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Changes in Chemical Composition of Natural Waters in Response to Technogenic Load (the Case of Tomsk City, Russia)

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Abstract

The article provides the analysis of chemical composition of the ground and surface waters on the left bank of the river Tom' within Tomsk area. This study is being conducted in context of active development of the area. The results obtained are compared with the analysis data of the earlier periods. It is concluded that the closed lakes have more changes in water chemical composition, which is caused by increasing content of petrochemicals, heavy metals, phosphorus and nitrogen compounds due to growing economical activities near the water bodies.

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Keywords: Natural waters, chemical composition, ecological state, water contamination;

1. Introduction

Modern urban areas are being developed at the expense of ecosystem integrity destruction, which leads to polluted air, poor quality of water and small number of recreation areas¹⁻⁴. The citizens of Tomsk, a Russian Siberian city located on the river Tom', face these environmental problems.

Currently, the left bank of the river Tom' within Tomsk borders is being actively developed: it is the area for a highway construction, increasing number of suburban settlements and summer houses. However, there is a unique ground water intake providing almost the whole city with high-quality drinking water. There are also numerous water bodies with great recreational potential. Thus, the revealed scope of the problems makes ecological and geochemical research of the natural waters of the area be very challenging task.

A lot of researchers, such as Udodov P.A., Smolentsev Yu.K., Rasskazov N.M., Shvartsev S.L., Korobkin V.A., Popov V.K., Yermashova N.A., Kolokolova O.V., Savichev O.G., have published papers devoted to the Ob'-Tom'

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interfluves⁵⁻¹¹. However, they studied the issue before the full-scale construction activities, the lakes of the area were not studied either.

The aim of the paper is to study the state of natural waters (both ground and surface) on the left bank of the river Tom' within Tomsk city.

2. Research methods and objects of research

In 2012-2013 years the ground and surface waters of the left bank of the river Tom' in Tomsk were studied (Fig.1). Such fast changing characteristics as redox and acid-basis properties, electric conductivity were measured in situ (at sampling sites) by means of a portable analyzer "Water Test".

The chemical water analysis was conducted in the accredited laboratory of Scientific Center "Water", TPU. Other chemical tests were done using the following methods: titrimetry, potentiometry, turbidimetry, photocolormetry, stripping voltammetry, flame emission spectrometry.

The sampling was carried out from different depths. The first three samples were taken on the Tom'-Burunduk interfluves area. The first well, which is 30 m depth, is located on the left bank of the river Tom', approximately 300-400 meters from the bank line. The well is a flowing one; the aquifer is attributed to the quaternary deposits. Well №2 is a flowing one, 48 m depth. It is located in the forest area near the U-shaped lake. The groundwater is recharged from the quaternary aquifer. Well №3 is also a flowing well, 96 m depth. It was drilled in 2012 for a private house water supply, 300 meters from the river Sukhaya (left bank tributary of the river Burunduk). The fourth sample is taken in a well which is 50m depth. It was drilled in 1980-s to pump water into lake Peschanoye in settlement Timiryazev from the Paleogenous deposits. The fifth sample is the water from the 15m depth well located in a private area in Nizhny Sklad near the coastal dam.

Surface water sampling was carried out from the rivers Tom', Kislovka, Burunduk and four lakes that are located on the left bank of the Tom' river (Belen'koye, Boyarskoye, Peschanoye, Toyanovo). These are favorite recreation areas of Tomsk citizens.



Fig.1 Water Sampling Map

3. Research results and their analyses

The studied waters are diverse in chemical composition. The water from well № 1 is moderately fresh, hydrocarbonate, magnesium-sodium-calcium, neutral, soft with high concentration of total iron. The water from well №2 is moderately fresh, hydrocarbonate-chloride calcium-sodium, alkaline, soft with high concentration of bromine. The water from well №3 is moderately fresh, chloride sodium-magnesium-calcium, neutral, very hard with high concentrations of total iron, manganese and bromine. The water from the well “Lake Peschanoye” is moderately fresh, hydrocarbonate magnesium-calcium, alkaline, soft. The water from the well “Nizhny Sklad” is moderately fresh, hydrocarbonate magnesium-calcium, neutral, soft with high iron concentration.

Chemical composition of the samples from well №1 and “Nizhny Sklad” is consistent with the background data¹⁰ in quaternary deposits. The well №2 sample is abnormally high in macro components.

The composition of the water from the well recharging Lake Peschanoye correlates with background data¹⁰ in the Paleogene deposits of the Ob'-Tom interfluvium, though being less hard. But the samples taken from well №3 are clearly abnormal.

Sodium chloride composition of the ground waters from wells № 2 and 3 is attributed to hydrogeochemical anomaly of the area, which is described in the monographs by Popov V. K., Lukashevich O.D., Korobkin V.A. et al.¹¹.

While comparing the chemical composition of the ground water samples (Table 1) with maximum permissible concentration (MPC) for non-centralized water supply systems^{12, 13}, it was discovered that iron (Fe) content exceeds MPC 13 times, silicon – 2 times and manganese (Mn) – 1.3 times in the sample from well №1. It was sampled in October, 2012. The sample №2, which is dated 2012, is characterized by chemical oxygen demand (COD) that exceeds the standard more than two times, high iron concentration (2.7-2.8 MPC) and high bromine content (2.4 MPC). Mn level exceeds the limits insignificantly (1.08 times). The quality of water from well №3 does not meet the standard requirements in the following components: COD (8.7-9.4 times excess), Cl⁻ (more than 1.5 times), total hardness (1.1 times), magnesium (1.3-1.4 times), total iron (more than 56 times), Mn (4.4-7.8 times), silicon (almost twice). In 2013 the concentration of petrochemicals (TPH) exceeds the standard by 1.5 times, bromine – more than 13 times and the BOD₅ (biochemical oxygen demand-5 day test) – 1.2 times. The water from the well “Lake Peschanoye” doesn’t meet the sanitary requirements for iron and silicon. There is also a slight excess of TPH (1.02 times). In “Nizhny Sklad” samples there is the only parameter that doesn’t meet the standards for non-centralized water supply systems: high ore content (5 times).

The surface waters of the studied area are fresh, calcium, rarely magnesium-calcium, mostly neutral, slightly alkaline, with high iron and manganese level. There is a detailed chemical composition of the studied rivers in O.G. Savichev’s monograph (2003 year)¹⁴. He summarized the data of a 30-year period and calculated the average values of the most common substances. Therefore, it was decided to compare the chemical composition of the samples taken in the period of 2012-2013 with the average values (Table 2). The comparison study shows that in 2013 the manganese concentration in the river Tom’ exceeded the average value by 20 times. The river Burunduk had copper level that also exceeded MPC. Other minerals (Mn, Cu, Pb, Zn) were either lower than the average values or equal to them. There are also high levels of the following substances:

- Phosphate PO₄³⁻ in the rivers Tom’ (above Tomsk) and Burunduk
- Ammonium ions NH₄⁺ in all the samples from the river Kislovka
- Silicon in the river Burunduk;

COD value exceeds the average level by 1.5-3 times in the rivers Kislovka and Burunduk. However, it is necessary to note that the level of Total Petroleum Hydrocarbon (TPH) in all river samples is 2-16 times lower than the average value. It may be explained by the time of sampling (high river discharge, light navigation).

The chemical compositions of lakes Boyarskoye, Belen’koye, Peschanoye and Toyanovo were compared with MPCs for recreational water use^{13, 15} and with MPCs for fishery waters¹⁶. The samples from lakes Belen’koye, Peschanoye and Toyanovo were also compared with the data obtained in 2006 by Tomsk State Special Ecological Inspection.

Table 1. Chemical composition of the ground waters

Well «Lake Peschanoye»	Well «Nizhny Sklad»		MPC ^{12,13}
	2012	2013	
5.8	6	4.8	-
7.7	7.7	6.9	6
7.4	7.35	6.6	
-30	-41	59	-
0.244	0.182	0.1	
0.219	0.197	0.24	-
13.8	6.92	9.65	15
0.82	0.83	0.26	2
7.2	7.04	42	-
185	175.68	130	-
<2	<2	20.6	500
1.4	0.5	14.3	350
0.73	0.35	<0.01	3.5
0.43	0.39	0.1	1.5 for N
<0.01	0.01	0.02	3.3
<0.1	0.1	2.3	45
2.7	2.2	2.8	10
32	34	38	-
13.42	6.1	10.98	50
10	10.76	6.26	200
0.87	0.51	1.04	-
0.84	1.13	1.5	0.3
0.086	0.063	0.049	0.1
11.23	10.66	7.69	10
0.055	0.102	0.039	0.1
242.69	227.55	221.18	1500
-	0.015	-	0.2
2.5	12	12	1000
<0.2	<0.2	<0.2	1
<0.2	2.9	0.34	10
<0.6	0.6	1.7	1000

Component	Dimension	Well No.1			Well No.2			Well No.3		
		2012	2013	2013	2012	2013	2013	2012	2013	2013
Temperature	°C	5.3	5.7	5.7	5.7	5.4	5.4	6.5	5.5	5.5
pH (Water Test)	pH unit	6.8	6.7	8.3	8.3	8.3	8.3	6.9	6.7	6.7
pH (Laboratory)	pH unit	6.7	6.68	7.8	7.8	7.63	7.63	6.6	6.3	6.3
Eh	mV	-32	-30	-121	-121	-128	-128	-10	-1	-1
Electrical conductivity (WaterTest)	mS/sm	0.273	0.24	0.54	0.54	0.611	0.611	1.226	1.56	1.56
Electrical conductivity (Laboratory)	mS/sm	0.271	0.247	0.554	0.554	0.637	0.637	1.998	1.84	1.84
COD	mgO ₂ /L	7.2	< 4	36.6	31.2	31.2	31.2	141.5	131	131
BOD ₅	mgO ₂ /L	0.99	0.59	0.78	0.37	1.31	1.31	2.35	2.35	2.35
CO ₂	mg/L	62.4	30.8	3.6	4.4	60	60	35.2	35.2	35.2
HCO ₃ ⁻	mg/L	207	204.96	171	173.24	85.4	85.4	87.84	87.84	87.84
SO ₄ ²⁻	mg/L	10.6	5.29	< 2	< 2	7.8	7.8	8.41	8.41	8.41
Cl ⁻	mg/L	3.4	2.8	133	131.35	530	530	553.8	553.8	553.8
PO ₄ ³⁻	mg/L	0.168	0.014	0.049	0.021	< 0.01	< 0.01	0.07	0.07	0.07
NH ₄ ⁺	mg/L	0.2	0.429	0.58	0.94	1.85	1.85	0.7	0.7	0.7
NO ₂ ⁻	mg/L	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
NO ₃ ⁻	mg/L	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.10	< 0.1	0.25	0.25
Total hardness (TH)	°H	2.5	2.2	2.9	2.6	11.4	11.4	11.8	11.8	11.8
Ca ²⁺	mg/L	30	28	32	32	122	122	120	120	120
Mg ²⁺	mg/L	12.2	9.76	15.86	12.2	64.7	64.7	70.76	70.76	70.76
Na ⁺	mg/L	25.4	25.68	78.9	84.7	110	110	119.71	119.71	119.71
K ⁺	mg/L	3.28	2.54	4.36	3.04	8	8	4.51	4.51	4.51
Fe _{total}	mg/L	4	3.92	0.81	0.84	17	17	16.81	16.81	16.81
Mn	mg/L	0.132	0.063	0.108	0.062	0.778	0.778	0.436	0.436	0.436
Si	mg/L	19.84	17.77	6.34	6.33	1.74	1.74	18.49	18.49	18.49
Petrochemicals	mg/L	0.048	0.01	0.046	0.013	0.057	0.057	0.15	0.15	0.15
Mineralization	mg/L	291.88	279.03	435.12	436.53	927.9	927.9	965.03	965.03	965.03
Br	mg/L	-	0.026	-	0.48	-	-	2.64	2.64	2.64
Zn	mg/L	3.9	3.6	3.9	12	6.2	6.2	4.2	4.2	4.2
Cd	mg/L	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
Pb	mg/L	0.21	0.21	0.22	0.54	< 0.2	< 0.2	0.27	0.27	0.27
Cu	mg/L	< 0.6	0.64	< 0.6	1.2	< 0.6	< 0.6	2.5	2.5	2.5

The samples from Lake Belen'koye (2013 year) show that the content of Fe, Mn, TPH, COD and Cu has increased since the previous year and exceeds not only MPCs for fishery waters but also MPCs for recreational water (apart from Cu). The content of ammonium and zinc ions doesn't meet the requirements for fishery water despite the fact that Zn level dropped in 2013.

If compared with the chemical analysis made in 2006 year the content of almost all the substances in Lake Belen'koye has increased considerably. These substances are nitrocompound, phosphates, iron, TPH and COD. The only parameter with lower value is BOD₅ (biological oxygen demand). It may be connected with the fact that the sampling taken in 2006 year was carried out in August when the water temperature is high enough to ensure fast biological processes.

In May 2012, it was only Fe, Zn and Cu that exceeded MPCs for fishery water in Lake Boyarskoye. In July 2013, the increasing anthropogenic load resulted in exceeding MPCs for TPH, Fe, nitrocompounds, COD. THP content reaches the MPC for recreational water use: 0.1 mg/l. There is also a slight increase in copper and BOD₅.

The water of Lake Peschanoye sampled in 2012-2013 doesn't meet the standards for recreational water use in THP, pH and BOD₅ (July 2012). THP content almost doubled over one year and increased 13 times over 7 years, which is caused by growing anthropogenous factor. Fe, Mn, Zn and Cu content in the lake exceeds MPC for fishery water

bodies. Such substances as phosphates and BOD5 exceeded MPCs in the samples taken from the lake in 2006. The corresponding samples of 2012-2013 years contained significantly less values of these components.

This difference may be explained by the fact that in 2006 the water was sampled in summer. It is the period of algae bloom, which produces phosphorus organic compounds.

The samples from Lake Toyanovo do not meet the fishery water use requirements for PO_4^{3-} , NH_4^+ , Fe, Mn, Zn and Cu. The content of COD, Fe and Mn exceeds not only MPC for fishery water but also for recreational water use. These results match the results of water sampling in August 2006. However, there is an increase in Fe and nitrates, which is caused by economic activities on the lakeshore. Though the samples showed the reduction in BOD5 content which used to increase the MPC 7 times, the content of other substances, such as ammonium ions, phosphates, iron and COD, still exceeds the limits.

4. Conclusion

In spite of short research period (about 2 years), its results allow us to make important conclusions on chemical composition of natural waters of the left bank of the river Tom' within Tomsk city:

1. The ground water from the studied wells, which are more protected from human influence, often falls short of sanitary-hygienic standards for non-centralized water supply in the following components: Fe, Si and Mn.
2. The surface water also does not meet the requirements in some substances, mostly total iron, manganese, which is common for the region. The concentrations of petrochemicals, heavy metals and other substances are increasing.
3. Continuing water quality impairment is observed in lakes Belen'koye, Boyarskoye and Peschanoye. Lake Toyanovo is less affected by these changes, due to the fact that it is a flowing water reservoir and most part of the contaminants is associated with the water flowing from the wetlands to the river Kislovka.
4. The quality of watercourse slightly improved due to high rivers in 2013, which makes it possible to analyze the nature of man-made substance in the water. Thus, the water quality of the river Tom' has improved significantly, which proves its anthropogenic contamination with such substances as THP, heavy metals and organic compounds. Unlike the river Tom', the water of the rivers Kislovka and Burunduk contains high amount of substances that doesn't depend on the river stage as this high content of substances is caused by natural factors.

Though the condition of the studied water bodies is not critical, the samples don't meet the standards in some parameters yet. The content of some substances (THP, phosphates, ammonium ions, heavy metals etc.) has increased recently due to eutrophication of the water bodies and developing economic activities in the area. Thus, the increasing anthropogenic load on the area can lead to the ecosystem degradation.

Table 2. Chemical composition of the surface waters

Dimension	Lake Belenkoye		Lake Boyarskoye		Lake Peschanoye		Lake Toyanovo		r. Tom (above Tomsk)		r. Tom (below Tomsk)		r. Kislavka		r. Burunduk (estuary)		MPC ¹⁶ MPC ^{13,15}
	2012-2006	2013	2012-2006	2013	2012-2006	2013	2012-2006	2013	1970-2002	1970-2002	1970-2002	1970-2002	1970-2002	1970-2002	1970-2002	1970-2002	
°C	-	12.3	9.85	-	12.45	-	9.15	-	9.0	-	12.5	-	6.0	-	13.0	-	-
pH unit	7.76	7.6	7.21	8.26	8.23	8.05	7.48	7.44	7.45	7.51	7.65	-	7.45	7.8	7.54	6.5-8.5	-
mgO ₂ /L	-	7.8	9.28	-	9.85	-	7.87	9.0	15.2	8.4	8.94	-	8.17	-	6.99	> 6	> 4
	17.9	24.12	16.33	17.9	21.26	53.6	55.7	11.44	-	14.44	< 4	21.76	55.35	19.81	38.1	-	30
	8.95	2.15	1.61	8.95	2.83	26.8	1.23	2.07	-	2.23	2.05	2.87	1.7	1.63	2.1	-	4
	-	6.45	8.49	-	8.35	-	8.79	8.8	-	7.91	-	14.9	-	11.5	-	-	-
	-	74.37	34.3	-	106.7	-	76.25	85.2	30.5	91.9	52.9	343.8	88.45	295.0	84.5	-	-
	<10.0	7.62	4.77	<10.0	6.12	<10.0	10.19	16.3	6.99	15.4	8.94	7.5	6.52	8.2	9.4	100	500
mg/dL	<10.0	4.93	6.48	<10.0	1.9	<10.0	2.67	7.1	2.5	6.6	1.95	5.0	5.55	2.7	3.35	300	350
	<0.1	0.09	0.02	0.42	0.07	0.2	0.27	0.041	0.1	0.086	0.07	0.660	0.41	0.022	0.3	0.15*	3.5
	0.15	0.36	0.14	0.15	0.33	1.07	1.04	0.724	0.14	0.642	0.2	0.641	1.12	3.915	0.84	0.5	1.5
	<0.02	0.02	0.01	<0.02	<0.01	0.04	<0.01	0.058	0.02	0.149	0.02	0.053	<0.01	0.048	<0.01	0.08	3.3
	<0.1	0.33	0.29	<0.1	0.28	0.55	1.15	1.202	0.93	1.470	1.32	6.330	1.52	3.060	1.05	10	45
	-	1.3	0.6	-	1.71	-	1.53	1.6	0.8	1.6	0.95	-	1.6	3.7	1.55	-	-
	-	21.33	8.33	-	23.67	-	26.5	23.9	13	23.8	14.5	-	26.5	55.8	25.5	180	-
	-	2.85	2.24	-	6.38	-	2.44	5.2	1.83	4.8	2.44	-	3.36	11.5	3.05	40	-
	-	4.44	3.39	-	7.89	-	3.87	-	3.11	-	3.82	-	4.28	-	3.99	120	200
	-	1.94	1.48	-	0.32	-	0.94	-	0.59	-	0.6	-	0.73	-	1.11	10	-
mg/L									8.1	3.7	11.2	4.42	-	5.01	22.1	5.1	-
	<0.1	0.42	0.38	<0.1	0.18	0.47	1.41	0.287	0.43	0.272	0.66	1.359	2.12	0.691	1.4	0.1	0.3
	-	0.162	0.06	-	0.04	-	0.158	0.013	-	0.006	0.13	-	0.19	0.227	0.096	0.01	0.1
	-	1.97	0.43	-	1.68	-	4.5	3.36	1.15	3.13	2.82	-	4.6	2.74	4.28	-	10
	0.02	0.096	0.062	0.02	0.181	0.02	0.033	0.373	-	0.357	0.057	0.050	0.019	0.271	0.04	0.05	0.1
	11.5	110.1	61.66	45	145.6	109.0	122.8	145.8	58.5	153.7	85.1	-	131.7	395.3	131.2	1000	1000
mcg/L	-	5.13	8.33	-	5.03	-	68	17.7	9.6	6.6	4.35	-	10	10.0	5.75	1	1000
	<0.2	<0.2	<0.2	-	<0.2	-	<0.2	-	<0.2	-	<0.2	-	<0.2	-	<0.2	5	1
	-	0.29	0.34	-	0.58	-	0.58	1.1	0.74	1.9	1.1	-	0.28	0.7	0.47	6	10
	-	1.56	1.87	-	0.9	-	1.95	3.2	1.6	2.6	2	-	1.9	1.3	3.3	1	1000

* - for mesotrophic water objects

Component	Temperature	pH	O ₂ (dissolved)	COD	BOD ₅	CO ₂	HCO ₃ ⁻	SO ₄ ²⁻	Cl ⁻	PO ₄ ³⁻	NH ₄ ⁺	NO ₂ ⁻	NO ₃ ⁻	Total hardness	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Na ⁺ + K ⁺	Fe _{total}	Mn	Si	Petrochemicals	Mineralization	Zn	Cd	Pb	Cu
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The research is the starting point for further monitoring of the natural waters of the area that is supposed to be developed in the nearest future.

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