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STRUCTURE AND SORPTION PROPERTIES OF THE IN-SHORE ZONE BOTTOM SEDIMENTS OF THE WESTERN PART OF THE GULF OF FINLAND

Olga Kurapova*[1], Valeria Lebedeva[1], Tatiana Shigaeva[2], Valentina Kudryavtseva[2] and Vladimir Konakov[1]

[1]St Petersburg State University, Saint Petersburg, Russia
[2] Scientific research center for ecological safety *RAS*, *St.Petersburg*, Russia

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Ecological problems of the Western part of Gulf of Finland

- The insertion of pollutants with effluents of flowing rivers,
- the construction of the oil terminals
- the construction of the alluvial territories
- rapidly growing civil engineering

ecological disequilibrium of the environment and the death of the aqueous biota

The goal of the work

the goal of present work was the investigation of the effect of the phase composition, particle size distribution and chemical composition of the in-shore bottom sediments of the Western part of the Gulf of Finland on their tendency to the heavy metal sorption (Cu^{2+} and Zn^{2+}).

Investigation techniques:

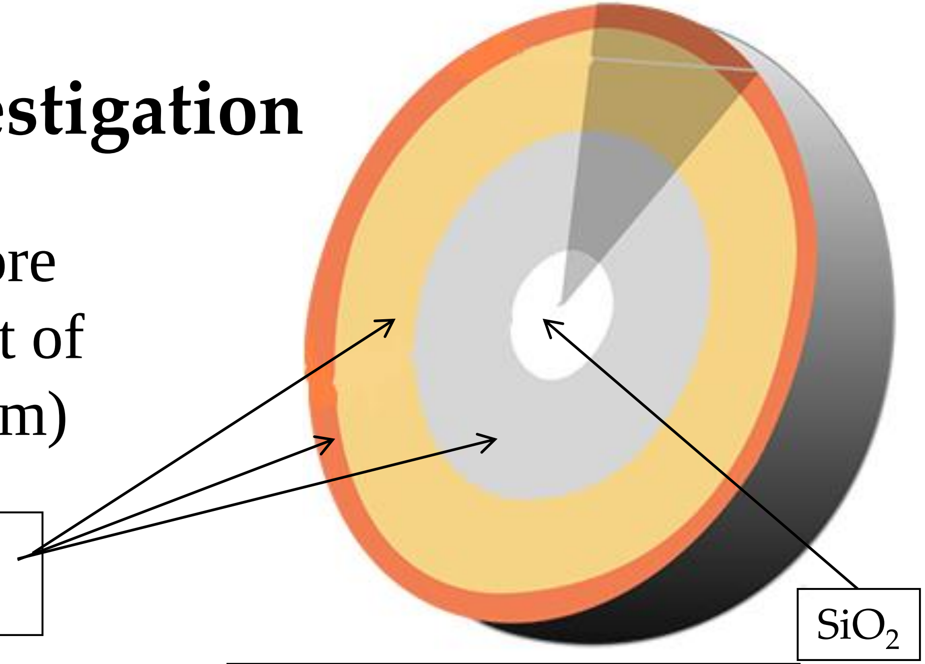
- X-Ray diffraction (XRD, SHIMADZU XRD-6000);
- Particle size distribution analysis (Horiba LA-950);
- Electrical conductivity of washing waters measurement (inoLab Cond7110)
- Scanning electron microscopy (SEM, Hitachi S-3400N with the equipment for energy dispersive X-Ray spectroscopy EDX analysis - EDX)*;
- Analytical investigation of the sorption properties

** Scanning electron microscopy and EDX analysis were performed by Vladimir Shilovskih at the Research park of St. Petersburg State University Center for Geo-Environmental Research and Modeling (GEOMODEL)*

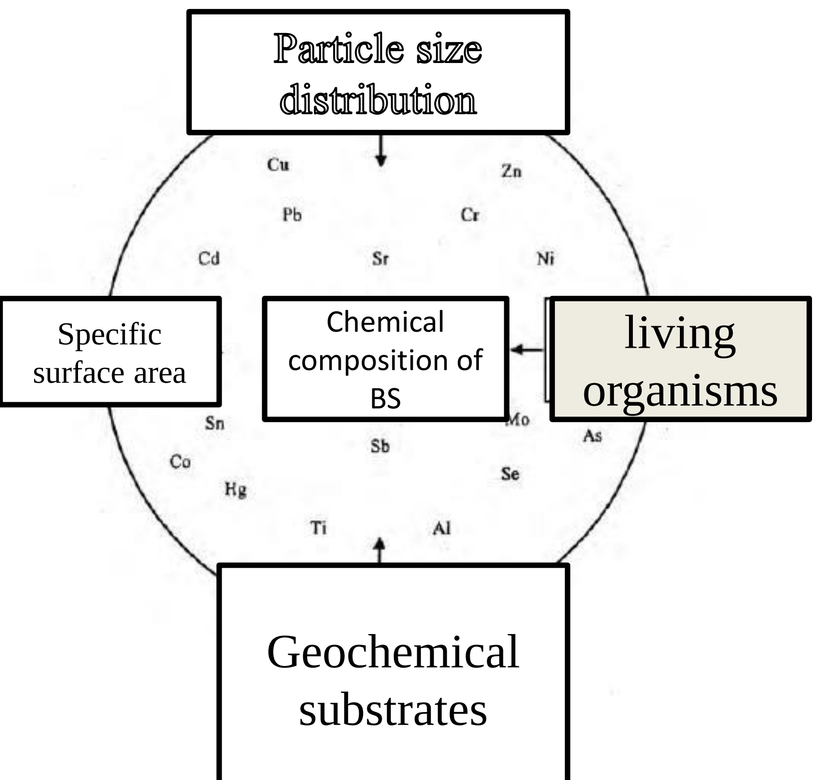
The object of the investigation

The upper layers (0-10 cm) of in-shore bottom sediments of the Western part of the Gulf of Finland (the depth is 0.5 m)

The alternation of the organic and inorganic layers

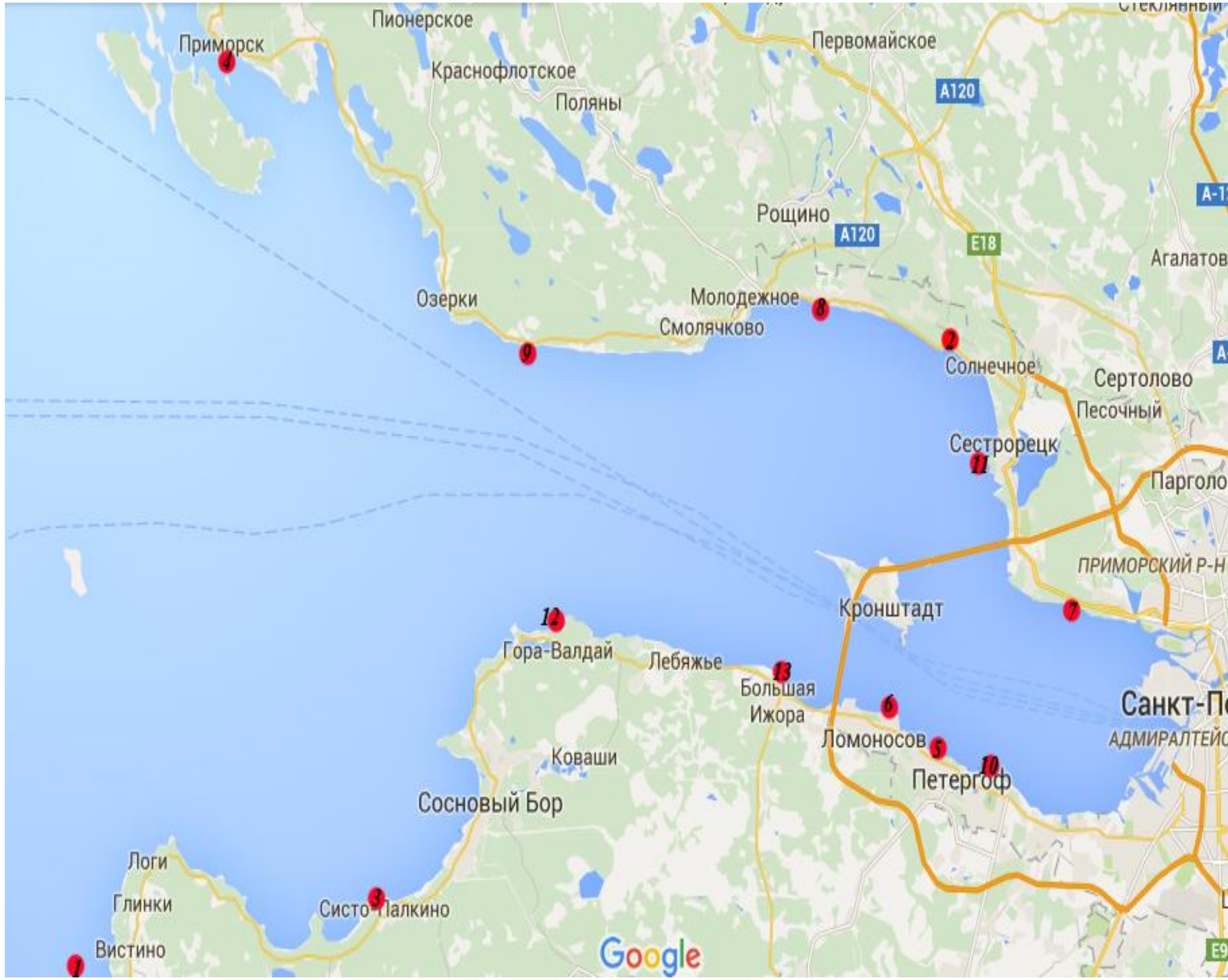


Multilayered sand particle



Bottom sediments — bottom silts and solid particles, formed and settled on the bottom of water system because of physical, chemical and biochemical processes (both natural and technogenic)

Grafskaya bay
Repino
Lomonosov
Sisto-Palkino
Sestroretsk
Luzhskaya guba
Primorsk
Martishkino
Olgino
Ushkovo
Bolshaya Izora
Cape Flotsky



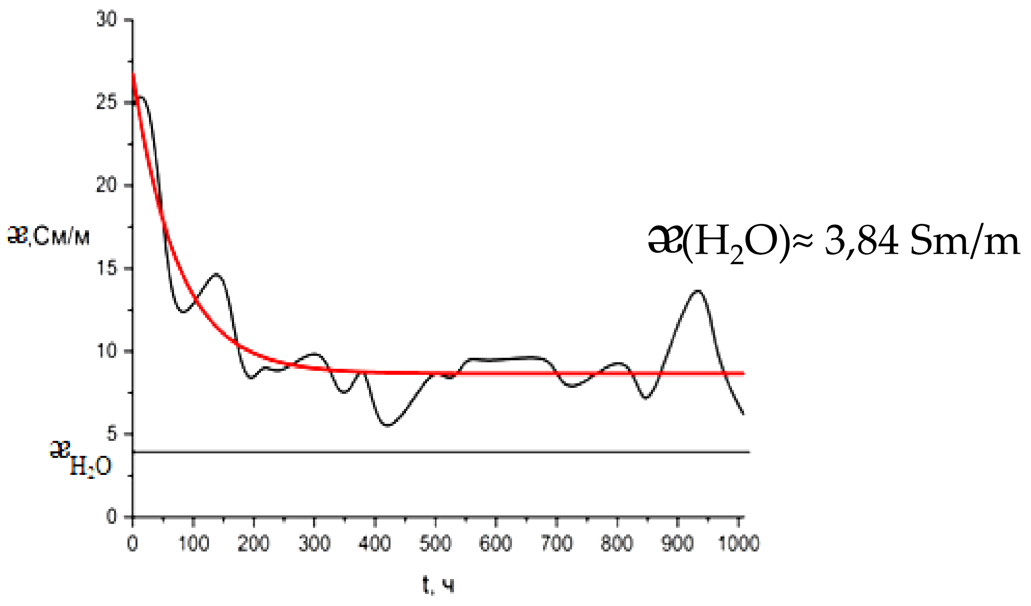
Chosen points in the in-shore zone of the Western part of Gulf of Finland for the observation

Sample preparation

➢Bottom sediments samples were dried at 30°C and then sieved using 1 mm cell sieve

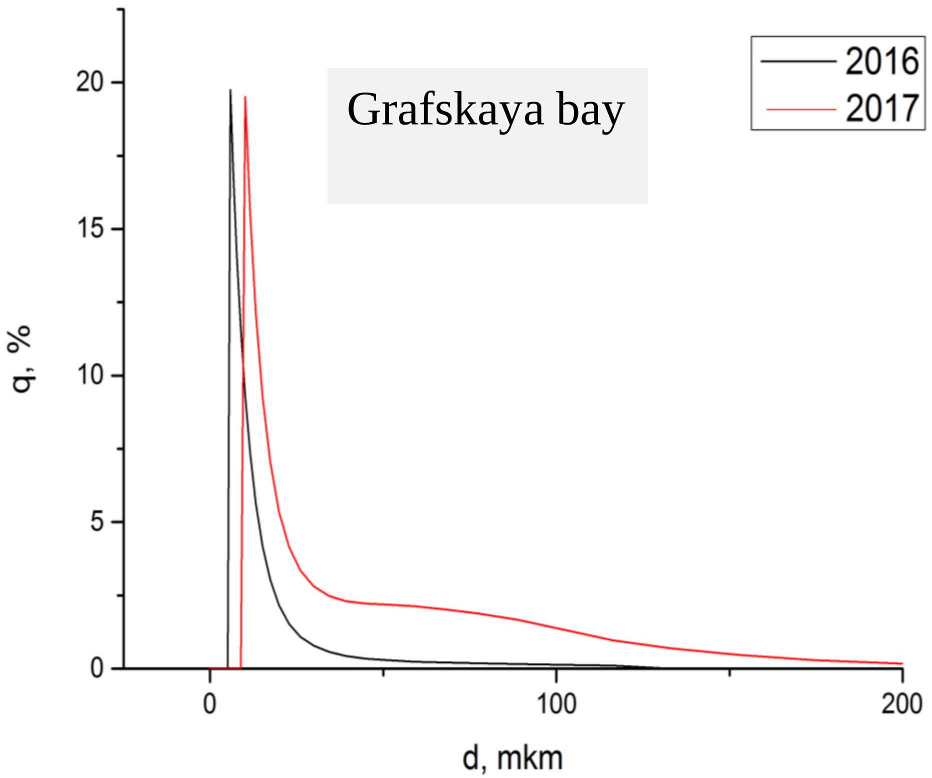
➢In order to eliminate the dynamic ion forms that could affect the sorption the samples were preliminary washed with distilled water.

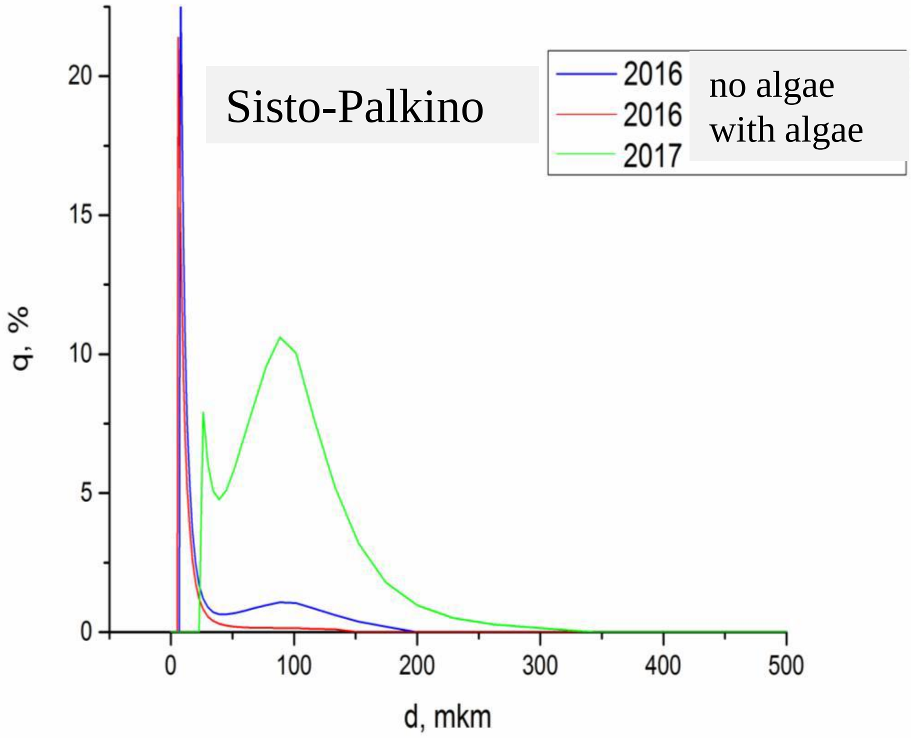
Sestroretsk



The dependence of the specific conductivity on the time of the samples washing

Particle size distribution analysis

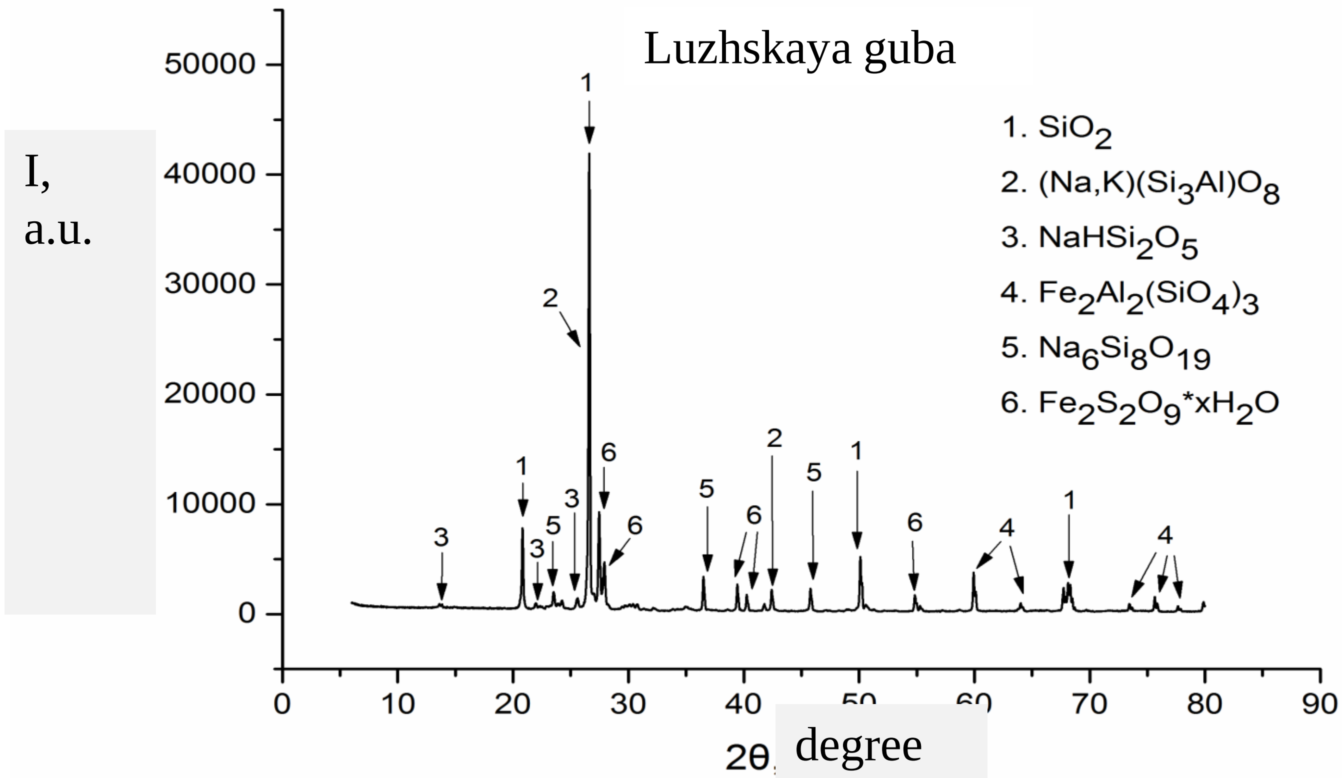




Mean particle size in the bottom sediments before and after ultrasound according PSD analysis

Control point	Year	no ultrasound		With ultrasound	
		d_N, mkm	d_V, mkm	d_N, mkm	d_V, mkm
Grafskaya bay	2016	10,19	200,82	7,91	140,50
	2017	24,46	140,50	8,00	135,43
Lomonosov	2016	106,62	163,58	106,14	160,04
	2017	111,94	153,49	108,09	153,39
Sisto-Palkino	2016	algae 16,59	algae 130,44	algae 8,41	algae 144,86
		no algae 9,76	no algae 557,10	no algae 8,39	no algae 321,76
	2017	72,51	221,29	8,84	199,44
Luzhskaya guba	2016	191,93	288,91	177,02	281,62
	2017	147,02	209,95	129,86	208,91
Sestroretsk	2016	226,91	511,11	221,80	416,68
	2017	156,32	365,87	153,55	399,76
Primorsk	2017	34,21	390,18	7,33	363,18
Bolshyaya izhora	2017	13,32	147,71	5,57	124,95
Cape Flotsky	2017	211,98	428,09	6,69	404,85
Martyskino	2015	5,66	120,11	5,33	103,45

Typical X-Ray pattern



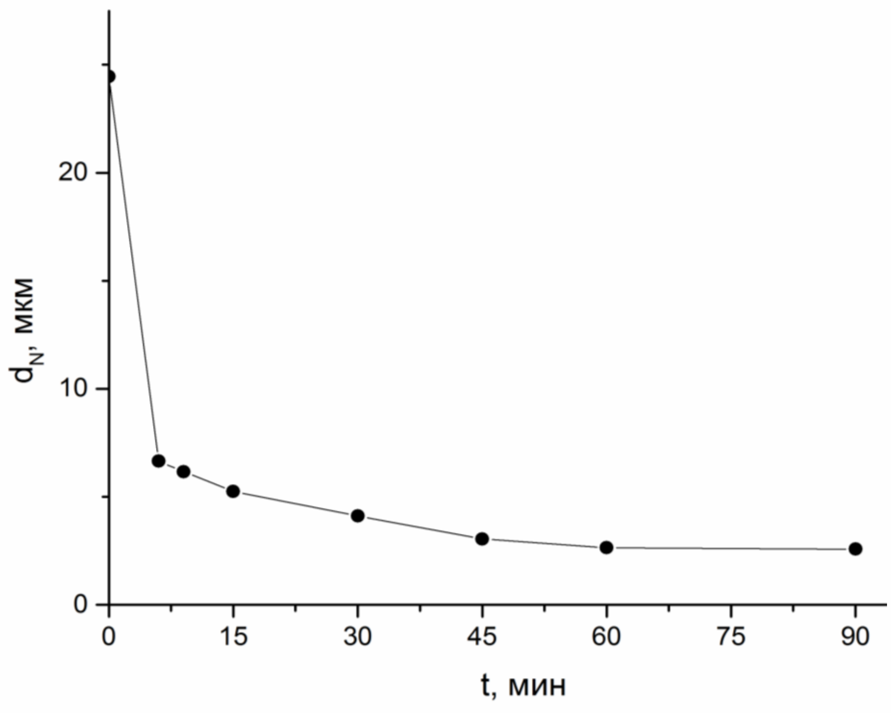
•SiO_2 is the main phase present in all bottom sediment probes.
Particles are multiphased, formed via the co-crystallization, which indicates the admixture phases baing natural
In general, the phase composition corresponds to the mineral composition of the region

Full Cu^{2+} exchange capacity data obtained for the bottom sediments

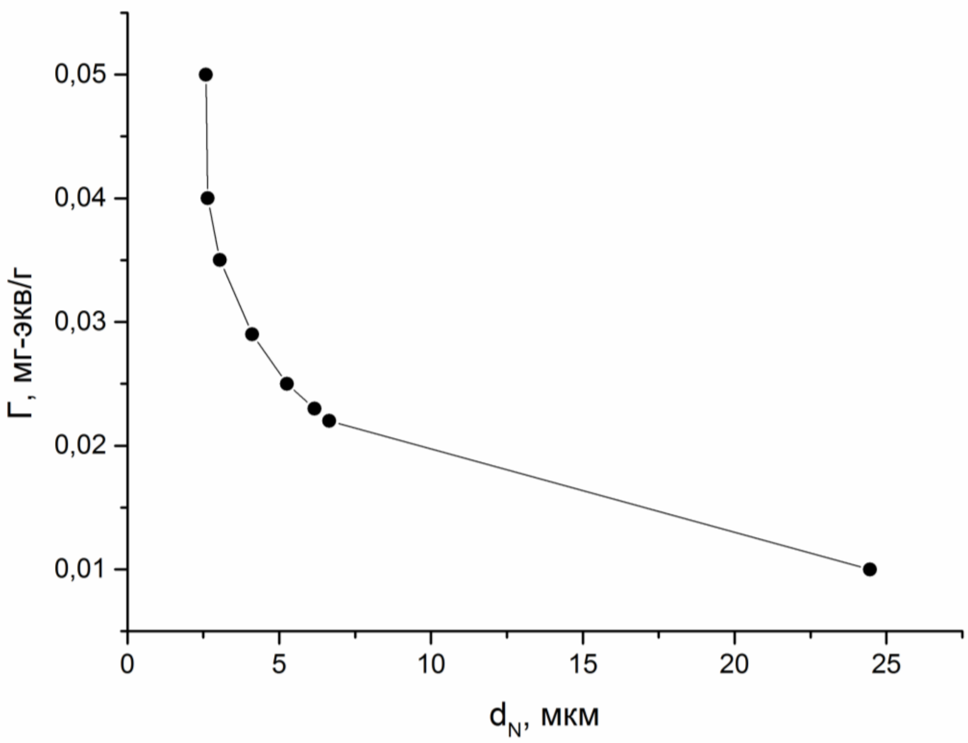
Control point of observation	d_N, mkm	d_V, mkm	Full cation exchange capacity Cu^{2+} (Γ, mg-ekv/g)
Martyshkino	5,66	120,11	0,040
Sestroretsk	156,32	365,87	0,025
Grafskaya Bay	24,46	140,50	0,010
Bolshaya Izhora	13,32	147,71	0,025
Luzhskaya Guba	147,02	209,95	0
Lomonosov	111,94	153,49	0,010
Sisto-Palkino	72,51	221,29	0,010

Full ion exchange capacity significantly depends on samples dispersity
Except BS collected at Sestroretsk .

Particle size effect on copper ions sorption by bottom sediments. Example for Grafskaya Bay (2017)

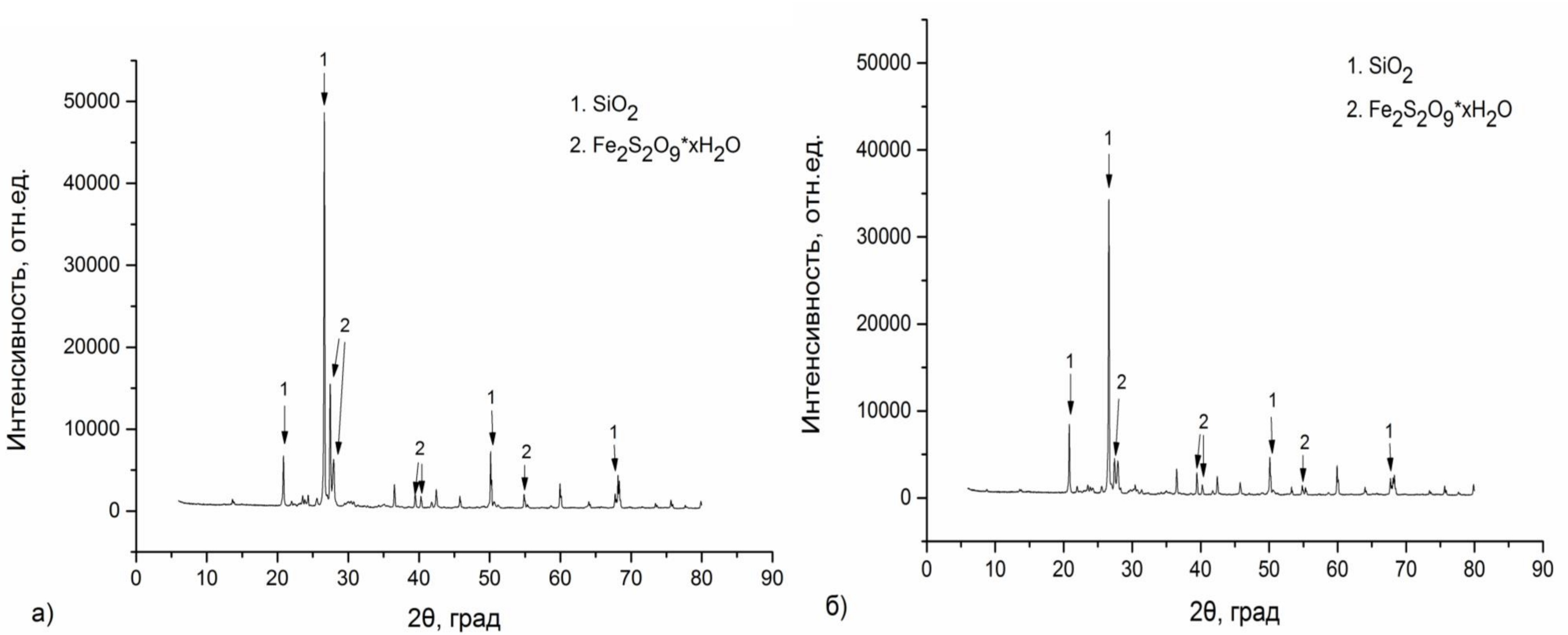


The effect of milling time on particle size of bottom sediments



The dependence of full Cu^{2+} exchange capacity on the bottom sediments mean particle size

X-Ray patterns of bottom sediments (BS) before and after washing

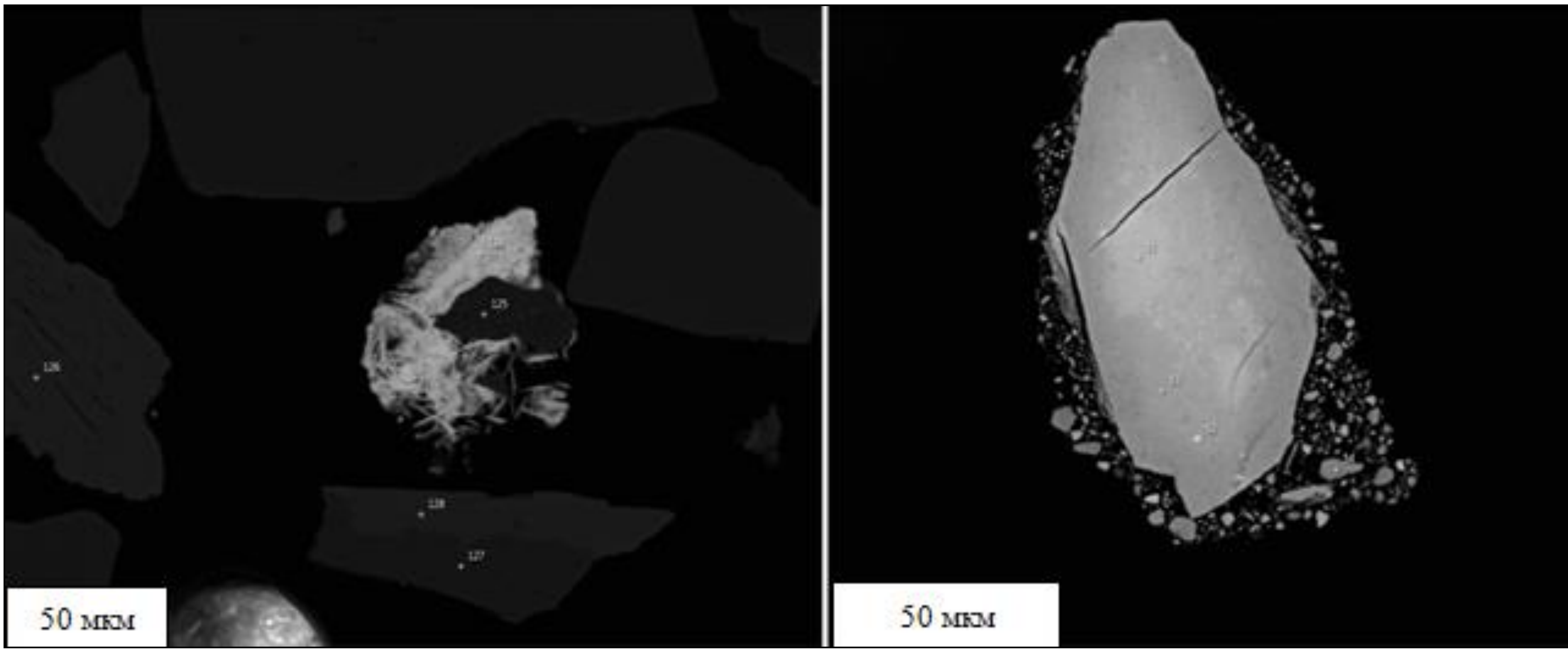


X-Ray patterns of BS collected in Sestroretsk for 2016 a) before washing, b) after washing

✓Full Cu^{2+} exchange capacity unwashed samples 0,025 mg-ekv/g, for the washed– 0,016 mg-ekv/g

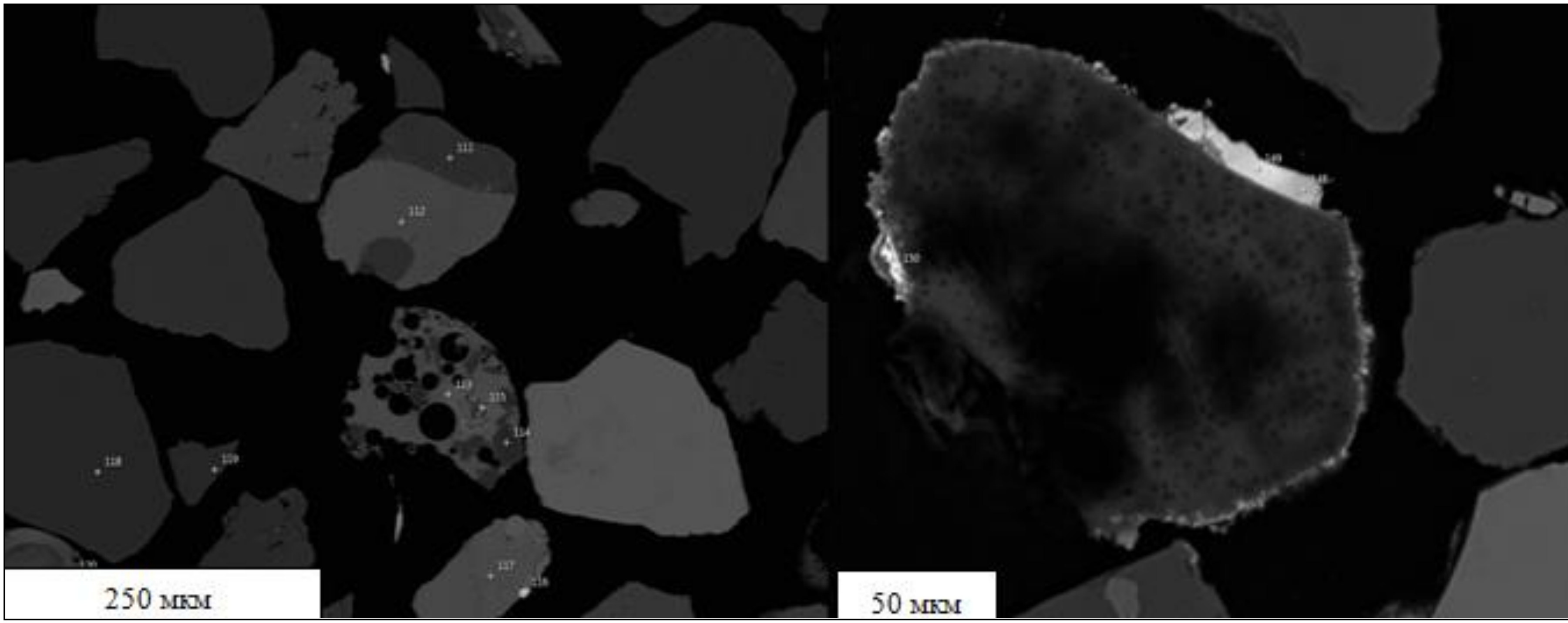
✓Washing leads to $Fe_2S_2O_9 \cdot xH_2O$ dissolution (see peak 2Θ=27,5-28 at degr)

SEM data of BS before washing with distilled water



BS collected at Sestroretsk, 2016

SEM data of BS after washing with distilled water



BS collected at Sestroretsk, 2016

The effect of biome (algae *Cladophora glomerata)* on the sorption properties of BS

The values of full Cu^{2+} exchange capacity

«Grafskya bay» increased from 0,010 to 0,085 mg-ekv/g,

«Luzhskaya guba» increased from 0 to 0,080 mg-ekv/g

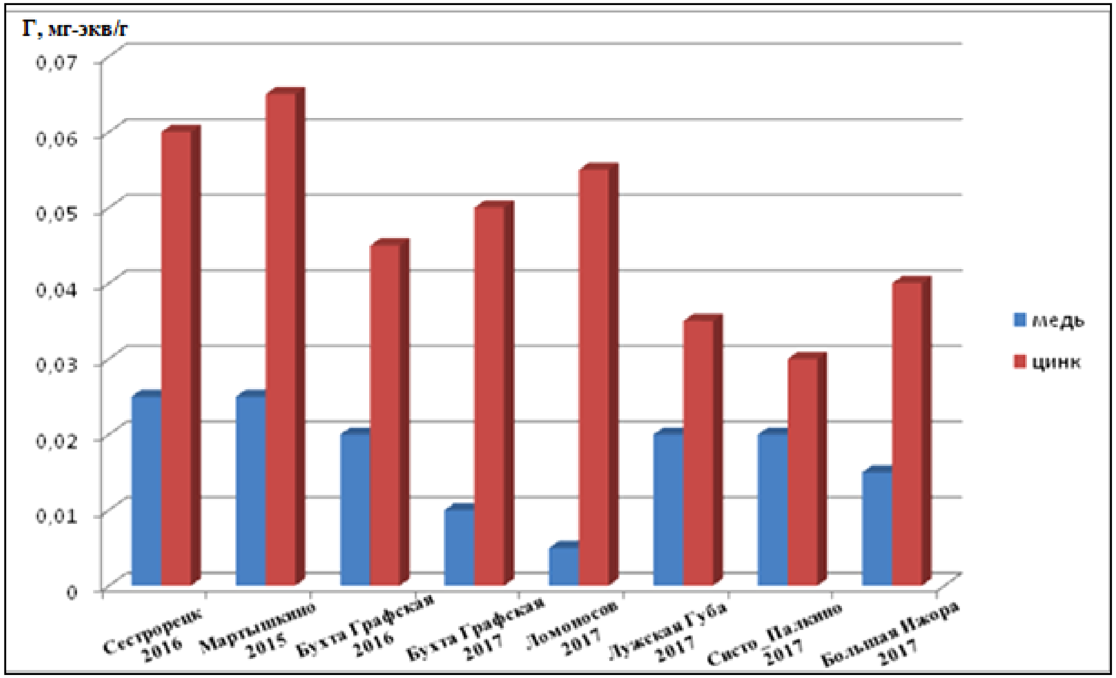
- ✓ Thus during the competition sorption of BS and biome, algae (biome) sorption is rather high.

Desorption properties of copper and zinc ions

There is no Zn^{2+} sorption neither in static and dynamic conditions.

The full Zn^{2+} exchange capacity is reached already.

Dynamic ion forms – the forms that can undergo desorption from the surface of sold particles upon pH decrease in water systems.



Full exchange capacity of the dynamic forms of copper and zinc ions for all observation points.

In order to evaluate the values of tull exchange capacity of the dynamic forms the samples were placed in 0.01N nitric acid solution for one week

pH value shift induce Zn^{2+} and Cu^{2+} desorption

Conclusions

1. using the probes collected in Grafskaya bay it was shown that mean particle size decrease from 24.46 to 2.58 mkm results in five times full Cu^{2+} exchange capacity increase;

2. using the probes collected in Sestroretsk it was proved that multilayered structure of bottom sediments as well as the presence of phases, able for the microelements accumulation i.e., for example, $Fe_2S_2O_9*xH_2O$, enhances their sorption ability considerably;

3. for the bottom sediments collected in Luzhskaya guba and Grafskaya bay it was established that the presence of algae significantly enhances Cu^{2+} sorption i.e. from 0 to 0.08 mg-ecv./g and from 0.01 to 0.085 for bottom sediments collected in Luzhskaya guba and Grafskaya bay, respectively;

4. Ion forms of zinc and copper are bio accessible, i.e. they can undergo desorption from bottom sediments upon pH value change. That can affect on the ecological balance of the water system.

Thank you for your attention!