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MARINE CHEMISTRY

The Biogeochemistry of Some Heavy Metals and Metalloids in the Ob River Estuary–Kara Sea Section

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Abstract—The biogeochemical behavior of the group of heavy metals and metalloids in the water (including their dissolved and suspended particulate forms), bottom sediments, and zoobenthos was studied in the Ob River estuary–Kara Sea section on the basis of the data obtained during cruise 54 of the R/V *Akademik Mstislav Keldysh* in September–October 2007. The changes in the ratios of the dissolved and suspended particulate forms of Fe, Mn, Zn, Cu, Pb, Cd, and As were shown, as well as the growth of the fraction of adsorbed forms in the near-bottom suspended particulate matter under the mixing of the riverine and marine waters. The features of the metals' accumulation in the typical benthic organisms of the Ob River estuary and the Kara Sea were revealed, and their concentrating factors were calculated based on the specific conditions of the environment. It was shown that the shells of the bivalves possessing a higher biomass compared to the other groups of organisms in the Ob River estuary play an important role in the deposition of heavy metals. The mollusks of the Ob River estuary accumulate Cd and Pb at the background level, whereas the Cu and Zn contents appear to be over the background level.

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INTRODUCTION

The study of the behavior of heavy metals at the river–sea geochemical barrier, where the primary transformations of the riverine runoff's composition proceed [5, 4], is of great importance for understanding the processes of the biogenic migration of heavy metals in the ocean. The activity of the living organisms (from bacteria to macrozoobenthos and macrophytes) extracting and concentrating the chemical elements constitutes the biological part of a marginal filter [11]. Benthic organisms are commonly used for the environmental monitoring of the heavy metal contamination of coastal zones of seas and oceans [17].

The Kara Sea is a high-latitudinal basin with the ice cover persisting for 8–9 months with a short vegetation period of about 3 months; the insolation is also very low there. The sea is an oligotrophic basin according to the primary production value [1]; i.e., it is characterized by a low phytoplankton biomass. The inhabitation of organisms under the highly severe and unfavorable conditions for bioproduction is reflected in the decreased bioaccumulation of heavy metals in the macrophytes at the Spitsbergen littoral compared to the temperate zone and the World Ocean as a whole [14]. Some of the heavy metals (Fe, Cu, Cd, Ni, and Pb) in the Ob River estuary show a conservative (simple dilution with a linear dependence on the water's salinity) and a nonconservative distribution (at which the metals are involved into various biogeochemical processes) [16].

The study aimed to research the biogeochemistry of the group of heavy metals (Fe, Mn, Zn, Cu, Cd, Ni, Co, Cr, Pb, Ag, and Hg) and of several metalloids (As, Se, and Sb) in the Ob River estuary–Kara Sea section, including the features of their bioaccumulation in the benthic organisms. To do this, the behavior of the metals was studied in the water mass (including their dissolved and suspended particulate forms), the near-bottom layer, the bottom sediment surface layer, and in the benthic organisms with the possible involving of the data on the organic carbon.

MATERIALS AND METHODS

The material for the studies was collected during cruise 54 of the R/V *Akademik Mstislav Keldysh* (September–October 2007) at the Ob River estuary–Kara Sea section. The section length amounted to over 900 km.

The water was sampled by means of a Rozette system. The suspended particulate matter was separated by filtration through nuclear filters with a 0.45 μm pore diameter manufactured at the Joint Institute of Nuclear Researches (Dubna). The filtrate was acidified with ultrapure Merck HNO_3 to pH 2. The samples of the bottom sediments from the water–bottom boundary layer were collected using a Neimisto tube. The macrozoobenthos (soft tissues and shells of bivalves, echinoderms, and crustaceans) was collected by means of a Sigsbee trawl. The fauna specimens were twice cleansed with small volumes of bidistilled water, prepared, and dried at $T^o \leq 70°C$. At the stationary laboratory, the samples of the suspended particulate matter and fauna were dried in desiccators and weighed with an electronic microbalance. The chemical preparation of the suspended particulate matter included decomposition of a mixture of concentrated ultrapure HNO_3 and 30% H_2O_2 (2 : 1 ml) in fluoroplastic vessels placed into an ultrasonic bath. In 12 samples of the near-bottom suspended particulate matter, the absorbed forms were determined by extraction with 25% CH_3COOH [6, 7, 20] and the following complete dissolution of the precipitate by 1 ml HNO_3 and 0.3 ml HF. The moisture of the bottom sediments was determined by gravimetry. The dried and pulverized samples of the bottom sediments were decomposed with a mixture of concentrated ultrapure HNO_3 and HF (2 + 1 ml), whereas the organisms were mineralized using 1.5 ml of a mixture of ultrapure Merck HNO_3 and H_2O_2 (2 : 1) for a 50-mg sample. The decomposition proceeded in fluoroplastic vessels of the MWS 2 microwave system (Berghoff, Germany). The volume of the substance obtained amounted to 15–20 ml.

The concentrations of the metals in the dissolved and suspended particulate forms were determined using atomic absorption spectrometry (AAS). The iron, Mn, Zn, and Cu were determined in a flame with a KVANT 2A spectrometer. For the Pb, Cd, Ag, and As, a graphite furnace and a KVANT Z.ETA spectrometer were used. The contents of the metals in the bottom sediments and the organisms were determined in three ways: by both AAS versions, as well as by neutron activation analysis (at the Vernadskii Institute for Geochemistry and Analytical Chemistry of the Russian Academy of Sciences). At that, the latter procedure was applied to determine the Fe, Zn, Sb, Se, Co, Cr, and As. The content of Hg was analyzed by the cold vapor procedure using a KVANT-Z.ETA spectrometer equipped with a GRG 106 attachment. Each of the samples was tested at least twice; the reproducibility of the analyses varied from 3% for Fe, Mn, Zn, and Cu to 7–15% for the other elements. The reliability of the analyses was controlled using the State Standard Samples (GSO) of the ions of the analyzed metals and the International Reference Materials: NIST SRM 2976 mussel tissue, IAEA MA-A-2/TM fish flash homogenate, and GSD 7. The standard deviation from the passport data of the standard samples amounted to 5–10% for Fe, Mn, Zn, Cu, Co, Cr, Pb, As, Ag, Cd, Se, and Sb and 15% for Hg. The content of C_{org} was determined by means of an AN 2975 M express analyzer.

RESULTS AND DISCUSSION

The metals in the water and the suspended particulate matter. The main source of the supply of dissolved and suspended particulate matter to the Kara Sea is the Ob and Yenisei riverine runoff. These rivers annually supply 1049 km^3 of freshwater and 22.4×10^6 t of suspended particulate matter, which amounts to about 70% of the total and solid runoff to the sea [12, 18]. Another important source of metals is their supply with aerosol matter, in which the contents of the toxic heavy metals such as Cu, Zn, Ag, Cd, and Sb occupy an intermediate level between the far distant background Arctic areas and the aquatic areas of the North and Baltic seas subjected to anthropogenic impact [21].

Table 1 includes the suspended particulate matter content and the ratios of the dissolved and suspended particulate forms of Fe, Mn, Zn, Cu, Pb, Cd, and As in the waters of the Ob River estuary compared to the average values for the rivers of the world [19] and of the Arctic [18]. The content of suspended particulate matter, as well as of dissolved and suspended particulate metals, in the Ob River estuary is close to the formerly published data [10, 18].

Our data on the dissolved forms of metals are close to the world average values, whereas, in the suspended particulate form, these latter are higher by 1–2 orders of magnitude than those in the Ob River estuary waters. This is quite reasonable because the Ob River is a lowland one draining areas with plain tundra relief with permafrost and a small thickness of the residual soil, which causes a decreased content of proper suspended particulate matter [11, 18].

Within the estuary, two zones are distinguished: (1) the riverine waters as such (stations 4993 and 4994) of 0.05 and 0.08‰ salinity and (2) the waters of the mixing zone (stations 4995–4999) of salinity from 3.55 to 29.69‰; to the north from station 5000, the salinity becomes typical for the Kara Sea (>30‰). The average turbidity of the riverine waters amounts to 37.5 mg/l (16 mg/l in the mixing zone). Under the riverine and marine water mixing, the migration forms of the metals vary in different modes. In the background of the almost tenfold decrease of both the dissolved and suspended particulate Fe forms, the latter is markedly prevailing and amounts to 66–99% of the total Fe content in the water of the mixing zone. In the balance of the Mn, Zn, and Pb forms, despite the considerable decrease of their concentrations in the suspended particulate matter (by a factor of 5–10), the suspended particulate form is also prevailing, accounting for 50 to 97%. Unlike these elements, the bulks of the Cu (66–92%), Cd (85–98%), and As (74–99%) occur in the dissolved form, and its fraction increases considerably with the turbidity decrease and the salinity increase of the waters (Table 1).

The spatial distribution of the suspended particulate matter and the suspended particulate forms of the metals in the water mass in the Ob River estuary–Kara Sea section is shown in Fig. 1. The concentration of the suspended particulate matter along the entire section decreases from 80 to 0.3 mg/l, i.e., by a factor of over 200 (Fig. 1a), with the most drastic decrease at the depths up to 20 m, where the salinity is 3‰ or below. In the near-bottom waters, the increased concentrations of suspended particulate matter are propagated somewhat farther: to the 30 m isobath and the 22‰

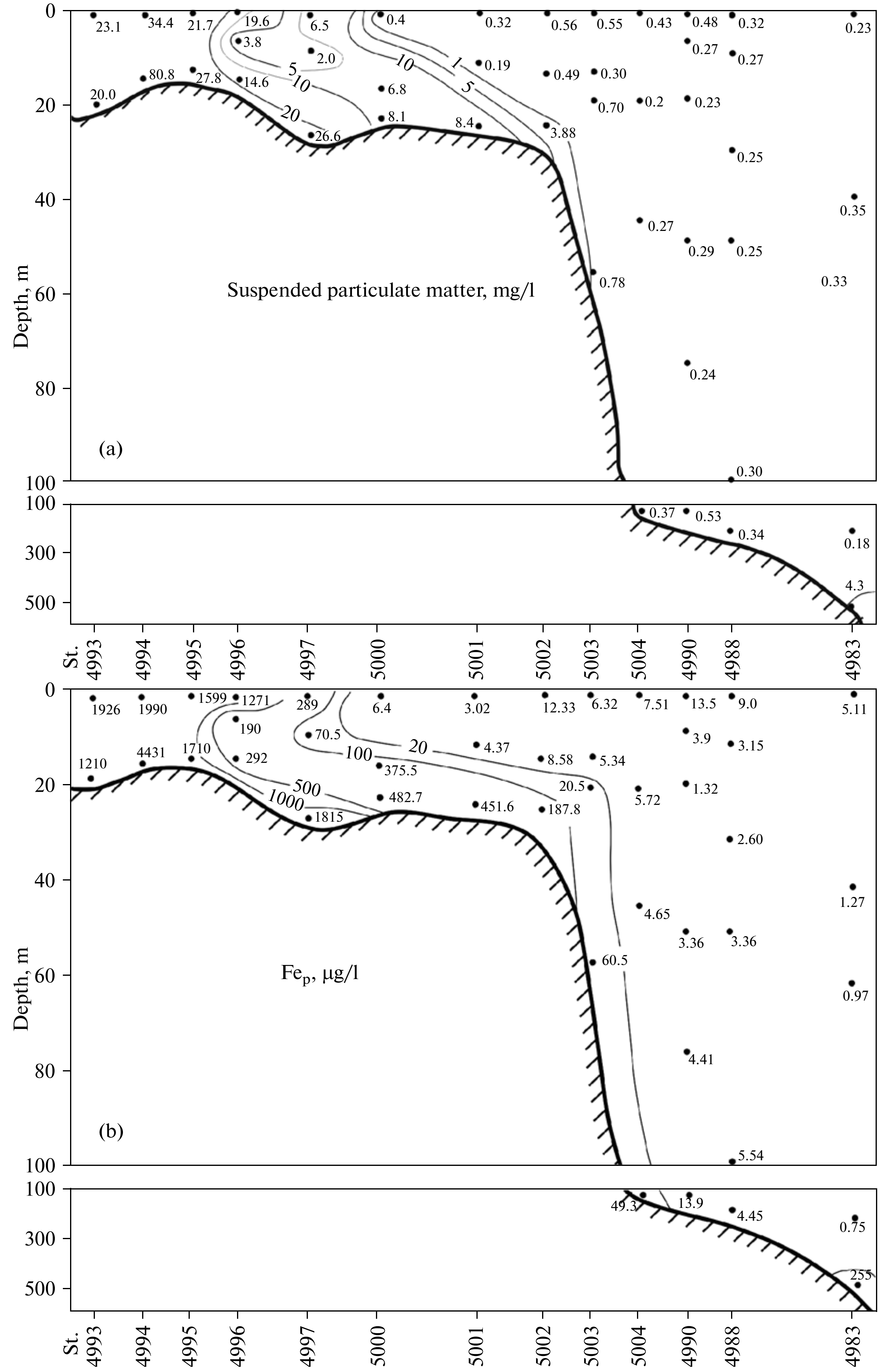

Fig. 1. The distribution of the suspended particulate matter (a) and the suspended particulate forms of Fe (b), Mn (c), Zn (d), Cu (e), and Pb (f) in the water mass over the Ob River estuary–Kara Sea section.

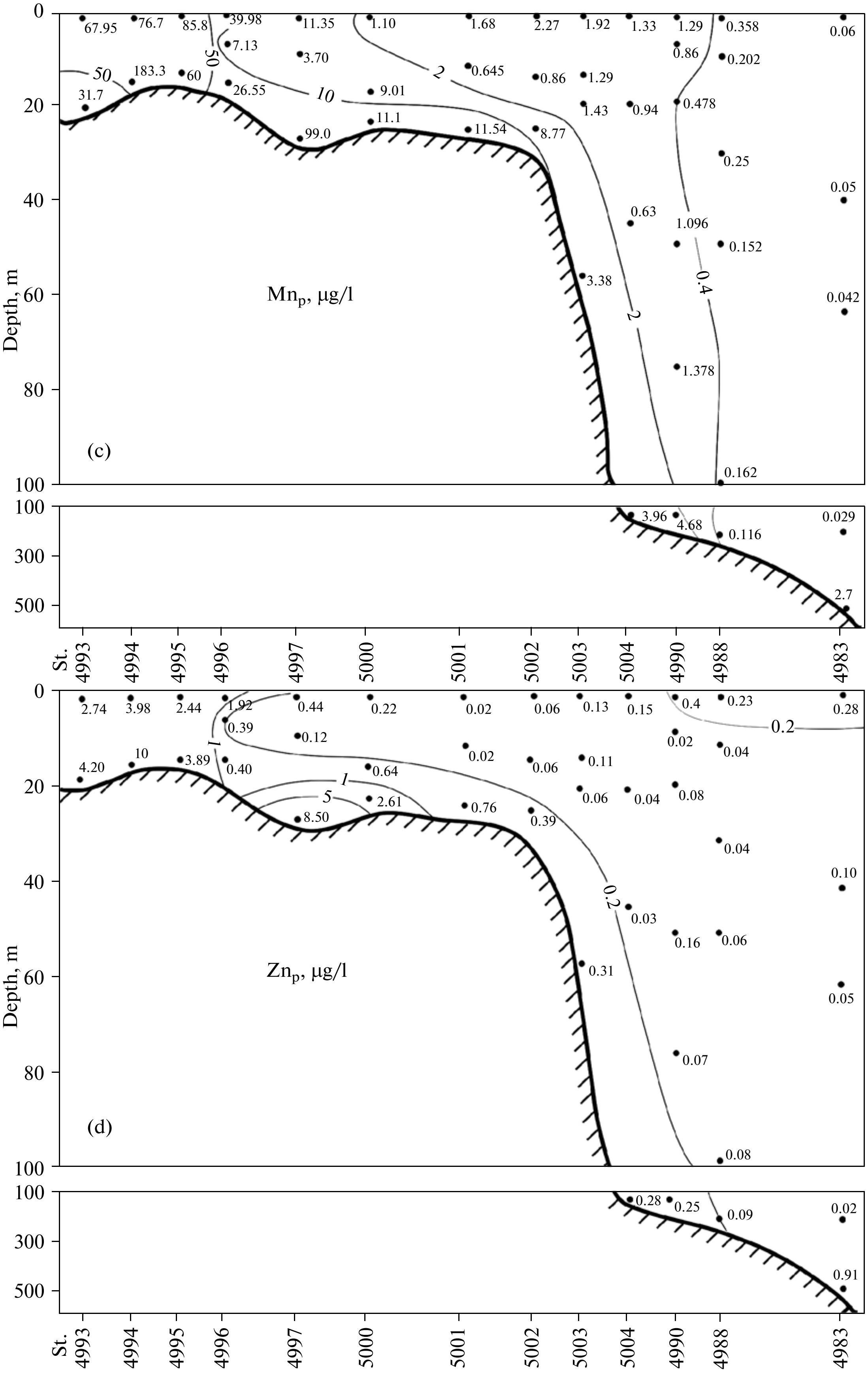
Depth, m
0
20
40
60
80
100
300
500
Mnp, μg/l
(c)
67.95
76.7
85.8
39.98
11.35
1.10
1.68
2.27
1.92
1.33
1.29
0.358
0.06
7.13
3.70
0.86
0.202
50
50
183.3
60
26.55
10
2
0.645
0.86
1.29
31.7
9.01
0.478
1.43
0.94
11.1
99.0
11.54
8.77
0.25
0.05
0.63
1.096
0.152
3.38
0.4
2
0.042
1.378
0.162
3.96
4.68
0.116
0.029
2.7
St.
4993
4994
4995
4996
4997
5000
5001
5002
5003
5004
4990
4988
4983
Znp, μg/l
(d)
2.74
3.98
2.44
1.92
0.44
0.22
0.02
0.06
0.13
0.15
0.4
0.23
0.28
0.39
0.2
0.12
1
0.02
0.04
0.02
0.06
0.11
4.20
10
3.89
0.40
0.64
1
5
2.61
0.06
0.04
0.08
8.50
0.76
0.39
0.04
0.10
0.2
0.03
0.16
0.06
0.31
0.05
0.07
0.08
0.28
0.25
0.09
0.02
0.91

Fig. 1. (Contd.)

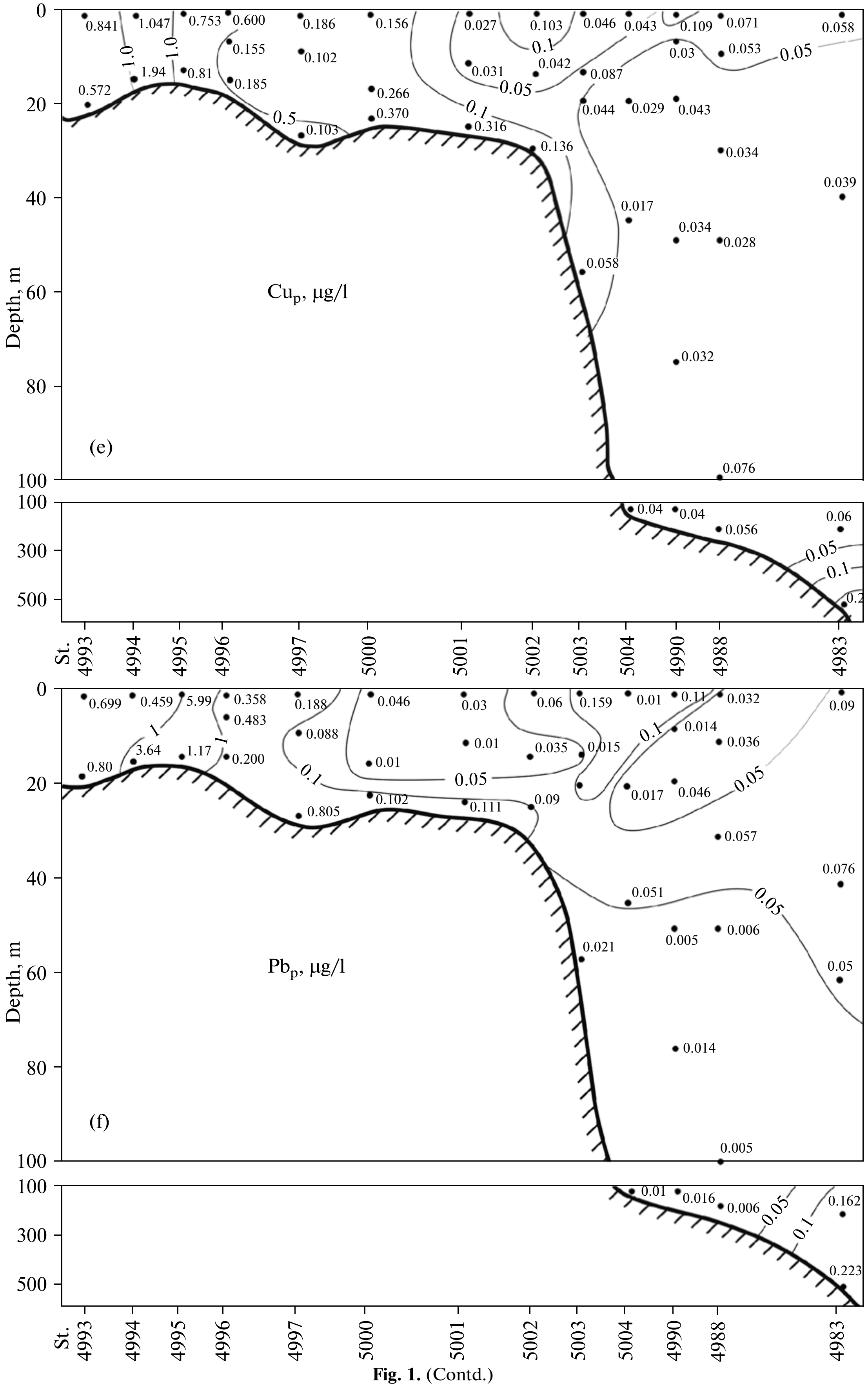
(e)
Cu$_p$, μg/l
Depth, m
0
20
40
60
80
100
300
500
0.841
1.047
0.753
0.600
0.186
0.156
0.027
0.103
0.046
0.043
0.109
0.071
0.058
0.155
0.102
1.94
0.81
0.185
0.572
0.266
0.370
0.103
0.031
0.042
0.087
0.03
0.053
0.316
0.044
0.029
0.043
0.136
0.034
0.039
0.017
0.034
0.028
0.058
0.032
0.076
0.04
0.04
0.056
0.06
0.2
1.0
1.0
0.5
0.1
0.05
0.1
0.05
0.05
0.1
St.
4993
4994
4995
4996
4997
5000
5001
5002
5003
5004
4990
4988
4983
(f)
Pb$_p$, μg/l
Depth, m
0.699
0.459
5.99
0.358
0.188
0.046
0.03
0.06
0.159
0.01
0.11
0.032
0.09
0.483
0.088
0.01
0.035
0.015
0.014
0.036
3.64
1.17
0.200
0.80
0.01
0.05
0.017
0.046
0.805
0.102
0.111
0.09
0.057
0.051
0.076
0.005
0.006
0.021
0.05
0.014
0.005
0.01
0.016
0.006
0.162
0.223
1
1
0.1
0.1
0.05
0.05
0.05
0.1
St.
4993
4994
4995
4996
4997
5000
5001
5002
5003
5004
4990
4988
4983

Fig. 1. (Contd.)

Table 1. Ratios of the concentrations of some metals in the dissolved and suspended particulate forms in the Ob River estuary–Kara Sea section compared to the world rivers and the Arctic rivers of Eurasia

Station	Layer, m	Suspended particulate matter, mg/l	Fe		Mn		Zn		Cu		Pb		Cd		As	
			dis-solved	sus-pended particu-late	dis-solved	sus-pended particu-late	dis-solved	sus-pended particu-late	dis-solved	sus-pended particu-late	dis-solved	sus-pended particu-late	dis-solved	sus-pended particu-late	dis-solved	sus-pended particu-late
4993	0	23.13	205	1926	1.3	67.95	1.3	2.74	2.10	0.84	0.11	0.70	0.02	0.029	0.41	0.24
			6	*94*	*2*	*98*	*32*	*68*	*71*	*29*	*14*	*86*	*41*	*59*	*63*	*37*
	21	20.07	620	1206	15.0	31.73	0.2	4.20	2.25	0.57	0.91	0.81	0.02	0.03	0.48	1.70
			34	*66*	*32*	*68*	*5*	*95*	*80*	*20*	*53*	*47*	*40*	*60*	*23*	*77*
4994	0	34.7	120	1990	2.5	76.7	0.2	3.98	1.70	1.05	0.23	0.46	0.04	0.015	0.65	0.36
			6	*94*	*3*	*97*	*5*	*95*	*62*	*38*	*33*	*67*	*72*	*28*	*36*	*64*
	16	80.8	110	4434	0.8	183.5	<0.1	9.9	1.20	1.94	0.08	3.70	0.09	0.013	1.02	0.54
			2	*98*	*0.5*	*99.5*	*<1*	*99*	*38*	*62*	*2*	*98*	*87*	*13*	*65*	*35*
4995	0	21.68	42	159	12.0	85.77	1.1	2.41	1.95	0.75	0.20	5.99	0.10	0.016	2.10	0.23
			21	*79*	*12*	*88*	*31*	*69*	*72*	*28*	*3*	*97*	*86*	*4*	*90*	*10*
	13.8	27.85	20	1709	18.0	60.04	0.7	3.89	1.55	0.81	0.32	1.17	0.18	0.006	6.74	2.41
			1	*99*	*23*	*77*	*15*	*85*	*66*	*34*	*21*	*79*	*97*	*3*	*74*	*26*
4996	0	19.57	53	1271	33.0	39.9	1.2	1.92	1.28	0.60	0.18	0.36	0.10	0.018	4.10	0.19
			4	*96*	*45*	*55*	*38*	*62*	*68*	*32*	*33*	*67*	*85*	*15*	*95*	*5*
	18.7	14.65	18	291.7	3.7	26.63	0.1	0.40	1.35	0.18	0.12	0.20	0.20	0.003	4.45	0.02
			6	*94*	*12*	*88*	*20*	*80*	*88*	*12*	*37*	*63*	*98*	*2*	*99*	*1*
4999	0	6.47	14	289	7.3	11.35	1.8	0.44	2.10	0.19	0.19	0.19	0.11	0.012	5.18	0.09
			5	*95*	*39*	*61*	*80*	*20*	*92*	*8*	*50*	*50*	*90*	*10*	*98*	*2*
Rivers of the world [19]		460	23500	10	500	0.6	115	250	1.5	37	0.03	16	0.01	0.3	–	2.3
Arctic rivers of Eurasia [18]]		36	87	1900	–	80	0.74	7.6	1.62	1.65	0.012	1.0	0.0034	0.025	–	0.68

Note: for each of the layers, the data in the upper lines are in μg/l; those in the lower lines (italicized) are in % of the sum(dissolved + suspended particulate).

Table 2. The adsorbed forms of some metals* in the suspended particulate matter of the near-bottom layer in the Ob River estuary–Kara Sea section

Station	Layer, m	Fe	Mn	Zn	Cu	Pb	Cd	Ag	As
4993	21	3.66/56	1351/79	76.7/34	12.22/40	4.11/94	0.14/84	0.04/68	4.20/5
4994	16	1.63/30	1708/75	23.0/19	5.49/23	10.37/23	0.02/12	0.01/9	0.46/7
4995	13.8	4.65/73	2061/92	82.65/57	18.51/62	43.67/68	0.11/52	0.03/98	20.0/80
4996	18.7	1.64/62	2284/95	19.02/53	11.77/68	5.52/30	0.22/86	0.19/95	2.02/81
4999	29	3.00/44	3150/85	82.97/26	16.48/43	17.55/59	0.16/21	0.01/27	5.97/27
5000	22.4	1.03/17	975/64	101.2/31	11.25/24	10.87/85	3.28/96	0.94/89	2.24/23
5003	60	4.07/55	3488/85	109.75/29	34.15/48	7.32/27	0.37/43	0.12/50	10.0/98
5004	110	8.13/64	7590/75	256.4/36	51.28/50	25.64/67	0.25/50	0.26/33	20.5/61
4983	528	0.66/13	267/47	41.26/21	4.30/10	20.72/43	0.11/53	0.13/50	1.18/3

* The numerator is the content of the metal in the adsorbed form (Fe is in % of the dry substance; the others are in μg/g of the dry substance); the denominator is the % of the total content in the suspended particalate matter.

salinity. Below, the turbidity is not higher than 1 mg/l over the entire water thickness. At the deepest station 4983 (528 m depth), the turbidity in the near-bottom waters increases to 4.3 mg/l. This is caused by the strong near-bottom current [8] roiling the bottom sediments and forming the nepheloid layer. It is seen from Fig. 1 that the suspended particulate forms of the metals per unit of volume (μg/l or ng/l) are distributed within the water mass similarly to the suspended particulate matter as such, e.g., Fe_p (Fig. 1b), Mn_p (Fig. 1c), Zn_p (Fig. 1d), Cu_p (Fig. 1e), and Pb_p (Fig. 1f). Iron is a metal with its content decreasing over the river–sea section to much a higher degree (by a factor of 1000) than that of the suspended particulate matter. This is provided by various biogeochemical processes, especially the flocculation and/or coagulation of colloids and organomineral complexes, the precipitation of amorphous hydroxides, and the intense Fe utilization from the solution and suspended particulate matter by the organisms of the living communities. Whereas the Fe_p and Mn_p contents decrease with the decrease of the turbidity and the increase of the salinity of the water (Figs. 1b and 1c), the distribution of Zn_p, Cu_p, and Pb_p in the central and northern parts of the section is characterized by local areas of alternating increased and decreased contents (Figs. 1d–1f). This is evidently caused by their higher geochemical mobility under the instability of the physicochemical parameters in the water mass.

Unlike the Me_p volume concentrations, their mass concentrations (% or μg/g of dry mass of the suspended particulate matter) allow one to characterize the metal enrichment of the suspended particulate matter itself depending on the biogeochemical parameters. As seen from Fig. 2, the riverine suspended particulate matter enriched in Fe (>5%) and Mn (>0.25% of the dry mass), with the increase of the salinity, is substituted by that with lower Fe and Mn contents in the water layer down to the 20 m depth (2.5 to <1 and <0.1% of the dry mass, respectively). However, this suspended particulate matter is of quite another composition constituted mainly of autochthonous organogenic substances formed as a result of the intense bioproduction by the phyto- and then zooplankton within the frontal zone of the estuary [15]. The suspended particulate matter in the near-bottom layer is also enriched in iron and manganese over the entire section. Our data show that a significant role in the composition of the near-bottom suspended particulate matter in the entire section belongs to the most labile and biologically assessable metal forms, i.e., to the adsorbed complex (Table 2). With the growth of the salinity, the fraction of the adsorbed forms of Fe, Mn, Zn, Cu, and As increases to reach its maximum in the seawaters (station 5004) associated with the maximum of the suspended particulate organic carbon (POC, 12.4%) [2]. The correlation between the distribution of the POC and the adsorbed forms of Fe, Mn (Fig. 3a), Zn, Cu, As, and Pb (Fig. 3b), probably, is caused by the influence of the biogenic factor on the changes in the migration forms of the metals in the section. Manganese is different from the other metals in the prevalence of the adsorbed form (77% on average) in the near-bottom suspended particulate matter (Table 2). The adsorbed complexes are of great importance for the other metals as well (on average, 35–58% of the total content). Note the drastic decrease of both the total Me_p concentrations (excluding Pb) and their adsorbed forms in the near-bottom waters at station 4983, i.e., at the northernmost and deepest one (528 m

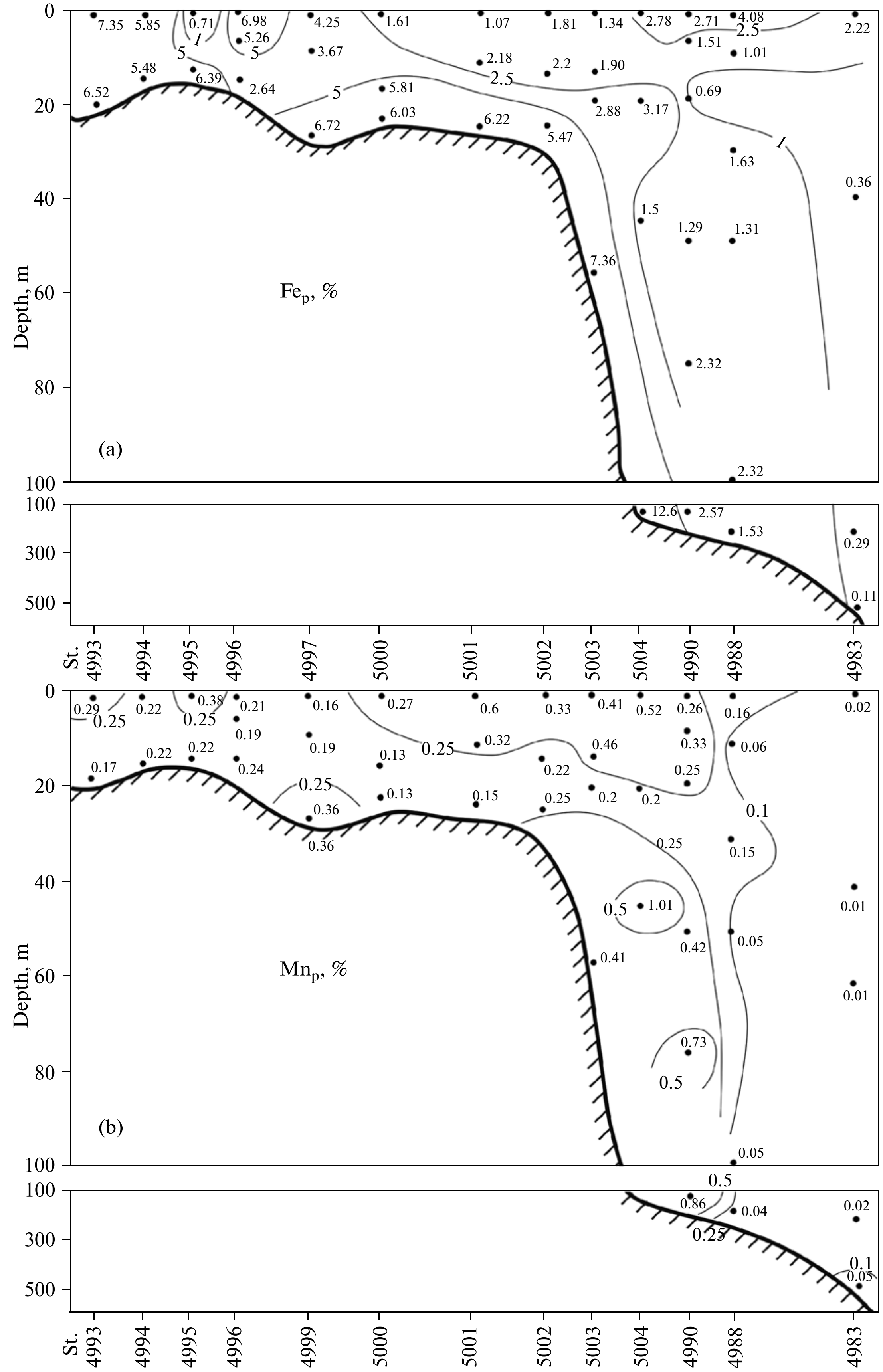

Fig. 2. The distribution of the Fe (a) and Mn (b) in the suspended particulate matter (% of the dry mass) over the Ob River estuary–Kara Sea section.

depth) located in the St. Anna Trench. Probably, this is caused by quite another source of the proper suspended particulate matter: a near-bottom water mass of Atlantic origin is found here, which flows from the Barents to the Kara Sea [8], as well as a thick nepheloid layer formed by a strong near-bottom currents.

The metals in the surface layer of the bottom sediments. The distribution of the metals in the water–sediment boundary layer is important for characterizing the habitat of benthic organisms. The bottom sediments in the area considered are characterized by low C_{org} contents (within 0.5–2.12% of the dry mass) [13], which is confirmed by our data as well (Table 3). Increased C_{org} contents (>2%) are characteristic for the sediments with increased contents of clayey matter (station 4995), as well as for the sapropel-like sediments (station 4993), which might have been formed owing to the sedimentation of high plankton biomasses below the pycnocline [15]. The water saturation of the bottom sediments and their enrichment in C_{org} provide favorable conditions for the fauna's habitation. The natural moisture of the bottom sediments is controlled by the grain-size composition of the particles, as well as the C_{org} content. Hence, it follows that there is a direct correlation between the C_{org} and the moisture of $R^2_{xy} = 0.78$. We also found a positive correlation with the moisture of the bottom sediments for Fe, Zn, Cu, and As ($R^2_{xy} = 0.81$, 0.80, 0.79, and 0.56, respectively), whereas only Fe correlated statistically with the C_{org} content ($R^2_{xy} = 0.58$).

It is seen from Table 3 that the variability of the contents of most of the metals in the surface layer of the bottom sediments is similar to that in the near-bottom suspended particulate matter. At the same time, Mn, as a metal of the highest geochemical sensitivity to the changes in the redox conditions, varies by more than an order of magnitude (from 445 to 6661 μg/g of dry mass). The maximum Mn content is registered in the clayey oozes of the deep-water part of the section (station 4990), where over 70% of its total content is represented by amorphous hydroxides probably formed under diagenetic Mn oxidation [7]. The maximum Fe, Co, Cr, Pb, Cd, Ag, Sb, and Se contents are found in the sapropel-like silty sediments of the estuary (stations 4994–4996). The minima of the metals are characteristic of the coarse-grained silty marine sediments (station 5001), in which, because of the oxygen deficiency in the near-bottom layer caused by its utilization for organogenic fluxes of precipitating nutrient matter, weakly reductive conditions are formed promoting the Mn and Fe reduction and their passing, together with the associated microelements, from the sediments to the solution.

In the surface bottom sediments at the Ob river section, the geochemically inert forms of Fe, Zn, Co, Cr, Ni, and Pb prevail: up to 80–95% of each of these metals are fixed in the crystal lattices of the loamy minerals or bound to the detrital minerals [7]. This form represents no direct danger to fauna. Unlike these metals, the Mn and Cu in the marine sediments of the section are characterized by the substantial role of the geochemically mobile forms (25–70%); at that, the hydroxide form is key for Mn; for Cu, this is the form bound to organic matter. In the riverine and estuarine sediments, the bulk of the Mn and Cu (about 80% on average) is fixed in the detrital matter [7].

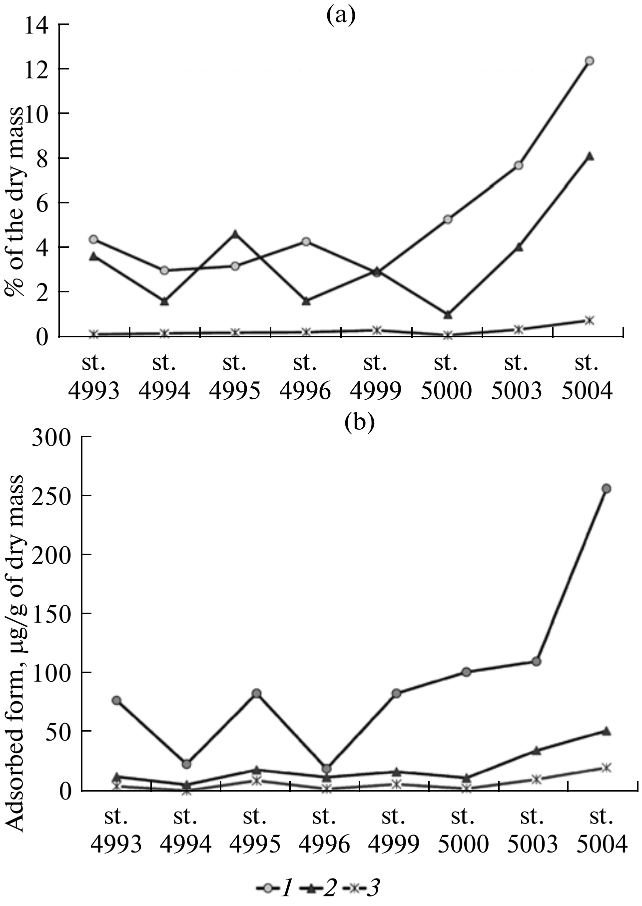

Fig. 3. The variations of the suspended particulate organic carbon [2] and the adsorbed forms of the metals in the particulate matter over the Ob River estuary–Kara Sea section: (a): *1*—POC, *2*—Fe, *3*—Mn; (b): *1*—Zn, *2*—Cu, *3*—As.

The metals in the benthic organisms. In the shallow waters of the Ob River estuary, bivalves and crustaceans prevail; at that, mollusks constitute the major part of the macrozoobetnos by their biomass and population density [9]. In the sea, particularly in its deeper part, echinoderms are dominant, especially their large forms [9]. With the growth of the salinity, quite a well-pronounced successive substitution of fresh- and saltwater taxons with their allied groups adapted to habitation in seawater is observed [3]. The benthic organisms treated are represented by the three main fauna groups typical for the Kara Sea: the bivalves *Portlandia*

Table 3. The natural moisture and the contents of organic carbon and heavy metals (μg/g of dry mass, excluding Fe) in the bottom sediments over the Ob River estuary–Kara Sea section

Station	Depth, m	Layer, cm	Moisture, %	C_{org}, %	Fe, %	Mn	Zn	Cu	Cr	Co	Pb	Cd	Ag	As	Se	Sb	Hg
4993	21	0.5–2.5	50.20	2.15	3.32	697	60.9	27.83	65.6	14.5	27.0	2.9	0.11	16.5	0.16	0.063	0.026
4994	16	0.5–1.0	48.38	0.89	6.37	1269	34.7	14.30	132	23.4	31.7	3.65	0.084	14.2	0.17	0.83	0.065
4995	17	0.5–1.5	66.67	2.39	6.66	3260	77.5	25.08	87.8	28.5	29.4	1.82	0.062	26.9	0.21	0.32	0.041
4996	17	0.5–1.5	56.89	1.95	6.38	2774	68.1	22.96	85.1	26.4	24.3	1.43	0.042	49.4	4.67	2.72	0.024
4999	27	0.5–1.5	44.15	0.85	4.02	770	47.3	15.05	80.7	14.9	14.93	0.85	0.05	28.3	2.6	0.17	0.022
5000	24	0–2.5	48.42	1.31	4.33	1089	53.3	16.90	77.6	19.3	14.52	0.59	0.041	34.4	0.37	0.42	0.045
5001	25	1.0–1.5	28.14	0.22	1.62	445	23.2	6.25	32.9	9.2	33.97	1.28	0.046	10.1	2.46	0.16	0.017
5003	60	0.5–1.0	41.42	0.51	3.13	868	27.8	11.08	61.1	9.72	16.53	0.74	0.032	26.7	0.49	0.51	0.015
4990	129	0.5–1.0	56.74	0.78	4.32	6661	52.7	23.9	77.9	23.4	15.1	0.67	0.02	46.7	1.03	0.79	0.019
4983	555	0.5–1.5	54.51	2.03	4.82	975	66.4	28.94	80.1	17.4	4.45	0.15	0.012	50.4	1.07	0.68	0.010

aestuariorum of brown color (evidently covered with a film of Fe and Mn hydroxides) and *Macoma* sp. of white color, *Opheopleura borealis*, *Stegophiura nodosa*, and *Asteroidea* (*Ctenodiscus crispatus*) echinoderms, as well as *Mesidothea sabini*, *M. sibirica*, *M. Entomon*, Cumacea, Amphipoda (*Anonyx nugax*) crustaceans.

The contents of the Fe, Mn, Zn, Cu, Cr, Co, Pb, Cd, Ag, and Hg heavy metals; the As, Se, and Sb metalloids; and the C_{org} in the typical fauna of the Kara Sea are presented in Table 4.

The peak concentrations of various metals are found in different organs of the examined organisms, which is caused by their different ability for metal accumulation. The shells of the *Portlandia aestuariorum* mollusk contain extremely high amounts of Fe (1.34%), Mn (2.09%), and Co (4.75 μg/g of dry mass), which is evidently caused by the presence of Fe and Mn hydroxides on their surfaces. The soft tissues of the *Macoma* sp. mollusk are enriched in Zn (253.3 μg/g). The maxima of Cu (100.8 μg/g), Cr (3.19 μg/g), Sb (3.67 μg/g), and Se (1.74 μg/g) are found in the body of the *Mesidothea sibirica* crustacean, whereas the bodies of the echinoderms are enriched in As (68.3 μg/g), Pb (4.65 μg/g), Cd (6.07 μg/g), and Hg (0.028 μg/g). The minimum contents of Zn, Cu, Cr, Ag, and Hg are characteristic for the shells of the mollusks; the minimum contents of Fe and Co, for the discs and rays of the echinoderms; and the minimum contents of Mn, Pb, As, Sb, and Se, for the bodies of the crustaceans (Table 4). Note that the C_{org} content is also quite variable: from the minimum (0.82%) in the carbonate shells of the mollusks via the intermediate values for the bodies of the echinoderms (5–14.85%) to the high contents in the soft tissues of the mollusks and crustaceans' bodies (27–28.6%). This confirms the idea proposed by A.P. Vinogradov over 50 years ago about the close relationship of the chemical compositions of the organisms with the features of their metabolism and the physiological functions of their individual organs.

The comparison of the heavy metal distribution in the bivalves of the two different species collected at different stations (Table 4) shows the following. The shells of *Macoma* sp. accumulate less metals than those of *Portlandia aestuariorum*; in the latter, the contents of Fe, Mn, Co, Zn, Cd, As, and Sb are the most drastically increased. In the soft tissues of both bivalves, the content of most of the metals, excluding Mn, varies within an order of magnitude. The soft tissues of *Portlandia aestuariorum* are considerably enriched in manganese compared to those of *Macoma* sp. (Figs. 4a and 4b). Evidently, the cause of the difference in the metal bioaccumulation between the two different mollusks should lie in the different habitat conditions (abiotic factors), as well as in the species' features and the nutrition types of these bivalves. In our case, both mollusk genera were collected in the shallow-water parts of the section but at different salinities: At station 4996 with a 17 m depth and 24.4‰ salinity, *Portlandia aestuariorum* was sampled, and *Macoma* sp. was collected at station 5000 with a 24 m depth and 32.13‰ salinity. The bottom sediments at station 4996 are more watered (10% higher moisture) and contain half as much again C_{org}. The total contents of the metals here are also higher by factors of 1.5–10 than those at station 5000 (Table 3). The brown color of the *Portlandia* shells is probably caused by the presence of films of Fe and Mn diffusing from the interstitial waters of the poorly reduced bottom sediments. In the near-bottom suspended particulate matter of station 4996, no significant excess over station 5000 was registered for the total contents of most of the metals and for their adsorbed forms, being the most digestible by the organisms. Thus, the difference in the levels of the concentrations of most of the heavy metals in the different organs of the *Macoma* sp. and *Portlandia aestuariorum* mollusks may be partly explained by the physicochemical and biogeochemical parameters of the environment; probably, a key reason is related to the species' features and/or other biological factors.

The concentrating function of the chemical elements F_c is characterized by means of the factor of the metal concentrating ($F_c = C_{Me, org}/C_{Me, hab}$). We evaluated the F_c value using the contents of the metal in the benthic organisms ($C_{Me, org}$) and in their habitat ($C_{Me, hab}$) using the example of the *Portlandia aestuariorum* mollusks (their shells and soft tissues) and the *Stegophiura nodosa* echinoderms (discs) collected at station 4996. Note that the total concentration of the metals in the solution and the suspended particulate matter (μg/l) was used to calculate the F_c, and, for the organisms, the content was converted to the wet mass (the dry mass content, on the average, was taken to be 0.25 of the wet mass). The F_c series are the following:

(1) *Portlandia aestuariorum* bivalve, soft tissues:

$$\begin{array}{ccccccccccccc} \text{Zn} & > & \text{Mn} & > & \text{Fe} & > & \text{Pb} & > & \text{Cd} & > & \text{Cu} & > & \text{As} \\ 8 \times 10^4 & & 3 \times 10^4 & & 4 \times 10^3 & & 3 \times 10^3 & & 2 \times 10^3 & & 2 \times 10^3 & & 7 \times 10^2; \end{array}$$

(2) *Portlandia aestuariorum* bivalve, shells:

$$\begin{array}{ccccccccccc} \text{Mn} & > & \text{Zn} & > & \text{Fe} & > & \text{Cu} & > & \text{As} & > & \text{Pb, Cd} \\ 7 \times 10^5 & & 1 \times 10^5 & & 4 \times 10^4 & & 1 \times 10^4 & & 6 \times 10^3 & & 1 \times 10^3; \end{array}$$

(3) *Stegophiura nodosa* echinoderm (discs):

$$\begin{array}{ccccccccc} \text{Zn} & > & \text{Cu, Cd} & > & \text{As} & > & \text{Mn, Pb} & > & \text{Fe} \\ 7 \times 10^3 & & 1 \times 10^3 & & 0.5 \times 10^3 & & 2 \times 10^2 & & 7 \times 10. \end{array}$$

The total content of the metals in the solution and the suspended particulate matter of the near-bottom layer at station 4996 decreases as follows: Fe (310) > Mn (30) > As (4.47) > Cu (1.50) > Zn (0.50) > Pb (0.32) > Cd (0.20). The comparison of this series to those for (1)–(3) shows the discrepancy of the series of the F_c decrease, on the one hand, and the total metal content in the near-bottom layer, on the other hand. Our data confirm the known thesis concerning the selectivity of the bioaccumulation of chemical elements by marine organisms. However, the comparison of rows (1)–(3) shows that the mollusks accumulate metals (both in the shells and soft tissues) to a higher degree than the echinoderms in their discs. The differences between the F_c values for the different metals amount to two orders of magnitude in each of the series. Among the metals, the highest F_c values in the mollusks are characteristic of the physilogically valuable metals: Zn, Mn, and Fe. In the shells, the maximum accumulation of Mn compared to the other metals is quite explicable by the mentioned existence of Fe–Mn hydroxide films, as well as by the Mn's capability for isomorphic substitution of Ca in the aragonite structure. By the data of the X-ray diffraction analysis (analyst O.M. Dara), aragonite constitutes 90–100% of the carbonate substance of the *Macoma* and *Portlandia* shells.

In the shells of the mollusks, each metal is concentrated to a tenfold degree compared to the soft tissues. By our data, the mass of the shells also appeared to be 10–15 times as high as that of the soft tissues of the mollusks. Hence, the shells of the bivalves play the main role in the deposition of heavy metals in the Ob River estuary.

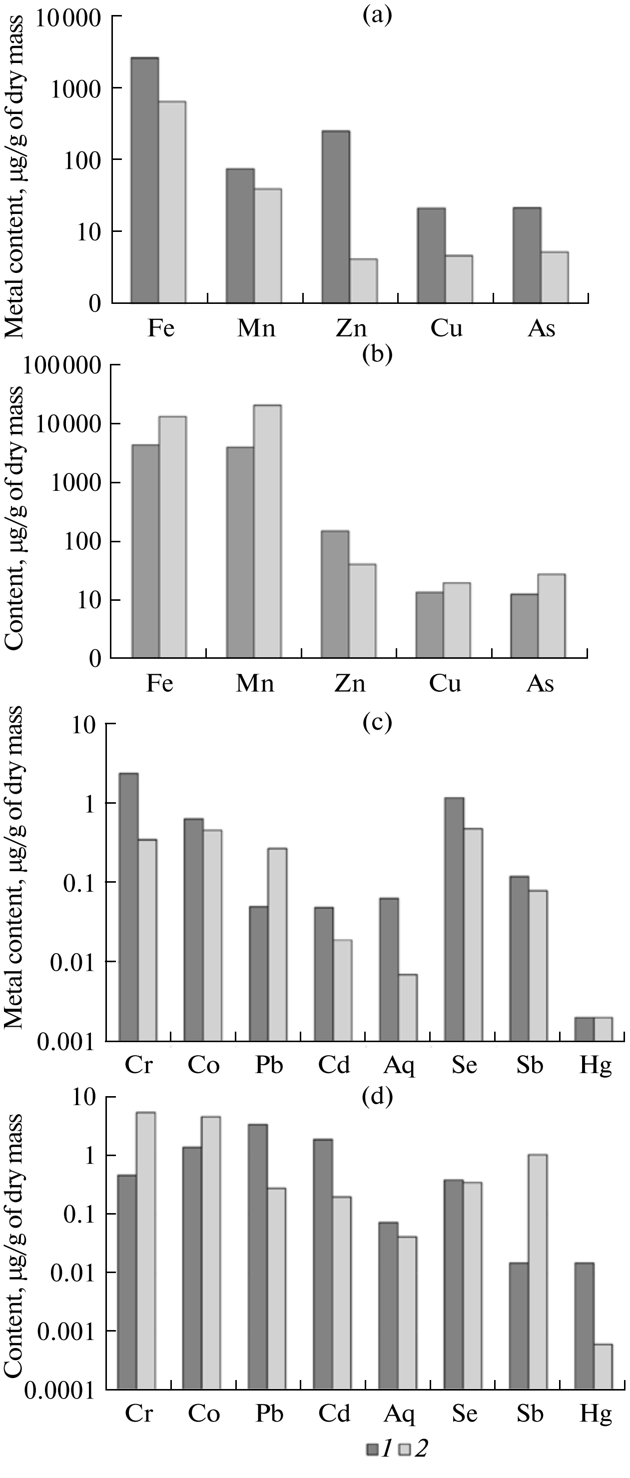

Fig. 4. The comparison of the microelement contents (μg/g of dry mass) in the bodies of the *Macoma* sp. (a, c) and *Portlandia aestuariorum* (b, d) bivalves. *1*—soft tissues, *2*—shells.

Table 4. The contents of some heavy metals (Fe in %, Hg in ng/g, and the others in μg/g of dry mass) and of organic carbon (%) in the benthic organisms over the Ob River estuary–Kara Sea section

Station	Organism (number of specimens)	Organ	Fe, %	Mn	Zn	Cu	Cr	Co	Pb	Cd	Ag	As	Se	Sb	Hg, ng/g	C_{org}
4994	*Mesidothea entomon* (2)	total	0.072	476	20.6	51.66	1.04	0.62	0.05	0.097	0.39	3.4	1.16	0.21	5.5	20.59
	“–” (4)	internals	0.093	54.15	150	51.3	1.15	0.54	3.12	0.145	0.443	12.8	0.1	0.01	6	27.0
	“–” (4)	body	0.16	697	51.4	32.45	2.41	0.47	0.05	0.02	0.345	3.94	1.44	0.39	8.7	21.46
4996	*Mesidothea sibirica* (1)	total	0.18	816	63.6	65.11	0.43	0.5	0.8	0.252	0.35	1.31	0.91	0.25	14.4	27.29
	Portlandia aestuariorum (10)	body	0.44	3990	153	13.68	0.47	1.42	3.48	1.94	0.072	12.6	0.39	0.02	15	27.16
	“–” (10)	shell	1.34	20904	41.1	19.76	5.6	4.75	0.28	0.2	0.041	27.7	0.35	1.05	0.6	4.2
4999	*Mesidothea sibirica* (1)	total	0.052	242	80.3	8.2	1.05	0.37	0.88	0.347	0.589	26.1	0.73	0.34	11.1	n.d
4999	*Stegophiura nodosa* (12)	discs	0.059	63	134	5.95	0.73	0.26	1.4	0.208	0.286	6.09	0.88	0.11	27.8	n.d
	“–” (12)	rays	0.043	34.1	21.8	2.89	0.44	0.09	1.01	0.113	0.092	4.25	0.72	0.01	0.7	n.d
5000	*Macoma* sp. (2)	body	0.26	75.9	253	21.63	2.39	0.64	0.05	0.049	0.064	21.8	1.18	0.12	2	28.6
	“–” (2)	shell	0.065	39.6	4.2	4.72	0.35	0.46	0.27	0.019	0.007	5.27	0.48	0.08	2.2	0.82
	“–” (2)	shell	0.052	44.5	3.6	3.8	0.37	0.12	0.19	0.017	0.008	1.99	0.84	0.14	5	n.d
5000	*Mesidothea sibirica* (1)	total	0.035	768	30.0	101	3.19	0.75	0.05	0.775	0.564	6.24	1.76	0.18	16.5	n.d
5000	*Mesidothea sibirica* (1)	total	0.11	328	75.1	91.2	0.59	0.43	0.05	0.702	0.561	7.58	0.79	0.01	16.7	n.d
5000	*Mesidothea sibirica* (1)	total	0.12	496	61.2	72	1.58	0.79	0.44	0.88	0.438	0.28	0.86	0.35	26.5	n.d
5000	*Mesidothea sabini* (1)	total	0.32	3468	57.6	79.2	1.69	1.66	2.56	0.677	0.29	12.5	0.67	1.74	22.9	n.d
5000	*Mesidothea sabini* (1)	total	0.88	5671	61.5	88.2	2.63	2.56	0.05	0.521	0.345	40.5	1.6	0.58	27.3	n.d
5000	*Mesidothea sabini* (1)	total	0.23	801	82.5	72.8	1.98	0.82	0.3	0.443	0.295	27.8	2.2	0.28	19.7	n.d
5002	Amphipoda (*Anonyx nugax*) (3)	total	0.38	23.8	202.0	36.0	2.78	1.46	0.05	2.47	0.386	29.3	1.17	0.19	0.6	20.22
5002	*Cumacea* (8)	total	0.33	274	72.1	75.9	2	0.6	2.97	1.40	0.301	5.63	1.54	0.31	0.9	22.01
5003	Ophiuroidea (*Ophiopleura borealis*) (2)	discs	0.001	37.7	62.1	2.47	0.39	0.08	0.07	0.319	0.139	68.3	0.67	0.01	14.2	7.55
5003	“–” (2)	rays	0.001	25.2	71.3	1.46	0.28	0.04	3.93	0.201	0.081	31.4	0.51	0.01	8.9	5.05
5004	Asteroudea (*Ctenodiscus crispatus*) (1)	total*	0.01	28.2	10.0	83.8	0.84	0.06	4.62	6.07	1.175	16.0	2.34	0.01	23.2	14.85

* A specimen with no stomach; n.d means “no data.”

As is known, bivalves are the most abundant benthic biocommunities in the coastal zones and are characterized by the high dynamics of their metabolism, which causes their intense accumulation of heavy metals. Because of this, they have long been used as biomonitors of the environmental conditions [17]. Resulting from the long-term international monitoring of estuarine ecosystems, the following background concentrations were specified for the toxic metals in the soft tissues of the bivalves (μg/g of dry mass): $Cd < 2$, $Pb < 5$, $Cu < 10$, and $Zn < 200$ [20]. Hence, one may note that the Cd and Pb toxic heavy metals do not exceed the background contents in the mollusks we tested in the Ob River estuary (Table 4), whereas Cu and Zn show only a small excess (by a factor of 1.5). This may testify to the absent or rather low anthropogenic contamination of the Ob River estuary with heavy metals.

CONCLUSIONS

In the Ob River estuary—Kara Sea section, under the riverine and marine water mixing, the processes of the dilution and transformation of the water composition are the most intense down to the 20 m depth, where the salinity is 3‰ or below, which is characteristic of the marginal filter [11]. The water turbidity decreases over the section by a factor of more than 200, and the salinity increases from 0.5 to 34.14‰. At that, the migration forms of all the metals considered are varied. Unlike the Ob riverine waters with the prevalence of suspended particulate forms, at the outlet of the estuary, in the waters of 29.5‰ salinity, from 50 to 97% of the Cd, As, Cu, Zn, and Pb in the water occur in the dissolved form. Iron and Mn exhibit an increase of the role of the dissolved forms, whereas their great amount in the estuarine waters remains bound to the suspended particulate matter. The contents of the microelements studied in the suspended particulate matter (μg/l) decrease by factors of 1000 for Fe_p, 500 for As_p, 200 for Mn_p, 100 for Zn_p, 50 for Cu_p and Pb_p, and 20 for Cd_p.

The variability of the mass concentrations of the suspended particulate forms ($10^{-4}\%$ of the dry suspended particulate matter) of Fe, Mn, Zn, Cu, Pb, Cd, Ag, and As is lower than that of the volume concentrations. This may be caused by the alternating of the adsorption and desorption processes in the section because of the local variations in the redox conditions depending on the C_{org} concentration and composition. The intense binding to the biogenic substances may cause an increase of the sorption processes even in the near-bottom suspended particulate matter in the case of its enrichment in organic matter. The peaks of the most geochemically mobile adsorbed forms of Fe_p, Mn_p, Zn_p, and Cu_p (valuable metals for bioproduction) coincide with the peak of the suspended particulate organic carbon (12.4% according to [2]). The primary for Mn (on average, 77% of the total content of the suspended particulate matter) and significant for other metals (35–58%) occurrence in the adsorbed form in the near-bottom suspended particulate matter increases markedly at the growth of the salinity in the section.

The surface layer of the bottom sediments, from the increased values of the moisture and the C_{org} content, as well as the presence of the heavy metals (especially of the toxic ones such as Pb and Cd) in the geochemically inert form, may be considered as a favorable environment for the development of benthic fauna. In general, the bivalves are the most enriched in the metals compared to the echinoderms and crustaceans. The different character of the heavy metal distribution in the *Portlandia aestuariorum* and *Macoma* sp. may be only partly explained by the difference abiotic parameters of their environment. In the both mollusk genera, the Cd and Pb concentrations are at the background levels, and those of Cu and Zn exceed the background by factors of 1.5–2.

The shells of the *Portlandia aestuariorum* mollusks are enriched in metals by an order of magnitude compared to their soft tissues. At that, the minimum F_c values in the mollusks are characteristic for the physiologically valuable metals (Zn, Mn, and Fe). Hence, the shells, having a great biomass, play an important role in the deposition of heavy metals in the estuary.

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