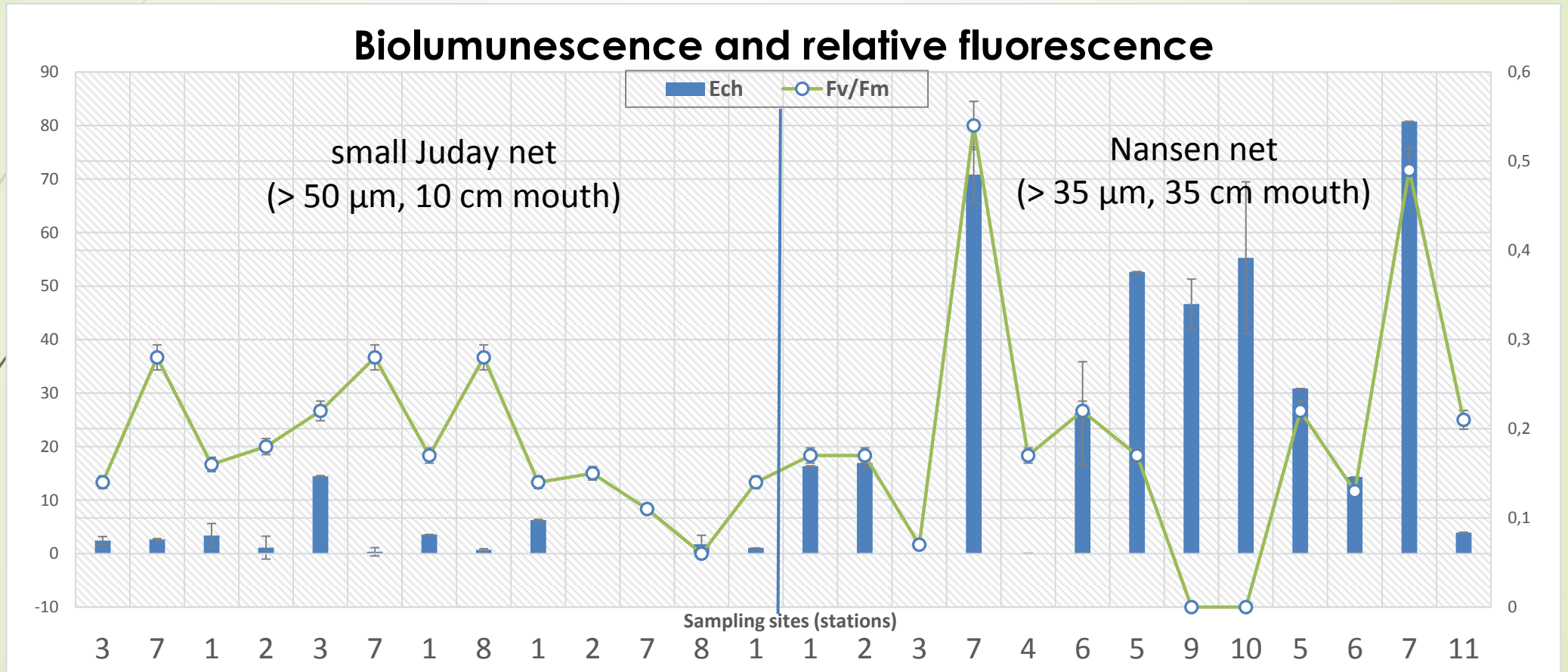


# Functional state of phytoplankton

- Phytoplankton organisms can emit **fluorescent** (in photosynthesis process) and **bioluminescent** light (several species)
- *Physiological processes which reflect functional state of closed communities:*
  - ❖ Fluorescence – when they are illuminated
  - ❖ Bioluminescence – when they are stimulated by waves, chemical affects, lights, x-rays etc.
- $F_v/F_m = (F_m - F_0)/F_m$  – Quantum yield of relative fluorescence of phytoplankton cells;
- $E_{ch}$  – Bioluminescent energy of phytoplankton under chemical stimulation (ethanol)



# Biophysical parameters of the phytoplankton activity



$F_v/F_m = (F_m - F_0)/F_m$  – Quantum yield of relative fluorescence of phytoplankton cells;  
 $E_{ch}$  – Bioluminescent energy of phytoplankton under chemical stimulation (ethanol)

# Biophysical parameters of the phytoplankton activity

In general view (on 30 samples):

- Bioluminescent energy under chemical stimulation correlated with concentration of **As** (0,62), **I**(0,77)
- Quantum yield of relative fluorescence correlated with **As**(0,63), **I**(0,7)

After excluding terrigenous and “water” elements, excluding small Juday samples, we analyzed results by PCA:

	Factor 1	Factor 2
<b>Biotic factor</b> { <b><math>F_v/F_m</math></b>	0,90	0,28
<b><math>E_{ch}</math></b>	0,97	-0,11
<b>I</b>	0,73	0,56
<b>Cr</b>	0,28	0,74
<b>Anthropogenic factor</b> { <b>Cu</b>	-0,20	0,83
<b>Zn</b>	0,23	0,46
Expl.Var	2,5	1,85
Prp.Totl	0,40	0,31



# Conclusions

- Major elements in shallow zone are terrigenous origin and extend to zone by coastal runoff, atmospheric precipitation and others ways
- The obtained results show that anthropogenic activity influence in phytoplankton exhibit in elemental pressure (Cr, Cu, Zn, Ag, Au and less Mo, Sb) on phytoplankton community and accumulated in living matter more than in terrigenous matter (on concentration levels)
- Bioluminescent and fluorescent activity of coastal phytoplankton are high in shallow water, but low in polluted shallow stations:
  - ❖ high abundance of diatoms and dinoflagellates in areas with big amounts of biogenic elements
  - ❖ Summer period of phytoplankton activity
  - ❖ Biotic factor (biophysical parameters and iodine concentrations) is small for medium deep water areas
- Functional state of coastal phytoplankton communities is influenced by hydrophysical and hydrochemical properties of the water mass and geochemical impact of the matter with terrigenous and anthropogenic origin



A satellite image of the Mediterranean Sea and surrounding landmasses. The sea is a deep blue, contrasting with the green and brown of the land. A red arrow points from the left edge towards the center. On the far left, there are several thin, curved, light-colored lines. The text "Thanks for your attention!" is centered over the sea in a white, bold, sans-serif font.

**Thanks for your attention!**

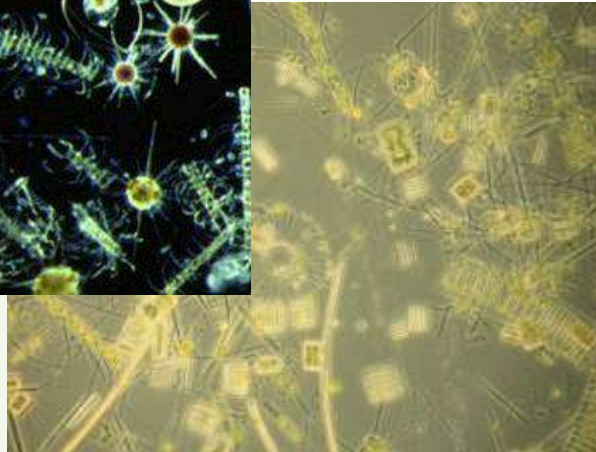
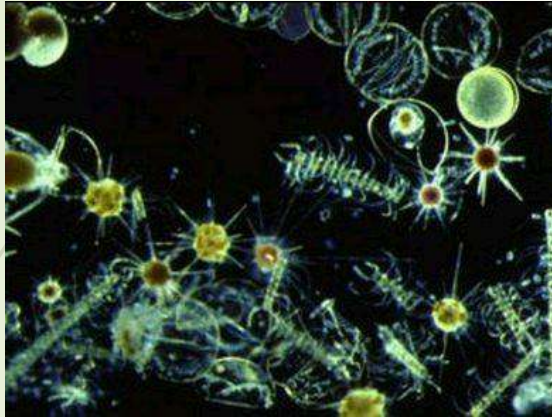




For questions



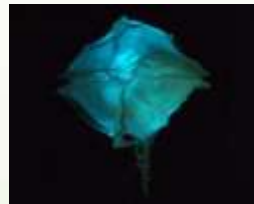
# Phytoplankton: what is it?



Marine phytoplankton is the most important producer of organic substances and the rate at which energy is stored up by these tiny organisms determine the basic primary productivity of the marine ecosystem. Phytoplankton are critical to other ocean biogeochemical cycles, as well. They take up, transform, and recycle elements needed by other organisms, and help cycle elements between species in the ocean.

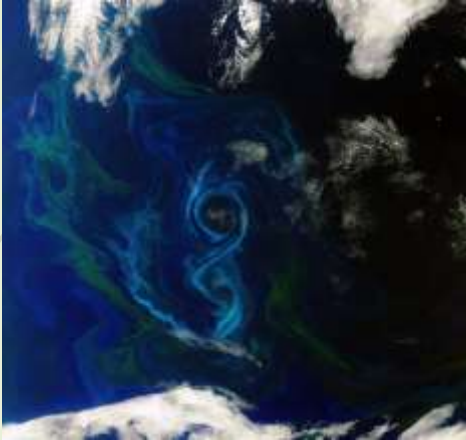
**Diatoms** are important oxygen producers in marine ecosystems (usually the first step in the food chain). Certain species produce harmful chemicals

**Dinoflagellates** are seasonally abundant and are one of the primary causes of red tides, seawater bioluminescence, and shellfish poisoning



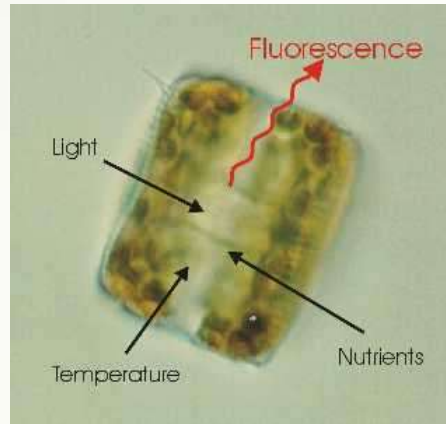
Different samples of seston on paper filters

# Behavior of phytoplankton cells



Chlorophyll patchiness

Phytoplankton organisms can emit **fluorescent** (in photosynthesis process) and **bioluminescent** light (several species)



Certain species produce harmful chemicals and are one of the primary causes of red tides and shellfish poisoning (*Noctiluca scintillans*)

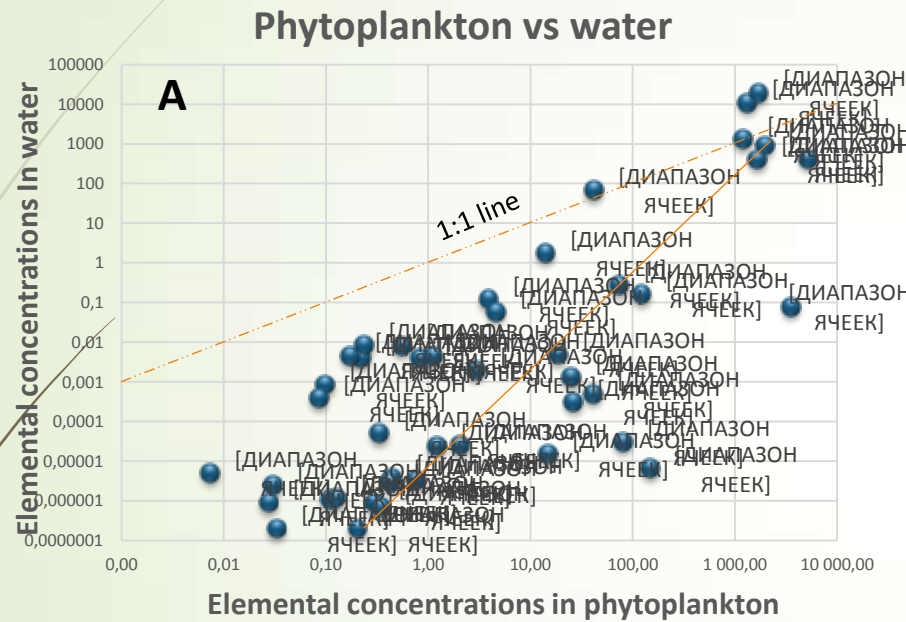


Physiological processes which reflect functional state of closed communities:

Fluorescence – when they are illuminated

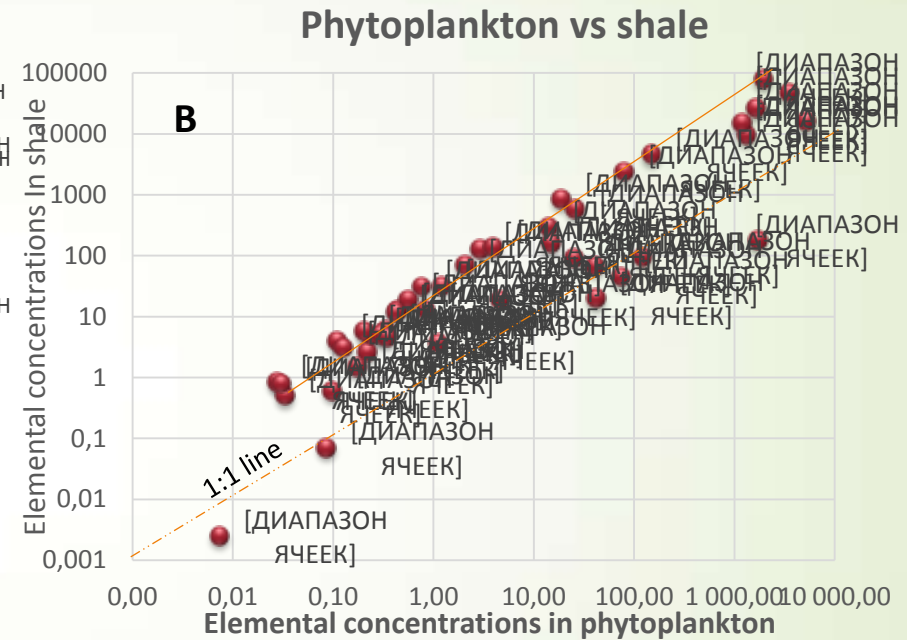
Bioluminescence – when they are stimulated

# Sources of elemental fluxes



A - average elemental concentrations in phytoplankton from 1 station and in water (Ryabinin et. al., 2006)

Fe, Ti, S, Ba, Ni, Cr, Zr



B - average elemental concentrations in phytoplankton from 1 station and in average shale (Li, 1991)

Cl, Zn, Cu, Ni, Br, Ag, Au

# Factor analysis of

	Factor 1	Factor 2	Factor 3
<b>Ech</b>	0,020288	0,925300	0,029772
Cr	0,905211	0,326862	0,145139
Ni	0,720082	-0,202906	0,323457
Cu	0,851292	0,192632	0,018576
Zn	0,901248	0,266802	-0,150609
Ag	-0,068271	-0,061089	-0,968929
I	0,404826	0,826963	0,028341
Expl.Var	3,043826	1,800080	1,089232
Prp.Totl	0,434832	0,257154	0,155605





Thanks for watching!

