ISSN 1875-3728, Geography and Natural Resources, 2011, Vol. 32, No. 4, pp. 333-336. © Pleiades Publishing, Ltd., 2011.
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ENVIRONMENTAL PROTECTION

The Ecologo-Geochemical State of Water Bodies in the Taz-Yenisei Interfluve

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Received March 16, 2011

Abstract—Presented are the results from investigating the chemical composition and quality of surface waters and bottom sediments in the Taz-Yenisei interfluve. The mean values of hydrochemical and geochemical indicators were determined, which can be used as background values in assessing the actual and allowable anthropogenic impact on water bodies. The elevated contents of a number of metals and organic and biogenic substances in the water are largely associated with the climatic conditions favorable for accumulation in aqueous medium of plant remains and products of their decomposition.

DOI: 10.1134/S1875372811040056

Keywords: chemical composition, surface waters, bottom sediments, Siberia.

Determination of the current ecologo-geochemical state of natural waters forms a groundwork for assessing the anthropogenic impacts on water bodies, and for planning environmental measures. This issue is a challenging problem facing all regions on the globe; however, it has particularly important current implications for the tundra and forest-tundra regions of Northern Eurasia where considerable reserves of hydrocarbon raw materials are concentrated, and anthropogenic impacts can give rise to severe, virtually irreversible disturbances in the functioning of terrestrial and water ecosystems. In this paper, this problem is examined by using, as an example, the rivers and lakes in the northeastern part of the West Siberian Plain within the Taz-Yenisei interfluve.

OBJECTS AND METHODS

The territory under consideration is situated in the forest-tundra province in the bog-taiga region of the West Siberian Plain and corresponds to the Purskii hydrological area exemplified by snowmelt spring floods peaking at the end of May, floods in summers and autumns, a long-lasting lowest-water period, and by a long persistent freezing-over period. River discharge alimentation is largely by snowmelt. Typically floods start in mid-May and end in the first half of August [1–3]. Based on these attributes, the analytical data obtained offer a means of assessing the hydrochemical conditions of the lowest-water period, without which, according to [4], an appraisal of the hydrochemical background is unfeasible.

During the progress of our investigations, we studied the catchments of the Russkaya river (the left tributary of the Taz river) and of the Bol. Kheta river (the left tributary of the Yenisei river). The catchments include: in the former case, the Russkaya, Tagul and Khurichangda rivers, the smaller streams and lakes, and in the latter case, the Bol. Kheta, Solenaya, Khochu and Varomyyakha rivers, and the smaller streams. The bulk of office work was done during the summer-autumn period of 2009 in the regional state institution "Tomsk regional Committee on Environmental protection and Natural Resources" (OGU Oblkompriroda). Chemical composition data for the smaller streams on the territory of the catchment of the Bol. Kheta river (7 samples) and for the lakes within the catchment of the Russkaya river (17 samples) as obtained during the summer-autumn and winter periods of the 2000s, were provided by the Krasnoyarsk Research institute of Geology and Minerals (KNIIGiMS).

Water samples were collected in accordance with Rosgidromet's requirements from the 0.3–0.5 m surface layer. In 2009, bottom sediment samples were concurrently collected (in the 0.2 m layer), followed by the separation of fraction of up to 1 mm in particle diameter. The analysis of chemical composition of the fluvial and lacustrine waters and bottom sediments was carried out largely in the laboratories operated by OGU Oblkompriroda, and partly in KNIIGiMS.

The determination of the hydrochemical and geochemical indices used the following methods: SO_4^{2-} and Cl^- – ion chromatography; Ca^{2+}, HCO_3^-, and COD – titrimetric method; BOD_5 – amperometric method, and pH – potentiometric method; nitrogen compounds and phenols – photometric method; Na^+, K^+, Fe, Zn, Pb, Cu, Mn, Ni, and Cr – atomic absorption ("KVANT Z. ETA"); oil products – fluorometric method, and suspended matter – gravimetric method [5]. The total num of samples of fluvial water, lacustrine waters and bottom sediments is 30, 20 and 13, respectively. The analysis of hydrochemical data for the presence of extreme values was done according to [4].

CHEMICAL COMPOSITION OF RIVER AND LAKE WATERS

Analysis of available information showed that the surface waters of the Taz-Yenisei interfluve beyond the areas of obvious anthropogenic impact are characterized, according to O.A. Alekin's classification [6], as freshwaters with low and moderate mineralization, and, for the winter months, as freshwaters with increased mineralization. In most cases, the fluvial waters are hydrocarbonate calcium waters, but there also occur hydrocarbonate sodium waters (the tributaries of the Bol. Kheta river). Compared to the fluvial waters, the lacustrine waters contain smaller amounts of dissolved salts, and the contribution of the Na^+ and K^+ ions in them is generally higher, which is accounted for by the significant role played by the atmospheric alimentation of the water bodies. At the lowest-water period, the fluvial waters are largely neutral and weakly alkaline waters, while the lacustrine waters are weakly acidic and neutral waters (Table 1).

A most comprehensive series of determinations of hydrochemical indices, compatible with respect to the water sampling time, were obtained largely for the Solenaya river, a relatively large right tributary of the Bol. Kheta river in its middle flow. Analysis of data intimated that mineralization of the water regularly increases toward the mouth, which is due to the increase in the influx of subterranean waters. No such correlation was revealed directly for the Bol. Kheta river because of the different sampling times in different sections of the river as well as due to the differences in content of dissolved salts in different tributaries during the autumn and winter months.

Fluvial waters and lacustrine waters alike contain considerable amounts of phenols, iron, copper, manganese, zinc and nickel, exceeding the fishery standards. The established standards for water bodies for domestic and drinking water purposes are exceeded in the case of chemical and biochemical oxygen demand (COD and BOD_5), and contents of iron, manganese and nickel (see Table 1). Also, there are breaches of the normative requirements for the indices of additive impact of chemical substances on water ecosystems in the form of sums of the ratios of actual and maximum allowable concentrations ($\sum\frac{C}{MAC}$). In particular, violations of this index were observed for water bodies of domestic and drinking water purposes as regards substances of hazard class 1 and 2 as well as the organoleptic and sanitary-toxicological limiting harmful index (LHI), and for water bodies for fisheries purposes as regards the toxicological and fisheries LHI. In accordance with the requirements [7], the fluvial waters are defined as alpha- and beta-mesosaprobic, which typically corresponds to polluted waters.

However, the chief cause for the aforementioned departures from the standard values is not the anthropogenic contamination and pollution of the water bodies but the entry of organic matter and organomineral compounds from swamped and tundra areas of the catchments. This is confirmed by the chemical composition data for the fluvial waters on the sites where the facilities of the oil and gas production complex are located. More specifically, the waters of a smaller river within the catchment of the Solenaya river did not reveal any significant changes (large errors of determination) in contents of oil products and phenols, the amount of ions, and a number of other indices downstream from the place of potential arrival of the overland runoff from the oil drilling platform. As of 2009, a similar situation is also observed generally for the other rivers in the study area; of course, it is not inconceivable in this case that individual smaller streams and lakes or local segments of larger water bodies are polluted.

One further evidence for the largely natural origin of most of the chemical composition agents for the surface waters in the area with production facilities is the absence of an abrupt increase in the values of indicators which include, in the case of a priority development of the oil and gas complex, oil products as well as sodium and potassium ions [8, 9]. It was found that standard values for fisheries facilities were exceeded mainly in the case of oil products in the tributaries of the Bol. Kheta river. Furthermore, the level of their content was below the usual values for bog-taiga landscapes of Western Siberia and was likely due to accumulation of decomposition products of plant remains [9]. This same factor is also responsible for the increased values of COD (higher than 15 mgO/dm^3). Some amounts of organic matter are mineralized to produce ammonium ions, while some organic acids produce compounds with Fe, Mn and with some other metals accumulating in water medium. As a result, the region's surface waters exhibit elevated concentrations of a number of components.

Thus the data obtained in the study area, in areas without any clearly pronounced anthropogenic impact, can be used as background values in a future monitoring of water bodies, and in standardizing pollutants discharges.

CHEMICAL COMPOSITION AND QUALITY OF BOTTOM SEDIMENTS

No standards of the quality for bottom sediments are available to date. Earlier (using the rivers of Tomsk Oblast), O.G. Savichev [10] suggested that four categories of bottom sediments be identified according to contents of oil products: 1) clean – up to 65 mg/kg; 2) clean (for smaller rivers with swamped catchments), and moderately polluted (in the other cases) – from 65 to 260 mg/kg; 3) polluted – from 260 to 550 mg/kg; 4) dirty - over 550 mg/kg. Concentrations exceeding 250 mg/kg for smaller rivers and 65 mg/kg for the

Table 1. Mean values of hydrochemical indices and errors of their determination for surface waters in the study area

Index	MAC_f	MAC_{dd}	Bol. Kheta river	Tributaries of the Bol. Kheta	Russkaya river	Tributaries of the Russkaya	Lakes
pH	6.5–8.5	6.5–8.5	7.63 ± 0.37	7.85 ± 0.23	7.85 ± 0.05	7.50 ± 0.12	6.36 ±0.19
BOD5, mgO_2/dm^3	2	2	1.30 ± 0.50	1.22 ± 0.17	2.40 ± 0.10	1.80 ± 0.10	2.45 ± 1.45
COD, mgO/dm^3	–	15	13.55 ± 0.25	19.88 ± 2.56	16.50 ± 1.50	17.50 ± 0.50	27.00 ± 22.0
				mg/dm^3			
Suspended substances	Background + 0.25	Background + 0.25	4.2 ± 0.85	2.2 ± 0.32	8.3 ± 0.25	7.7 ± 2.35	5.6 ± 1.85
$\Sigma_и$	1000	1000	212.8 ± 109.8	195.6 ± 61.5	73.8 ± 8.6	69.1 ± 8.9	46.4 ± 12.9
Ca^{2+}	180	–	19.8 ± 4.1	12.5 ± 4.0	9.2 ± 0.2	8.0 ± 0.6	4.4 ± 0.9
Mg^{2+}	40	50	10.3 ± 5.8	8.4 ± 2.2	4.1 ± 0.1	2.7 ± 0.7	1.6 ± 0.4
Na^+	120	200	16.7 ± 13.9	14.2 ± 8.1	5.2 ± 0.1	6.1 ± 2.3	6.4 ± 3.1
K^+	50	–	7.8 ± 6.3	6.5 ± 3.7	1.8 ± 0.1	2.7 ± 1.1	2.9 ±1.4
HCO^{3-}	–	–	113.0 ± 41.2	128.0 ± 35.4	42.8 ± 0.8	42.0 ± 4.6	16.2 ± 2.0
SO_4^{2-}	100	500	41.7 ± 36.7	20.6 ± 7.1	5.0 ± 1.0	2.9 ± 1.3	1.4 ± 0.4
Cl^-	300	350	3.5 ± 1.8	5.4 ± 2.5	5.9 ± 0.1	4.9 ± 1.3	13.5 ± 7.4
Oil products	0.05	0.3	0.004 ± 0.001	0.091 ± 0.022	0.013 ± 0.001	0.012 ± 0.005	0.043 ± 0.012
Phenols	0.001	0.1	0.010 ± 0.002	0.004 ± 0.001	0.008 ± 0.001	0.006 ± 0.003	0.005 ± 0.001
ASAS	0.1	0.05	0.013 ± 0.001	0.013 ± 0.001	0.021 ± 0.008	0.042 ± 0.016	0.080 ± 0.012
$N–NH_4^+$	0.39	1.5	0.295 ± 0.015	0.262 ± 0.012	0.200 ± 0.010	0.217 ± 0.033	0.609 ± 0.102
$N–NO_2^-$	0.024	1.00	0.003 ± 0.001	0.003 ± 0.001	0.003 ± 0.001	0.002 ± 0.001	0.034 ± 0.021
$N–NO_3^-$	9.03	10.16	0.120 ± 0.010	0.473 ± 0.111	0.115 ± 0.005	0.329 ± 0.256	0.656 ± 0.114
$Fe_{tot.}$	0.1	0.3	0.250 ± 0.060	0.804 ± 0.172	0.765 ± 0.015	0.643 ± 0.015	0.996 ± 0.579
				μg/dm^3			
Zn	10	1000	5.2 ± 1.1	98.4 ± 23.7	73.0 ± 6.1	13.5 ± 1.5	6.0 ± 1.1
Cu	1	1000	7.1 ± 0.4	6.7 ± 1.3	16.5 ± 2.5	8.0 ± 1.2	13.5 ± 3.5
Pb	6	10	1.8 ± 1.1	1.4 ± 0.1	2.8 ± 0.5	5.9 ± 2.9	2.2 ± 0.9
Ni	10	20	31.0 ± 0.1	19.5 ± 6.8	50.0 ± 8.0	43.5 ± 18.5	26.5 ± 9.5
Mn	10	100	51.5 ± 3.5	103.6 ± 16.3	139.5 ± 19.5	112.5 ± 22.5	56.0 ± 31.0
Cr	20	50	19.3 ± 11.8	4.7 ± 0.8	4.3 ± 1.5	5.5 ± 0.1	3.0 ± 1.5

Note. The error of determination of the arithmetical mean is calculated by the formula $\delta_A = \frac{\sigma}{\sqrt{N}}$, where σ is a standard deviation, and N is the sample size; MAC_f is maximum allowable concentration for fisheries; MAC_{dd} is maximum allowable concentration for domestic and drinking water; BOD_5 is biochemical oxygen demand for five days; COD is chemical oxygen demand; ASAS stands for anionic surface-active substances.

other rivers, give evidence, with >90% probability, for anthropogenic pollution of the water bodies [9, 10]. The bottom sediments of the rivers and lakes in the study area can be categorized as “clean” having regard to this classification (Table 2), which points to the absence of any severe anthropogenic impact.

According to [10], such an approach cannot be applied to a classification of bottom sediments from contents of the other substances because of their less clearly pronounced dependence on anthropogenic impacts and, perhaps, of a more significant association with geological structural patterns of the catchment territories. Nevertheless, as far as trace elements are concerned, it would be appropriate to use, as the boundary values between characteristic categories, the first (25%) and the third (75%) quartiles of the empirical probability curve. In this case, unlike oil products, these categories reflect not only the degree of pollution of bottom sediments but also the peculiarities of the natural formation conditions for their chemical com-

Table 2. Mean values of the index of matter composition of bottom sediments (mg/kg) for rivers and lakes in the study area

Index	Quartile of the empirical probability curve [10]		Catchments		Lakes
	25%	75%	Bol. Kheta river	Russkaya river	
pH	–	–	7.29 ± 0.05	6.98 ± 0.02	7.20 ± 0.10
$N–NH_4^+$	–	–	10.0 ± 0.1	10.0 ± 0.1	10.0 ± 0.1
Oil products	258.9	64.8	43.7 ± 6.7	33.0 ± 8.0	61.0 ± 8.0
Fe*	30 000	1868	8124 ± 1102	2744 ± 207	9034 ± 684
Zn*	70.0	21.0	13.9 ± 2.5	3.0 ± 0.4	26.7 ± 7.0
Cu*	30.0	7.7	8.3 ± 0.8	1.8 ± 0.3	10.3 ± 1.6
Pb*	20.0	4.0	8.5 ± 0.9	5.5 ± 0.6	8.2 ± 1.2
Mn*	1312.7	300.0	261.1 ± 21.6	177.8 ± 14.7	190.0 ± 49.0
Ni*	40.0	20.0	13.5 ± 6.5	6.9 ± 1.2	8.9 ± 1.9
Cr*	200.0	85.0	7.3 ± 0.7	6.1 ± 1.8	7.6 ± 1.0

* Acid-soluble forms of metals.

position, which, as far as it goes, is of great interest.

With this taken into account, bottom sediments can be categorized as ‘arbitrarily clean’ and ‘moderately clean’ according to contents of Fe, Zn, Cu, Pb, Mn, Ni and Cr (see Table 2). A section of the Solenaya river stands out with a rather high content of nickel, or 52 mg/kg. Considering that this fact was recorded upstream from the potential pollution source, its natural origin might be suggested. In general, the bottom sediments in the streams used in this study can be assessed as being in a satisfactory state, and the resulting characteristics of their chemical composition can be used as background ones.

CONCLUSIONS

As of 2009, chemical composition of the surface waters on the study territory of the Taz-Yenisei interfluve is formed largely over the course of naturally occurring processes and exhibits increased values of COD (averaging 14–27 mgO/dm^3), phenol concentrations (0.004–0.010 mg/dm^3), NH_4^+ (0.2–0.6 mgN/dm^3), Fe (0.25–1.0 mg/dm^3), and Mn (0.052–0.140 mg/dm^3). Breaches of the established quality standards of the aforementioned substances are quite a typical phenomenon as regards the cold, humid conditions of the bog-taiga region in general and the forest-tundra province in particular [3]. Noteworthy also is some difference of the study area from the taiga provinces in the region involved, implying higher concentrations of heavy metals, specifically nickel, in the surface waters.

The anthropogenic influence on the ecologo-geochemical state of the surface water bodies has thus far been limited to local areas and makes itself evident in some increase in concentrations of oil products (up to 0.16 mg/dm^3), Na^+ (up to 57 mg/dm^3), and Cl^- (up to 138 mg/dm^3), which is observed in individual small streams and lakes. Taking into consideration the possibility of quantifying the Na^+ and Cl^- concentrations in the field, it is advisable to include these indices in ecological monitoring programs for the territories of development of the oil and gas complex in the Taz-Yenisei interfluve area, with the greatest possible sampling of the water bodies, and with a more comprehensive study into chemical composition of the surface waters and bottom sediments in areas with increased contents of these ions.

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