

## Speciation of Some Heavy Metals in Bottom Sediments of the Ob and Yenisei Estuarine Zones

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**Abstract**—The speciation of Fe, Mn, Zn, Cu, Co, Ni, Cr, Pb, and Cd was studied in 52 samples of bottom sediments collected during Cruise 49 of the R/V *Dmitrii Mendeleev* in estuaries of the Ob and Yenisei rivers in the southwestern Kara Sea. Immediately after sampling, the samples were subjected to on-board consecutive extraction to separate metal species according to their modes of occurrence in the sediments: (1) adsorbed, (2) amorphous Fe–Mn hydroxides and related metals, (3) organic + sulfide, and (4) residual, or lithogenic. The atomic absorption spectroscopy of the extracts was carried out at a stationary laboratory. The distribution of Fe, Zn, Cu, Co, Ni, Cr, Pb, and Cd species is characterized by the predominance of lithogenic or geochemically inert modes (70–95% of the bulk content), in which the metals are bound in terrigenous and clastic mineral particles and organic detritus. About half of the total Mn amount and 15–30% Zn and Cu is contained in geochemically mobile modes. The spatiotemporal variations in the proportions of metal species in the surface layer of sediments along the nearly meridional sections and through the vertical sections of bottom sediments cores testify that Mn and, to a lesser extent, Cu are the most sensitive to changes in the sedimentation environment. The role of their geochemically mobile species notably increases under reducing conditions.

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### INTRODUCTION

The study of the physicochemical speciation of chemical elements, in particular, some heavy and transitional metals in marine bottom sediments is important for several reasons. The speciation of elements reflects the processes that result in the accumulation of metals in bottom sediments, which serve as a habitat for benthic organisms. The microelemental composition of these organisms is largely controlled by the composition of the bottom sediments. In studying the bioavailability, it is important to know not only the total metal contents but also the modes of their occurrence, because, as has been established experimentally, mobile species of metals, i.e., organic particles adsorbed on clay, and/or hydroxides bound with Fe and Mn, are largely available for the bottom biota [1, 2]. Marine bottom sediments are commonly characterized by pH ranging from 6 to 8. As pH drops, metals are released from sediments and pass into bottom water. Thereby, their minor concentrations are vital for the biota, whereas elevated concentrations may be toxic for it. Heavy metals of anthropogenic origin come to the environment largely as inorganic complexes or hydrated ions, which are readily adsorbed on the surface of settling and suspended particles from the dissolved stream flow and are held by relatively weak physical and/or chemical bonds. Therefore, the specia-

tion of metals in bottom sediments may be used to estimate the anthropogenic impact on the sedimentation region.

These investigations are especially important in such key zones of the geochemical migration of elements as the zone of mixing of river and marine waters, where sedimentary materials supplied by river-runoff are modified and largely control the behavior of elements in the marine environment. Acad. A.P. Lisitsyn [3] regards the zone of river and marine water mixing as a global marginal filter that combines a complex of sedimentation processes that are driven by abrupt changes in the hydrodynamic, biological, and physicochemical parameters.

The behavior of chemical elements in arctic zones of mixing attracts interest because of the still insufficient quantitative assessment of geochemical processes with the participation of heavy and transitional metals that hampers the prediction of their effect on the ecosystems of shelf seas.

Our research was focused on studying the spatiotemporal distribution of physicochemical Fe, Mn, Zn, Cu, Co, Ni, Cr, Pb, and Cd species in the bottom sediments of the southwestern Kara Sea, including the estuaries of the Ob and Yenisei rivers, with the aim of quantitatively assessing the contribution of the main processes to the deposition of heavy metals in this region.

## MATERIALS AND METHODS

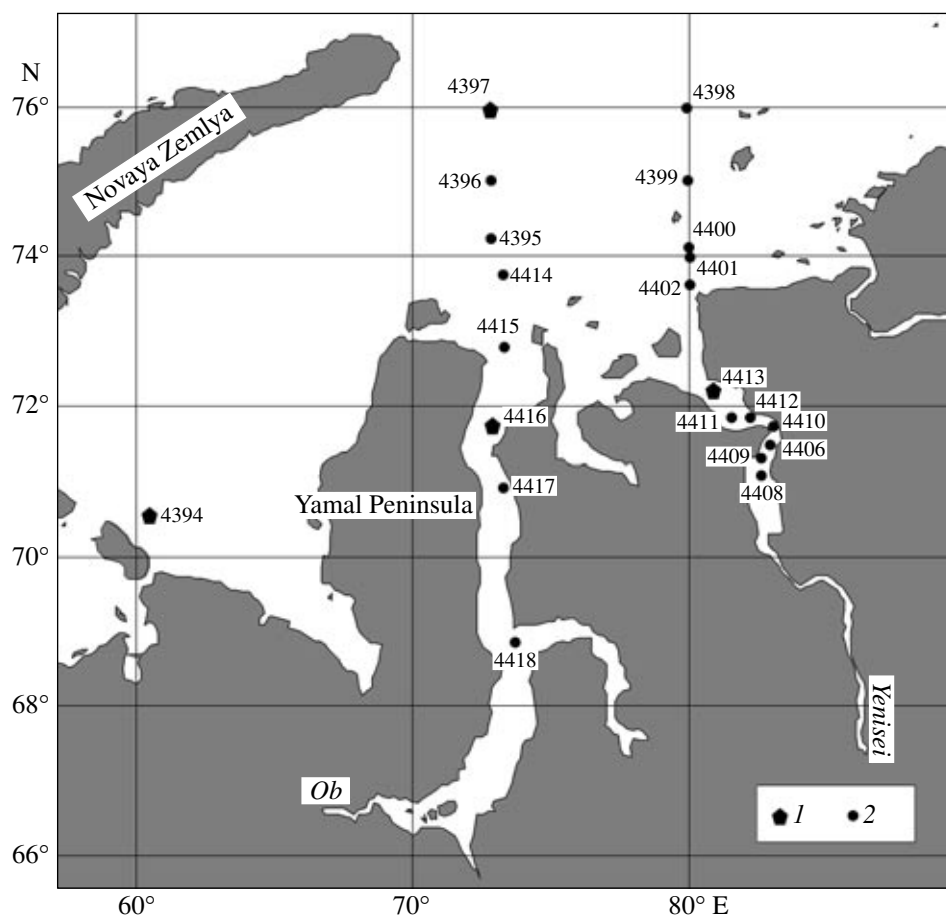
This study was conducted on 52 samples of bottom sediments taken during Cruise 49 of the R/V *Dmitrii Mendeleev* conducted by the Shirshov Institute of Oceanology, RAS, in the Kara Sea in September–October, 1993.

Samples of bottom sediments from the surface layer (0–1 cm) were taken with Ocean-0.25 dredgers and box corers and four columns of bottom sediments 365–421 cm long were obtained with geological shock tubes 127 mm in diameter. The sampling was carried out along two nearly meridional sections, provisionally referred to as Ob (12 stations) and Yenisei (8 stations). The northern points of the Ob and Yenisei sections (stations 4397 and 4398, respectively) are located at 76° N; thus, the extent of the sections is 800–900 km. Furthermore, the samples from the column of bottom sediments at Station 4394 in the southwestern Kara Sea near the Karskiye Vorota Strait have been analyzed. An index map of stations is shown in Fig. 1.

The physicochemical species of metals in bottom sediments were separated with the consecutive chemical leaching of the initial sediment samples at their natural moisture. Thereby, the fractions of element differ-

ently bound with bottom sediments consecutively passed into solution.

In the course of the expedition, each bulk sediment sample was divided on board into two subsamples within six hours after the raising of the corers and dredgers. One subsample was used to determine the natural moisture with the weight method and then retained in a plastic container for the subsequent stationary analysis of its bulk composition. Another subsample went to the chemical treatment in two sequential stages. During the first of these stages, the samples were treated with an acetate buffer solution (pH 4.8), which is traditionally applied to extract the exchange complex of metals adsorbed on various sorbents and bound with carbonates; thereby, the first, reactive adsorbed species of metals passed into solution. Between the extraction stages, the samples were separated from the reagent by filtering through a double paper filter, washed on the filter with doubly distilled water, dried up to a constant weight at 60°C, ground in an agate mortar, and weighed. During the second stage, a mixture of 25% acetic acid and 1M hydroxylamine hydrochloride (Chester reagent [4]) was used to extract amorphous Fe and Mn hydroxides and coprecipitated



**Fig. 1.** Index map of stations of bottom sediments sampling in the estuaries of the Ob and Yenisei rivers in the Kara Sea. (1) Sampling stations of vertical columns of bottom; (2) sampling stations of bottom sediments from the surface layer.

**Table 1.** Speciation of metals in the bottom sediments of the Ob and Yenisei estuaries and the southern Kara Sea; Fe is given in wt %, other metals in ppm of dry material

Station	Depth, m	Interval, cm	Fe 1	Fe 2	Fe 3	Fe 4	Mn 1	Mn 2	Mn 3	Mn 4	Co 1	Co 2	Co 3	Co 4
4394	138	0–5	0.32	0.2	0.23	4.88	185	194	39	620	0.2	0	1.7	17
		30–35	0.39	0.15	0.22	4.89	413	124	39	580	0.9	0	2.6	26
		60–65	0.41	0.15	0.18	5.04	140	96	42	410	1.1	0	0.6	26
		150–155	0.47	0.18	0.15	4.51	87	40	31	390	0.7	0	1.9	34
		240–245	0.36	0.13	0.16	4.45	82	85	28	370	0.5	0	0	20
		300–3205	0.3	0.06	0.2	4.14	72	49	68	380	0.3	0	2.5	12
		360–365	0.31	0.21	0.19	4.2	47	80	225	380	0.1	0	1.5	14
4395	30	0–10	0.09	0.13	0.06	1.49	77	525	24	765	0.2	0.2	0.2	9
4396	32	0–10	0.02	0.07	0.03	2.41	265	50	8	480	0.1	0.1	1.1	12
4397	150	0–10	0.01	0.47	0.18	6.29	1061	13308	584	18792	0.1	18.7	4	37
		20–25	0.33	0.18	0.08	5.8	380	167	22	1313	1.3	0.6	0.1	31
		60–64	0.47	0.14	0.08	5.12	430	110	21	1058	2.3	0.1	3.2	40
		96–100	0.36	0.18	0.04	5.55	380	37	42	1117	2.7	0.1	4	26
		166–170	0.37	0.14	0.05	5.62	823	257	55	1148	1.9	0.1	4.6	26
		191–200	0.41	0.12	0.06	4.63	413	133	44	1376	0.6	0.1	5.4	23
		320–330	0.43	0.08	0.03	5.41	339	196	28	1021	2.4	0.1	3.2	34
		370–380	0.36	0.1	0.02	5.68	558	193	36	1510	2.3	0.12	3.8	34
4398	62	0–10	0.08	0.09	0.06	3.89	113	95	74	500	0.7	0.1	1.6	23
4399	41	0–2	0.02	0.1	0.04	4.88	466	51	25	1080	0.1	0.1	4.8	17
4400	29	0–5	0.11	0.05	0.03	3.21	118	31	17	970	0.3	0.1	1.4	17
4401	33	0–5	0.19	0.13	0.04	6.6	225	93	375	832	0.2	0.1	3.7	29
4402	39	0–2	0.2	0.03	0.05	4.75	156	26	18	667	0.2	0.1	1.2	17
4406	20	0–3	0.06	0.1	0.07	2.35	75	12	17	621	0.1	0.1	0.1	14
4408	17	0–5	0.01	0.14	0.1	2.84	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
4409	14	0–5	0.14	0.17	0.34	5.98	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
4410	21	0–5	0.32	0.1	0.19	4.82	280	152	41	875	1.2	0.1	4.9	29
4411	29	0–5	0.38	0.05	0.28	5.12	520	29	182	1361	0.1	0.1	6.6	23
4412	21	0–10	0.06	0.05	0.07	6.42	158	189	16	416	0.3	0.1	2.4	34
4413	14	0–2	0.04	0.1	0.13	5.19	232	271	52	1040	0.1	0.1	1.9	34
		20–25	0.26	0.08	0.16	5.37	155	116	379	977	0.1	0.1	4.8	29
		50–53	0.43	0.08	0.15	5.62	229	151	44	1075	0.6	0.1	4.8	23
		100–105	0.12	0.1	0.52	6.6	386	570	517	1574	0.1	0.1	7.3	29
		140–145	0.47	0.11	0.47	6.42	276	330	213	1204	0.1	0.1	8.2	26
		200–205	0.47	0.14	0.22	6.66	258	265	97	1180	0.1	0.1	5.5	34
		270–275	0.6	0.19	0.21	6.6	289	325	97	1147	0.1	0.1	4.2	17
		290–295	0.66	0.13	0.27	7.03	295	260	100	1082	0.1	0.1	4.6	34
		305–310	0.64	0.18	0.19	6.42	264	288	90	1326	0.1	0.1	5	31
		345–350	0.63	0.16	0.19	6.72	311	47	66	1154	0.1	0.1	4.6	34
		380–385	0.67	0.13	0.14	6.66	1511	559	74	2126	0.5	0.1	3.8	31
		400–405	0.45	0.04	0.15	6.23	376	85	56	1490	0.2	0.1	3.4	31
		415–421	0.46	0.14	0.16	6.11	1472	741	84	3515	0.5	0.1	5.4	20
		4414	25	0–5	0.05	0.46	0.34	6.67	607	244	121	2189	0.1	0.1
4415	25	0–5	0.05	0.37	0.17	4.2	452	121	94	1267	0.1	0.1	2.2	12
4416	18	0–6	0.46	0.14	0.11	5	437	136	21	1470	0.2	0.1	2	20
		20–25	0.55	0.15	n.a.	4.38	562	354	n.a.	1167	2	0.1	n.a.	14
		50–55	0.45	0.17	0.08	5.31	1028	280	20	2192	0.8	0.1	0.9	29
		150–155	0.19	0.2	0.07	5.31	795	488	24	5925	1.4	0.1	1.3	23
		245–250	0.67	0.19	0.12	5.62	1300	380	43	4204	0.8	0.1	0.8	23
		295–300	0.72	0.2	0.09	5.37	4637	173	32	5385	0.5	0.1	2	23
		406–408	0.53	0.12	0.13	5.74	1412	443	25	4360	0.3	0.1	0.1	20
		4417	23	0–5	0.24	0.08	0.04	2.29	158	40	12	545	0.1	0.1
4418	14	0–10	0.48	0.2	0.06	4.2	736	284	17	3042	4.4	0.1	0.1	20

Table 1. (Contd.)

Station	Depth, m	Interval, cm	Cu 1	Cu 2	Cu 3	Cu 4	Zn 1	Zn 2	Zn 3	Zn 4	Cr 1	Cr 2	Cr 3	Cr 4
4394	138	0-5	0	0.7	2.2	16.4	14.5	7.7	9.3	107.2	1	0.73	0	79
		30-35	0.1	0.4	1.9	16.4	3.9	3.2	8.9	84.7	0.6	0.32	0	84
		60-65	0.2	0.6	2	16.4	2.5	3.3	8.7	90.8	0.7	0.49	0	81
		150-155	0	0.1	3.4	14	3.2	4.4	10.6	77.1	1.3	0.51	0	79
		240-245	0	0.3	1.8	18	1.8	3.6	7.7	89.8	0.7	0.37	0	86
		300-3205	0	0.1	2.3	12	2.1	1.8	8.6	78.3	0.1	0	0	74
		360-365	0	0.7	1.9	16.4	3.1	6.1	8	90.8	0.3	2.49	1	79
4395	30	0-10	0.3	0.5	1.6	3.4	1.4	2.7	8	22.7	0.24	0.08	0.05	38
4396	32	0-10	0.4	0.7	1.1	10.4	0.7	2.1	3.5	40.2	0.1	0.1	0.1	46
4397	150	0-10	0.1	2	3.8	24	4.4	10.3	9.6	109	0.2	0.5	0.2	81
		20-25	0.05	2.6	19.4	26	3.9	7.1	8.5	97	0.4	0.9	1.4	84
		60-64	0.05	1.2	20.2	24	3	5	8.8	93	0.4	0.2	0.2	79
		96-100	0.05	1.4	40.3	67	2.6	6.7	16.3	447	0.3	0.2	0.2	84
		166-170	0.05	1.2	18.6	26	1.4	4.8	10.3	94	0.3	0.2	0.4	91
		191-200	0.05	0.6	17.2	24	0.8	3.7	9.3	77.5	0.2	0.2	1	86
		320-330	0.05	0.8	27.3	32	1.3	2.7	6.9	98	0.3	0.3	1.7	96
		370-380	0.05	1.1	23.4	36	1.6	3.4	8.1	105	0.2	0.2	1.5	98
4398	62	0-10	0.05	0.8	14.3	18	8.3	2.7	7.3	59.3	0.1	0.35	0.7	67
4399	41	0-2	0.05	0.8	16.2	20	0.5	9.1	10.7	71.4	0.1	0.22	1.1	70
4400	29	0-5	0.05	0.2	25.8	70	1.5	2.3	8.7	50.3	0.1	0.07	0.5	55
4401	33	0-5	0.05	0.8	30.4	76	2.8	4.8	10.4	56	0.1	0.55	0.5	93
4402	39	0-2	0.05	0.05	22.4	28	2.1	1.1	7.1	84	0.1	0.1	0.8	79
4406	20	0-3	0.07	0.3	0.7	8	6	6	7.3	70	0.1	0.13	0.5	50
4408	17	0-5	0.05	0.6	n.a.	4	5.6	5.6	n.a.	29.4	0.1	0.1	n.a.	34
4409	14	0-5	0.15	1.2	8.7	40	8.9	5.8	2.3	107	0.1	0.15	5.3	88
4410	21	0-5	0.05	0.7	19	26	2.4	4.8	13.7	74	0.1	0.5	6.6	88
4411	29	0-5	0.05	0.05	22	28	3.6	0.6	17.3	85.8	0.1	0.1	6.4	88
4412	21	0-10	0.05	0.3	13.3	27	1.9	1.7	5	96	0.1	0.09	1.4	59
4413	14	0-2	0.05	0.4	25.8	32	1.1	4.3	11.4	92.2	0.1	0.37	5.2	77
		20-25	0.05	0.8	37.7	39	0.9	4.3	13.1	93.7	0.1	0.5	4.8	93
		50-53	0.1	0.55	30	43	1.2	6.9	12.4	101.2	0.1	0.48	5.3	91
		100-105	0.05	0.57	21	87	0.1	3.5	13.2	343	0.1	0.81	7	91
		140-145	0.05	0.57	32.2	51	0.03	3.2	14	115.2	0.1	0.8	6.6	88
		200-205	0.05	0.55	30.5	45	0.3	3.2	16	103.2	0.1	0.78	8.9	91
		270-275	0.05	0.8	11.4	47	1.3	4.6	9.5	105.2	0.1	1.2	5.2	93
		290-295	0.05	0.7	12.1	49	0.02	3.3	5	112.2	0.1	0.5	5.4	96
		305-310	0.05	0.7	11.1	63	0.2	3.7	10	115.2	0.1	0.92	5.3	96
		345-350	0.05	0.2	11.4	43	0.7	6.1	11.4	106.7	0.1	0.74	6.5	93
		380-385	0.05	0.6	9.5	270	1.2	3.8	8.6	103.3	0.1	0.81	5.8	100
		400-405	0.05	0.05	9.1	43	0.6	1.4	8.5	105.2	0.1	0.2	4.6	91
		415-421	0.05	0.9	10.5	43	2.5	3.8	9.4	107.2	0.1	0.62	4.8	88
4414	25	0-5	0.2	1.6	5.7	28	0.3	6.1	10.6	90.8	0.1	0.35	3.4	74
4415	25	0-5	0.2	0.9	3.3	22	0.4	14.4	6	55.6	0.1	0.21	1.3	65
4416	18	0-6	0.05	0.5	1.7	18	2.4	7.2	7.4	71.9	0.1	0.39	1.4	62
		20-25	0.05	1	n.a.	16	1.9	6.6	n.a.	58.8	0.34	0.15	n.a.	58
		50-55	0.1	0.6	1.3	20	1.5	3.3	3.2	65.8	0.1	0.07	1	60
		150-155	1	0.7	0.8	18	3	18.2	2.7	66.6	0.1	0.22	0.1	62
		245-250	0.05	1.1	0.9	18	1.1	21.5	3.6	66	0.1	0.42	0.5	60
		295-300	0.05	0.6	1.2	18	1.7	6.1	3.6	63.3	0.1	0.1	0.1	61
		406-408	0.05	1	0.5	22	1.5	1.5	4.6	70.6	0.31	0.1	0.4	72
4417	23	0-5	0.05	0.05	0.1	8	2.1	2	1.5	34.9	0.1	0.2	0.1	38
4418	14	0-10	0.05	1.80	0.4	18	2.5	7.7	2.2	66	0.22	0.3	0.6	62

**Table 1.** (Contd.)

Station	Depth, m	Interval, cm	Cd 1	Cd 2	Cd 3	Cd 4	Pb 1	Pb 2	Pb 3	Pb 4	Ni 1	Ni 2	Ni 3	Ni 4
4394	138	0–5	0.08	0.15	0.02	0.4	0.4	2.9	0.1	54	0.1	0.1	3.9	65
		30–35	0.19	0.05	0.02	0.5	1.3	3.4	0.1	38	0.1	0.1	4.2	61
		60–65	0.11	0.02	0.02	0.5	0.1	7.3	0.1	38	0.1	0.1	3.8	52
		150–155	0.05	0.02	0.02	0.4	0.5	2.9	0.1	38	0.2	0.1	2.1	63
		240–245	0.12	0.1	0.02	0.4	0.1	3.2	0.1	22	0.1	0.1	4.1	61
		300–3205	0.02	0.02	0.02	0.2	0.7	0.8	1.7	22	0.3	0.1	6.6	61
		360–365	0.14	0.3	0.02	0.4	0.1	6.8	0.1	54	0.5	0.1	5.2	54
4395	30	0–10	0.02	0.02	0.02	0.2	0.1	0.2	0.1	22	0.1	0.1	1.4	42
4396	32	0–10	0.02	0.02	0.02	0.3	0.05	1.8	0.05	38	0.1	0.1	0.6	42
4397	150	0–10	0.02	0.13	0.02	0.6	0.05	3.4	0.05	38	0.1	3.3	4.7	98
		20–25	0.02	0.55	0.02	0.4	0.05	6.1	0.05	22	1.3	1.3	3.8	69
		60–64	0.1	0.02	0.02	0.5	0.5	2.6	0.05	70	1.1	1.6	4.4	75
		96–100	0.02	0.3	0.02	0.4	0.6	5.2	0.05	54	1.9	0.1	8.2	70
		166–170	0.02	0.02	0.02	0.4	0.05	4.2	0.05	54	1.4	1.5	6.3	81
		191–200	0.02	0.02	0.02	0.4	0.05	5	0.05	70	0.1	1.2	7.2	73
		320–330	0.1	0.02	0.02	0.4	0.05	2	0.6	70	1.5	0.6	4.7	69
		370–380	0.06	0.02	0.02	0.3	0.05	3.4	0.05	54	1.4	0.4	6.6	68
4398	62	0–10	0.16	0.02	0.02	0.5	0.05	3	0.05	54	0.3	0.3	4.7	52
4399	41	0–2	0.02	0.07	0.02	0.6	0.05	1.9	0.05	38	0.4	0.1	5.7	70
4400	29	0–5	0.02	0.02	0.02	0.3	0.05	3.7	0.05	38	0.7	0.1	3.2	69
4401	33	0–5	0.02	0.02	0.02	0.5	0.05	4.9	0.05	38	0.2	0.1	4.8	86
4402	39	0–2	0.06	0.02	0.02	0.6	0.05	0.1	0.05	38	0.4	0.1	2.8	65
4406	20	0–3	0.02	0.02	0.02	0.1	0.05	0.05	0.08	22	0.1	0.1	3.4	46
4408	17	0–5	0.02	0.06	n.a.	0.3	0.05	1.3	n.a.	21	0.1	2.3	n.a.	37
4409	14	0–5	0.02	0.02	0.02	0.4	0.05	5.8	0.05	54	0.1	0.1	8.6	76
4410	21	0–5	0.12	0.18	0.02	0.4	0.05	1.7	0.05	54	0.7	0.1	5.7	74
4411	29	0–5	0.02	0.1	0.02	0.6	0.05	0.05	0.05	38	0.1	0.1	8.8	62
4412	21	0–10	0.02	0.03	0.02	0.4	0.05	0.1	0.05	37	0.1	0.1	3.2	42
4413	14	0–2	0.02	0.12	0.02	0.4	0.05	0.1	0.05	70	0.1	0.1	5	71
		20–25	0.02	0.3	0.02	0.35	0.05	0.9	0.05	54	1	0.1	5.6	78
		50–53	0.02	0.36	0.02	0.4	0.05	3.8	0.05	38	0.9	0.1	7	79
		100–105	0.02	0.12	0.02	0.5	0.05	2.5	4.7	86	0.1	0.6	10.7	81
		140–145	0.02	0.02	0.03	0.4	0.05	2.4	3.8	54	0.1	0.1	7.4	78
		200–205	0.02	0.02	0.03	0.5	0.05	2.4	2.5	38	0.1	0.2	8.2	77
		270–275	0.02	0.02	0.02	0.3	0.05	1.6	0.05	54	0.1	0.6	6.4	81
		290–295	0.02	0.02	0.02	0.3	0.05	1.7	0.05	54	0.1	0.1	7.9	80
		305–310	0.06	0.02	0.02	0.4	0.05	1.1	2.1	70	0.1	0.9	8.6	79
		345–350	0.02	0.02	0.02	0.4	0.05	0.35	1	70	0.1	0.1	6.9	84
		380–385	0.02	0.02	0.02	0.3	0.05	2.8	0.05	101	0.1	0.5	6.2	76
		400–405	0.02	0.02	0.02	0.5	0.05	0.1	0.05	54	0.1	0.1	5.5	98
415–421	0.02	0.02	0.02	0.6	0.05	3.2	0.05	38	0.1	0.6	6.7	104		
4414	25	0–5	0.02	0.02	0.02	0.3	0.8	4.3	1.9	54	0.1	0.1	6.2	89
4415	25	0–5	0.02	0.02	0.02	0.2	0.05	1.9	0.5	38	0.1	0.1	2.2	56
4416	18	0–6	0.02	0.02	0.02	0.3	0.5	5	0.05	54	0.5	0.1	2.3	50
		20–25	0.05	0.1	n.a.	0.3	0.05	1.4	n.a.	70	0.1	0.1	n.a.	46
		50–55	0.02	0.02	0.02	0.4	1.1	2.8	0.2	54	0.1	0.1	2.2	60
		150–155	0.02	0.02	0.02	0.2	0.05	1.9	1	53	0.2	0.4	3	56
		245–250	0.1	0.07	0.02	0.02	0.05	3.6	0.8	22	0.6	0.8	2.2	63
		295–300	0.1	0.02	0.02	0.3	1	4.5	0.05	54	0.4	0.6	3.1	61
		406–408	0.06	0.02	0.02	0.3	0.05	9.5	0.05	55	0.3	0.1	2.6	57
4417	23	0–5	0.08	0.02	0.02	0.1	0.05	4.5	0.05	38	0.1	0.1	1.6	58
4418	14	0–10	0.09	0.02	0.02	0.3	1.1	7.6	0.05	54	1.9	0.1	1.8	53

Note: Speciation of metals: 1 – adsorbed, 2 – amorphous Fe and Mn hydroxides and related metals, 3 – organic and sulfide, 4 – bulk content.  
n.a. is not analyzed

metals, i.e., the second reactive hydroxide species of metals.

The third stage of extraction of the dried sediments with 30% perhydrol, acidated with nitric acid to pH 2 using the method proposed in [5], was performed at a stationary laboratory in Moscow. This procedure resulted in the separation of the third (organic + sulfide) species of metals.

Thus, the first three modes of metals are reactive, geochemically mobile compounds, which can be transformed by variations in such physicochemical parameters of the environment as pH, Eh, salinity, and organic matter (OM) content.

The extracts of the acetate buffer containing adsorbed metals were forwarded directly to atomic absorption spectroscopic analysis (flame version); the reference samples were also prepared on the basis of the acetate buffer. The extracts of the second and third stages were converted to 10% HCl solutions. The bulk metal contents after the complete breakdown of the sample with a mixture of concentrated HCl, HNO<sub>3</sub>, and HF were determined simultaneously. The metal content in the residual bottom sediment after three consecutive stages of extraction was determined as a difference between the bulk content and the sum of the first, second, and third species. The residual (clastic), or geochemically inert species is represented by terrigenous particles, where the metals are fixed in crystal lattices of minerals.

The blanks were determined on each stage of the chemical treatment. The accuracy of analysis was checked against state standard samples SDO-2; the determined concentrations of all of the metals were no less than 85% of the certified values. The Fe, Mn, Zn, Cu, Co, Ni, Cr, Pb, and Cd contents were measured on a Perkin-Elmer 403 flame atomic absorption spectrophotometer at the analytical laboratory of the Shirshov Institute of Oceanology, RAS. The accuracy of measurements was 5% for Fe, Mn, Ni, Zn, and Cu and 10% for Cd, Co, Cr, and Pb. The analytical results are given in Table 1.

#### LITHOLOGY AND GEOCHEMISTRY OF THE STUDIED BOTTOM SEDIMENTS

The central Kara Sea, where the sediments of the Ob and Yenisei sections have been investigated (Ob–Yenisei Zone), has a shallow depth, and sedimentation occurs there largely at the expense of the suspended material supplied by the Ob and Yenisei rivers. The river water spreads by currents from the Ob and Yenisei mouths far to the north, up to 75° N, as follows from the mean perennial silicon content in the surface water of the Kara Sea [3]. About 30–40% of the dissolved and more than 90% of the solid stream fluxes are held up by the marginal filter and do not reach the open Kara Sea [6].

In the southwestern Kara Sea, where the deepwater column at Station 4394 was sampled, the abrasion of the Yamal Peninsula coast and continental surroundings is the main source of the supplied sedimentary material.

A considerable part of the Ob and Yenisei drainage basins is located in the tundra plain with a thin weathering zone and a minor solid flux (tundra and taiga landscapes with permafrost). The cold-water Kara Sea is characterized by an elevated content of free carbon dioxide that promotes the dissolution of carbonates. The bottom sediments are carbonate-free (<2 wt % CaCO<sub>3</sub>); according to their average contents of silica (62.1 wt %) (largely in the form of quartz) alumina (8.02%), and C<sub>org</sub> (1–2 wt %), they are classified as terrigenous [7]. On the basis of its primary production, the sea is classed with oligotrophic seas [8, 9], i.e., those characterized by a low phytoplankton biomass.

According to the sedimentation facies conditions, the upper Quaternary bottom sediments of the area are subdivided into several groups [10]: (1) river sediments of the Ob (stations 4417–4419) and Yenisei (stations 4406–4413); (2) sediments in zone of river and sea water mixing (stations 4414–4416 for the Ob and stations 4401, 4402 for the Yenisei river); and (3) marine sediments of zones of erosion, transit, and accumulation (stations 4395–4400).

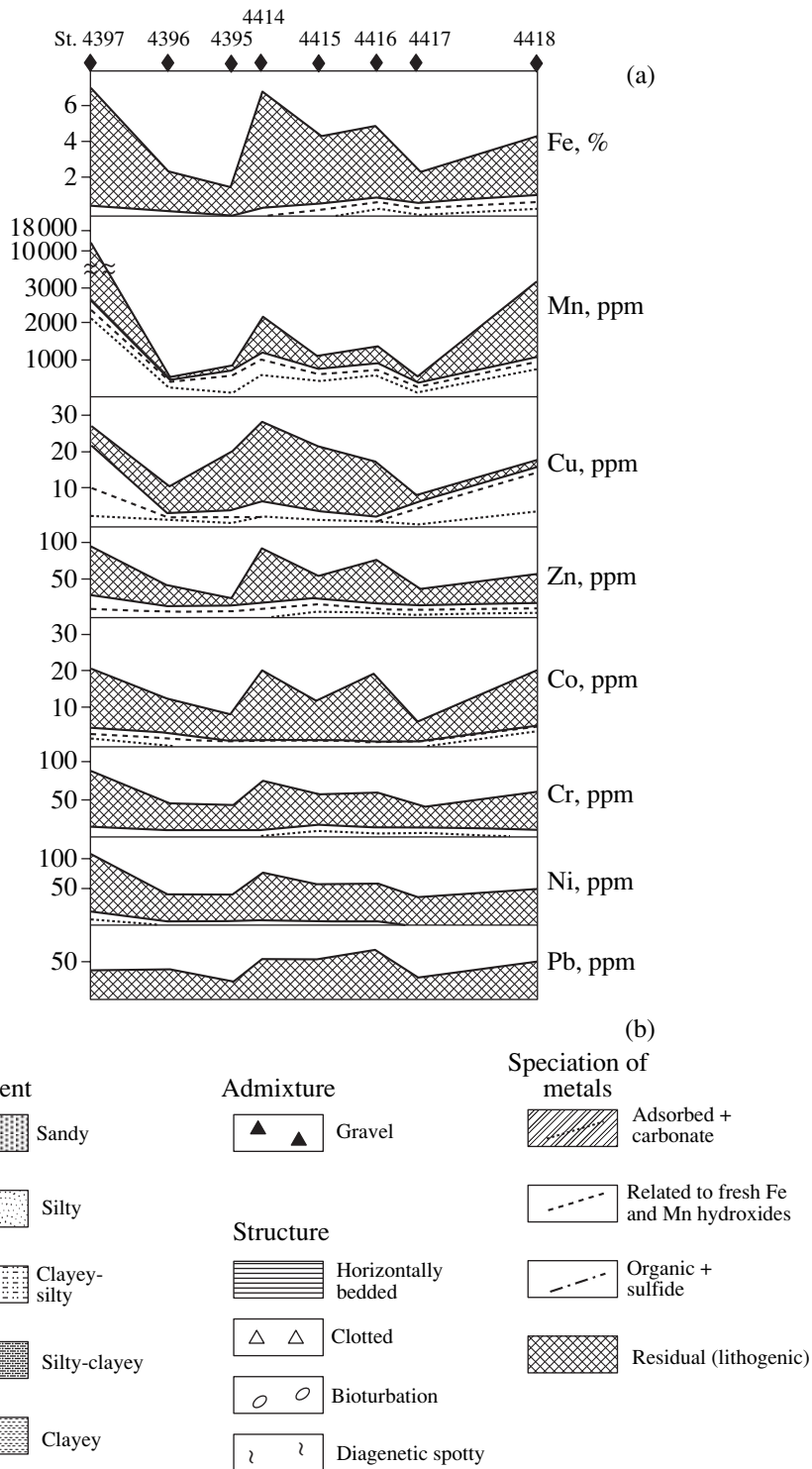
In the southern portions of both sections, the bottom sediments consist of Holocene river sand and silt; the salinity of the bottom water is close to zero, pH is about 7.4, and the bottom water temperature is 7–9°C. The shallow-water river sediments are characterized by intercalation of poorly sorted silts and sands of various grain size, locally with an admixture of perfectly rounded pebbles and plant detritus. The partially reduced sediments with diagenetic spots occur beneath the upper (2–3 cm) layer of oxidized sediments; in places, the oxidized layer is absent.

The horizontal layering of olive-colored and black silty–clayey and clayey muds, as well as signs of bioturbation are characteristic of sediments in the zone of mixing.

The marine sediments in the northern parts of the sections are composed of gray silty and silty–clayey muds with a diagenetic spotty structure; the Holocene sediments oxidized at the surface (Eh ranges from +101 to +461 mV) and slightly reduced in deeper units [11] are prevalent. The biogenic component consists mainly of benthic foraminifers. The bottom water temperature in the north of sections varies from 0 to –1°C and is thus much lower than in the south; the salinity (33–35‰) and pH (8.4, on average) correspond to the typical marine conditions.

#### RESULTS AND DISCUSSION

Consider the spatial distribution of bulk contents and particular species of metals in the surface layer of sediments along the Ob and Yenisei sections.



**Fig. 2.** (a) Bulk content and speciation of metals in the surface layer of sediments in the Ob section and (b) legend to Figs. 2-7.

In the southern portion of the Ob section, i.e., precisely in the estuary of the river (stations 4417 and 4418), the deposits consist of the sandy-silty river sediments characterized by the absence of the upper oxi-

dized layer and plant detritus. The water column at these stations is characterized by the maximum biomass of zooplankton, amounting to 10 g/m<sup>3</sup> [8], a high rate of sedimentation, and, hence, a reducing environ-

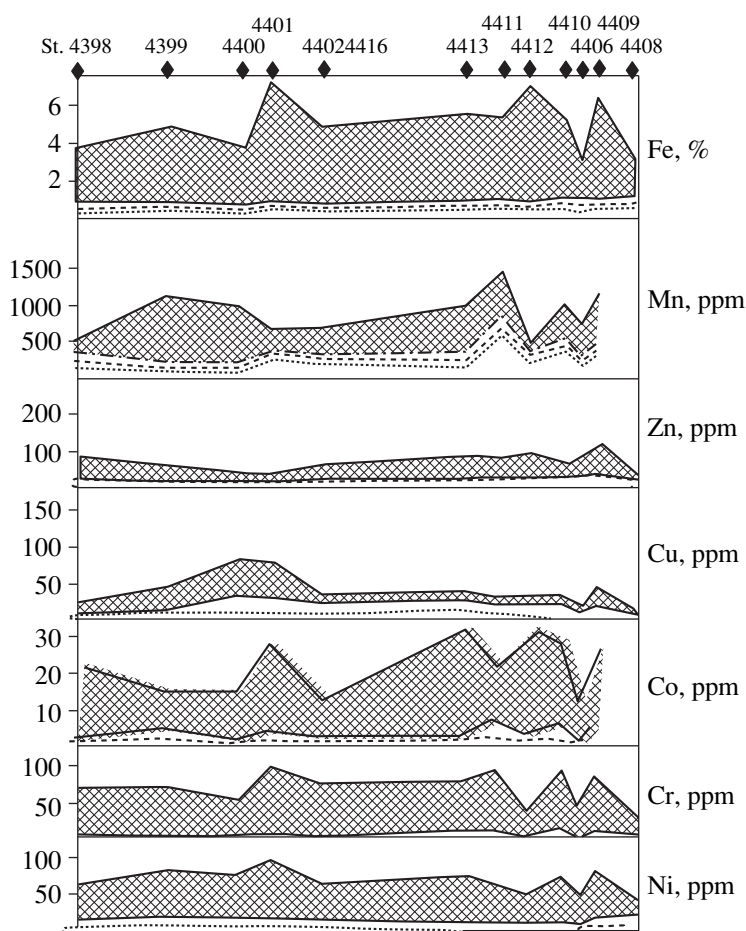


Fig. 3. Bulk contents and speciation of metals in the surface layer of sediments in the Yenisei section. See Fig. 2 for legend.

ment. Further to the north, these deposits are gradually replaced by finer silty-clayey sediments of the mixing zone (stations 4414–4416) and by mainly pelitic marine sediments in the northern part of the section (stations 4395–4397). The bulk Fe, Zn, Cu, Co, Cr, Ni, and Pb contents reveal fluctuations (1.5–2.0 times), and judging from the curves shown in Fig. 2, these fluctuations are similar for all the metals. The sawtooth character of variation of bulk metal contents along the section can probably be explained by the following causes. First, as was mentioned above, there are three facial regions in the section, distinct in grain size and redox conditions. As is known, heavy and transitional metals are mainly related to the fine-grained clayey sediments, while the coarse-grained sediments (first of all, sands) are, on the contrary, depleted in these metals, because quartz, prevailing in sand and coarse silt, dilutes the metals in bottom sediments. Second, in the bottom areas with a slightly reducing environment, the sediments are depleted in Mn and related microelements (Cu, Co, Zn, Ni, etc.).

The appreciable (1.5–2.0 times) increase in the Fe, Zn, Cu, Co, Ni, and Pb contents and a sharp enrichment

in Mn from 0.31 to 1.88 wt % of dry material, i.e., almost six times, is detected in the surface layer of marine sediments (stations 4395–4397). Station 4397 is located behind a steep scarp at a much greater depth (140 m) in comparison with other stations of this section, and the physicochemical conditions are such that the slightly oxidized and reduced sediments (Eh from +20 to –160 mV) occur beneath a 20-cm surface oxidized layer (Eh = +358 mV). As can be seen from Fig. 2, the abrupt increase in the bulk Mn content occurs almost completely at the expense of hydroxide species that contains 71% of the bulk manganese. It may be suggested that the Mn hydroxide was formed owing to the diagenetic migration of Mn from the underlying reduced sediments (in which it occurred as  $Mn^{2+}$  dissolved in pore water), and its oxidation to  $Mn^{4+}$  under oxidizing conditions of the surface layer. Recall that more than 100 years ago, Murray and Irvine [12] first drew attention to a possible postsedimentation migration of Mn in arctic bottom sediments. Upon studying the surface bottom sediments of the Kara and Barents seas, Bruevich [13], suggested a mechanism of the enrichment of sediments in Fe and Mn as a result of



**Table 2.** Al and Si contents (after E.G. Gurvich), natural density and moisture of sediments, and the Me/Al ratio in the surface layer of bottom sediments in the Yenisei section

Station	Al, wt % of dry material	SiO <sub>2</sub> , wt % of dry material	Density, g/cm <sup>3</sup>	Moisture, %	Si/Al	Fe/Al	Co/Al	Cu/Al	Zn/Al	Cr/Al	Cd/Al	Pb/Al	Mn/Al	Ni/Al
4400	9.35	66	44.3	1.62	3.31	0.34	0.18	0.17	0.54	0.59	0.003	0.4	0.103	7.37
4401	6.87	51.5	56.1	1.45	3.52	0.96	4.22	10.18	8.15	13.5	0.072	5.53	0.121	12.5
4402	6.17	60.5	56.4	1.45	4.6	0.77	2.75	4.54	13.6	12.8	0.097	6.15	0.108	10.53
4413	7.64	58.6	49	1.54	3.6	0.67	4.45	4.2	12.1	10.1	0.052	9.16	0.136	9.29
4411	6.01	53.1	37	1.6	4.14	0.85	3.82	4.65	14.3	14.6	0.1	6.32	0.226	10.3
4410	6.33	60.9	41.2	1.65	4.42	0.76	4.58	4.1	11.67	13.9	0.063	8.53	0.138	11.7
4409	7.4	59.8	59.6	1.4	3.79	0.81	3.9	5.4	14.4	11.9	0.054	7.29	0.141	10.3
4408	1.33	88.6	n.a.	n.a.	31.3	2.13	10.5	18	22.1	25.5	0.22	15.7	n.a.	27.8

their postsedimentation migration from the underlying reduced layers to the surface, where they are oxidized and repeatedly precipitated. It is interesting to note that on the surface of sediments at Station 4395, where the saucer-shaped Fe–Mn nodules were observed, we have measured the minimum rate of sedimentation that corresponds to a low flux of sedimentary material (9.4 mg/m<sup>2</sup> per day) collected by sedimentary traps.

Geochemically inert species of Fe, Zn, Co, Cr, Ni, and Pb are predominant along the Ob section: up to 80–85% of each metal is contained in the residual fraction. Approximately half of 15–20% Fe contained in geochemically mobile species (the sum of modes 1 + 2 + 3), or 7–10% of the bulk content, occur as amorphous oxide–hydroxide films; Zn, Co, and Cr are also associated with such films. A very insignificant amount of Fe, Zn, Co, and Cr (about 5–10% of the bulk contents) is bound with organic matter and sulfides. Note that Ni and Pb almost completely (more than 95%) are contained in residual modes. In contrast to these metals, Mn and Cu in the Ob section mostly occur as geochemically mobile species. Thus, while, the bulk of Mn and Cu is contained in the river and estuarine sediments in clastic material (~80% of the bulk contents), the marine sediments, conversely, contain 25–70% of the bulk Fe concentration in the form of adsorbed, hydroxide, and organic + sulfide species. Thereby, hydroxides are the major species for Mn, whereas species related to organic matter and sulfides predominate for Cu. The Mn and Fe hydroxides have been known for about half a century [14] to be efficient sorbents of transitional metals from natural waters, and the relation of Cu in bottom sediments to organic matter and its close association with Mn have also been reliably documented [15].

Areas of the accumulation, transit, and erosion of sediments alternate on the bottom surface along the Yenisei section (Fig. 3) in compliance with the seafloor topography and the hydrodynamics of the bottom water. The unstable line of the shallow-water shelf, with alternating small highs and deeps in the Yenisei estuary leads to the variation in the density and mois-

ture of the sediments. The depressions are commonly characterized by wetter sediments enriched in a finely dispersed pelitic fraction, as a rule, with elevated metal contents.

According to [16], the bimodal grain size distribution of bottom sediments in the Yenisei estuary affects their chemical composition very strongly. In the southern segment of the section, within the estuary, predominant particles have sizes 20–30 and 400–500 μm. To the north, the grain size diminishes, and the particles of sizes 10–20 and 100–200 μm become prevalent. In the marine sediments proper (stations 4398–4400), the bimodal distribution of the grain size disappears, and the sediments are composed largely of particles 20–80 μm in size.

As can be seen from Fig. 3, the spatial distribution of the bulk metal contents along the Yenisei section is comparable with that along the Ob section (see above). The greatest variations in the bulk metal contents are detected in the river sediments and sediments from the mixing zone; neither drastic change nor appreciable increase in the metal contents is noted in the marine sediments proper, perhaps, because of their more monotonous grain size.

One can see from Table 2 that the Si/Al and Me/Al ratios are maximal at the southern extremity of the section, i.e., in the river sediments (Station (4408), where the sedimentation of coarse-grained river material proper with high Si content (41.6 wt % of dry material) and low Al content (1.33 wt % of dry material) probably ended (both the above estimates are from [7]). The minimum salinity (<1‰) was detected precisely in this area (stations 4406–4408); to the north, the salinity increases to 10–12‰ [17]. The Si/Al and Me/Al ratios markedly decrease northward. The growth of salinity in the zone of river and sea water mixing is known to give rise to the flocculation and coagulation and, thus, to the enlargement of suspended particles carried by the river flow and their settling.

In the surface layer of the bottom sediments, metals occur mainly in the residual, geochemically inert mode,

which consists of terrigenous clay and clastic minerals in combination with crystallized Fe and Mn hydroxides and related microelements. The contribution of Fe, Co, Ni, Cr, Pb, and Cd to this species reaches 70–100% of the bulk contents and decreases to 60% for Mn and Zn. Thereby, the predominant mode of Mn is adsorbed, while the Zn mode is hydroxide films. The Cu distribution differs from other metals in that about 70% of the bulk of this element occurs throughout the entire section in geochemically mobile species, largely as organic + sulfide species that largely control the behavior of Cu in the section.

The total Fe and Mn contents and concentrations of other metals are elevated in the oxidized layers (Station 4417) and depressed in the reduced sediments. In shallow-water shelf environments in the presence of free hydrogen sulfide, Mn hydroxides are unstable and may be reduced to Mn(II). According to Lein *et al.* [11], bacterial sulfate reduction with formation of pyrite and monosulfide sulfur proceeds already in the surface layer (0–20 cm) of the bottom sediments in the Yenisei estuary (Station 4402), and free hydrogen sulfide is produced by sulfate-reducing microorganisms. The predominance of reducing conditions in the surface layer results in the precipitation of copper sulfides from the mud water rich in Cu [18].

Bottom sediments in the zone of the river and sea water mixing in the Yenisei section are characterized by a similar distribution of metal species.

According to [19], about 70–80% of the bulk metal contents in the river suspension of the arctic Yukon River occur in crystal lattices of different minerals. Our data on the proportions of metal species in the surface layer of the bottom sediments in the Ob and Yenisei sec-

tions, especially in their southern and central segments, are very close to these estimates.

This fact and the aforementioned lithological and geochemical characteristics of the bottom sediments suggest that the distribution and speciation of metals in bottom sediments within estuaries of the Ob and Yenisei rivers and the adjacent marine sediments are controlled by the river suspension. As a result, the metal species typical of the river suspension are “inherited” by sediments in the zone of mixing and, to some extent, by marine sediments also.

Let us now consider the temporal distribution of metals and their species (Fig. 4–7). All the core columns are composed of Holocene sediments.

At Station 4394 located in the western Kara Sea not far from the Karskie Vorota Strait, the upper 20 cm of deposits consist of brownish, silty–clayey sand (43.5% of pelitic material + 43.5% of sand + 13% of silt) with a thin oxidized bed that overlies the grayish olive-colored, slightly reduced pelitic mud (>75% of pelitic material) with a spotty diagenetic structure. Note that the lowered bulk contents of all of the metals were detected in the surface layer as a consequence of variations in the granulometric composition (enrichment in sand).

The bulk Fe and Zn contents insignificantly decrease down the column 4394 (Fig. 4) while the Cr, Ni, Cd, Co, and Cu contents remain virtually unchanged. The Mn content reaches a maximum in the surface layer and then diminishes with depth. Further downward, two minima are noted for all of the metals within two intervals with zero magnetic susceptibility. The vertical variation of the bulk Mn is determined by geochemically mobile species, mainly adsorbed and hydroxide, that yield 55–90% of the bulk content. The

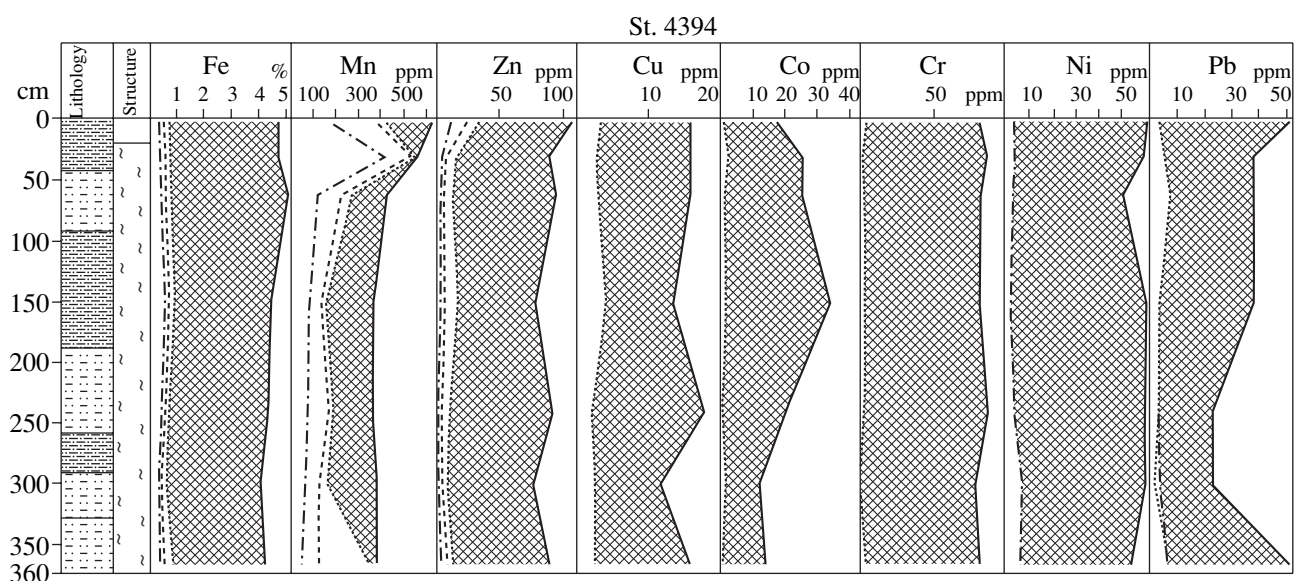
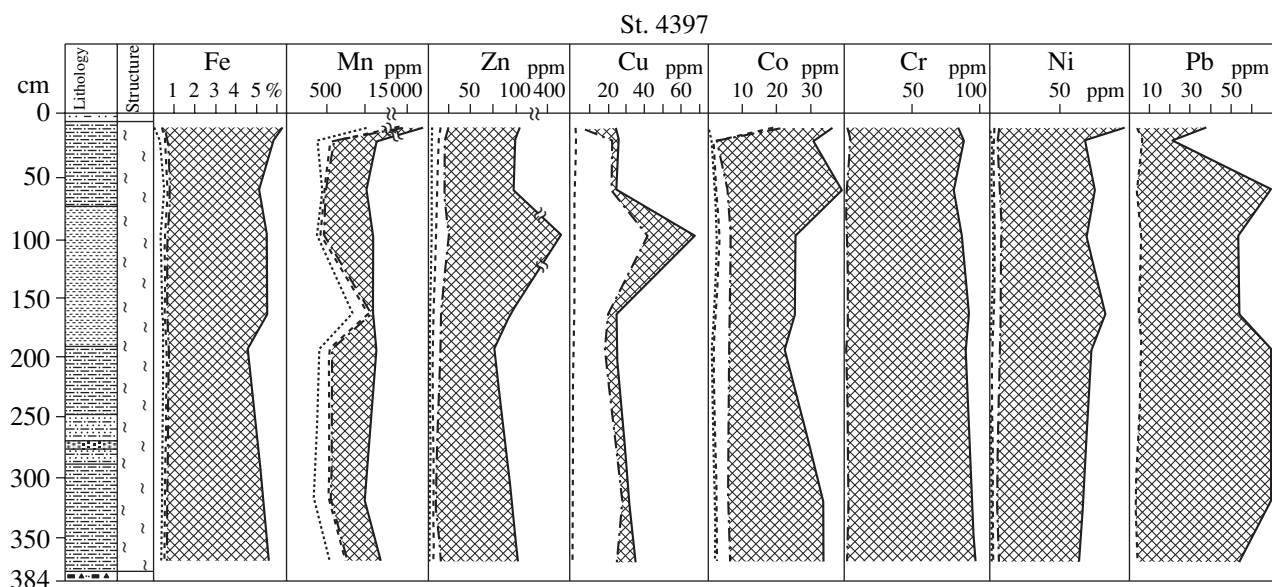
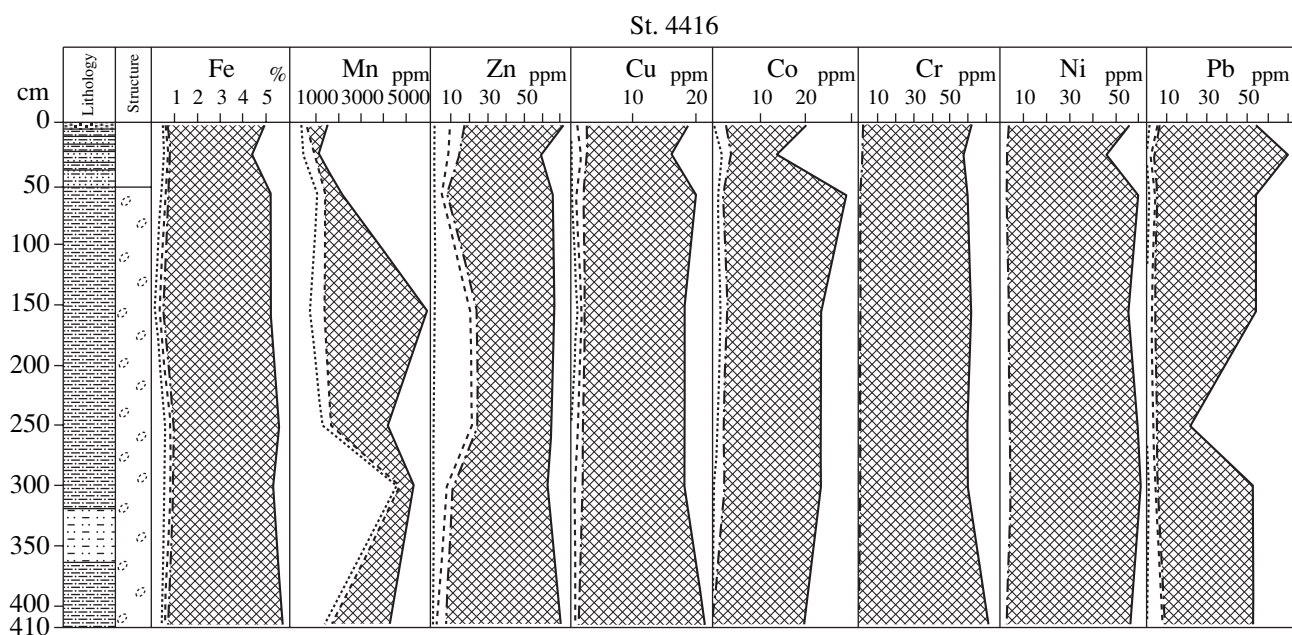


Fig. 4. Distribution of the bulk content of metals and their speciation in the column at Station 4394.



**Fig. 5.** Distribution of the bulk content of metals and their speciation in the column at Station 4397.



**Fig. 6.** Distribution of the bulk content of metals and their speciation in the column at Station 4416 in the estuary of the Ob River.

maximal total content of these species falls on the interval of 30–35 cm, where free hydrogen sulfide was detected. For other metals, the residual modes of occurrence are predominant and vary from 85% for Fe to 95% for Cr. The contribution of this mode for Zn and Cu is much lower (65–75% of the bulk content).

The vertical distribution of the bulk contents through column 4397 (Fig. 5) located at the northern extremity of the Ob section is largely controlled, simi-

larly to other stations, by the physicochemical conditions. The slightly reducing conditions and correlation of Mn with Eh throughout the entire column length led to the occurrence of Mn mainly as geochemically mobile species (55–85% of the bulk Mn content, including 20–30% that fall on the adsorbed mode and 15–25% on the hydroxide mode). Residual modes are predominant for other metals, and the percentage of geochemically mobile modes varies from 10% (Cr) to 25% (Fe, Zn) of the bulk contents. If the mobile Mn and

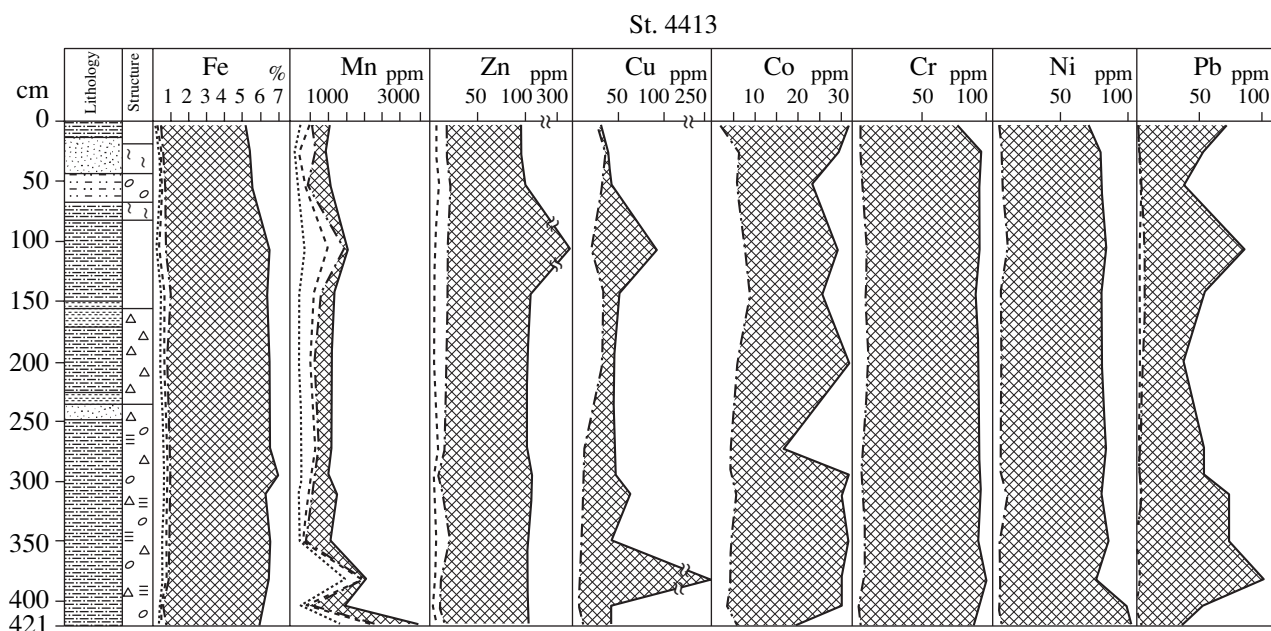


Fig. 7. Distribution of the bulk content of metals and their speciation in the column at Station 4413 in the estuary of the Yenisei River.

Fe modes are mainly the adsorbed complex and hydroxide, most of mobile Cu, Zn, Co, Ni, Cr and Pb modes are organic + sulfide species, as is especially evident for intervals of 10–70, 130–150, and 290–350 cm (Fig. 5), in which hydrotroilite coatings were found. The highest content of adsorbed Co in the interval of 0–20 cm is correlated with a high Mn content. The elevated contents of the residual (clastic) Fe, Zn, Cu, and Cr modes were detected in the lower portion of the column composed of glacial–marine sediments, in which a sand unit was detected. The radiocarbon age of sediments (Station 4397) is estimated at 7.7 ka at a depth of 190 cm and at 9.1 ka at a depth of 280 cm [20]. The composition of the sediments testifies to the strong effect of river sediment supply at 8 ka and earlier.

The column of bottom sediments at Station 4416 was taken from the frontal zone of the Ob River water and seawater mixing. The bulk contents of all of the metals, except Mn, vary within rather narrow limits (Fig. 6), and all the elements display a minimum at 30 cm, where a sand interbed was found. Down the column, the percentage of the pelitic fraction increases, giving rise to some enrichment in metals. The proportions of metal species along the column are generally similar to those in the open Kara Sea (Station 4397), indicating that a difference in facial conditions does not induce a change in the contribution of various processes to the accumulation of metals in the sedimentary column.

Station 4413 is situated in the Yenisei River estuary. The bottom sediments are enriched in organic carbon (1.3–2.0 wt %) and have diagenetic spotty and bioturbation structures, with abundant hydrogen sulfide. The bacterial sulfate reduction of the sediments results in a

gain of reduced sulfur compounds irrespective of water freshening and the activity of hydrodynamic regime, the temperature of the bottom water, the redox conditions, and the basin depth [11].

The bulk Fe, Co, Ni, Cr, Pb, Cd, Zn, and Cu contents in columns of bottom sediments in the Ob and Yenisei estuaries (Fig. 7) are practically identical, while the Mn content in the Yenisei sediments is 3.5–4.0 times lower than in the Ob sediments, probably owing to the reducing conditions that determine the prevalence of Mn(II) contained mainly in mud water. Like in the two previous columns, the vertical Mn distribution is controlled by geochemically mobile modes, largely by the adsorbed complex (25–95% of the bulk Mn), see Fig. 7; the amount of the adsorbed Mn is much greater than in the Ob column. Peaks in the bulk Mn contents (2500 and 3500 ppm) are noted at depths of 370 and 430 cm, where Mn is contained almost exclusively as the adsorbed complex. This fact can be explained by an abrupt increase in the redox potential and/or enrichment in pelitic material. Because no specific information on this issue is available, we cannot suggest any plausible interpretation.

Geochemically mobile Cu species amounts to 20–95% of the bulk Cu content in the column at Station 4413, and these species are more important in the vertical distribution of Cu than in the Ob column. The bulk of Cu is contained in the form of organic + sulfide species. Judging from the proportion of Co modes, 10–30% of which fall on organic + sulfide species and species adsorbed on Fe–Mn hydroxides, Co is also more mobile here than in the Ob column. This also applies to Fe, Zn, Ni, and Pb, which is quite understandable, tak-



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