Atlantis Highlights in Material Sciences and Technology (AHMST), volume 1
International Symposium "Engineering and Earth Sciences: Applied and Fundamental Research" (ISEES 2019)

Physical and Chemical Modeling of the Composition of River Waters Affected by Technogenic Sources(Angara River, Baikal Region)

Poletaeva V.I.
Laboratory of Environmental Geochemistry and Physico-Chemical Modeling
Institute of Geochemistry named after A.P. Vinogradov, SB of the RAS
Irkutsk, Russia
alieva@igc.irk.ru

Pastukhov M.V.
Laboratory of Environmental Geochemistry and Physico-Chemical Modeling
Institute of Geochemistry named after A.P. Vinogradov, SB of the RAS
Irkutsk, Russia
mpast@igc.irk.ru

Bychinsky V.A.
Laboratory of Environmental Geochemistry and Physico-Chemical Modeling
Institute of Geochemistry named after A.P. Vinogradov, SB of the RAS
Irkutsk, Russia
val@igc.irk.ru

Abstract **- The model for mixing wastewater and river water was built using Selector software. Chemical analysis of highly mineralized wastewater from the Usolye industrial zone which is one of the main pollutants of the Angara river, and river water in the area before and after exposure to technogenic sources was carried out. Forms of migration of Al, Cu, Zn, As, Cd, Pb, Hg in the geochemical systems and their transformations have been identified. Due to a high self-cleaning ability of the Angara river, concentrations of toxic elements can decrease to the background values. Technogenic pollution changes forms of these elements in the aquatic environment and increases the environmental hazard to the aquatic ecosystem.**

Keywords – river; sewage; physical and chemical modeling; element forms.

I. INTRODUCTION

Currently, industrial wastewater discharged into the environment has a significant impact on all components of aquatic ecosystems [1, 2]. Potentially toxic elements deteriorate quality of the water body as a source of drinking water supply [3, 4] and aquatic organisms are accumulated during migration along the food chain [5, 6].

Fresh water of the Angara river contain a low concentration of microelements. However, industrial effluents and products of economic activities entering the reservoir significantly change the hydrochemical composition of the river. Total concentration of elements in wastewater and river water cannot always provide complete information to assess negative effects of pollution of the aquatic ecosystem. To analyze migration characteristics of pollutants and predict further development of the ecological and geochemical environment in the river, the process of mixing water with various hydrochemical parameters was simulated. Ecological-geochemical problems have already been simulated before [7, 8]. The purpose of the article is to determine forms of elements of anthropogenic origin in waste and river waters, and in zones of mixing natural and technogenic waters using physical and chemical modeling.

II. METHODS AND MATERIALS

A distinctive feature of Angara river is uniformity of the river flow throughout the year. The share of the Baikal flow remains significant. Water of the Angara river is low-mineralized, HCO3-Ca. An increase in the concentration of most elements in the water is due to natural (lithology, tributaries, etc.) and technogenic factors. The Usolye Industrial Zone (UIZ) contributes to the technogenic emission of chemical elements in the ecosystem of the Angara river (Fig. 1). The zone includes chemical, pharmaceutical and salt-mining enterprises, machine-building and power plants, etc. Large-scale mercury contamination of the abiotic and biotic components of the river is associated with one of the enterprises of the UIZ (Usolyekhimprom) [9]. At present, industrial wastewater contains significant amounts of mercury entering from the highly polluted industrial site of Usoliekhimprom into the river.

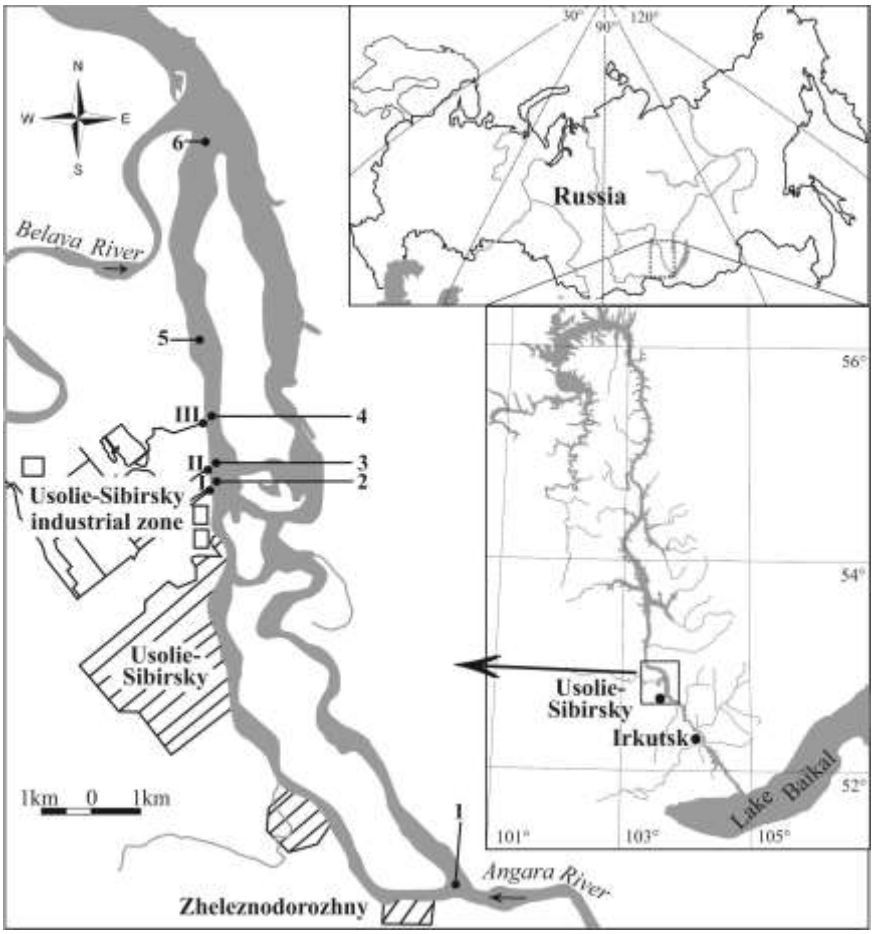

Fig. 1. Map of stations sampling wastewater and water of the Angara river in the Usolye industrial zone. Sampling points: I - GZU; II - VP; III - DK; 1 – the Angara river (Zheleznodorozhny); 2 - 50 m below GZU; 3 - 50 m below VP; 4 - 50 m below the drainage ditch; 5 – the Angara river (1.5 km below the discharge zone); 6 - p. Angara (5 km below the discharge zone).

Assessment of the impact of technogenic UIZ sources on the composition of river water was based on the results of chemical analysis of UIZ wastewater, water samples from the Angara river on the background area and the area of possible pollution. During the sampling period, the industrial discharge of the plant included wastewater of the hydraulic ash disposal (HAD) and drainage ditch (DD) - organized industrial rain showers of industrial facilities and surface drainage receivers from the territory of the Usoliekhimprom company (Fig. 1). The wastewater of the third source of pollution (VP) is the direct discharge of the Usoliekhimprom company. The site located 5 km above the wastewater discharge (Zheleznodorozhny) was chosen as a conditional background section.

A. Analysis

Analysis was carried out using the research equipment of the Siberian branch of the RAS (Irkutsk). Concentration of Al, Cu, Zn, As, Cd, Pb in water was determined by the ICP-MS method using an ELEMENT-2 mass spectrometer (Thermo Finnigan, Bremen, Germany); concentration of Hg was determined using an atomic absorption analyzer RA-915 + with RP-91 by the method of "cold steam". Cations (Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}) and anions (HCO_3^{-}, Cl^{-}, SO_4^{2-}, F^{-}) were determined using standard methods described in [10].

B. Physico-chemical modeling

The modelling principles for physicochemical processes in multi-reservoir systems by minimizing the Gibbs free energy are described in [11]. The chemical thermodynamics apparatus is used to study chemical interactions in multicomponent, multi-unit, heterophase systems, taking into account precipitation processes - dissolution, oxidation - reduction, adsorption and complex formation. Therefore, the study of evolution of natural systems, taking into account the flows of mobile groups of phases and local equilibria in reservoirs, allows us to construct a model that reflects natural objects, despite the fact that in real processes complete equilibrium is difficult to achieve. The model imitating the physicochemical evolution can adapt to changes in the overall chemical composition: some independent components can be removed from the system which causes evaporation, adsorption, etc. The physicochemical model was designed in Selector software [12].

The physicochemical model for mixing industrial effluents with water of the Angara river is presented as a set of nine reservoirs (Fig. 1: wastewater - 3 reservoirs, segments of the Angara river in the zone of influence of wastewater - 6 reservoirs) where metabolism through a specified flow of water solutions conjugated with river water occurs. Each reservoir is

an equilibrium area where the composition of the wastewater and natural water is calculated in ratios corresponding to real conditions. The substance is transferred between the reserovirs in discrete portions of mobile groups of phases (water, suspension). The model includes 18 independent components: C, Cd, Cl, S, As, Hg, Ca, Pb, Al, Cu, F, K, Mg, Na, Zn, H, O, e (e - electron) and 850 dependent components (gases, aqueous solution and solid phases). Thermodynamic properties of solutes, solid phases, and gases are taken from [13], [14], and [15], respectively.

III. RESULTS

The river waters of the background area belong to low-mineralized (112.6-123.1 mg / l), with a predominance in the ionic composition of HCO3- and Ca2 + and concentrations of trace elements (Table 1) significantly lower than the permissible concentrations regulated for drinking water [16].

The composition of the VZW wastewater in various time periods is extremely diverse. During the study period, the wastewater had a pronounced sodium chloride composition, with trace elements content tens and thousands of times higher than the concentration in the water of the background area r. Hangars (Table 1). The greatest contribution to the technogenic intake of trace elements is made by highly mineralized (16321 mg / l) wastewater GZU. In the waters of CAP and DC, the value of mineralization is less (11926 and 7858 mg / l, respectively). The pH value in water GZU is in the range of weakly acidic (6.3), in VP and DK - weakly alkaline waters (8.1-8.9).

TABLE I. CONCENTRATION OF MAIN IONS AND MICROELEMENTS IN WASTE AND ANGARA RIVER WATER

Components	Background area	**Wastewater**			**The Angara River**				
		HAD	***VP***	***DD***	***50 m away from HAD***	***50 m away from VP***	***50 m away from DD***	***1.5 km away from* the source of pollution**	***5 km away from* the source of pollution**
	mg/l								
HCO_3^-	77.1	30.3	280.6	157.6	68.3	73.2	76.6	74.7	73.2
Cl^-	2.8	9720.7	7000.2	4600.6	800.0	278.6	475.2	117.7	39.7
SO_4^{2-}	10.0	180.1	140.4	90.0	20.0	18.0	14.0	14.0	9.5
Ca^{2+}	20.0	189.0	27.0	68.3	30.0	21.0	25.0	25.0	24.0
Mg^{2+}	5.5	6.7	6.7	12.2	4.3	4.3	4.9	2.4	0.5
Na^+	2.4	6187.7	4465.0	2921.3	355.5	138.4	262.4	73.8	20.3
F^-	0.13	1.00	0.48	0.62	0.22	0.18	0.20	0.16	0.15
K^+	0.9	6.4	6.5	8.1	1.8	1.4	1.7	1.2	1.1
	ug/l								
Al	13.8	587.0	266.0	168.0	107	12.5	11.5	12.6	11.0
Cu	0.93	3.84	0.44	0.29	1.03	0.46	0.39	0.43	0.44
Zn	1.19	16.00	10.70	1.24	5.4	0.48	0.15	0.34	0.20
As	0.18	1.47	0.61	2.14	0.38	0.29	0.25	0.38	0.33
Cd	0.012	0.500	0.031	0.029	0.066	0.013	0.01	0.009	0.008
Pb	0.025	1.210	0.310	0.170	0.188	0.015	0.008	0.017	0.020
Hg	0.001	2.390	0.399	1.990	0.239	0.016	0.204	0.008	0.003

Physicochemical modeling showed that wastewater differs from the natural forms of elements in the solution (Table 2). Ionic forms of Cd, Zn and Cu are predominant forms of migration; Al, Pb and As are present as hydroxo complexes, Hg migrates in the form of HgO^0 oxide. In highly mineralized wastewater, the share of chloride (Pb, Cd, Hg, Zn, Cu) and fluoride (Al) complexes increases.

Forms of migration of arsenic in the HAD and VP wastewater and river water are similar. In the DD wastewater, As is present in the form of solid phases due to the flow of wastewater from the Usoliekhimprom enterprise where As is in the mineral form. Similarity of the presence of Zn in natural and waste waters determines its presence in the form of simple ions. A distinctive feature is the presence of $ZnOH^+$ hydroxo-complexes in natural water, while its solubility in wastewater is controlled by a high chlorine content.

Wastewater entering the Angara river is dispersed in the water column which decreases its concentration (Table 1) due to dilution and sorption on suspended particles. At the same time, mineralization is high (535-1280 mg/l). The difference in hydrochemical types of wastewater and natural water entering the mixing zone changes the ratio of the forms of most elements (Table 2). Concentration of chloride and fluoride complexes in wastewater decreases for Hg and Cd; for Al, Pb, Zn, Cu, it is minimal. The dominant forms of elements are hydroxocomplexes (Al, As, Pb, Zn) and simple cations (Cd), characteristic of the background region. However, the forms of elements in the water of the background area and mixing zone have some differences (Table 2). In the zone of waste and river water, the share of free Zn^{+2} ion decreases, $ZnOH^+$ hydroxide is dominant. The ionic form of copper (80% in the background area) does not exceed 10% after the wastewater has entered the river. Its share is less than that of CuO^0.

TABLE II. FORMS OF MIGRATION OF CHEMICAL ELEMENTS (%) IN NATURAL AND WASTE WATERS

Forms of elements	**Background area**	***HAD***	***50 m away from HAD***	**VP**	***50 m away from VP***	**DD**	***50 m away from DD***	***1.5 km away from* the source of pollution**	***5 km away from* the source of pollution**
Aluminum									
$Al(OH)_4^-$	45	2	64		63	3	63	63	63
AlO_2^-	25	1	35		36	1	36	36	36
$Al(OH)_2F$	13	45				53			
$HAlO_2^0$	12		1		1	3	1	1	1
$Al(OH)_3$	3								
AlF^{+2}		31		62		26			
AlF_3		14				7			
AlF_2^+		4		35		4			
Al^{+3}				1					
$AlSO_4^+$				1					
AlF_4^-				1					
Arsenic									
$As(OH)_3^0$	70	69	66	69	61	100 (solid phases As_2O_5)	61	61	61
$HAsO_2^0$	30	31	29	31	26		26	26	26
$As(OH)_4^-$			2		5		5	5	5
$H_2AsO_3^-$			2		4		4	4	4
AsO_2^-			1		4		4	4	4
Cadmium									
Cd^{+2}	99	6	83	9	74	12	70	70	70
$CdCl^+$	1	55	17	59	25	64	28	28	28
$CdCl_20$		38		32	1	24	1	1	1
$CdOH^+$							1	1	1
Mercury									
HgO^0	98		80		95		89	89	89
$HgCl_2^0$	2	26	20	41	5	60	11	11	11
$HgCl_4^{-2}$		60		43		25			
$HgCl_3^-$		14		16		15			
Lead									
$PbOH^+$	84	8	99		99	17	99	99	99
Pb^{+2}	16	20	1	27	1	30	1	1	1
$PbCl^+$		44		50		40			
$PbCl_2^0$		22		20		12			
$PbCl_3^-$		4		2		1			
$PbCl_4^{-2}$		2		1					
Zinc									
Zn^{+2}	90	80	47	85	24	88	24	24	24
$ZnOH^+$	10	1	53		75	1	75	75	75
$ZnCl^+$		15		13		10			
$ZnCl_2^0$		3		2		1			
$ZnCl_3^-$		1							
ZnO^0					1		1	1	1
Copper									
Cu^{+2}	83	78	9	82	1	85	1	1	1
$CuOH^+$	8	1	9		4	1	4	4	4
CuO^0	9		82		95		95	95	95
$CuCl^+$		21		18		14			

1.5 and 5 km away from the sources of pollution, concentrations of most of the main ions and microelements, except for Cl-, Na +, As and Hg, are close to the background values. Despite the fact that in this area there is an increase in the share of river water, the forms of migration of elements remain inherited from the mixing zone of the last discharge (DD) (Table 2). 5 km below the discharge, the ratios of the forms of migration of elements do not restore.

The most toxic form that has a large impact on the living organisms is the main contaminant element of mercury [17]. The lack of thermodynamic data on forms of mercury does not allow to take into account its combination with organic ligands. However, it can be assumed that in the wastewater, by analogy with seawater [18], Hg associated with organic substances is absent due to high concentration of chloride ion. On the contrary, in the river water, at lower concentrations of Cl-, mercury can be represented by organic complexes with fulvic

and humic acids [7]. This is also confirmed by the results of [19] which shows that downstream from wastewater (the Angara River, Bratsk Reservoir), the share of methylated mercury entering plankton from the aquatic environment is about 50% of its total concentration.

IV. CONCLUSION

Quantitative analysis of concentrations of elements showed that under the influence of intensive mixing and a high degree of aeration, technogenic elements are dispersed in the river water. 5 km away from the sources of pollution, most of the concentrations of elements, except for mercury, arsenic, chlorine and sodium ions, are equal to the background values. However, comparison of the forms of elements in the Angara River water in the background area and 5 away from the sources of pollution shows that their composition does not restore to the background values. This means that changes in mobility of toxic elements can increase the levels of their accumulation in bottom deposits, especially in trophic chains of hydrobionts.

Thus, the physicochemical modeling of transformations of the forms of chemical elements in the natural-man-made system, in combination with traditional research methods, can be used for assessing changes in their biogeochemical cycles.

Acknowledgment

The research is part of the state assignment on Project IX.127.1. (0350-2016-0027) supported by the RFBR grant No.17-45-388089 r-a.

References

[1] A.B. Azizi, M.P.M. Lim, Z.M. Noor, N. Abdullah, “Vermiremoval of heavy metal in sewage sludge by utilising Lumbricus rubellus”, Ecotoxicology and Environmental Safety, vol. 90, pp. 13–20, 2013.

[2] D. Dietler, M. Babu, G. Cissé, A.A. Halage, E. Malambala, S. Fuhrimann, “Daily variation of heavy metal contamination and its potential sources along the major urban wastewater channel in Kampala, Uganda”, Environ Monit Assess, no. 191 (2), pp. 52, 2019.

[3] N. Gul, M.T. Shah, S. Khan, N.U. Khattak, S. Muhammad, “Arsenic and heavy metals contamination, risk assessment and their source in drinking water of the Mardan District, Khyber Pakhtunkhwa, Pakistan”, Journal of Water and Health, vol. 13 (4), pp. 1073–1084, 2015.

[4] H. Chappells, L. Parker, C. Fernandez, C. Conrad, J. Drage, G. O’Toole, N. Campbell, T.J.B. Dummer, “Arsenic in private drinking water wells: an assessment of jurisdictional regulations and guidelines for risk remediation in North America”, Journal of Water and Health, vol. 12 (3), pp. 372–392, 2014.

[5] D.M.K. Ongeri, J.O. Lalah, S.O. Wandiga, K.-W. Schramm, B. Michalke, “Seasonal Variability in Cadmium, Lead, Copper, Zinc and Iron Concentrations in the Three Major Fish Species, Oreochromis niloticus, Lates niloticus and Rastrineobola argentea in Winam Gulf, Lake Victoria: Impact of Wash-Off into the Lake”, Bulletin of Environmental Contamination and Toxicology, vol. 88, pp. 166–171, 2012.

[6] P. Spanopoulos-Zarco, J. Ruelas-Inzunza, M.E. Jara-Marini, M. Meza-Montenegro, Bioaccumulation of arsenic and selenium in bycatch fishes Diapterus peruvianus, Pseudupeneus grandisquamis, and Trachinotus kennedyi from shrimp trawling in the continental shelf of Guerrero, México: Environ Monit Assess, 2015, pp. 187–700.

[7] A.V. Savchenko, L.M. Gramm-Osipov, A.A. Mar'yash, “Physicochemical modeling of the behavior of microelements (As, V, Cr, Co, and Hg) under the mixing of riverine and marine waters (the Razdol'naya River-Amur Bay System)”, Oceanology, vol. 49, no. 1, pp. 45–52, 2009.

[8] S.Kh. Pavlov, K.V. Chudnenko, “Formation of nitrogen-rich hot springs: Modeling physicochemical interactions in a water-granite system”, Geochemistry International, vol. 51, no 12, pp. 981–993, 2013.

[9] P.V. Koval, G.V. Kalmychkov, S.M. Lavrov, Yu.N. Udodov, E.V. Butakov, F.W. Fifield, V.I. Alieva, “Anthropogenic Component and Balance of Mercury in Ecosystem of the Bratsk Hydropower Reservoir”, Doklady Earth Science, vol. 388, no. 2, pp. 225–227, 2003.

[10] L.V. Boeva, Guide to the chemical analysis of a surface water of sushi. Rostov-on-Don: NOK, 2009, 1046 p.

[11] I.K. Karpov, K.V. Chudnenko, D.A. Kulik, V.A. Bychinskii, “The convex programming minimization of five thermodynamic potentials other than Gibbs energy in geochemical modeling”, American Journal of Science, vol. 302, no 4, pp. 281–311, 2002.

[12] K.V. Chudnenko, Thermodynamic modeling in geochemistry: the theory, algorithms, the software, applications, Novosibirsk: Academic publishing house “Geo”, 2010, 287 p.

[13] D.A. Sverjensky, E.L. Shock, H.C. Helgeson, “Prediction of the thermodynamic properties of aqueous metal complexes up to 1000 °C and 5 kb”, Geochimica et Cosmochimica Acta, vol. 61, pp. 1359–1412, 1997.

[14] L. Richard, H.C. Helgeson, “Calculation of the thermodynamic properties at elevated temperatures and pressures of saturated and aromatic high molecular weight solid and liquid hydrocarbons in kerogen, bitumen, petroleum, and other organic matter of biogeochemical interest”, Geochimica et Cosmochimica Acta, vol. 62, pp. 3591–3636, 1988.

[15] R.C. Reid, J.M. Prausnitz, T.K. Sherwood, The properties of gases and liquids. New York: McGraw-Hill, 1977.

[16] WHO, Guidelines for drinking water quality, 4th edn. Geneva: World Health Organization, 2011.

[17] S.M. Ullrich, T.W. Tanton, S.A. Abdrashitova, “Mercury in the aquatic environment: a review of factors affecting methylation, Critical Reviews”, Environmental Science and Technology, vol. 31, no. 3, pp. 241–293, 2001.

[18] M. Leermakers, C. Meuleman, W. Baeyens, “Mercury speciation in the Scheldt estuary”, Water, Air & Soil Pollution, vol. 80, pp. 641–652, 1995.

[19] V. Perrot, V.N. Epov, M.V. Pastukhov, V.I. Grebenshchikova, C. Zouiten, J.E. Sonke, S. Husted, O.F.X. Donard, D. Amouroux, “Tracing Sources and Bioaccumulation of Mercury in Fish of Lake Baikal − Angara River Using Hg Isotopic Composition”, Environmental Science & Technology, vol. 44, no. 21, pp. 8030–8037, 2010.