SPECIAL ASPECTS OF ASSESSING THE ELEMENTAL COMPOSITION OF PHYTOPLANKTON AND SESTON USING NEUTRON ACTIVATION ANALYSIS

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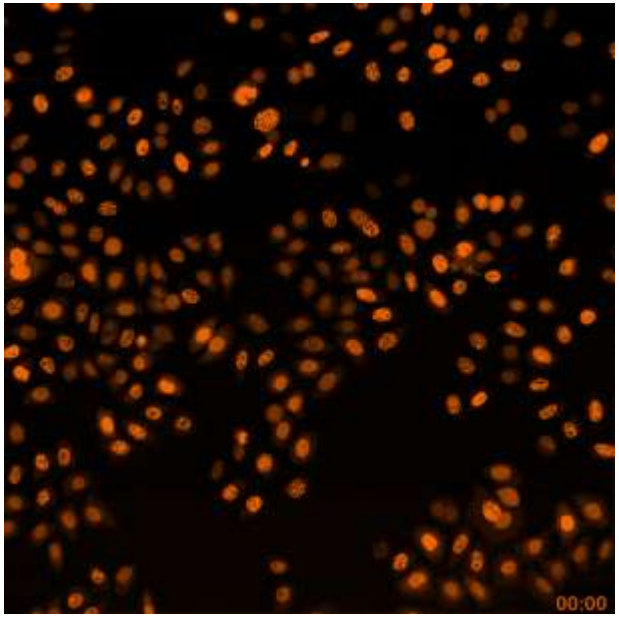
How to study mobile (versatile) matter?

- The life period of cell is one-two days
- The horizontal and vertical speed of moving in water is 50-100 cm/hour (speed of waves and currents)
- The number of phytoplankton species in water column is more than 5000 (The Black Sea)



The period of phytoplankton cell growth and fission in culture

Objects, suspended in water

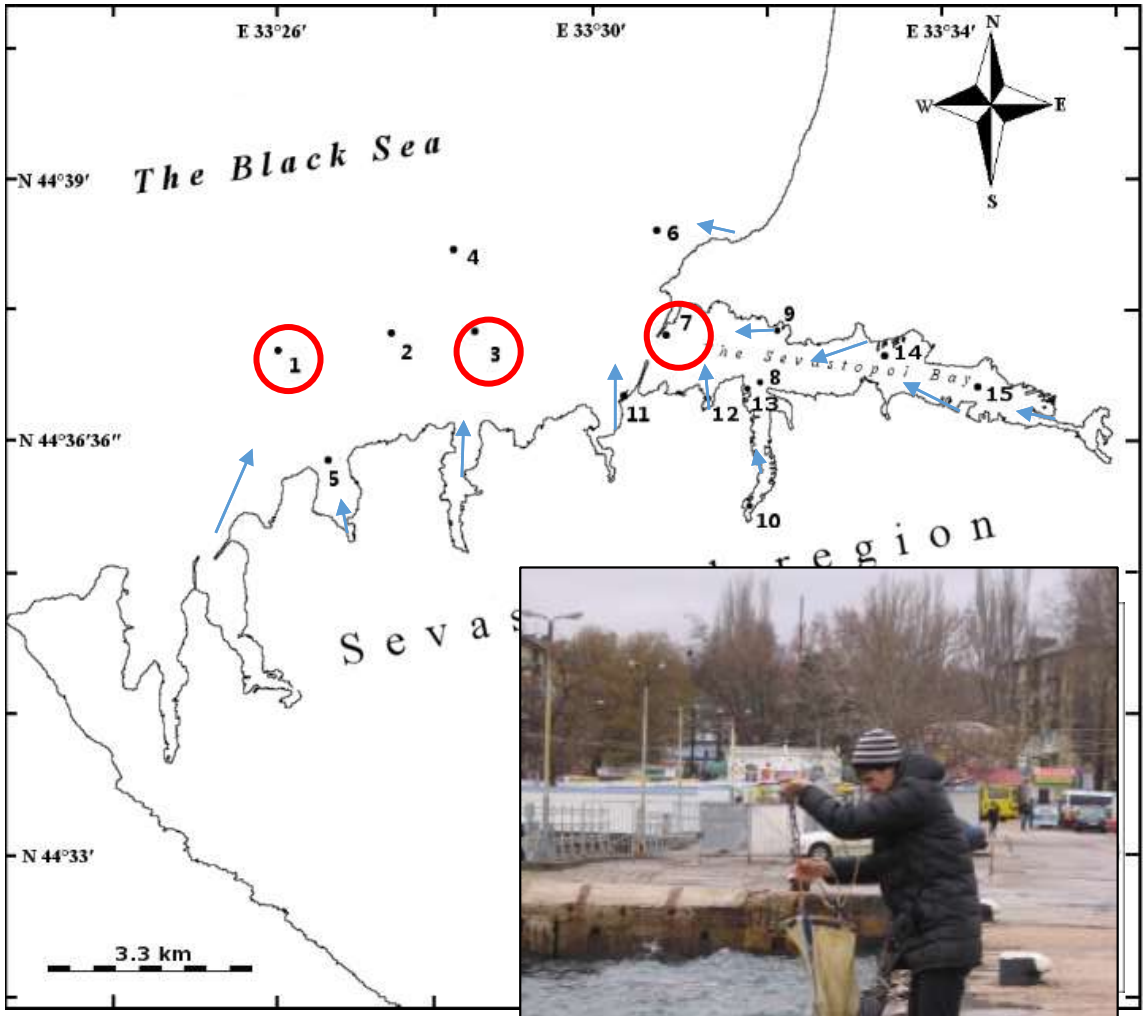
- Seston – organisms and non-living matter (plankton + detritus)
- Phytoplankton – autotrophic organisms
- Zooplankton – heterotrophic organisms

Presumptions

- Small variability of phytoplankton state in one period of time
- Stable state of the hydrological structure, variability of taxonomic structure in ecosystem
- Small number of zooplankton organisms (because of small speed of net towing)
- Minimal grazing activity of zooplankton and growth rate of phytoplankton from sampling to fixation

Sampling

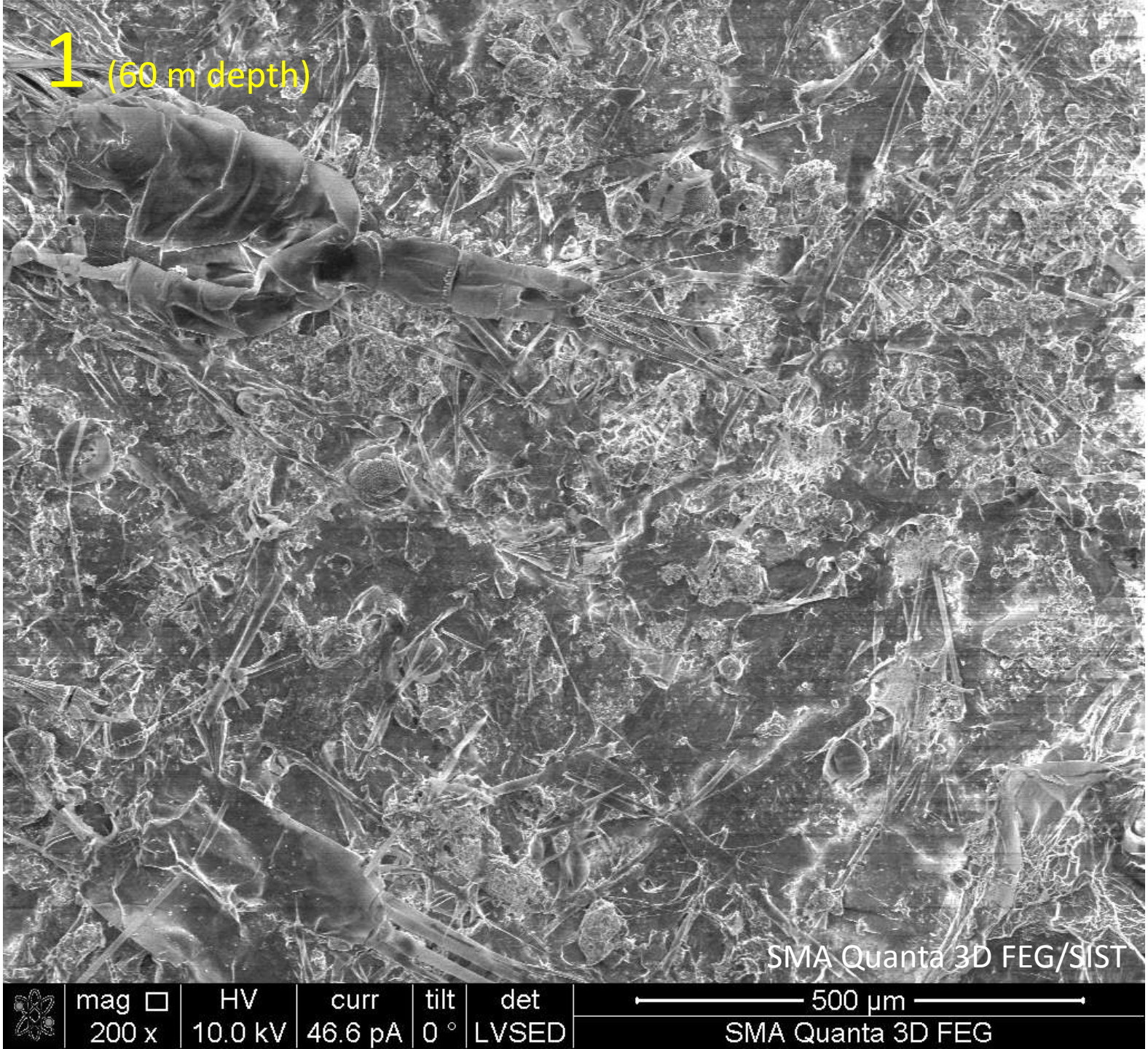
We study the microfraction (cells and particles with more than 35 µm sizes) of 50 samples from 15 st. in Summer and winter of 2013

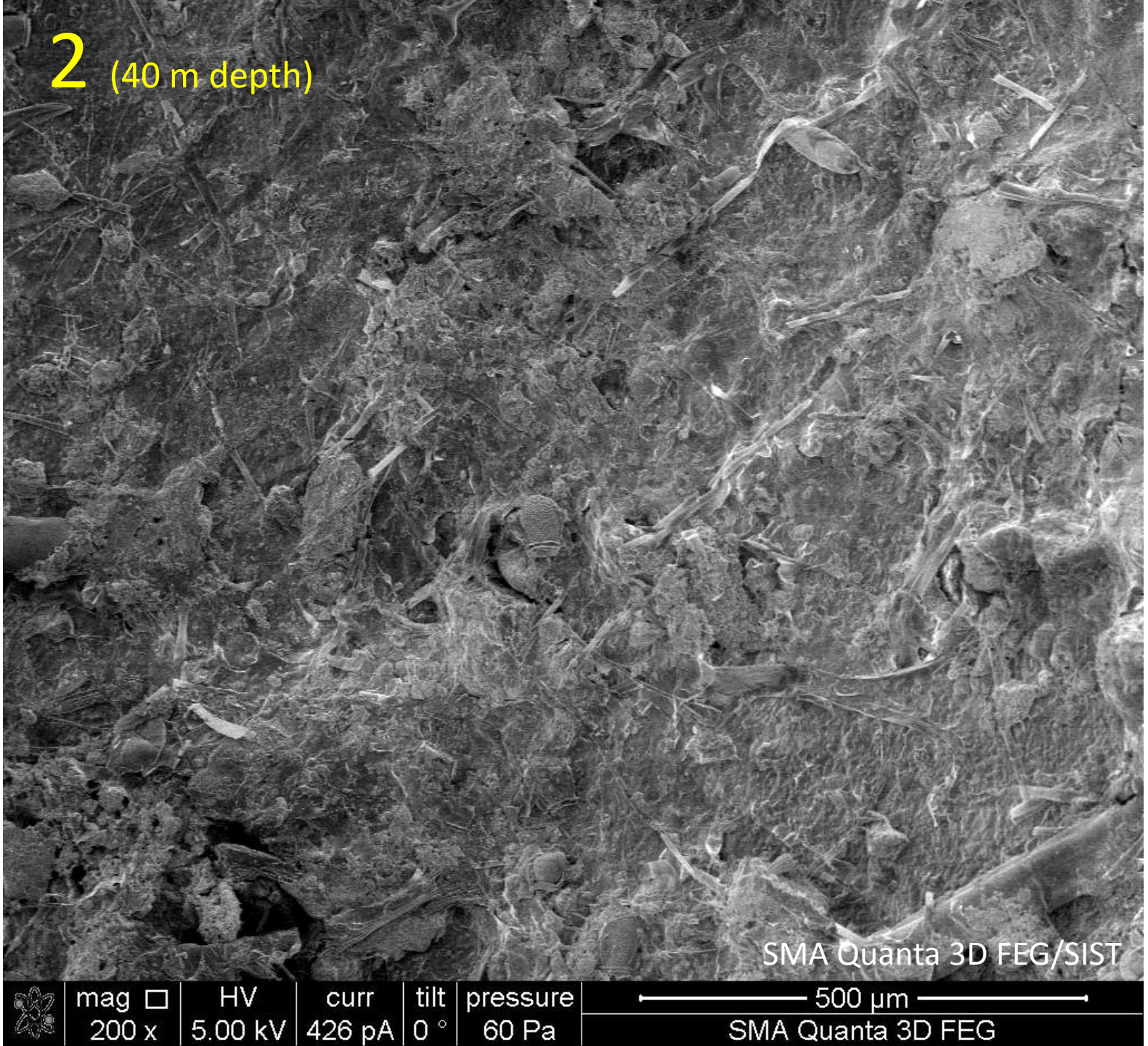


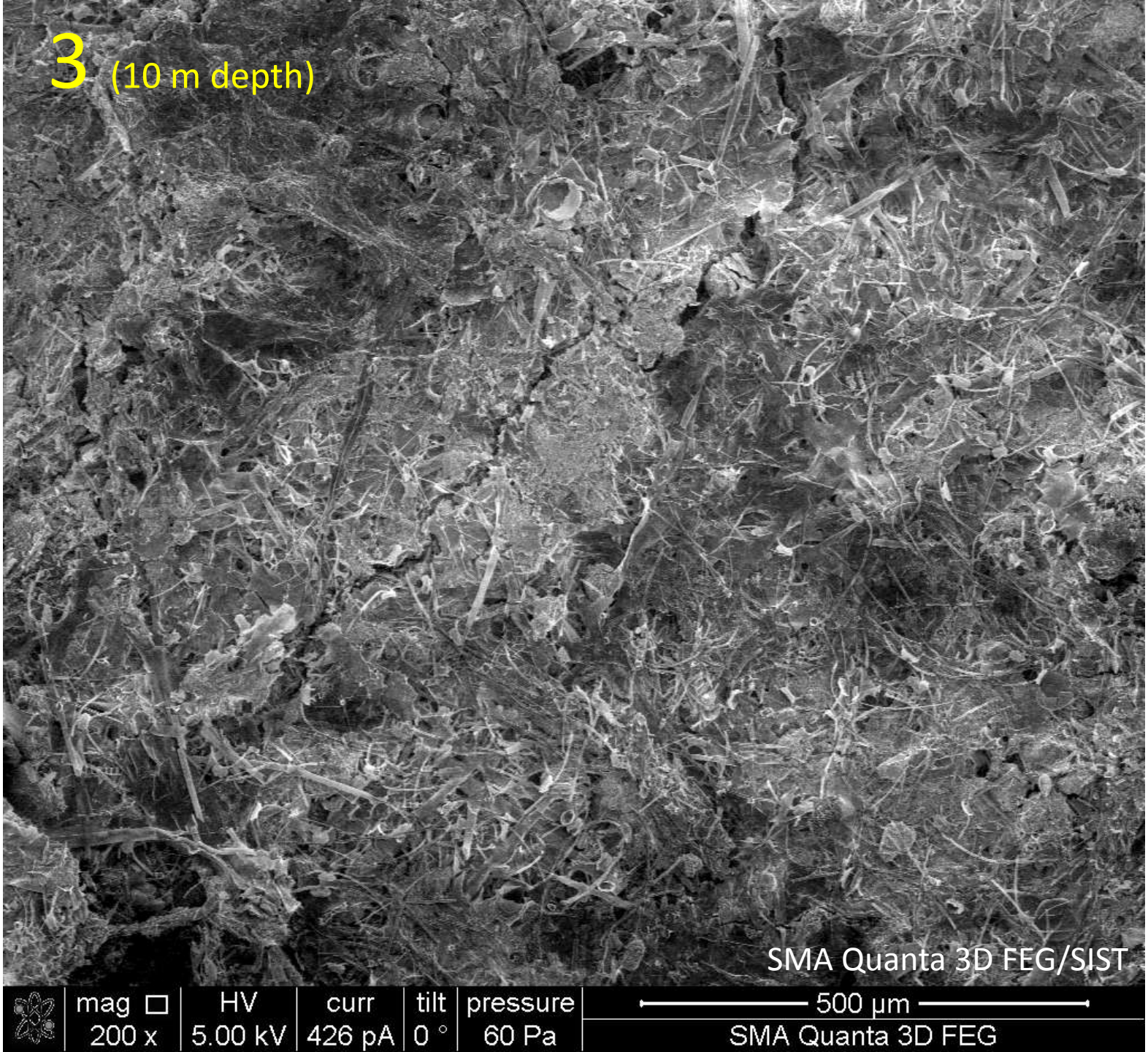
Taking into account:

- Site
- Depth (volume of water)
- Time and season
- Lapse (interval) from sampling to fixation

Net sampling is the best method for collecting average sample of water column without a small fraction


1 (60 m depth)
SMA Quanta 3D FEG/SIST
mag
200 x
HV
10.0 kV
curr
46.6 pA
tilt
0 °
det
LVSED
500 µm
SMA Quanta 3D FEG


2 (40 m depth)
SMA Quanta 3D FEG/SIST
mag
200 x
HV
5.00 kV
curr
426 pA
tilt
0 °
pressure
60 Pa
500 µm
SMA Quanta 3D FEG


3 (10 m depth)
SMA Quanta 3D FEG/SIST
mag
200 x
HV
5.00 kV
curr
426 pA
tilt
0 °
pressure
60 Pa
500 µm
SMA Quanta 3D FEG

Special preparing for Neutron Activation Analysis

- Fixation (90% ethanol)
- Homogenization (stirring and shaking)
- Precipitation on filters (vacuum filtration with precleaning)
- Drying (20-30 °C)
- Dilution on SLI and LLI

Assessment of elemental concentrations

- 40 elements in each sample were identified
- The mass fraction of elements in matter of paper filters (preliminary washed by distilled water) was determined 5 times in the same sample sets
- The “real” concentrations of elements in the matter of phytoplankton were calculated by subtraction concentration of element in filter blank from assessed in total matter of samples:

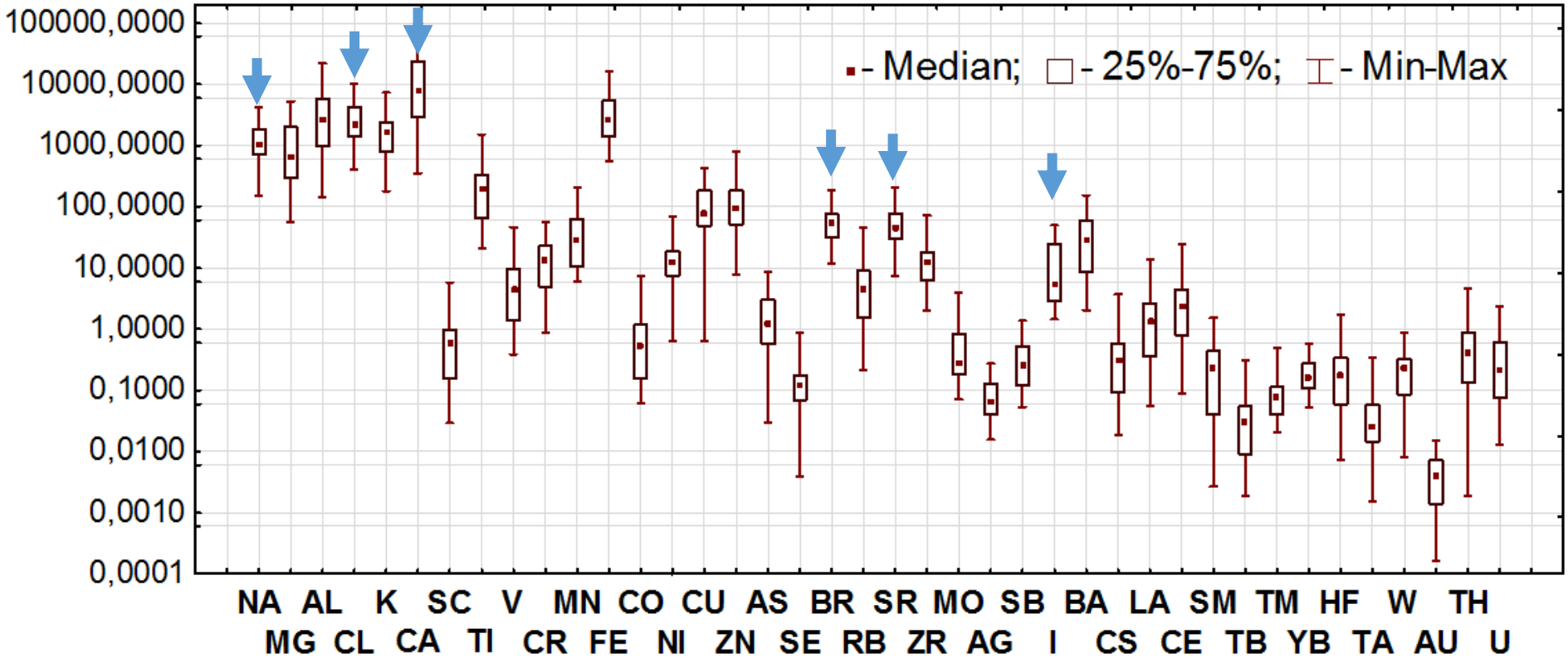
$$C_r = C_t - C_b,$$

C_r – “real” phytoplankton concentration, C_t – concentration in total matter of filter with sample,

C_b – concentration in filter blanks

In case if $C_r < 0$ was considered that element was not identified in sample and its concentration was equal to analytical minimum

Concentrations of elements



Features of phytoplankton samples in coastal regions:

- High amounts of terrigenous elements (Al, Ti, Sc, Zr, REE, Th)
- High amounts of relative elements
- High amounts of elements from sea salt and water (Na, Cl, I, Br etc.)

The main problem

- How to separate the terrigenous, biogenic and anthropogenic elements in phytoplankton matter?

✓ Analysis of elements after chemical purifying (lose the metals on surfaces of cells)

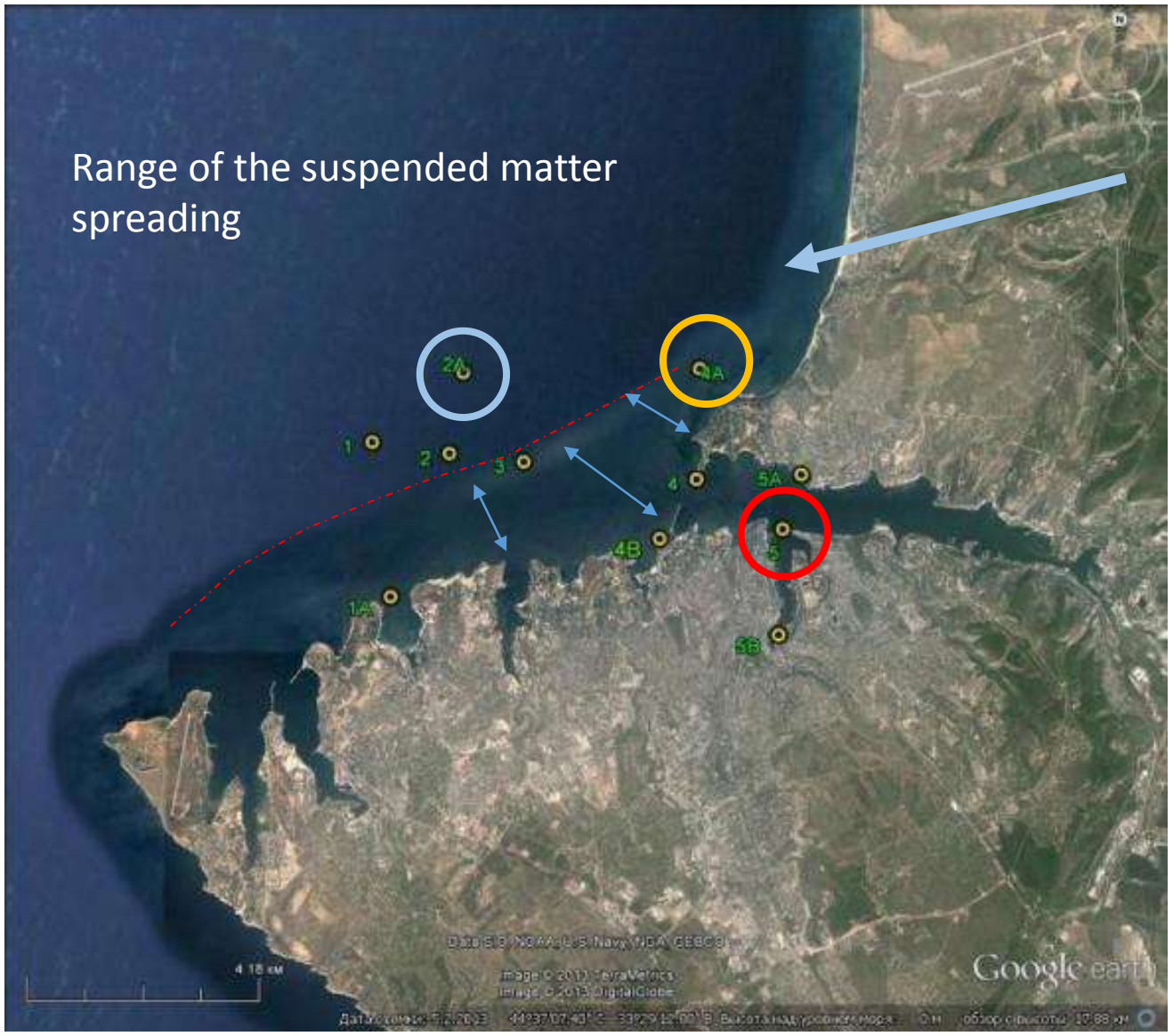
✓ Assess the amounts of ash after burning of the phytoplankton sample (lose the sample)

✓ Studying and comparison the different water areas (pristine, polluted, rich of suspended particles – river runoff)

✓ Estimation of Coefficients of biological accumulation (variability of water content)

✓ Estimation of Enrichment factors (reference elements: Al, Ti, Sc, Th) (reference of terrigenous elements)

Suspended matter



Biological accumulation

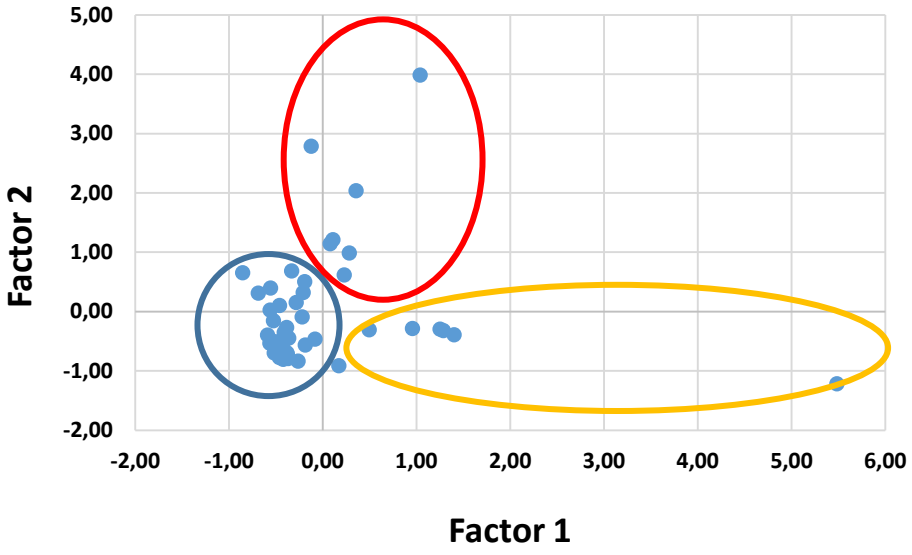
[redacted]

[redacted]

Kb	EF	Summer	Winter
Kb>4	EF>10	Cu, Zn	Cu
Kb>2	EF>10	Ag, Au	Zn, Au
Kb>2	EF>2	As, Sr, Sb	As, **Se**, Sr, **Mo**, Ag, Sb, **I**, **W**

Factor analysis

Factor 1 – Natural origin (terrigenous and biogenic elements)
Factor 2 – Anthropogenic origin



Overlapping of Natural and Anthropogenic factors. Superposition in deep pristine waters

	F1	F2	F3	F4	F5
NA	0,19	-0,22	-0,89	0,03	-0,01
MG	0,88	0,35	-0,11	0,20	0,06
AL	0,94	0,13	0,04	0,25	0,14
CL	-0,10	-0,27	-0,89	0,08	0,05
K	0,86	0,10	0,02	0,19	-0,20
CA	0,72	0,21	0,13	0,37	0,28
SC	0,98	0,11	0,00	0,08	0,03
TI	0,91	0,06	0,15	0,16	-0,06
V	0,96	0,08	0,05	0,19	0,13
CR	0,47	0,75	0,11	0,22	0,06
MN	0,82	0,31	0,05	0,36	0,18
FE	0,90	0,30	0,04	0,15	0,10
CO	0,96	0,07	0,10	0,06	-0,12
NI	0,27	0,78	-0,02	-0,15	0,13
CU	-0,01	0,80	0,07	0,04	-0,08
ZN	0,06	0,76	0,10	0,23	-0,38
AS	0,90	0,23	-0,03	0,26	0,07
SE	0,89	-0,24	0,08	0,13	0,04
BR	0,34	0,19	-0,17	0,71	-0,16
RB	0,97	0,16	0,00	0,14	0,05
SR	0,84	0,20	-0,08	0,25	0,06
ZR	0,95	0,12	-0,01	-0,15	-0,03
MO	0,12	0,04	0,02	0,75	0,23
AG	-0,03	0,08	-0,17	-0,05	-0,01
SN	0,02	0,22	-0,06	0,02	-0,60
SB	0,07	-0,04	0,08	0,29	-0,17
I	0,55	0,44	0,04	0,48	0,18
CS	0,91	-0,27	0,00	0,13	0,16
BA	-0,17	-0,11	0,46	0,11	-0,71
LA	0,98	0,13	0,01	0,06	0,04
CE	0,89	0,10	0,09	0,31	0,10
W	0,70	-0,11	0,35	0,16	-0,03
AU	0,31	0,05	0,33	0,17	0,47
TH	0,97	0,11	0,01	0,17	0,11
U	0,09	-0,05	0,50	-0,39	-0,43
Expl.Var	23,05	3,91	2,48	2,60	1,94
Prp.Totl	0,55	0,09	0,06	0,06	0,05

Modified method for terrigenous matter assessment

$$El_{nt} = El_i - El_s \cdot \frac{Sc_i}{Sc_s},$$

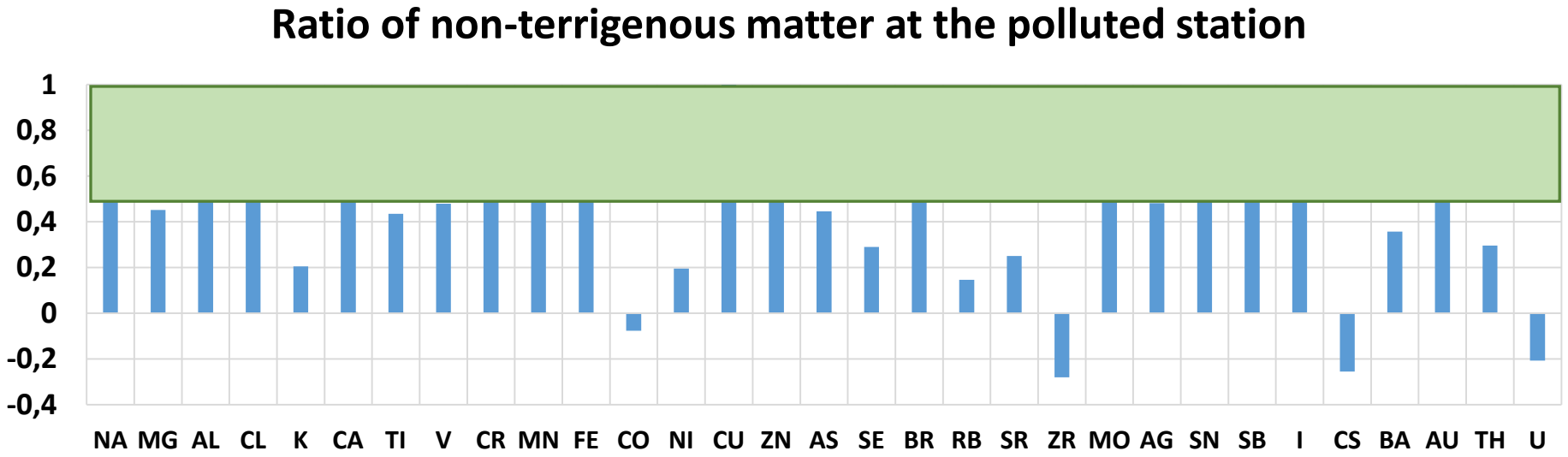
El_{nt} –non-terrigenous concentration of element

El_i –total concentration of element

[redacted] –concentration of element at the station with the highest amounts of **sediments**

–ratio between total concentration of scandium at the current station and at the "**sediment" station**

Modified method for terrigenous matter assessment



Na, Cl, Ca, Cr, Mn, Cu, Zn, Br, Mo, Sn, Sb, I, Au:

- Cr, Cu, Zn, Br, Mo, Sn, Sb and Au were probably anthropogenic origin
- Na, Cl – due to chemical content of water
- Ca, Mn and I – due to biogenic accumulation

Co, Zr, Cs, U (and REE) accumulated due to terrigenous matter

Conclusions

- The special aspects of neutron activation analysis of the phytoplankton matter were discussed
- The elements with the highest concentrations with different origin in phytoplankton matter were defined
- For the Black sea phytoplankton: such elements as Cr, Cu, Zn, Br, Mo, Sn, Sb and Au were probably anthropogenic origin, Na,Cl were accumulated due to high concentrations in water, Ca, Mn and I – due to biogenic accumulation
- The method of normalizing the data of concentrations in phytoplankton on reference element (Sc) in sediment-rich waters helped to separate the elements with different origin
- Results which obtained after factor analysis, calculation of coefficients of biological accumulation and enrichment factors, ratio of non-terrigenous matter allowed to separate the terrigenous group of elements (in microphytoplankton samples (with more then 35 µm cell size): Co, Zr, Cs, U (and REE) accumulated due to terrigenous matter
- The influences of large scale fraction of detritus on the accumulation of elements in marine environment by phytoplankton were discussed
- The suggested approach can be applied in any study of marine organisms and its elemental content

Thank you for your attention!