Distribution of Metals in Water, Bottom Silt, and on Suspensions in the Arms of the Selenga Delta

Z. I. KHAZHEEVA, A. K. TULOKHONOV and S. D. URBAZAEVA

Baikal Institute of Nature Management, Siberian Branch of the Russian Academy of Sciences, Ul. Sakhyanovoy 6, Ulan Ude 670047 (Russia)

E-mail: zkhazh@binm.bscnet.ru

(Received July 7, 2005; revised February 28, 2006)

Abstract

Distribution of heavy metals in water, bottom silt, and on suspensions in the mouth area of the river and in the arms of the Selenga delta has been investigated. It has been found that significant part of Pb and Cu is sorbed on suspension. Cu, Fe, and Mn content in the water of the arms before the confluence into Lake Baikal increases in the spring and exceeds the admissible concentration limit for fish-economic water bodies. The analysis of seasonal dynamics of the content of elements in water demonstrates that maximal content of Pb, Zn, Cu, Fe, and Mn in water is observed in the spring and in winter; in the rest of the time of year, it flattens at a level of minimal autumn values.

INTRODUCTION

The average long-term magnitude of the run-off of suspended load of the Selenga is as large as about 2080 thousand tons [1, 2]. This characteristic is given for a hydrologic section of the Mostovoy siding located 127 km from the mouth of the Selenga, which is the vast delta involving arms, lakes, bogs, and sores with water and water-air vegetation that facilitates the deposition of the load. Long-term researches of the dynamics of deposits in the Selenga, in its delta, and on the mouth beach have demonstrated that from 44 to 74 % of the load precipitates in the delta.

The run-off distribution of the Selenga over the delta arms is extremely irregular, and it varies according to the water level. The bulk of the run-off (50–60 % in the summer and up to 90 % in winter) occurs through the Kharauz and the Levoberezhnaya main arms that are arranged near the left edge of the delta, and no more than 3–5 % of the total run-off of the river passes through its central part (the Kolpinnaya and the Srednyaya arms) even under conditions of an elevated water content.

From the middle of winter and to the spring, the Kolpinnaya and the Srednyaya arms freeze up, and there is practically no run-off here. In the right part of the delta, the Lobanovskaya is the arm that contains the greatest amount of water (30–40 % of the run-off of the river during summer period and about 10 % in winter) [3].

To determine the current level of pollution of the ecosystem of the Selenga delta and to reveal the changes that have been caused by the disposal of municipal and industrial sewage in the water of the river and by the activity of agricultural and cattle-breeding farms, complex investigations of water, bottom silt (BS), and suspensions have been made in the mouth zone of arms and in the Selenga (the settlement of Kabansk). During 2001–2005, the institutes of the Siberian Branch of the Russian Academy of Sciences (SB RAS) performed regular investigations of the Selenga delta within the framework of Integration projects of the SB RAS (Nos. 90, 99).

This work summarizes the results of the determination of content of metals in water, BS, and on suspensions of the mouth zone of the river and the arms of its delta.

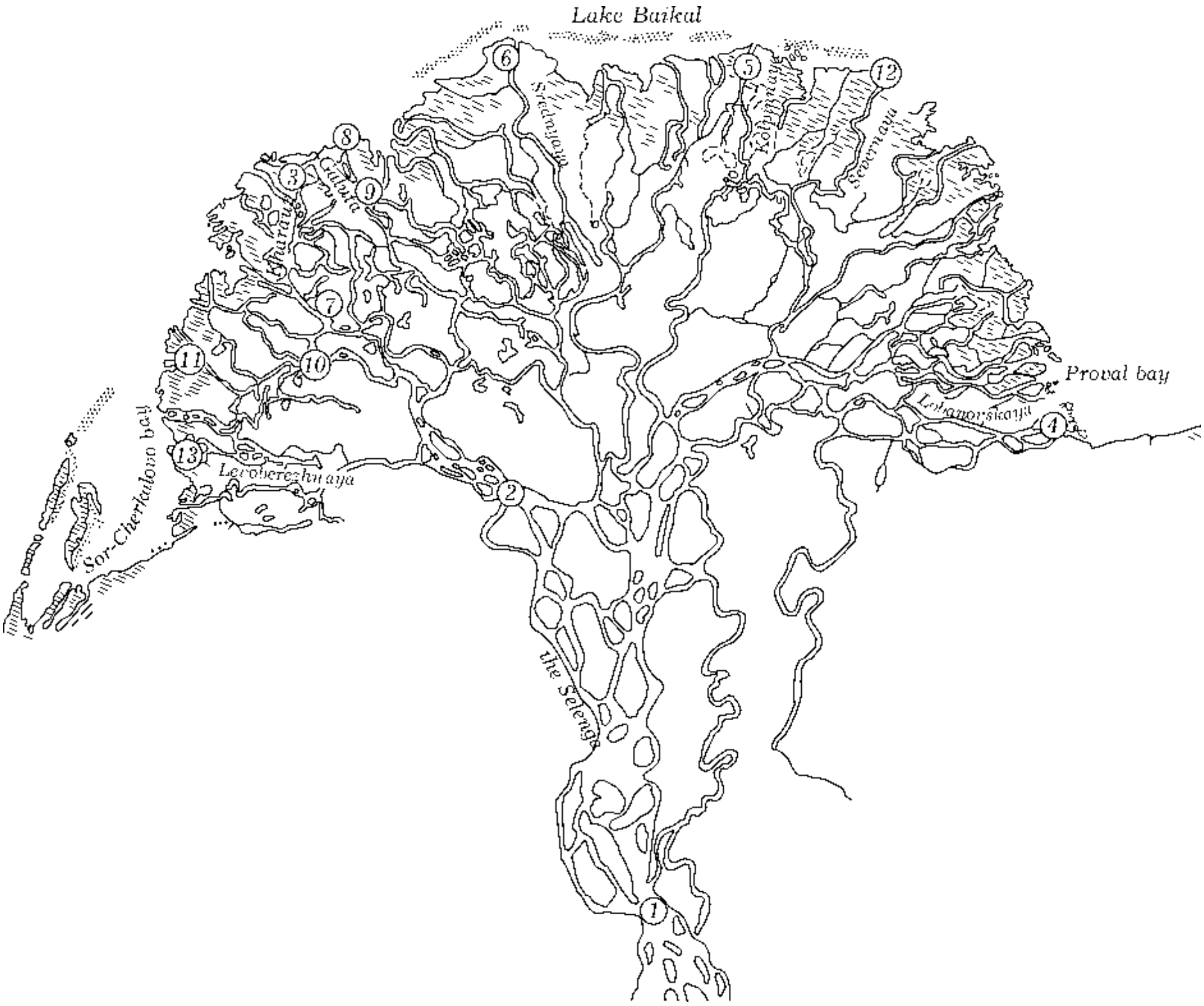

Fig. 1 Schematic map of the Selenga River delta: *1* − Selenga River (the settlement of Kabansk), *2* − the Selenga (Murzino), *3* − the Kharauz arm (mouth), *4* − the Lobanovskaya arm (mouth), *5* − the Kolpinnaya arm (mouth), *6* − the Srednyaya arm (mouth), *7* − the Zavernyaikha Lake, *8* − the Galuta arm (mouth), *9* − the Galuta arm, *10* − the Selenga (Semenovskiy Is.), *11* − the Shamanka arm (mouth), *12* − the Northern arm (mouth), *13* − the Levoberezhnaya arm (mouth).

EXPERIMENTAL

Samples of water, BS, and suspensions have been selected from the arms during expeditions in mouth sites of the river and the delta arms. The schematic diagram of the disposition of hydrochemical sections of the sampling is presented in Fig. 1. Water samples were filtered through a 0.45-μm filter before their preservation. BS samples and suspensions were taken in the same places. BS samples were taken using of the Peterson dredge that captured a high layer of BS, 6−8 cm in thickness, then they were placed in double polyethylene packages to prevent the loss of volatile elements and hyperfine fractions. Suspension samples have been received by way of settling great volumes of water (50−80 l) during 3−4 days.

Concentrations of trace elements in the studied components of the ecosystem were determined by the method of atomic absorption spectrometry with flame atomisation at SOLAAR spectrophotometer. The acetylene−air mixture was used for the flame atomisation. The accuracy of the procedure estimated from 10 measurements of a standard sample with the known concentrations of metals comprises 5−15 % for various metals. The reproducibility of analysis results estimated from 10 measurements of a standard sample amounts to 2−3 %. Total concentrations of Pb, Cu, Zn, Cd, Fe, and Mn were determined.

TABLE 1

Content of heavy metals in water of mouths of the Selenga and of arms of the delta, μg/l

Section of observation	Year season	Fe	Mn	Zn	Cu	Pb	Cd
the Selenga, settlement of Kabansk	Winter	100	70	8	9	8.0	0.4
	Spring	1600	120	9	9	2.0	–
	Summer	960	20	8	20	0.2	–
	Autumn	110	8	1	4	0.1	–
Kharauz arm, mouth	Winter	100	50	3	6	6.0	0.5
	Spring	1200	80	4	8	2.0	–
	Summer	400	10	1	16	0.5	–
	Autumn	120	8	2	16	0.1	–
Lobanovskaya arm, mouth	Winter	120	60	7	20	6.0	0.4
	Spring	900	70	6	7	2.0	–
	Summer	600	15	8	18	0.5	–
	Autumn	170	15	1	2	0.1	–
Kolpinnaya arm, mouth	Winter	600	120	4	6	0.5	2.0
	Spring	600	60	15	15	1.0	–
	Summer	600	30	15	20	0.2	–
	Autumn	200	10	4	8	0.1	–
Srednyaya arm, mouth	Winter	450	100	3	5	0.5	1.0
	Spring	600	60	10	20	1.0	–
	Summer	600	40	15	20	0.3	–
	Autumn	250	20	2	10	0.2	–
Levoberezhnaya arm, mouth	Winter	100	50	7	7	4.0	0.8
	Spring	900	70	7	6	3.0	–
	Summer	800	20	8	18	0.3	–
	Autumn	110	10	1	14	0.1	–

RESULTS AND DISCUSSION

The results of the research testify that variations in the content of heavy metals (HM) on suspensions, in water and BS in the mouth area of the river and in the arms of the Selenga delta are highly diversified. Specifically, when moving downwards to the outlet along the arms, spatial variation in the content of chemical elements should be expected in the delta because of the decrease in the water flow rate as well as owing to a high density of water vegetation that forms underwater meadows in numerous arms.

Superficial water

Waters of the Selenga and its delta arms fall into hydrocarbonate-calcium type as to the composition of the main ions. On evidence of the Limnological Institute (LIN, SB RAS, Irkutsk) [4], permanganate oxidizability of the delta water-currents is 3.5–6.6 mg O/l, bichromate one is 4.2–34.3 mg O/l. Hydrochemical indexes vary according to a hydrological year season and according to flowage extent of the water-currents. As a consequence of this, the range of annual oscillations of the mineralization comprises 115–824 mg/l for the arms Kolpinnaya, Srednyaya, whereas in the Kharauz, the Levoberezhnaya, the Lobanovskaya (active nonfreezing arms), the oscillations of the mineralization are close to those in the Selenga (112–182 mg/l). During the open channel period the mineralization and concentration of the main ions in active arms is virtually identical [4].

On freeze-up the content of the dissolved iron in water varies in an interval of 100–

250 μg/l in water-currents with a high dynamic water exchange both in the mouth area of the Selenga (the settlement of Kabansk) and in mouths of the main arms (the Kharauz, the Lobanovskaya) (Table 1). But in water of mouths of Kolpinnaya and Srednyaya arms, which freeze in winter and have a low water exchange, the iron content is more, and it varies within the limits of 450–600 μg/l. These values 2–12 times exceed the admissible concentration limit for fish hatchery basins [5].

The content of the dissolved manganese in water of mouths of the Kharauz and Lobanovskaya main arms varies within the limits of 50–70 μg/l, and it comprises 100–120 μg/l in mouths of arms with a little water exchange (the Kolpinnaya, the Srednyaya). Manganese concentrations 2 times exceed the admissible concentration limit for fish hatchery basins [5].

Concentrations of Zn and Cu dissolved in water of arms and the Selenga mouths (s. Kabansk) during freeze-up are practically close and they vary in the intervals of 3–8 and 5–20 μg/l, respectively. According to admissible concentration limits for fish hatchery basins, Zn concentration is within the normal range, while Cu content exceeds the limit by a factor of 5–20.

Concentrations of dissolved Pb in the mouth of Kharauz and Lobanovskaya arms and in the mouth of the Selenga (s. Kabansk) vary within the limits of 6–8 μg/l and do not exceed the limit for fish hatchery basins. The content of the dissolved lead in water of mouths of arms with a low water exchange (the Kolpinnaya, the Srednyaya) does not exceed 0.5 μg/l.

Concentration of dissolved Cd in mouths of the arms with a high water exchange (the Kharauz, the Lobanovskaya) and in the Selenga does not exceed 0.6 μg/l, and in mouths of arms of the central delta (the Kolpinnaya, the Srednyaya), it rises up to 2.0 μg/l.

During spring high water, the content of Fe and Zn dissolved in water increases, whereas that of Pb drops to 1–3 μg/l. Practically no dissolved Cd is also registered (see Table 1). The content of dissolved Fe rises up to 800–1600 μg/l, and that of Zn ranges up to 15 μg/l in mouth area of the Selenga (the settlement of Kabansk) and of Kharauz, Lobanovskaya main arms. In mouths of arms of the central delta (the Kolpinnaya and the Srednyaya) it is as great as 500–600 μg/l. Maximal concentrations of Zn and Cu (15 and 20 μg/l, respectively) are noticed in mouths of arms with a low water exchange (the Kolpinnaya, the Srednyaya).

During summer-autumn period the content of the studied dissolved elements in water of the river and the delta arms decreases, except for the dissolved Cu, the content of which rises up to 20 μg/l in all arms in summer and drops to 4–16 μg/l in autumn.

Suspended substances

Suspended material (SM) represents an isolated phase that is made up of particles of an alive or inanimate nature and that shows various chemical composition and the dimensions which vary from 0.1 to 100 μm [6]. The predominance of a fine-grained material renders the suspension into a powerful adsorbent of many chemical elements and pollutants. The active surface of the suspension and thus its sorption capacity are increased considerably with decreasing size of the suspension particles. The main body of suspension of fresh river waters is made up of phytoplankton and detritus. Among anthropogenic components which have a substantial influence on the qualitative composition of the suspension mention should be made of petroleum hydrocarbons [7]. Fine-grained particles of iron hydroxides and manganese dioxides possess a high adsorptive activity and they may be related to the major carriers of HM in natural waters. Thus SM generally serves as a natural indicator for HM content in the ecosystem of the delta, since it sorbs maximum quantity of HM and at the same time provides a mobile part of the solid run-off.

The maximal turbidity of water (up to 150 g/m^3) during the spring high water and summer high waters is characteristic for Kolpinnaya and Srednyaya arms. In steady channels of Kharauz and Lobanovskaya arms water turbidity coincides with the turbidity appropriate to transport capability of the stream and varies in the range from 50 to 90 g/m^3. The average monthly load of the Selenga waters with suspended particles at arm sources of the delta is 70–90 g/m^3 during this period.

TABLE 2

Content of heavy metals in suspended matter in the mouth of the Selenga and in the arms of the delta, mg/kg

Section of observation	Year season	Fe	Mn	Zn	Cu	Pb	Cd
the Selenga, settlement of Kabansk	Spring	29 000	900	130	300	750	4
	Summer	28 000	900	140	350	600	4
Kharauz arm, mouth	Spring	28 000	900	120	320	780	4
	Summer	29 000	1000	140	350	800	4
Lobanovskaya arm, mouth	Spring	28 000	950	140	300	800	4
	Summer	27 000	1000	130	320	750	4
Kolpinnaya arm, mouth	Spring	33 000	1000	120	200	400	4
	Summer	32 000	1000	140	250	450	4
Srednyaya arm, mouth	Spring	33 000	1000	130	200	450	4
	Summer	32 000	1000	130	250	450	4
Levoberezhnaya arm, mouth	Spring	28 000	900	120	300	750	4
	Summer	28 000	950	130	320	750	4

Table 2 presents data of the analysis of HM distribution over the SM in arm mouths and the Selenga. Spatial distribution of Pb is appreciably of anthropogenic nature. Its content in the suspension of the main arms and of the Selenga is 18–20 times higher as compared to that in clay of sedimentary rocks [8]. Concentration of Pb on suspensions in arm mouths of the central sector (the Kolpinnaya, the Srednyaya) decreases by a factor of two. Cu is concentrated on SM in a similar way: its content on suspensions of Kharauz and Lobanovskaya main arms and of the Selenga mouth is 15–18 times more than in clays of sedimentary rocks, whereas in the arms of the central sector (the Kolpinnaya, the Srednyaya) the content decreases and just 3–4 times exceeds that in clay of sedimentary rocks. An increase of copper concentration in SM is also related to entering of hydrobionts, which have finished their annual life cycle.

Content of Zn and Cd in the suspension is independed of the flowage degree of the currents, and in the case of zinc, it is close to that in clay of sedimentary rocks, whereas in the case of Cd, it is 10 times more.

Content of Fe and Mn in SM in the arms with active water exchange (the Kharauz, the Lobanovskaya, and mouth of the Selenga) 1.2 times exceeds abundance ratio for clays of sedimentary rocks [8], and in the arms of the central part of the delta (the Kolpinnaya, the Srednyaya), the content increases by the factor of 1.5 due to passing arms on the marshy sites.

An increase in chemical run-off occurs, as a rule, during the spring high water at the period of intensive snow thawing and entry of chemicals, including metals, from the drainage area into the channel network. So in 2002, during the spring high water, the content of dissolved Pb in mouths of the Selenga (the settlement of Kabansk) and of Kharauz and Lobanovskaya main arms attained 120 μg/l, although the like values were not noticed in next years. Along with HM, organic matter is sorbed on SM, the content of the matter being not over 3–8 % in the mouths of the arms and the river.

Bottom silt

Suspended and bed loads of the river during the spring and summer high water, as well as products of washout and redeposition of ancient alluvial depositions within the limits of modern delta serve as the source of BS. They may be classed with aleurite oozes by the content of predominant fraction in BS of the arms and the mouth zone of the river. During the flood phase of the river regime, as much as 70 % of fractions less than 0.05 mm are delivered to the mouth of the river (the settlement of Kabansk), and these fractions are

TABLE 3

Content of heavy metals in bottom silt of the mouth of the Selenga and of the delta arms

Section of observation	Number of samples	Content*, mg/kg					
		Fe/100	Mn/10	Zn	Cu	Pb	Cd
the Selenga, settlement of Kabansk	72	270/40	45/10	85/20	15/5	20/9	2.0/0.3
Kharauz arm, mouth	76	290/40	55/12	110/20	40/20	45/10	20/0.3
Lobanovskaya arm, mouth	76	290/40	55/10	70/25	40/15	35/10	0.8/0.1
Kolpinnaya arm, mouth	72	310/100	65/30	100/30	90/10	40/10	0.7/0.3
Srednyaya arm, mouth	76	300/110	60/25	90/30	80/10	30/10	0.8/0.3
Levoberezhnaya arm, mouth	76	270/30	50/10	70/20	30/10	30/10	0.6/0.1

*The first value is the maximal content, the second value is the minimal one.

settled on the swells along the riber bed and in the arms of the delta. Bottom silt in the mouths of Kharauz, Kolpinnaya, and Srednyaya arms is composed of fine clay sands and aleurites that alternate with loamy and oozy layers. BS of the Lobanovskaya arm shows a somewhat different lithologic structure, the BS being composed of sandy deposits that are covered in some places with finely elutriated flood deposits.

Table 3 lists the data on the content of HM in BS of the mouth of the Selenga and mouths of the arms of the delta in 2004. The decrease of the water flow speed in channels of the arms of the delta leads to active sedimentation of SM and thus to an increase in the HM content in the mouths of the arms as compared to the mouth of the Selenga. From the data of Table 3 it will be obvious that the great flow speed over the main arms (the Kharauz and the Lobanovskaya) weakens the process of accumulation of metals by an average of almost 1.5–2 times as compared to the Kolpinnaya and Srednyaya arms. These differences in the HM accumulation degree are related to a decrease in sedimentation rate of fine fractions of SM. The concentration of Mn in BS of Kolpinnaya and Srednyaya arms is 1.5 times more, and that of Fe is 1.2 times more than in the arms with active water exchange (the Kharauz and the Lobanovskaya), and these concentrations do not exceed the values that have been presented in the work [9]. Maximal contents of Pb and Zn (40–45 and 100–110 mg/kg, respectively) are observed in the mouths of Kharauz and Kolpinnaya arms and they practically do not exceed the data that have been presented in the work [9]. Maximal concentrations of Cu (80–90 mg/kg) have been noticed in the Kolpinnaya and Srednyaya arms. Content of Cd in BS of mouths of arms and the river is the same and it is as great as 0.2–2.0 mg/kg.

Physicochemical distribution of HM at the BS/water interface can be expressed quantitatively by concentration coefficients, to take an example, by molar concentration coefficient that has been calculated from experimental data: K_c = HM(BS)/HM(W), where HM(BS), HM(W) are the concentrations of HM in BS and water, respectively (in mmol/kg and μmol/l, respectively). For the samples that were selected in 2004, K_c varies with the nature of metal: 2500–260 000 for Fe, 1000–65 000 for Mn, Pb – 1200–450 000, Cu – 500–45 000, Zn – 1300–55 000, and Cd – 200–6000. The received values can be represented by the following succession: $Pb \approx Fe > Zn \approx Cu \approx Mn > Cd$, where cadmium stands out, since water-soluble species make significant contribution to its total concentration in water.

The work [10] presents experimental data on the content of metals in solution and SM, as well as results of extracting the metals into BS due to the sedimentation from suspension. Significant part of Pb was sorbed on SM, which led to a sharp decrease of its content in water. Sorption of Cu on SM is less effective; therefore a less noticeable decrease of the copper content in water and a smoother increase on the suspension were evident. Concentrations of dissolved Zn and Cd dropped less effectively as well, which is also determined by a smaller degree of the metal sorption on suspension. Correlation between effective sorption and the fraction of neutral complexes of metals in the solution caused Zn and Cd which showed the lowest fraction of uncharged complexes in water to be the least effective for entering into BS.

Considerable part in processes of HM extraction into BS plays planktonic community, whose effect becomes more intensive during the period when the channels of the water-currents are open. Planktonic organisms are capable to sorb HM from a solution and to remove them into BS, which leads to appreciable decrease in the content of the studied dissolved elements in delta water-currents when the channels of the arms are open, especially in summer-autumn.

Acquired experimental results on the distribution of HM in water, on SM and BS are in a good agreement with data of the work [10] that is devoted to mesosimulation of the pollution of a water body.

CONCLUSIONS

Seasonal variability of the concentration of HM in water of the Selenga and its delta has been observed. Concentrations of copper, iron, and manganese in water exceeds the admissible concentration limits for fish-economic water bodies. It has been demonstrated that the concentration of these elements increases in spring. During the period of open water of the channels of the water-currents, especially at the end of summer, the concentration of the mentioned elements flattens, and in autumn it drops to a minimum level.

Efficiency of sorption of metals on a suspension and their removal from the bulk of water into BS decreases in the order: Pb > Cu > Zn > Cd. Considerable part in processes of HM removing into BS plays planktonic community, the action of which becomes more intensive when the channels of the water-currents are open. Notwithstanding the fact that significant seasonal increase of HM concentration is noted in surface waters of the delta, the accumulation extent of these elements in BS of the delta does not exceed data of the work [9].

REFERENCES

1 T. G. Potemkina, V. A. Fialkov, *Vod. Res.*, 6 (1993) 663.
2 T. G. Potemkina, *Geogr. i Prirod. Res.*, 1 (1995) 75.
3 V. N. Sinyukovich, N. G. Zharikova, V. D. Zharikov, *Ibid.*, 3 (2004) 64.
4 L. M. Sorokovikova, A. K. Tulokhonov, V. N. Sinyukovich, *Ibid.*, 1 (2005) 73.
5 Kontrol' khimicheskikh i biologicheskikh parametrov okruzhayushchey sredy, Ekometriya, St. Petersburg, 1998.
6 I. G. Orlova, *Tr. GOIN*, 203 (1992) 46.
7 A. I. Simonov, N. A. Afanasyeva, I. M. Nazarov, *Meteorol. i Gidrol.*, 3 (1984) 64.
8 A. Kabata-Pendias, H. Kabata-Pendias, Mikroelementy v pochvakh i rasteniyakh [Russian translation], Mir, Moscow, 1989.
9 V. A. Vetrov, A. I. Kuznetsova, Mikroelementy v prirodnykh sredakh regiona ozera Baikal, Izd-vo SO RAN, Novosibirsk, 1997.
10 B. S. Smolyakov, S. B. Bortnikova, M. V. Zhigula *et al.*, *Vod. Res.*, 31, 3 (2004) 365.