Available online at www.sciencedirect.com
SCIENCE DIRECT®

Applied Geochemistry 19 (2004) 593–610

Applied Geochemistry

www.elsevier.com/locate/apgeochem

Geochemical behaviour of major and trace elements in suspended particulate material of the Irtysh river, the main tributary of the Ob river, Siberia

V.V. Gordeev[a], V. Rachold[b,*], I.E. Vlasova[a]

[a] *P.P. Shirshov Institute of Oceanology, Russian Academy of Sciences Nakchimovsky Prospect 36, Moscow 117991, Russia*
[b] *Alfred Wegener Institute for Polar and Marine Research, Telegrafenberg A43, 14473 Potsdam, Germany*

Received 17 January 2003; accepted 14 August 2003
Editorial handling by C. Reimann

Abstract

In July 2001, samples of surface suspended particulate material (SPM) of the Irtysh river in its middle and lower reaches (from Omsk City to the confluence with the Ob river) and its main tributaries were collected (18 stations along 1834 km). The SPM samples were analyzed for major and trace element composition. The results show that the geochemistry of Irtysh river SPM is related to landscape and geochemical peculiarities of the river basin on one hand and to industrial activities within the drainage area on the other hand. In the upper basin polymetallic and cinnabar deposits and phosphorite deposits with high As content are widespread. The open-cut mining and developed oil-refining, power plants and other industries lead to the contamination of the environment by heavy metals and other contaminants. The territory of the West Siberian lowland, especially the Ob-Irtysh interfluve, is characterized by the occurrence of swamps and peat-bogs. Tributaries of the Irtysh river originating in this region, have a brown color and the chemical composition of the SPM is specific for stagnant water. In the first 500–700 km downstream from Omsk City the Irtysh river has the typical Al–Si-rich suspended matter composition. After the inflow of the tributaries with brown water the SPM composition is significantly changed: an increase of POC, Fe, P, Ca, Sr, Ba and As concentrations and a strong decrease of the lithogenic elements Al, Mg, K, Na, Ti, Zr can be observed. The data show that Fe-organic components (Fe-humic amorphous compounds, which contribute ca. 75–85% to the total Fe) play a very important role in SPM of the tributaries with brown water and in the Irtysh river in its lower reaches. Among the trace metals significant enrichments relative to the average for global river SPM could only be observed for As and Cd (coefficient of enrichment up to 16 for As and 3–3.5 for Cd). It can be shown that the enrichment of As in the SPM is related to natural processes, i.e. the weathering of phosphate containing deposits with high As concentrations in the upper Irtysh basin and the high As–P affinity in the swamp peaty soil. Dissolved P and As are absorbed by amorphous organic C/Fe oxyhydroxide components which act as carriers during the transport to the main stream of the Irtysh river. The role of anthropogenic factors is probably insignificant for As. In contrast, the enrichment of Cd is mainly related to anthropogenic input. The threefold enrichment of Cd in the SPM just below Omsk City and its continuous decrease down to background level at a distance of 500–700 km downstream points quite definitely to the municipal and industrial sewage of Omsk City as the main source of Cd in the SPM of the Irtysh river.

* Corresponding author.
E-mail address: vrachold@awi-potsdam.de (V. Rachold).

0883-2927/$ - see front matter
doi:10.1016/j.apgeochem.2003.08.004

1. Introduction

During recent years the region of the Russian Arctic has attracted the attention of scientists not only in connection with expected climate changes but also with the developing and processing of new oil and gas deposits and the probable subsequent increase of anthropogenic impact on the environment. The rivers are the most important pathways for dissolved and particulate material, including contaminants, from the land to the sea.

The first analyses of major and trace elements in dissolved and particulate forms in the main rivers of the former Soviet Union, including the Russian Arctic, were started at the beginning of the 1950s during the last century in the framework of the USSR Hydrometeorological Survey (Konovalov, 1959; Konovalov et al., 1968). Similar research was carried out by specialists of the Geological Institute of the USSR Academy of Sciences (Glagoleva, 1959; Nesterova, 1960 and Kontorovich, 1968, for Siberia). However, adequate methods of sampling, treatment and analyses of water and suspended particulate matter (SPM) had not been developed at that time. The use of metallic water samplers, paper filters and analytical chemical–spectral methods of low sensitivity did not allow obtaining reliable data, especially for dissolved heavy metals (HM).

Monitoring of HM levels in river water and other environments of the Russian Arctic was performed in the 80–90s of last century by the State System for Observation and Control of Environmental Pollution of the USSR State Committee for Hydrometeorology. An "Atlas of Environmental Pollution of the aquatoria and coastal seas of the Russian Arctic" was prepared by the Regional Center for Monitoring of the Arctic of the Russian Federal Survey on Hydrometeorology and Monitoring of the Environment (Melnikov, 1999) under the umbrella of the Arctic Monitoring and Assessment Program (AMAP).

Concentrations of Fe, Mn, Cu, Zn, Ni, Co, Cd, Pb, Cr and Sn in unfiltered surface waters and SPM of the Pechora, Ob, Yenisey, Khatanga, Lena, Indigirka and Kolyma rivers were presented in this atlas. However, the interpretation of these data is problematic, because it has to be expected that parts of the particulate elements were transferred into dissolved form due to acidification of the water samples.

Geochemical studies of the Russian arctic rivers (Lena, Ob, Yenisey) were carried out in the framework of the "Scientific Program on Arctic and Siberian Aquatorium (SPASIBA)" from 1989 to 1995. Modern methods of sampling and analyses were applied in 3 expeditions to the estuaries of the Ob and Yenisey rivers and to the delta of the Lena river; reliable data for some trace elements (Fe, Cu, Zn, Ni, Pb, Cd, Hg, As) in river and estuarine waters were obtained (Martin et al., 1993; Gordeev and Sidorov, 1993; Kravtsov et al., 1994; Dai and Martin, 1995; Gordeev and Shevchenko, 1995; Guieu et al., 1996; Cossa et al., 1996; Cauwet and Sidorov, 1996; Nolting et al., 1996). The results of these studies clearly documented that previous data on dissolved HM in the arctic rivers were largely overestimated and that the actual concentrations of HM in dissolved and particulate forms in the lower courses of the 3 studied rivers were comparable to the average concentration in global river discharge or even lower.

In the following years the geochemistry of major and trace metals in the Siberian rivers (Lena, Yana, Khatanga, Yenisey) was considered in details within the studies of the Russian-German projects "The Laptev Sea System" and "Siberian river-Runoff (SIRRO)" (Rachold et al., 1996; Rachold, 1999; Rachold and Hubberten, 1999; Lara et al., 1998; Lukashin et al., 1999; Beeskow and Rachold, 2003). It could be shown that HM concentrations in the Lena river SPM do not exceed the World river average. The elevated content of As, Bi and Sb in the Yana river SPM could be related to granitic intrusions forming the source of Au and Sn ore-deposits in the Yana basin. High Co, Cu, Fe, Ni and V concentrations in the SPM of the Khatanga river are a result of basaltic rocks of the Siberian Traps in its basin (Rachold, 1999). In summary, it could be concluded that the chemical composition of the SPM of these Siberian rivers is controlled primarily by the types of rocks and sediments in the basins.

At the same time scientific groups from the USA paid significant attention to the geochemical features of the Siberian rivers (Moran and Woods, 1997; Guay and Falkner, 1998; Huh et al., 1998, and other). Moran and Woods (1997) determined the concentrations of Cd, Cr, Cu, Ni and Pb in filtered water, SPM and bottom sediments of the middle Ob and a few samples of the lower Irtysh river, the Ob's major tributary (Fig. 1). Dissolved Cd, Cr, Cu and Ni concentrations were similar to or slightly higher than those of other Russian arctic and World rivers and estuaries. The comparison between trace metal ratios in crustal material and suspended and bottom sediments suggested that the source of Cr, Cu and Ni was continental weathering. Particulate Cd and Pb concentrations were elevated relative to their crustal abundance, and the authors suggested an additional source for these two elements, although the nature of the source could not be determined.

Shvartsev et al. (1996) stated that within the last few decades a dramatic decrease of river water quality that led to significant changes in the ecosystem took place in the Ob river basin. In 1997 the International Research Center on Physics of Environment and Ecology of the Siberian Branch of the Russian Academy of Sciences established a complex ecological research program in the Ob basin. Three river expeditions and 2 workshops "Ecology of the Poymas of Siberian rivers and Arctic" (1999, 2000) were organized and scientific reports

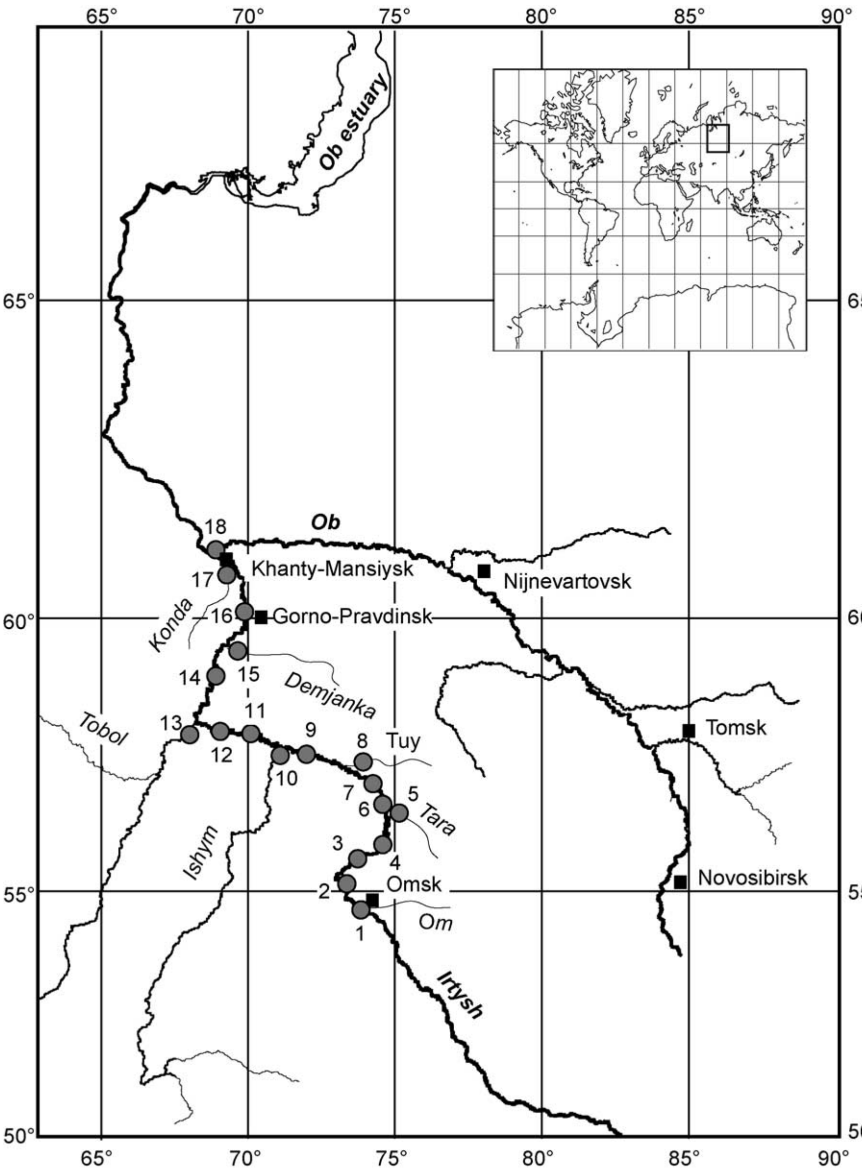

Fig. 1. Sampling locations in the Irtysh River and its tributaries (July 2001).

including the results of the HM determinations in the middle reaches of the Ob river and some of its tributaries were published (Shvartsev et al., 1999; Sorokovikova et al., 1999; Leonova et al., 2000). Shvartsev et al. (1999) collected 20 water samples along the stream of the middle Ob river below its tributary the Tom river and analyzed 9 HM in dissolved form. Sorokovikova et al. (1999) obtained 53 samples of the Tom river and the middle Ob river and 9 HM in filtered water samples were determined by ICP–MS. However, in both studies the interpretation of the results is very limited. Shvartsev et al. (1999) note an increase of Zn and Mn from south to north along the Ob river. They consider that this increase is a result of the association of metals with organic acids, the concentrations of which increase to the north due to the inflow of tributaries with water of swamp genesis. Sorokovikova et al. (1999), on the other hand, did not identify any definite tendency in concentration changes along the rivers but report an unsystematic scatter of concentrations. Leonova et al. (2000) collected water samples of the Ob river (below Novosibirsk City) and the Tom river (from Tomsk City down to the mouth of the river). The analyses showed that the Tom river is much more contaminated by HM than is the Ob river. Especially high concentrations of Hg were determined in the lower course of the Tom river: Hg diss. = 0.045–1.5 μg/l and Hg part. = 8–32 μg/g in the Tom river ($n = 5$); Hg diss. < 0.02 μg/l and Hg part. = 0.4–1.7 μg/g in the Ob river ($n = 4$).

As a result of the combined action of strong anthropogenic impact and specific natural geochemical anomalies (geochemical provinces), the concentrations of many HM in the upper Irtysh river and its tributaries in the territory of Kazakhstan appear to be extremely high (Panin and Sibirkina, 2000; Panin, 2002). The analyses of large volume water samples performed in 1984–1996 show that the average concentrations of dissolvable metals in the upper Irtysh basin are (in μg/l): Mn: 33.1 ± 4.2 ($n = 832$), Zn: 80.5 ± 20.8 ($n = 1289$), Cu: 51.9 ± 12.1 ($n = 1277$), Pb: 14.4 ± 2.2 ($n = 916$), Cd 2.64 ± 0.46 ($n = 788$), Cr: 5.2 ± 0.6 ($n = 687$), Co: 1.85 ± 0.25 ($n = 1006$), Mo: 10.0 ± 1.1 ($n = 934$). Unfortunately, no information about sampling, filtration and other treatment of the water samples was presented in the papers except for a reference to ''Unified Methods of Water Analyses in the USSR'' (1978) and a note on the analytical methods, which were ICP–OES and GF–AAS (for Cd determinations) (Panin, 2002). Thus, the reliability of these data remains questionable, especially because the term ''dissolvable form'' is usually related to the sum of the dissolved content and a part of the leachable fraction of the SPM.

During the third expedition of the program ''Ecology of the Poymas of Siberian rivers and Arctic'' 3 small groups of geochemists including a group of two co-authors of the present paper (VVG and IEV) participated in sampling. The preliminary results of this expedition to the middle and lower courses of the Irtysh river (July 2001) and some additional data were published in the report ''Ecologo-geochemical investigation in the Ob river basin''. Sazonova and Shvartsev (2002) analyzed dissolved major cations and anions, nutrients, organic C and 10 dissolved trace elements. The total mineralization of the Irtysh river water decreased from 250 mg/l below Omsk City to 115 mg/l near the confluence with the Ob river with an average of 205 mg/l. The authors state that low mineralization of the southern tributaries and technogenic influence of Omsk City are the main reasons for this tendency. The highest concentrations of dissolved Zn and Cu were detected below Omsk City (20–37 μg/L Zn and 4–6 μg/l Cu) and dissolved Pb concentrations of up to 9.4 μg/l were determined near Tobolsk City. The other elements (Cd, Li, Sr, Br, F, Hg) did not exceed the maximum allowed concentrations (MAC).

Kovalskaya et al. (2002) analyzed 26 major and trace elements in 40 SPM samples of the Irtysh river and its tributaries. river water was filtered through paper filters ''blue line'' with a pore size of 2.5 μm and the samples were analyzed by XRF with synchrotron radiation. The results were reported in μg/l units but SPM concentrations were not provided. The authors could not detect any trends in the elemental composition of SPM along the Irtysh river between Omsk City and Khanty-Mansiysk City and the comparison between the right and left tributaries did not show significant differences.

Preliminary results for 10 dissolved metals (Fe, Mn, Cu, Zn, Ni, Co, Pb, Cd, Cr and Hg) and for particulate major and trace elements, which were obtained by the authors of the present paper in the middle and lower courses of the Irtysh river, are reported in the above mentioned report (''Ecologo-geochemical investigation in the Ob river basin'') and in Gordeev and Vlasova, 2002 and Gordeev et al., 2002. The results and conclusions of this earlier study will be shown in the following in context with the results of the present paper. However, it should be noted here that the consistency of the analytical results obtained by the 3 groups involved in the program ''Ecology of the Poymas of Siberian rivers and Arctic'' was quite poor.

Summarizing, this short review of available data on the geochemistry and the level of contamination of Russian arctic rivers and estuaries by HM demonstrates that the results of different authors exhibit significant inconsistencies. The concentrations along the main stream of the rivers appear to vary unsystematically. Many features of the geochemical behavior of the trace elements in dissolved and particulate form in river discharge are still studied insufficiently. Thus, a critical review and new assessments of HM concentrations and their fluxes in the Russian arctic rivers was published recently (Gordeev, 2001).

This study concentrates on the geochemistry of the suspended particulate matter (SPM) of the Irtysh river, the main tributary of the Ob river, East Siberia, Russia. The main objectives are to characterize the behaviour of major and trace elements in the SPM and to identify natural and anthropogenic sources of the particulate load. Sampling was conducted in July 2001 and extended from Omsk City down to the confluence with the Ob river along a distance of 1834 km. As discussed above, the upper Irtysh river waters are polluted by HM in dissolvable form but SPM data are not available (Panin, 2002). Information on HM in the middle and lower courses of the Irtysh river is very scarce. In particular, the role of the tributaries with brown acid waters of swamp genesis in the transformation of the chemical composition of water and SPM is unknown.

1.1. Study site

The Irtysh river is the largest western tributary of the Ob river (Fig. 1). Its water and suspended sediment discharges are 99.8 km^3/a and 15.2×10^6 t/a, respectively (Lisitzina, 1974). The upper stream of the Irtysh river is located in the middle and high mountains of the Altay. The most widespread rocks are granites, clayey sandstones and limestones. To the north, in the lower mountains of the Kazakhstan hills, Paleozoic deposits consisting of quartzite, limestones, sandstones and shales are more common.

Below Omsk City the Irtysh river flows through the lowlands of the East Siberian Plain, which comprise numerous peat swamps and lakes interrupted by ice ridges, hills and thermokarst trenches. The western part of the basin between the Irtysh and Ob rivers is occupied by a huge swamp system (approximately 800×350 km). The level of swampiness reaches 50–80% and reed overgrowths are the dominating type of vegetation in these swamps (Panin, 1972).

Numerous deposits of polymetals are concentrated in the Irtysh river basin, especially in its southern part in the territory of Kazakhstan, and a large-scale extractive industry is developed. Today the bare surfaces of mine sites and their dumps and tailings deposits outflows from metallurgical, chemical, engineering industries and power plants and of the construction industry and agriculture results in significant HM pollution of the environment (Panin and Sibirkina, 2000; Panin, 2002).

2. Sampling and analytical methods

The small vessel ''Mirazh'' (34 t deadweight) was used to collect water samples along the Irtysh river from Omsk City to the confluence with the Ob river at 18 stations during 21–28 July 2001 (Fig. 1). To avoid any contamination by the ship, surface water samples were taken by a plastic bucket from the bow boom 2–3 m in front of the ship during slow movement. Filtration was carried out immediately after sampling inside a small cabin. The cabin walls were covered by polyethylene film to minimize contamination. The SPM was separated by vacuum filtration through 47 mm Nuclepore filters of 0.4 μm pore size (for chemical analyses) and through glass-fiber GF/F filters of 0.7 μm pore size (for organic C determinations) in plastic Millipore funnels. The filtered water volume varied between 0.1 and 1.0 l depending on sediment load.

Total suspended matter concentrations were estimated from the weight difference between the clean and the sediment-loaded filters after freeze-drying. Acid digestions of the sediment loaded Nucleopore filters were performed in PTFE vessels using ultrapure HNO_3, $HClO_4$ and HF. The residues were redissolved in HNO_3 and diluted with H_2O to a final volume of 20–50 ml depending on the sediment load. Analyses of Al, Fe, Mn, Ti, Mg, Ca, Na, K, P, Ba, Co, Cu, Ni, Pb, Sr, Zn and Zr were carried out by ICP–OES (Perkin-Elmer Optima 3000 XL), Cd and As by GF–AAS (Perkin-Elmer SIMAA 6000). Accuracy of the determinations was checked by the analysis of the international standard reference material (MESS-1, BCSS-1, GSD-9 and others). The analytical precision was better than 5% for major elements and better than 10% for trace elements except for P, Co, Cr and Zr (up to 20%).

The sediment-loaded GF/F filters were hand-ground in a mortar and the powder was analyzed for particulate organic C concentrations by a carbon auto-analyzer (ELTRA) after removal of carbonate. The analytical precision was better than 5%.

3. Results

The chemical composition of the SPM and the total sediment load of the Irtysh river are presented in Table 1. In addition to the SPM samples collected along the main river, 7 samples were taken in its tributaries (Fig. 1). The lowermost station (St. 18) was in the mixing zone between the Irtysh and Ob river waters.

The water of the middle Irtysh river (downstream Omsk City) has a yellow-gray color due to clayey-silty suspensions. The Tuy river, the first tributary with brown water of swamp genesis (Table 1), is quite small and the color of the main river does not change after its confluence. The same holds true for the Ishym river. However, after the inflow of the Tobol river the Irtysh river itself changes to a brown color and remains such down to the confluence with the Ob river.

Fig. 2 shows the variations of total SPM, Al_2O_3, Fe_2O_3, CaO and POC along the main course of the Irtysh river. The SPM concentration of the Irtysh river is 10–29 mg/L; the highest SPM concentration was detected in the Tara river (average 38.9 mg/l). Generally, the brown water tributaries are characterized by lower pH (6.5–7.1) and SPM content (8–17 mg/l). Al_2O_3 content is stable up to the Tobol river (12–14%) and decreases down to 8.17% at the confluence with the Ob river. Fe_2O_3 concentrations remain constant up until the Tara river inflow (5.0–5.5%) and later increase up to 15%. Similarly, CaO demonstrates a monotonous increase from 1.3–1.5% to 2% after the Tara inflow. POC concentrations vary within a range of 0.7–1.0 mg/l (except St.1 near Omsk City) and increase up to 1.3 mg/l below the inflow of the Tobol river. The variations of K_2O, MgO, Na_2O and TiO_2 along the river are almost identical to that of Al_2O_3, the concentrations remain stable in the middle river and significantly decrease in the lower river. The behavior of P is analogous to POC. The concentration of MnO is stable down to St. 6 (Tara river) and later increases from 0.28 up to 0.40%. The majority of the trace elements show a quite stable behavior, especially Cu, Ni, Co, Cr, Zn. Variations of Zr along the river are very similar to that of Al_2O_3. Barium shows an insignificant increase from 360–420 μg/g in the middle course to a maximum of 540 μg/g in Sts. 11 and 12 and a slight decrease in the lower reaches of the river. Vanadium increases from 110 μg/g up to 160 μg/g at St. 11 and remains at this level down

Table 1
Chemical composition of SPM from the Irtysh River and its tributaries[a]

Station	River	Distance from Ob River (km)	Type of water[b]	pH	SPM (mg/L)	Al_2O_3	CaO	Fe_2O_3	K_2O	MgO	MnO	Na_2O	P_2O_5	TiO_2	POC	As	Ba	Cd	Co	Cr	Cu	Ni	Pb	Sr	V	Zn	Zr
1/A	Irtysh	1834 (Omsk)	yl	6.7	29.0	13.89	1.53	5.43	2.04	1.82	0.20	1.17	0.26	0.71	8.35	17	415	1.14	17	78	41	49	30	128	112	148	179
1/B	Irtysh	1834 (Omsk)	yl	7.0	22.1	12.61	1.39	5.47	1.77	1.70	0.32	0.62	0.54	0.52	7.68	23	370	1.43	26	118	54	68	42	111	117	197	124
2	Irtysh	1800	yl	7.2	20.3	11.96	1.48	5.07	1.66	1.67	0.27	0.64	0.51	0.52	3.98	29	383	3.58	<	180	<	<	45	116	102	192	122
3	Irtysh	1735	yl	7.15	19.0	12.17	1.39	5.02	1.75	1.65	0.25	0.65	0.48	0.53	5.44	18	359	3.25	21	104	44	51	34	109	105	151	126
4	Irtysh	1620	yl	–	11.7	12.44	1.35	5.19	1.77	1.67	0.28	0.62	0.60	0.52	5.82	21	421	2.81	<	115	49	59	37	111	110	226	123
5	Irtysh	1520	yl	7.3	10.7	13.14	1.37	5.47	1.81	1.75	0.28	0.76	0.47	0.61	8.82	28	434	1.45	<	129	53	65	36	122	117	158	144
6	Tara	1488	yl	6.9	38.9	15.08	1.82	9.03	1.99	1.95	0.18	0.58	0.68	0.72	4.18	25	529	0.80	24	110	37	58	31	130	145	156	136
7	Irtysh	1330	yl	7.1	13.3	12.89	1.50	6.84	1.82	1.75	0.31	0.59	0.65	0.60	6.15	29	551	2.77	<	145	43	59	38	129	135	211	131
8	Tuy	1198	br	7.1	16.4	7.10	4.02	15.53	0.93	1.18	0.18	0.34	2.81	0.35	9.24	87	884	–	<	125	<	48	–	273	101	202	76
9	Irtysh	1120	yl	–	14.5	13.50	1.60	7.59	1.81	1.81	0.33	0.56	0.68	0.60	5.07	39	556	0.78	<	167	45	63	37	137	147	161	132
10	Ishym	1050	mx	7.35	12.0	11.43	2.80	9.20	1.62	1.81	0.49	0.49	1.51	0.57	6.75	111	637	1.30	<	138	<	61	39	231	139	170	117
11	Irtysh	852	yl	7.3	18.1	14.63	1.67	8.31	1.99	1.95	0.37	0.59	0.69	0.65	4.22	44	542	0.95	30	99	46	63	43	144	161	205	138
12	Irtysh	820	yl	7.25	22.8	14.74	1.63	8.28	2.05	1.96	0.37	0.63	0.67	0.66	4.40	37	541	0.69	29	76	47	60	35	141	159	298	142
13	Tobol	666	br	6.65	14.8	8.62	1.79	12.42	1.09	1.27	0.47	0.41	1.43	0.44	6.18	57	375	1.28	34	127	48	56	33	139	158	176	93
14	Irtysh	565	br	6.95	16.3	11.46	1.71	10.25	1.52	1.58	0.44	0.49	1.11	0.55	5.70	52	473	0.97	35	115	40	58	35	144	158	149	116
15	Demjanka	332	br	6.5	7.9	7.74	2.92	16.39	0.94	1.10	0.19	0.30	2.18	0.39	12.46	66	569	1.29	<	133	<	47	44	198	136	192	85
16	Irtysh	225 (Gorno-Pravdinsk)	br	7.05	17.3	11.60	1.80	10.90	1.51	1.59	0.37	0.49	1.08	0.55	6.97	52	494	1.70	30	135	44	65	43	147	166	269	114
17	Konda	90	br	6.55	11.5	6.48	1.95	18.10	0.86	1.04	0.36	0.32	2.09	0.33	11.80	67	440	0.94	<	128	36	56	33	149	115	171	73
18	Ob	0	br	7.1	14.7	8.17	1.97	15.17	1.08	1.18	0.27	0.53	1.21	0.39	9.04	60	475	0.79	30	116	52	54	35	145	145	137	115

[a] Major elements in weight%, trace elements in μg/g, < = below detection limit, – = not determined.
[b] yl: yellow-gray water, br: brown water, mx: mixed water (at St.10 sampling was performed in the mixing zone between Ishim and Irtysh waters).

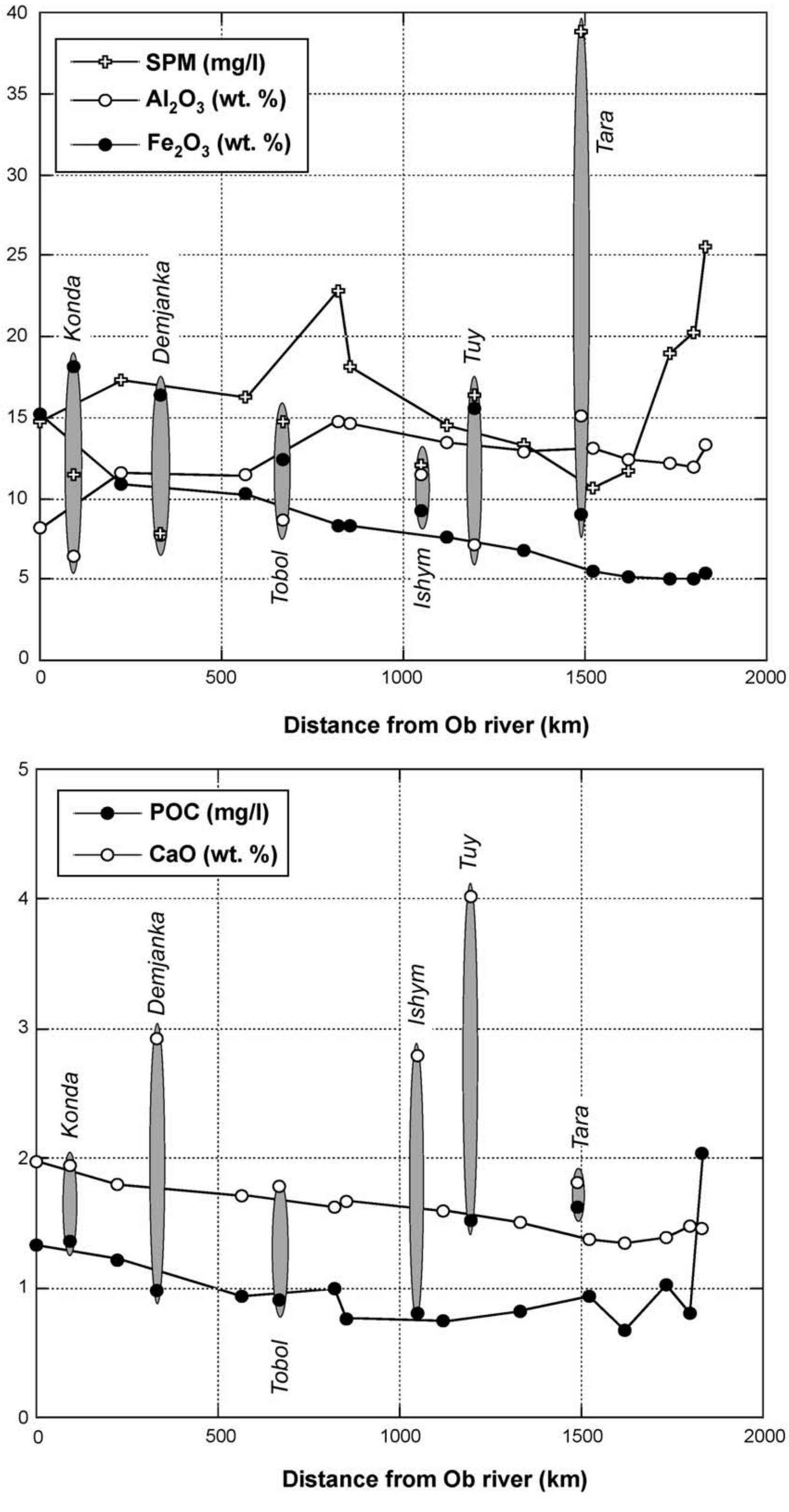

Fig. 2. Variations of SPM, Al_2O_3 and Fe_2O_3 (top) and POC and CaO (bottom) in SPM along the Irtysh River. Shaded vertical bars mark concentrations in the tributaries.

to the confluence with the Ob river. Finally, Sr follows CaO along the entire river course.

In the following, the authors will focus on the variations of Al_2O_3 and Fe_2O_3 and show that their behavior provides the key to understand the main factor controlling the SPM geochemistry of the Irtysh river. Fig. 3 displays the interrelationship between Al_2O_3 and Fe_2O_3 and clearly shows that the samples can be divided into 3 groups.

Group 1 includes the stations of the Irtysh river (Sts. 1, 2, 3, 4, 5, 7, 9, 11, 12) and the tributary Tara (St. 6). For these stations a direct correlation between Al_2O_3 and Fe_2O_3 can be observed. Al_2O_3 and Fe_2O_3 are present in silicate crystalline form; the Fe/Al ratio of 0.61 is typical for silicate rocks. The highest concentrations of Al_2O_3 and Fe_2O_3 for the samples of Group 1 were found in the Tara river SPM—15.08 and 9.03%, respectively. SPM concentrations in the Tara river are the highest of all samples—up to 58.7 mg/l, averaging 38.9 mg/l ($n=3$). It is obvious from Fig. 3 that in respect of the Fe/Al ratio the composition of the Tara river SPM does not differ from that of the upper Irtysh SPM. The first tributary with clean brown water of swamp genesis is the Tuy river (St. 8). Its SPM has a high Fe_2O_3 (15.53%) and a low Al_2O_3 (7.10%) content and the position in Fig. 3 is far away from the Group 1 stations. Consequently, this sample is included in another group (Group 2: the brown water tributaries), which also comprises 4 additional stations of other tributaries with brown water (Tobol, St. 13, Demjanka, St. 15; Konda, St. 17, and Ob, St. 18).

After the inflow of the Tobol river the influence of brown waters in the Irtysh main river becomes obvious (see above). As a result, the composition of SPM at St. 14 and 16 significantly differs from that of the upper Irtysh SPM. These two stations belong to Group 3, which describes intermediate waters, and in Fig. 3 the two stations plot between Group 1 and Group 2. The Ishym river (St. 10) belongs to the brown water rivers. However, the Ishym sample was collected in the mixing zone between Ishym and Irtysh waters and, therefore, plots in the field of Group 3 (intermediate waters). It is worthy of note that in Group 1 a direct positive correlation between Fe and Al is seen whereas in Group 2 a negative correlation between the two elements occurs. In Group 3 the correlation is practically absent.

It is obvious from the above considerations that in the middle reaches of the Irtysh river (below Omsk City) the SPM is dominated by typical silicate material (Table 2). However, the variations of Al_2O_3 and Fe_2O_3 discussed above suggest that the inflow of brown water

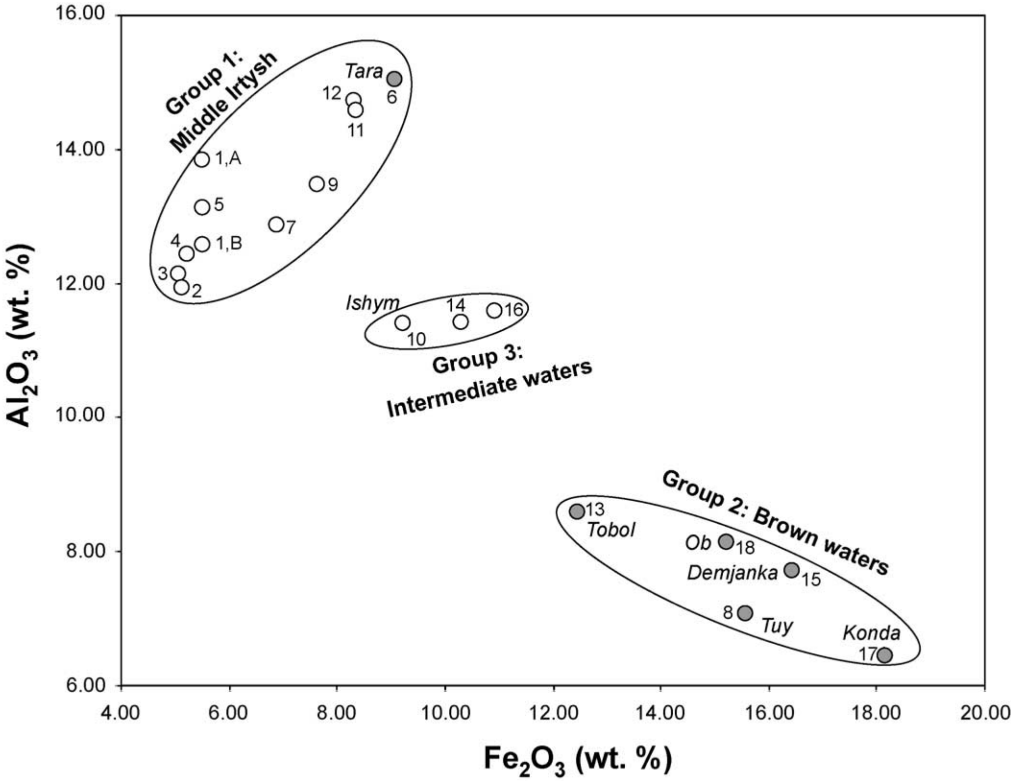

Fig. 3. Interrelations between Al_2O_3 and Fe_2O_3 in SPM of the Irtysh River and its tributaries. Group 1: SPM of middle Irtysh River including Tara River; Group 2: SPM of tributaries with brown water; Group 3: mixed yellow-gray and brown waters (Sts. 14 and 16) including the Ishym River (St. 10) where sampling was performed in the mixing zone of Ishym and Irtysh waters.

Table 2
Average chemical composition of SPM in (1) the middle Irtysh, (2) intermediate Irtysh waters and (3) brown water tributaries and Ob River[a]

Element, component	(1) Middle Irtysh (Sts. 1–5, 7, 9, 11,12)	(2) Intermediate water (Sts. 10, 14, 16)	(3) Brown water tributaries (Sts. 8, 13, 15, 17, 18)	(4) Representative lower Irtysh (Sts. 14, 16)	(3)/(1) ratio
SPM	18.1	15.2	13.1	16.8	0.57
POC	1.09	0.98	1.22	1.07	1.67
Al_2O_3	13.20	11.50	7.62	11.50	0.58
Fe_2O_3	6.27	10.11	15.53	10.6	2.55
CaO	1.49	2.10	2.53	1.75	1.70
K_2O	1.85	1.55	0.98	1.52	0.54
MgO	1.77	1.66	1.15	1.59	0.65
MnO	0.30	0.43	0.29	0.41	0.80
Na_2O	0.68	0.49	0.38	0.49	0.60
P_2O_5	0.55	1.23	1.94	1.10	3.52
TiO_2	0.59	0.56	0.38	0.55	0.65
As	29	52	67	52	2.39
Ba	457	534	548	480	1.18
Cd	1.88	1.32	1.07	1.33	0.58
Co	25	32	–	$\leqslant$32	–
Cr	121	129	126	125	1.05
Cu	47	42	45	42	1.00
Ni	60	61	52	62	0.87
Pb	38	39	36	39	1.00
Sr	125	174	155	145	1.36
V	115	154	131	162	1.00
Zn	195	196	175	209	0.92
Zr	136	116	88	115	0.65

[a] The representative composition of the Irtysh River (4) at the confluence with the Ob River is shown as well (SPM and POC in mg/l, major elements in weight% and trace elements in μg/g, – = not determined).

tributaries strongly affects the geochemical characteristics of the Irtysh SPM. The existence of this type of waters is very common in this region if one remembers that a great area of the basin is occupied by swamps. The average SPM composition of these brown water rivers is presented in Table 2. In comparison to the SPM of the middle Irtysh, this material is characterized by a significantly higher content of POC (POC brown water/POC yellow-gray water = 1.67), P_2O_5 (3.52), Fe_2O_3 (2.55), CaO (1.7) and the trace elements As (2.39), Sr (1.36), Ba (1.18). In contrast, total SPM (0.57), Al_2O_3 (0.58), K_2O (0.54), MgO (0.65), Na_2O (0.60), TiO_2 (0.54–0.65), MnO (0.80), and trace metals Cd (0.58), and Zr (0.65) show lower concentrations. For other trace elements the difference between the two SPM types is insignificant; the ratio for Cu, Cr, Pb, V, Zn, Ni is in the range of 0.9–1.05. The average SPM composition in the lower course of the Irtysh river (in the following called ‘‘representative Irtysh’’) represents a mixture between the two components SPM of the middle Irtysh—typical silicate material and SPM of brown water tributaries.

Dissolved major and trace element data have been obtained during the same expedition by Sazonova and Shvartsev (2002) and Gordeev and Vlasova (2002). Table 3 presents average dissolved concentrations for the 3 groups of stations, which had been identified based on the particulate Al_2O_3 and Fe_2O_3 distribution shown in Fig. 3. The data in Table 3 demonstrate that the brown waters are significantly enriched in Mn and Fe, and to a lesser degree in Zn, Ni and P_2O_5. The concentrations of Ca and Sr in brown waters are ca. 10% higher. The trace metal concentrations (Cu, Pb, Cr and Hg) are practically the same in all types of water, Cd concentrations are even higher in the main stream of the middle Irtysh river than in brown water tributaries.

Although a detailed comparison of dissolved trace metals with published results is not the task of this paper it is noted that data published by Moran and Woods (1997), who analyzed 4 samples of the lower Irtysh river and 1 brown water sample of the Tobol river, exhibited identical dissolved Cu concentrations, 1.5–3.0 times higher Cr and Ni and ca. 3–7 times higher Cd concentrations. However, it must be mentioned that the samples described in Moran and Woods (1997) were collected in June 1995 when the SPM concentrations were 58 mg/l in the Irtysh river and 52 mg/l in the Tobol river, which is 3.4 and 3.5 times higher than during the authors' field season. Considering the

Table 3
Average concentrations of dissolved elements (in μg/L) in the middle Irtysh before (1) and after (2) the inflow of brown waters, brown water tributaries (3), and the lower Irtysh River (4) at the confluence with the Ob River

Element, component	(1) Middle Irtysh, before inflow of brown waters (Sts. 1–5, 7)	(2) Middle Irtysh, after inflow of brown waters (Sts. 9, 11–12)	(3) Brown water tributaries (Sts. 8, 13, 15, 17, 18)	(4) Respresentative lower Irtysh (Sts. 14, 16)	(3)/(1) ratio
Fe	20.9	228.2	364	110	17.4
Mn	1.1	23.5	57	4.0	51.8
Cu	2.69	3.20	2.90	3.0	1.07
Zn	0.97	1.5	2.5	1.600	2.58
Ni	4.6	5.5	7.0	6.2	1.520
Pb	0.55	0.43	0.41	0.40	0.75
Cd	0.052	0.020	0.020	0.020	0.38
Cr	0.56	0.49	0.42	0.32	0.75
Hg	0.018	0.011	0.019	0.018	1.05
Ca	27 400	–	30 000	–	1.09
Sr	0.22	–	0.24	–	1.1
PO_4	48	–	90	–	1.9

Fe–Hg data are taken from Gordeev and Vlasova (2002); Ca, Sr and PO_4 data from Sazonova and Shvartsev (2002) [– = in Sazonova and Shvartsev (2002) water samples on Sts.9, 11–12, 14 and 16 were not obtained].

different years of sampling and the significant differences in SPM concentrations, the authors therefore, consider these results to be satisfactorily comparable with the dissolved concentrations published by Sazonova and Shvartsev (2002) and Gordeev and Vlasova (2002).

4. Discussion

4.1. Role of main oxides/oxyhydrates and organic matter

It is a well-known fact that Al, Fe and Mn oxides/oxyhydrates as well as organic matter and carbonates are the most important carriers for trace elements in river SPM. The results indicate that Fe-organic complexes are the dominant phases in the SPM of brown water rivers. Fig. 4 shows the relationship between Fe_2O_3 and POC, a positive correlation is clearly visible for SPM of the brown water tributaries. The negative correlation between Al_2O_3 and POC testifies against the presence of any Al–organic compounds in the SPM of these type of waters. The third element which is able to form oxyhydrates and metal–organic complexes, Mn, does not show any correlation with POC.

After filtration through nucleopore filters with 0.4 μm pore size, the filtered water practically looses its brown color and becomes colorless clean water. This fact coupled with the relation between Al_2O_3 and Fe_2O_3 (Fig. 3) indicates that amorphous Fe–organic (Fe–humic) particles are responsible for the brown color but not dissolved or colloidal components. If it is assumed that Al_2O_3 in brown water SPM is entirely present in silicate form the contribution of amorphous Fe to the total Fe can be quantified as 83.5% for SPM of the Konda river and about 77% for SPM of the average for the brown water tributaries.

In this context, the following point should be noted. Meade et al. (2000) emphasized that between Tobolsk and Khanty-Mansiysk in the course of the lower Irtysh (Fig. 1) in the middle of the 70s the water discharge increased by 30% and at the same time the SPM discharge became twice as high. This increase could not be attributed to the two small tributaries Demjanka and Konda, both of which have low SPM concentrations. Meade et al. (2000) found the reason to be intensive shore erosion in this part of the river. They concluded (with a reference to Lisitzina, 1974) that the SPM concentration was 1.6 times higher near Khanty-Mansiysk than at the confluence between the Tobol and Irtysh rivers. However, the present results do not document an increase of SPM concentrations in the course of the lower Irtysh. The authors suggest that the erosion activity is highest during spring flood time and significantly decreases during periods with lower water level. The present sampling was performed at the end of July when the water level was significantly lower than immediately after spring flood. However, if it were correct that shore erosion during spring flood produces a significant increase of SPM in the lower course of the Irtysh river this process would change the SPM composition towards that of the middle course of the river, i.e. silicate material. The consequence would also be a pronounced seasonality in the SPM composition of the lower Irtysh river. Unfortunately no information is available about seasonal variation of the chemical composition of SPM and water of the Irtysh river.

Fig. 5 presents the average Al-normalized major and trace element concentrations of Irtysh SPM

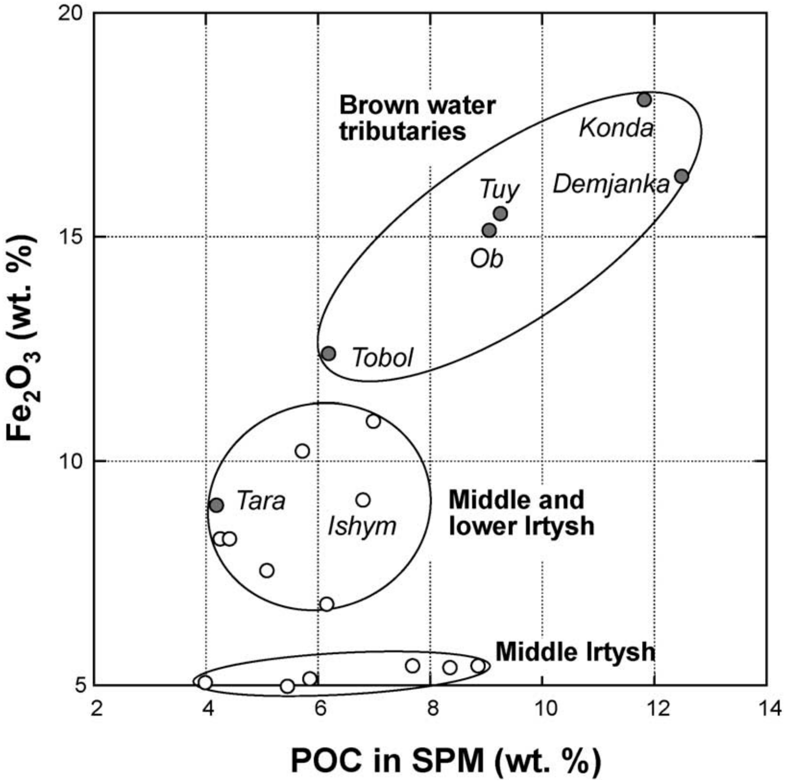

Fig. 4. Correlation between Fe_2O_3 and particulate organic C (POC) in SPM of the Irtysh River and its tributaries.

(lower = ''representative'' Irtysh) in comparison to average shale (Wedepohl, 1971, 1991). In general, average shale can be regarded as the weathering product of the upper continental crust after subtracting the ''soluble'' elements. Aluminium normalization was applied to compensate for dilution by organic material. Except for some elements (P, Cd, As which will be discussed below) a general agreement between the middle Irtysh SPM and average shale is seen indicating that the chemical composition of the middle Irtysh SPM as a whole is not very different from the world average. The SPM of the lower (''representative'') Irtysh on the other hand shows more pronounced deviations, especially an elevated Fe/Al ratio can be observed in Fig. 5.

4.2. Role of peat in the formation of SPM

As shown above the composition of SPM of brown water tributaries draining swamps significantly differs from that of typical silicate SPM of the middle Irtysh. It is interesting to compare the SPM composition with the average composition of peat of the West Siberian lowlands. The most representative data were recently published by Inisheva and Tsibukova (1999). The authors have investigated 950 peat samples from 28 representative peat deposits in 4 swamp regions of the Tomsk district (Table 4). They divided all peat samples into two groups in accordance with the type of deposits—upper layer and low-lying peat with significantly different chemical composition. Table 4 displays the chemical composition of the two peat units in comparison to that of the brown water SPM; the last two columns give the concentration ratios. These ratios cannot serve as direct evidence of the peat origin of the elements in the SPM of brown waters but they show the direction of trends. In general, the composition of the river SPM is closer to that of the low-lying peat. Unfortunately, organic C, Al, P, As and Cd concentrations were not analyzed by Inisheva and Tsiburova (1999). However, the available data show that the low-lying peat deposits might be a source of Ca, Sr and to lesser degree Ba.

Considering the higher contents of POC and P_2O_5 in SPM of brown-water rivers in comparison with silicate SPM of the middle Irtysh, it is also suggested that the peat deposits may be a source of these components.

It would be important to study the behavior of Fe, P, Ca, Sr and other elements during the transit from acid swamp waters to the tributaries with brown water and, finally, to the Irtysh river in relation to pH and redox changes. Unfortunately, the available data are very limited. The comparison of the ratios between dissolved and particulate elemental concentrations in brown and

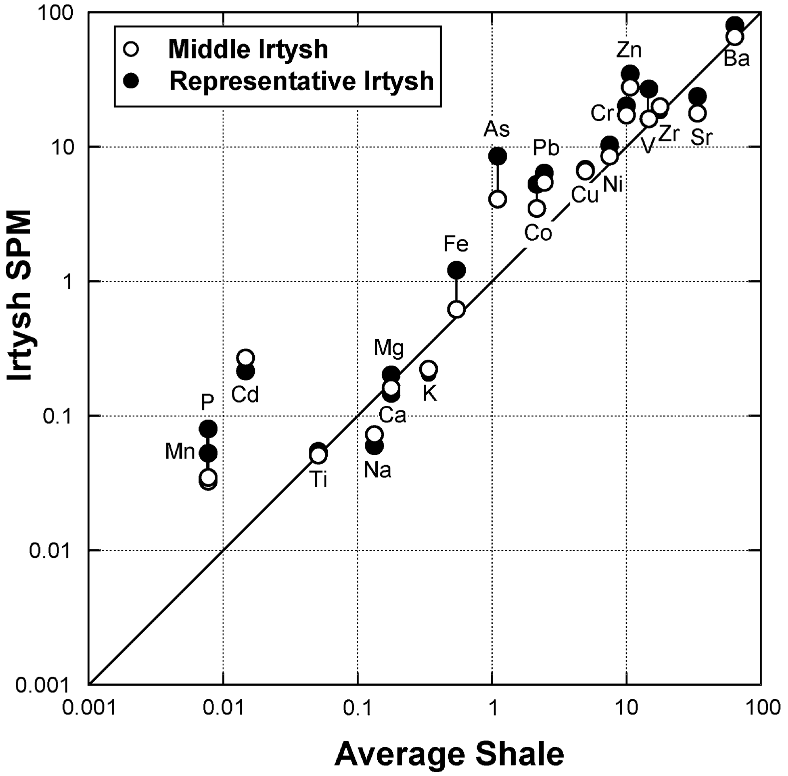

Fig. 5. Average chemical composition of SPM from the middle Irtysh River (below Omsk City) and from the lower Irtysh River ("representative" Irtysh SPM). The *x*-axis corresponds to the composition of average shale (Wedepohl, 1971, 1991). The diagonal represents the straight line of identical values. Al normalized concentrations based on weight ratios (major elements) and weight ratios 10^4 (trace elements) are displayed.

Table 4
Average composition of the West Siberian lowland peat (Inisheva and Tsibukova, 1999) and SPM of brown-water rivers as well as their ratios for the investigated chemical elements (major elements in weight%, trace elements in µg/g,– = no data)

Element/oxide	SPM of brown waters	Upper layer peat (UP)	Low-lying peat (LP)	UP / SPM_{bw}	LP / SPM_{bw}
Fe_2O_3	15.53	0.28	1.28	0.018	0.082
MnO	0.29	0.012	0.077	0.041	0.26
CaO	2.50	0.40	5.90	0.16	2.36
Na_2O	0.38	0.031	0.065	0.081	0.17
As	67	–	–	–	–
Ba	548	47	275	0.085	0.50
Cd	1.07	–	–	–	–
Co	32	1.1	2.4	0.034	0.075
Cr	126	7.6	12.3	0.06	0.10
Cu	45	7.0	10.8	0.15	0.24
Pb	36	3.1	4.9	0.086	0.13
Sr	156	80	338	0.51	2.16
Zn	175	6.6	15.5	0.038	0.088
V	131	2.1	11.7	0.015	0.089

yellow-gray waters shows that in the brown waters the ratios for Fe and Mn are 80–100 times higher than those in the middle Irtysh river (yellow-gray water). At the same time the ratios for Ca, Sr and P are practically identical in both types of waters. It is necessary to note here that in the case of dissolved P the concentrations of inorganic PO_4 are referred to, whereas the particulate P is the sum of organic and inorganic P forms.

Table 5
Trace metal concentrations in SPM of the Irtysh River and other Arctic rivers (in μg/g, – = no data)

River	Cu	Zn	Ni	Co	Cr	Pb	Cd	As	V	Reference
Representative Irtysh	42	209	62	$\leqslant$32	125	39	1.33	52	162	This study
Ob–Irtysh	25.8	–	28.8	–	49.8	14.9	0.58	–	–	Moran and Woods (1997)
Ob	50	104	38	19	–	16	0.53	–	–	Gordeev et al. (2003)
Yenisey	144	220	77	23	–	30	1.3	–	–	Gordeev et al. (2003)
Yenisey	87	194	83	38	–	23	0.66	13	175	Beeskow and Rachold (2003)
Lena	28	143	31	–	–	23	–	–	–	Martin et al. (1993)
Lena	28	160	34	13	–	36	0.25	–	–	Gordeev and Shevchenko (1995)
Lena	42	185	42	–	–	42	0.96	–	–	Nolting et al. (1996)
Lena	35	141	53	18	–	24	0.65	9.1	97	Rachold (1999)
Yana	30	130	39	17	–	23	0.32	36.7	110	Rachold (1999)
Khatanga	82	104	84	35	–	12	0.22	9.3	349	Rachold (1999)
Average Russian Arctic river	55	138	47	19	–	22	0.63	–	118	Gordeev (2001)
Average World river	80	250	84	20	100	35	0.7	5.0	130	Martin and Gordeev (1986) (with corrections)

It is assumed that acidic conditions in the swamps are responsible for the primary migration of some elements including Fe in dissolved form. The concentration of total dissolved Fe in stagnant water at pH = 3–4 reaches 17 mg/l (Inisheva et al., 2000). It is very likely that during the mixing with waters of the Irtysh tributaries with pH = 6.5–7.1 Fe flocculates and is transformed into particulate form. Considering the sharp decrease of dissolved Mn from the brown to the yellow-gray waters it is reasonable to suggest that a part of dissolved Mn is coprecipitated with Fe-floccules and/or flocculates separately. This transformation of dissolved to particulate Mn is clearly seen from elevated Mn concentrations in SPM of the lower Irtysh river (up to 0.41%).

4.3. Sources of heavy metals in the Irtysh SPM

Taking into account the aforementioned ecological situation in the river basin and the significant enrichment of the dissolved HM Cu, Zn, Pb, Cd, Co, Cr, Mo in the upper reaches of the Irtysh and its tributaries (2–16 times according to Panin, 2002), it is reasonable to expect higher concentrations of some HM in the Irtysh SPM as well. Table 5 presents a comparison of HM data of the SPM of the Irtysh river, other Arctic rivers and the averages for the World rivers. A direct comparison is possible for the data of this study with those published by Moran and Woods (1997). One can see that the results of their analyses for Cu, Ni, Cr, Pb and Cd in the SPM of the Irtysh river are lower than the present data and also lower than data for other arctic rivers. A possible reason for this discrepancy could be the sample preparation applied by Moran and Woods (1997): the SPM was leached in 2 M HNO_3 for 6 weeks and not totally dissolved as in the present study.

To assess the degree of HM enrichment of the Irtysh SPM below Omsk City and near the confluence with the Ob river Al-normalized enrichment factors EF were calculated:

$$EF_{HM} = (HM/Al)_{SPMsample}/(HM/Al)_{SPMworld\ average}$$

Among all studied trace elements only 2 elements—As and Cd—have an enrichment factor of more than 2: As—7.5 for the middle Irtysh SPM and 16.1 for lower Irtysh SPM and, Cd—3.5 and 2.9, respectively. In the following the possible reasons for their enrichment will be discussed in detail.

Extensive information on the distribution of As in soil-forming rocks and soils of West Siberia has been presented by Mal'gin and Puzanov (1996). Soil-forming rocks of southern West Siberia of loamy and clayey composition are characterized by an average As concentration of 13.2 ± 0.7 μg/g (n = 155). High contents of As are explained, firstly, by geochemical and genetic features of the upper cover of the Quaternary deposits of the flat territories of Southern West Siberia. These deposits have been formed from weathering products of the phosphorite-bearing rocks of the Altai-Sayany mountain area and are, therefore, characterized by enrichment of P and As, which shows a strong affinity to P (Il'in and Syso, 2001). Secondly, numerous polymetallic deposits within the Altai-Sayany mountain area serve as a source of As. Thirdly, anthropogenic As sources are the processing of As-ores, burning of coal and oil and the processing of S and P minerals. The coal ash contains 60–90 μg/g As and in the tailings deposits of the open-cut mines of polymetallic ores As concentrations of up to 1000 μg/g have been determined (Mal'gin and Puzanov, 1996). Additionally, heat and power plants in southern West Siberia introduce significant quantities of As into the environment.

Summarizing, it can be stated that the mountain areas of Southern West Siberia constitutes an extensive

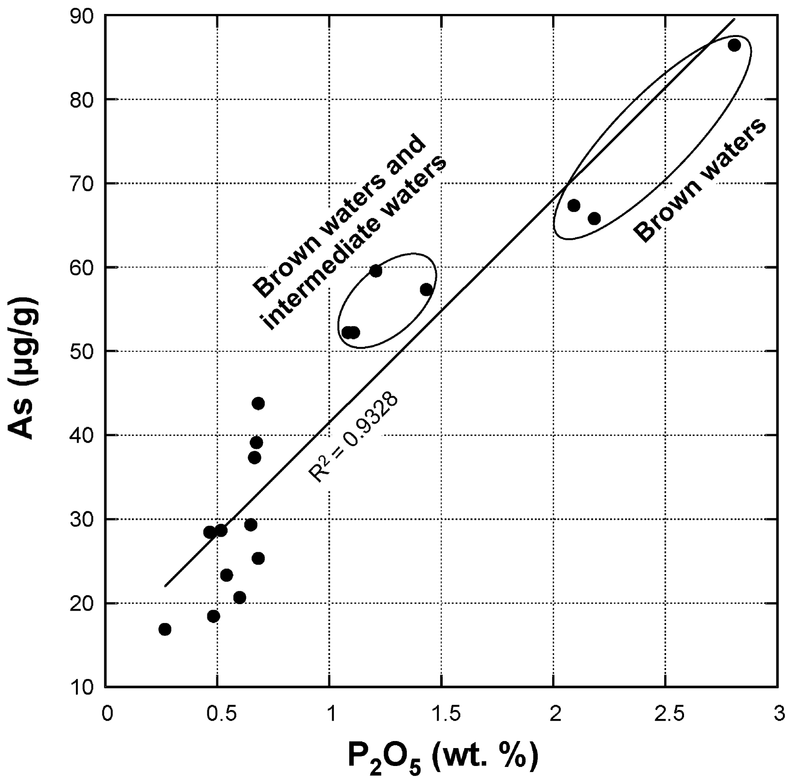

Fig. 6. Correlation between P_2O_5 and As in SPM of the Irtysh River and its tributaries. Sample St.10 (111 μg/g As) is considered as contaminated and not included here.

biogeochemical province with high As content (Il'in and Syso, 2001). The marsh soils of the taiga zone are characterized by high background concentrations of As—on average 23.9 μg/g (Polyakov, 1996), and meadow-marsh peaty soils of the Altai plains contain 26.2–159.6 μg/g of As (Mal'gin and Puzanov, 1996).

Fig. 6 shows the direct correlation between As and P_2O_5 in SPM of the Irtysh river and its tributaries and underpins the conclusion of Mal'gin and Puzanov's study about the As–P affinity in the weathering products of the Irtysh drainage area. The authors suggest that the main portion of P and As in the acid swamp waters originates from natural sources (phosphate deposits) and not from anthropogenic input. The highest As concentrations are observed in the SPM of the brown waters (57–87 μg/g As, on average 76 μg/g) (Table 1). Additionally, a high positive correlation exists between Fe_2O_3 and As (Fig. 7). The direct correlation between Fe_2O_3 and POC (Fig. 4) and Fe_2O_3 and P_2O_5 (not shown here) documents a very close interrelationship between Fe, P, POC and As in the SPM of brown waters. Generally, in an acidic environment the main P-bearing compounds, i.e. apatites, are remarkably soluble (Wedepohl, 1978). Iron-organic dissolved and colloidal compounds flocculate during the process of transport from swamp waters to brown and yellow-gray river waters and adsorb dissolved P and As. Thus, the high positive correlation between As and Fe-POC-P indicates that natural sources of As in the SPM of brown waters and later in the Irtysh waters are dominating.

In contrast to As, Cd is not correlated with P_2O_5. The marsh soils of the taiga zone are characterized by a low Cd background (0.02–0.63, on average 0.17 μg/g) (Polyakov, 1996). Some conclusions about the sources of Cd in the Irtysh SPM can be drawn from the variations of the Cd concentrations along the river from Omsk City to the confluence with the Ob river (Fig. 8). St. 1 is located in the area of Omsk City near the western shore of the river in a small channel behind an island. It has to be noted that Omsk City itself is situated mainly on the eastern shore of the Irtysh river. At St. 1 a Cd concentration of 1.14–1.43 μg/g was determined in the SPM (Table 1). However, at the next station (St. 2, 34 km below Omsk City) the Cd content increases up to 3.58 μg/g. Further northward the Cd concentration smoothly decreases down to 0.7–0.9 μg/g at a distance of about 700 km from Omsk City and remains at this level down to the confluence with the Ob river (only at St. 16, near Gorno-Pravdinsk city, another high Cd value is observed—1.7 μg/g). It is likely that already in the Irtysh headwaters the SPM is enriched in

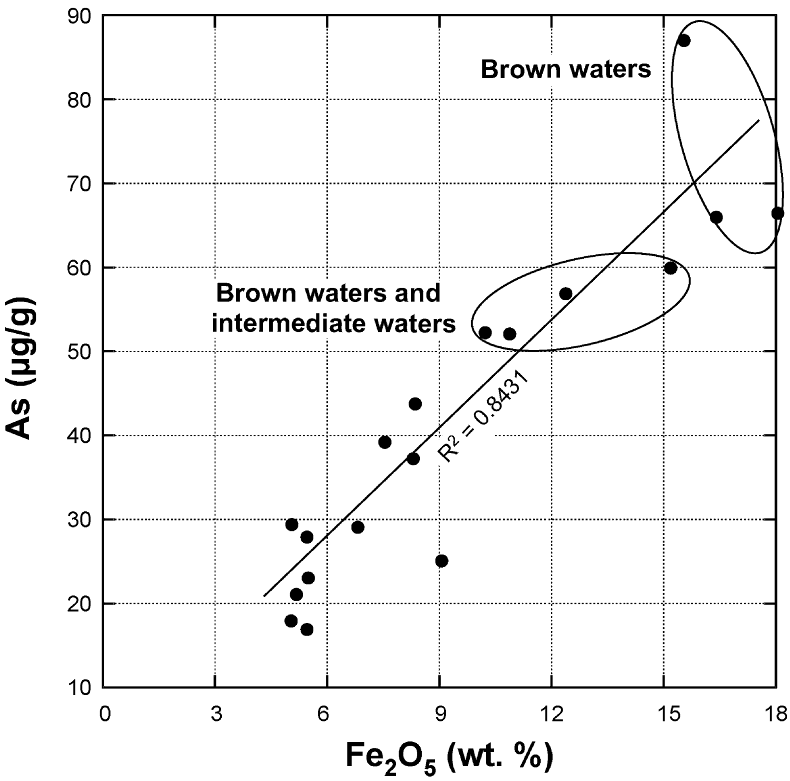

Fig. 7. Correlation between Fe_2O_3 and As in SPM of the Irtysh River and its tributaries. See note on Fig. 6.

Cd due to the exploitation of polymetallic deposits and the development of metallurgical industries. The Cd concentration at St. 1 is already higher than the average concentrations in other arctic rivers and in average World rivers (Table 5). However, the main Cd input is obviously attributed to the influence of Omsk City and clearly documented in the peak concentration north of the city. Omsk City is a large-scale industrial and transport center with a population of 1.2×10^6 and it is not possible to identify any specific Cd sources. The Omsk oil-refining enterprise and two large heat and power plants are potential sources of air-pollution. The most important sources of sewage (204.8×10^6 m^3 in 1999) are housing and communal services (91%), chemical and oil-refining industry (2.8%), electro-energetic (2.1%) and engineering industry (1.6%). Considering the multitude of potential pollutants it is surprising that other HM (Cu, Zn, Pb, Ni, Co, V, Cr) do not reveal any significant enrichment.

5. Conclusions

The analyses of major and trace elements in the SPM of the Irtysh river, the largest western tributary of the Ob river, show that the specific character of its chemical composition is determined by the peculiarities of the river watershed. In the upper basin numerous polymetallic deposits and a large biogeochemical province with high As content play an important role. The middle and lower reaches are characterized by the widespread distribution of swamps, peaty soils and peat deposits. Mining, metallurgical and oil-refining industries and other types of industries are frequent in the basin; large cities such as Semipalatinsk, Pavlodar, Omsk and others are situated on the shores of the Irtysh river and contribute to the environmental pollution of the region.

SPM collected downstream of Omsk City up to a distance of 500–700 km along the river consists mainly of silicate material typical of the SPM of the World rivers. However, after the inflow of several tributaries with brown water of swamp genesis the composition of the SPM significantly changes. The SPM of these tributaries (Tuy, Ishym, Tobol, Demjanka, Konda) is characterized by a strong depletion in lithogenic elements (K_2O, MgO, Na_2O, TiO_2) and an excess of POC, Fe_2O_3, P_2O_5. The comparison between brown water SPM and peat of West Siberia shows that peat-bogs may serve as a source of Ca, Sr and Ba, and probably of POC and P_2O_5 in the river SPM. Peat is strongly depleted in Fe and it is assumed that the total dissolved Fe (up to 17 mg/l in

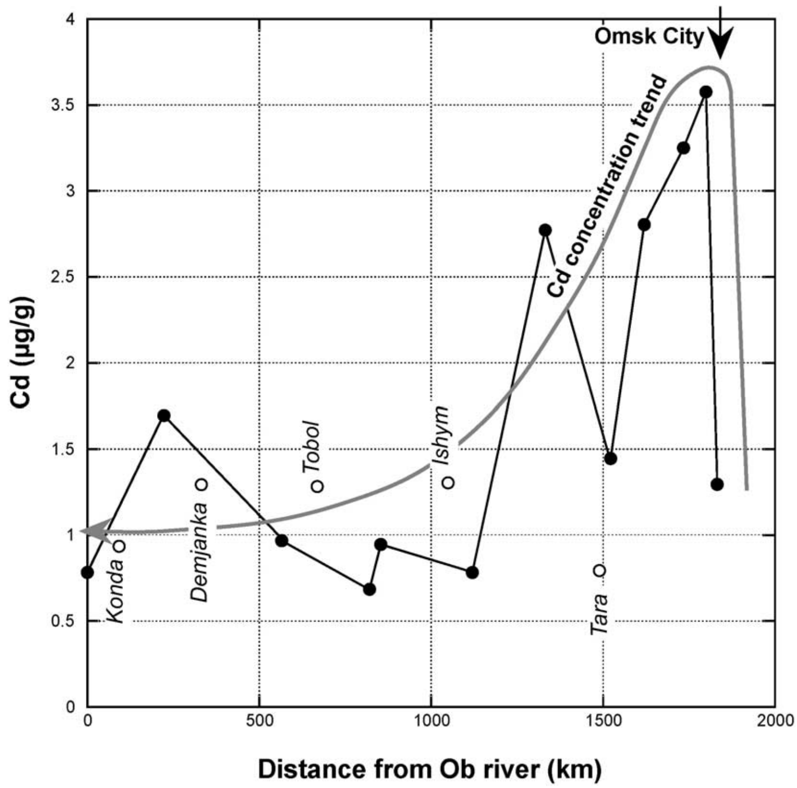

Fig. 8. Cd variations in SPM along the Irtysh River.

stagnant water) is flocculated in the mixing zone between stagnant waters (pH = 3–4) and river waters (pH = 6.5–7.1), which results in the enrichment of amorphous Fe-organic compounds in the river SPM. The assessments show that this amorphous form of Fe contributes about 75-85% to the total particulate Fe in brown-water rivers.

Among the investigated trace elements (Cu, Zn, Ni, Co, Cr, Pb, Cd, As, Sr, V, Ba, Zr) only As and Cd are noticeably enriched in the SPM of the Irtysh river. High As background concentrations of the soil-forming rocks and soils in the upper basin of the Irtysh river have been reported in the literature. The As biogeochemical province is located in the southeastern part of the West Siberian plain. In accordance with published information, a strong correlation between As and P was observed, which indicates that both elements are the products of weathering of phosphorite-bearing rocks of the As biogeochemical province. Anthropogenic factors for the high As concentrations cannot be excluded but play a minor role.

Cadmium concentrations are highest in SPM collected directly downstream of Omsk City (3.6 µg/g), slowly decrease to a value of 0.7–0.9 µg/g at a distance of about 700 km and remain at this level down to the confluence with the Ob river. Most probably the sewage of the large industrial center Omsk City are the reason for the Cd enrichment of the Irtysh SPM.

Acknowledgements

The authors wish to thank Prof. V.V. Zuev for inviting VVG and IEV to take part in the expedition on the Irtysh river. The assistance of the captain and the crew of R/V "Mirazh" is greatly acknowledged. Special thanks go to A. Eulenburg for supporting the analytical work at AWI. Constructive reviews of Dieter Garbe-Schönberg and one anonymous reviewer are appreciated.

References

Beeskow, B., Rachold, V., 2003. Geochemical processes in the Yenisey river and estuary. In: Stein, R., Fahl, K., Fuetterer, D.K., Galimov, E. (Eds.), Siberian River Run-off in the Kara Sea: Characterization, Quantification, Variability, and Environmental Significance. Proceedings in Marine Sciences, Elsevier (in press).

Cauwet, G., Sidorov, I.S., 1996. The biogeochemistry of Lena river: organic carbon and nutrients distribution. Mar. Chem. 53, 211–227.

Cossa, D., Coquery, M., Gobeil, C., Martin, J.-M., 1996. Mercury fluxes at the ocean margins. In: Baeyens, W. et al. (Eds.), Global and Regional Mercury Cycles: Sources, Fluxes and Mass Balances. Kluwer Academic, Dodrecht, pp. 229–247.

Dai, M., Martin, J.-M., 1995. First data on trace metal level and behavior in two major arctic river–estuarine systems (Ob and Yenisey) and in the adjacent Kara Sea. Earth Plan. Sci. Lett. 131, 127–141.

Glagoleva, M.A., 1959. Migration forms of the elements in river water. In: On the Diagenesis of Sediments. USSR Acad. Sci. Publ. House, Moscow, 5–28 (in Russian).

Gordeev, V.V., 2001. Heavy metals in the Russian arctic rivers: concentrations and fluxes. In: Pacyna, J.M. (Ed.), Proc. AMAP Workshop on Sources, Emission and Discharges. Norwegian Inst Air Research, Kjeller, Norway, pp. 79–100.

Gordeev, V.V., Sidorov, I.S., 1993. Concentrations of major elements and their outflow into the Laptev Sea (Russia). Mar. Chem. 43, 33–46.

Gordeev, V.V., Shevchenko, V.P., 1995. Chemical composition of suspended sediments in the Lena river and its mixing zone. In: Kassens, H. et al. (Eds.), Russian–German Cooperation: Laptev Sea System. Rep. Polar Res. 176, pp. 154–169.

Gordeev, V.V., Vlasova, I.E., 2002. Dissolved heavy metals in the Ob'-Irtish basin: is the technogenic pollution level high? In: Ecologo-biogeochemical investigations in the Ob river Basin. Publ. House "RASKO", Tomsk, pp.72–86 (in Russian).

Gordeev, V.V., Rachold, V., Vlasova, I.E., 2002. Major and trace elements in the Irtish river suspended matter. In: Ecologo-biogeochemical Investigations in the Ob river Basin. Publ. House "RASKO", Tomsk, pp.27–50 (in Russian).

Gordeev, V.V., Paucot, H., Wollast, R., Aibulatov, N.A., 2003. Distribution of chemical elements in grain-size spectrum of suspended and bottom sediments of the Ob and Yenisey estuaries (in preparation).

Guay, C.K., Falkner, K.K., 1998. A survey of dissolved barium in the estuaries of major arctic rivers and adjacent seas. Cont. Shelf Res. 18, 859–882.

Guieu, C., Huang, W., Martin, J.-M., Yong, Y.Y., 1996. Outflow of trace metals into the Laptev Sea by the Lena river. Mar. Chem. 53, 255–268.

Huh, Y., Tsoi, M.-Y., Zaitsev, A., Edmond, J.M., 1998. The fluvial geochemistry of the rivers of Eastern Siberia: 1. Tributaries of the Lena river draining the sedimentary platform of the Siberian Craton. Geochim. Cosmochim. Acta 62, 1657–1676.

Il'in, V.B., Syso, A.I., 2001. Pedogeochemical provinces in the Ob–Irtysh interfluve: causes and consequences. Siberian J. Ecol. 8, 111–119 (in Russian).

Inisheva, L.I., Tsibukova, T.N., 1999. Ecologo-geochemical assessment of the peat of the South-East of West Siberia plane. Geog. Natural Resour. 1, 45–51 (in Russian).

Inisheva, L.I., Stroitelev, A.D., Inishev, N.G., 2000. Geochemical peculiarities of waters of upper marshes. In: Ore Deposits, Mineralogy, Geochemistry. Tomsk, Tomsk State University 2, pp. 132–139 (in Russian).

Konovalov, G.S., 1959. Transport of trace elements in major USSR rivers. Rep. USSR Acad. Sci. 129, 912–915 (in Russian).

Konovalov, G.S., Ivanova, A.A., Kolesnikova, T.Kh., 1968. Dispersed rare elements dissolved in water and contained in suspension of the main USSR rivers. In: Strakhov, N.M. (Ed.), Geochemistry of Sedimentary Rocks and Ores. Nauka, Moscow, pp. 72–87 (in Russian).

Kontorovich, A.E., 1968. Migration forms of elements in the rivers of humic zone (West Siberia and other regions). In: Strakhov, N.M. (Ed.), Geochemistry of Sedimentary Rocks and Ores. Nauka, Moscow, pp. 88–102 (in Russian).

Kovalskaya, G.A., Pavlov, V.E., Karbyshev, S.F., 2002. Elemental composition of the Irtish river suspended material. In: Ecologo-biogeochemical Investigations in the Ob river Basin. Publ. House "RASKO", Tomsk, 51–59 (in Russian).

Kravtsov, V.A., Gordeev, V.V., Pashkina, V.I., 1994. Labile dissolved forms of heavy metals in the Kara Sea waters. Oceanology 34, 673–680 (in Russian).

Lara, R.J., Rachold, V., Kattner, G., Hubberten, H.W., Guggenberger, G., Skoog, A., Thomas, D.V., 1998. Dissolved organic matter and nutrients in the Lena river, Siberian Arctic: characteristics and distribution. Mar. Chem. 59, 301–309.

Leonova, G.A., Anoshin, G.N., Il'ina, V.N., Badnaev, J.O., Androsova, N.V., 2000. Biogeochemical indication of natural and technogenic concentrations of heavy metals in water ecosystem (on the Ob and Tom examples). In: Ecology of poimas and Siberian rivers and Arctic. Proc. II Conference. Tomsk, pp. 124–130 (in Russian).

Lisitzina, K.N., 1974. Suspended sediment discharge of Siberian rivers. Leningrad, State Hydrol. Inst. Proc. 210, 48–72 (in Russian).

Lukashin, V.N., Ljutsarev, S.V., Krasnjuk, A.D., Shevchenko, V.P., Rusakov, V.Yu., 1999. Suspended particulate matter in the Ob and Yenisey estuaries. In: Matthiesen, J., Stepanets, O.V., Stein, R., Fuetterer, D.K., Galimov, E.M. (Eds.), The Kara Sea Expedition of R/V Acad. Boris Petrov 1997. Rep. Polar Res. 300, pp. 155–178.

Mal'gin, M.A., Puzanov, A.V., 1996. As in soil of the West Siberia. Siberian J. Ecology 3, 199–212 (in Russian).

Martin, J.-M., Gordeev, V.V., 1986. river input to ocean systems: a reassessment. In: Estuarine Processes: An Application to the Tagus Estuary. Proc. UNESCO/IOC/CNA Workshop. Paris, UNESCO, pp.203–240.

Martin, J.-M., Guan, D.M., Elbaz-Poulichet, F., Thomas, A., Gordeev, V.V., 1993. Preliminary assessment of the distributions of some trace elements (As, Cd, Cu, Fe, Ni, Pb and Zn) in a pristine aquatic environment: the Lena river estuary (Russia). Mar. Chem. 43, 185–200.

Meade, R.H., Bobrovitskaya, N.N., Babkin, V.I., 2000. Suspended sediment and fresh-water discharges in the Ob and Yenisey rivers, 1960-1988. Internat. J. Earth Sci. 89, 461–469.

Melnikov, S.A. (Ed.), 1999. Atlas of Environmental Pollution of the Aquatoria and Coastal Seas of the Russian Arctic. Regional Centre "Monitoring of Arctic", Roskomhydromet, AMAP, St-Petersburg (in Russian).

Moran, B.S., Woods, W.L., 1997. Cd, Cr, Cu, Ni and Pb in the water column and sediments of the Irtysh–Ob rivers, Russia. Mar. Poll. Bull. 35, 270–279.

Nesterova, I.L., 1960. Migration forms of elements in the Ob river. Geochem. 4, 355–362 (in Russian).

Nolting, R.F., van Dalen, M., Helder, W., 1996. Distribution of trace and major elements in sediment and pore waters of the Lena Delta and Laptev Sea. Mar. Chem. 53, 285–300.

Panin, N.A., 1972. Resources of Surface Waters of the USSR,

v. 15. Altai and West Siberia. Pt. 2. Gidrometeoizdat, Middle Ob, Leningrad (in Russian).
Panin, M.S., 2002. Technogenic pollution by heavy metals of the Irtysh basin. Geochem. 7, 759–768 (in Russian).
Panin, M.S., Sibirkina, A.R., 2000. Technogenic pollution by copper of the Irtysh river watershed within the Kazakhstan territory. Geochem. 2, 187–196 (in Russian).
Polyakov, G.V., 1996. Ecogeochemistry of the West Siberia. Heavy metals and radio nuclides. Novosibirsk (in Russian).
Rachold, V., 1999. Major, trace and rare earth element geochemistry of suspended particulate material of East Siberian rivers draining to the Arctic Ocean. In: Kassens, H., Bauch, H.A., Dmitrenkro, I., Eicken, H., Hubberten, H.-W., Melles, M., Thiede, J., Timokhov, L.A. (Eds.), Land–ocean Systems in the Siberian Arctic—Dynamics and History. Springer-Verlag, Berlin, pp. 199–222.
Rachold, V., Hubberten, H.-W., 1999. Carbon isotope composition of particulate organic material in East Siberian rivers. In: Kassens, H., Bauch, H.A., Dmitrenkro, I., Eicken, H., Hubberten, H.-W., Melles, M., Thiede, J., Timokhov, L.A. (Eds.), Land–ocean Systems in the Siberian Arctic—Dynamics and History. Springer-Verlag, Berlin, pp. 223–238.
Rachold, V., Alabyan, A., Hubberten, H-W., Korotaev, V.N., Zaitsev, A.A., 1996. Sediment transport to the Laptev Sea—hydrology and geochemistry of the Lena river. Polar Res. 15/2, 183–196.
Sazonova, M.V., Shvartsev, S.L., 2002. Ecologo-geochemical conditions in the Irtish river. In: Ecologo-biogeochemical Investigations in the Ob river Basin. Publ. House "RASKO", Tomsk, pp. 60–71 (in Russian).
Shvartsev, S.L., Savichev, O.G., Vertman, G.G., et al., 1996. Ecologo-geochemical conditions of waters in the middle Ob river basin. Water Resources 22/6, 723–731 (in Russian).
Shvartsev, S.L., Savichev, O.G., Khvashevskaya, A.A., Kopylova, Yu.G., Zarubina, R.F., Trifonova, N.A., Nalivaiko, N.G., Maruleva, U.M., Efimova, A.N., 1999. Complex ecologo-geochemical investigations of the Ob river waters. In: Ecology of Poimas and Siberian rivers and Arctic. Novosibirsk, SB RAS Publ. House, pp. 110–115 (in Russian).
Sorokovikova, L.M., Netsvetaeva, O.G., Khodjer, T.V., Kobeleva, N.A., Chebukina, E.P., Golobokova, L.P., Chubarov, M.P., 1999. Chemical composition and water quality of the Ob river. In: Ecology of Poimas and Siberian rivers and Arctic. Novosibirsk: SB RAS Publ. House, pp. 116–122 (in Russian).
Wedepohl, K.H., 1971. Environmental influences on the chemical composition of shales and clays. In: Ahrens, L.H., Press, F., Runcorn, S.K., Urey, H.C. (Eds.), Physics and Chemistry of the Earth, Vol. 8. Pergamon, New York, pp. 305–333.
Wedepohl, K.H. (Ed.), 1978. Handbook of Geochemistry.v.II/1. Phosphorus (15). Springer Verlag, Berlin/Heidelberg/New York.
Wedepohl, K.H., 1991. The composition of the upper earth's crust and the natural cycles of selected metals. Metals in natural raw materials. In: Merian, E. (Ed.), Metals and their Compounds in the Environment. VCH-Verlagsgesellschaft, Weinheim, pp. 3–17.