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Geochemical groundwater peculiarities of Paleogene sediments in S-E Western Siberia artesian basin

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Abstract. The geochemical peculiarities of groundwater in Paleogene deposits in southeastern part of Western Siberia artesian basin are considered in the paper. Landscape, climate, geostructural and hydrogeological conditions define the water composition and quality peculiarities in this region. It has been established that ion-saline composition, mineralization and water quality changes arre governed by the horizontal zonal distribution. Groundwater of taiga landscapes generally is in equilibrium with kaolinite and quartz, mainly involving Ca-and Mg-montmorillonite, illite, carbonate minerals, sometimes barite. Groundwater in woodland grass and grassland, together with previously mentioned minerals, is usually in equilibrium with barite, colestine, and particularly, fluorite and gypsum. As a result, all relevant elements are removed from the groundwater and their accumulation level is restricted.

1. Introduction

The most important and priority issue today is to supply a population with good quality water. Numerous scientists are paying more and more attention to this problem. Health and environmental effects, sanitary and epidemiological safety, environmental comfort and safety are reliant on the quality of the water [1-4]. This issue is more acute for arid and semi-arid regions where natural waters are usually unconditional due to the existing level of some components. A prime example is southern Siberia.

Paleogene aquifer system is widely distributed throughout and is the major supply of drinking water. Urban and rural water supply is from these groundwaters and provides the central water supply of Tomsk, Tumen and Barnaul, whereas small water catchment areas and wells supply water for small populated areas.

Hydrogeological, hydrogeochemical conditions of West Siberian Platform sedimentary cover have discussed by different scientists. In spite of this fact, such issues the peculiarities of fresh groundwater distribution and its quality are still underinvestigated. Updated methodical basis and software mapping of the hydrogeochemical conditions, as well as analysis of hydrogeochemical processes allows furthers a possibly new approach in solving the above-mentioned issues. This research is a continuation of previous research investigations [3-5]. The research target is the analysis of

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groundwater chemical composition changes in Paleogene deposits, mechanisms of water quality by studying its equilibrium with water bearing rock minerals and secondary minerals.

2. Materials and methods

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Research base is factual data of JST "Tomskgeomonitoring" which includes water chemical composition from wells of water catchment areas of populated places. Groundwater chemical composition analysis was based on modern certificated analytic methods in the laboratories of JST "Tomskgeomonitoring", TPU and several regional geological organizations.

Methods of mathematic statistics and GIS technologies were used for information generalization and processing via programs EXCEL, Statistica, ArcGIS, as well as physico-chemical calculations by HydroGeo. The use of the software HydroGeo for solving various problems has been shown by us earlier [6 - 8]

3. Results and Discussion

3.1. Chemical composition of groundwater

The generalized chemical composition data are represented in table 1. Regionally, groundwater embraces various chemical compositions and is characterized by significant mineralization alterations. Variety of landscape and climate conditions (fig.1), zonal changes of wetness conditions and infiltration charge, aquifer lithofacies peculiarities determine the main features of Paleogene deposit groundwater formation. This, in its turn, reflects the horizontal zonal changes of Paleogene waters ion-saline composition and salinity (fig. 2, 3). Fresh water is located within most of the territory. TDS regularly increases from east-northward and eastward to west-southward (fig.1) and westward from moderate wetting and overwetting charge zones to zones with difficult water exchange conditions and underwetting. Groundwater chemical composition (fig.3) and its quality also alters directionally. It is estimated that 80 % of the above-described territory embraces fresh water with TDS of up to1 g/l,

It is estimated that 80 % of the above-described territory embraces fresh water with TDS of up to 1 g/l, while water with mineralization of more than 1 g/l are within 20% of this territory. Groundwater with mineralization of 5 g/l was found only within 7 % of the territory.

 Table 1. Paleogene deposits groundwater chemical composition.

| Components | | TLV | Amount | Mean | Min | Max | % higher TLV |
|------------------------|--|-------|--------|--------|---------|--------|-----------------|
| Generalized components | TDS, mg/l | 1000 | 4168 | 851.7 | 56.7 | 4993.5 | 42.9 |
| | рН | 6-9 | 3854 | 7.4 | 6.0 | 10.9 | - |
| | Eh, мВ | - | 94 | 23.57 | -187.00 | 210.00 | - |
| | Total hardness, mg-eq/l | 7 | 4113 | 6.9 | 0.3 | 59.9 | 45.3 |
| | Permanganate oxidation, mgO ₂ /l | 5 | 1820 | 2.67 | 0.01 | 39.0 | 26.1 |
| pəs | Oil-products, mg/l | 0.1 | 481 | 0.026 | 0.0005 | 1.77 | 5.6 |
| Generaliz | Anionic surfactant, mg/l | 0.5 | 24 | 0.03 | 0.009 | 0.09 | - |
| | Detergent, mg/l | 0.5 | 73 | 0.023 | 0.008 | 0.2 | - |
| | Phenolic index | 0.25 | 340 | 0.003 | 0.0001 | 0.062 | - |
| | Phenols, mg/l | 0.001 | 52 | 0.0016 | 0.0001 | 0.012 | 3.8 |
| Macrocomponents | Hydrocarbonate (HCO ₃ -), mg/l | - | 4166 | 449.3 | 20.0 | 1281.0 | - |
| | Carbonate (CO ₃ ²⁻), mg/l | - | 202 | 11.1 | 0.2 | 150.0 | - |
| | Chlorides (Cl ⁻), mg/l | 350 | 4087 | 75.9 | 0.14 | 2906.0 | 31.5 |
| | Sulfates (SO ₄ ²⁻), mg/l | 500 | 3491 | 71.9 | 0.01 | 1819.0 | 7.4 |
| | Calcium (Ca ²⁺), mg/l | - | 4168 | 60.7 | 0.15 | 502.4 | - |
| | Magnesium (Mg ²⁺), mg/l | 50 | 4156 | 38.4 | 0.28 | 372.0 | 38.2 |
| | Sodium (Na ⁺), mg/l | 200 | 4162 | 125.1 | 0.2 | 1612.0 | 49.5 |
| | K ⁺ , mg/l | - | 359 | 1.8 | 0.25 | 59.88 | - |
| | Ammonium (NH ⁴⁺), mg/l | 1.5* | 2555 | 0.32 | 0.001 | 12.61 | 4.6 |
| | Nitrate (NO ₃ ⁻), mg/l | 45 | 2169 | 1.1 | 0.001 | 44.0 | - |
| | Nitrites (NO ₂ -), mg/l | 3 | 1507 | 0.019 | 0.00005 | 2.97 | 0,2 |
| o o n po | Aluminium (Al), mg/l | 0.5 | 180 | 0.039 | 0.0001 | 0.056 | - |

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| Barium (Ba), mg/l | 0.7 | 293 | 0.1 | 0.0001 | 0.6 | - |
|--|--------|--------|----------|---------|--------|-----------------|
| Beryllium (Be), mg/l | 0.0002 | 99 | 0.00011 | 0.00002 | 0.2 | 8.1 |
| Boracium (B), mg/l | 0.5 | 132 | 0.13 | 0.002 | 1.42 | 6.8 |
| Bromide (Br), mg/l | 0.2 | 130 | 0.11 | 0.002 | 6.5 | 13.1 |
| Components | TLV | Amount | Mean | Min | Max | % higher TLV |
| Protoxidic iron form (Fe ²⁺), mg/l | - | 147 | 0,.68 | 0.04 | 51.12 | 86.2 |
| Oxide iron form (Fe ³⁺), mg/l | - | 199 | 0.2 | 0.001 | 27.2 | 63.9 |
| Iodine (I), mg/l | - | 147 | 0.17 | 0.003 | 5.0 | - |
| Cadmium (Cd), mg/l | 0,001 | 159 | 0.00027 | 0.00001 | 0.00 | 8.8 |
| Silicium (Si), mg/l | 10 | 473 | 6.98 | 0.2 | 35.9 | 24.3 |
| Lithium (Li), mg/l | 0.03 | 143 | 0.0046 | 0.00003 | 0.047 | 2.1 |
| Manganese (Mn), mg/l | 0.1 | 475 | 0.16 | 0.00001 | 2.45 | 74.3 |
| Copper (Cu), mg/l | 1 | 969 | 0.01 | 0.00003 | 0.92 | - |
| Molybdenum (Mo), mg/l | 0.25 | 259 | 0.003 | 0.00003 | 0.2 | - |
| Arsenium (As), mg/l | 0.05 | 199 | 0.0038 | 0.0001 | 0.04 | 0.5 |
| Nickel (Ni), mg/l | 0.1 | 231 | 0.0069 | 0.00063 | 0.08 | - |
| Polyphosphates (PO ₄), mg/l | 3.5 | 382 | 0.096 | 0.001 | 3.49 | - |
| Hydrargyrum (Hg), mg/l | 0.0005 | 135 | 0.000081 | 0.00001 | 0.0006 | 0.7 |
| Plumbum (Pb), mg/l | 0.03 | 427 | 0.0021 | 0.0001 | 0.25 | 0.7 |
| Selenium (Se), mg/l | 0.01 | 49 | 0.00051 | 0.0001 | 0.005 | - |
| Strontium (Sr), mg/l | 7 | 439 | 0.33 | 0.00004 | 5.9 | - |
| Fluoride (F ⁻), mg/l | 1.5 | 780 | 0.25 | 0.00048 | 1.4 | - |
| Chromium (Cr), mg/l | 0.05 | 262 | 0.0066 | 0.0007 | 0.043 | - |
| Zink (Zn), mg/l | 5 | 765 | 0.012 | 0.0002 | 4.43 | - |

N o t e * Normalized by ammonia (by nitrogen).

Water chemical composition changes from hydrocarbonate calcium and sodium to chlorite sodium, pH increases, however, iron and organic substance content decreases (fig.2).

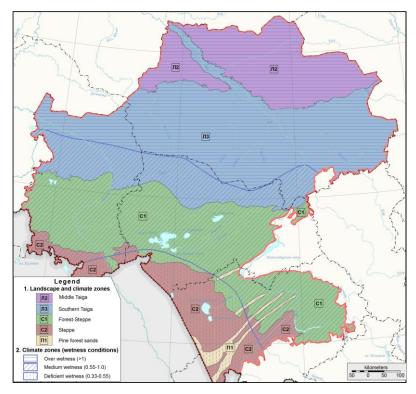


Figure 1. Landscape and climate zones.

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Hydrocarbonate calcium and magnesium-calcium, fresh water (TDS up to 450 mg/l), often acid and neutral (pH less than 7) with increased oxidability and iron and manganese content are widely distributed in central taiga conditions. It has been estimated, there are wells with off-spec water with iron is 95%, manganese - 74%, and oxidability - 56%.

Hydrocarbonate calcium and magnesium-calcium or sodium-calcium, fresh water (TDS 400-800 mg/l), neutral and weakly alkaline (pH 7-7.7) water with relatively increased Fe and Mg content, sometimes organic substances and total hardness are widely distributed in south taiga and sub-boreal taiga conditions. It has been estimated, there are wells with off-spec water where iron is 93%, 37% - manganese, 10% - oxidability, whereas total hardness – 7%.

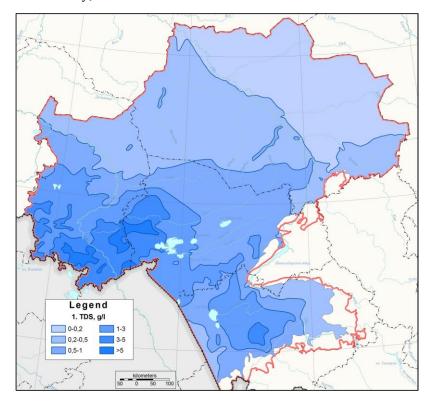
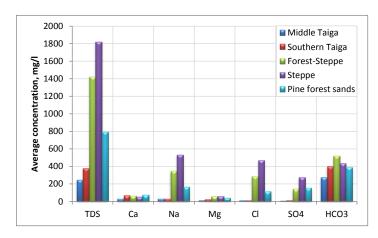


Figure 2. Paleogene deposits groundwater mineralization.

TDS growth is the result of total macrocomponent decrease (Cl, SO₄, HCO₃, Na, Mg, Ca).



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Figure 3. Mean content of macrocomponents in groundwaters of different landscape zones.

Both saltish and fresh water are typical for woodland grass zones. The saltish waters are widely distributed in typically grassland landscape with deficient wetness conditions and continental salt accumulation processes. Significantly high concentrations of sulfates (540—610 mg/l and over 1000 mg/l in Altai region), chlorides (over 350 mg/l) and high hardness are noted in mineralized Cl-SO₄, SO₄-HCO₃, SO₄ and SO₄-Cl water types. Wells with water of over 7 mg-eq/l composes 50% of Paleogene deposits in Kulundin artesian basin. Ground water in grassland and woodland grass zones comparable to taiga zones differ by high microcomponent concentrations.

3.2 Physico-chemical calculations of complexable and mineral-forming groundwater capacity

The complexable formation calculation results show that the role of compounds in microcomponents migration is insignificant. For example, tenth percent of Na migrates as complex compounds. Complex calcium and manganese compounds are more prevalent in migration, i.e. Mg migration - from 3,3 to 4,6 % and Ca migration – from 3,3 to 4,7 % of total content. Complex compounds of these elements are represented by hydrocarbonate forms.

Among the considered microcomponents the migration prevalence involves native ions ions, mainly ferrous iron. Ferrous complex compounds are only from 5.7 to 9.1% of total content. They are mainly carbonate and hydrocarbonate complex compounds.

Native ions also play an important role in the migration of manganese and zinc, i.e. from 66 to 79% and from 72 to 87%, respectively of total manganese and zinc content. The predminate complex compounds are carbonate and bicarbonate.

Comparable to micronutrients, Fe, Cu and Pb migration involves mainly complex compounds, i.e. only 0.03 - 0.24; 1.38 - 6.18 and 3.29 - 7.07%, respectively. Iron oxide migration involves prevailing carbonate and hydroxide, Pb - carbonate, bicarbonate and hydroxide, Cu - carbonate and bicarbonate compounds. In the groundwater of woodland grass and grasslands the water migration - chemical element relation transfers to complex compounds, mainly bicarbonate, carbonate, and even, sulfate (table 3).

Table 3. Macrocomponents (Na, Mg, Ca) and microcomponents (Mn, Fe, Cu, Zn, Pb) migration types in regional groundwater.

| Landsoanos | Migration compounds | | | | |
|---------------|--|---|--|--|--|
| Landscapes | Major | Secondary | | | |
| Central taiga | Na ⁺ , Mg ²⁺ , Ca ²⁺ , Mn ²⁺ , Fe ²⁺ , (FeOH) ²⁺ , | (MgHCO ₃) ⁺ , (CaHCO ₃) ⁺ , (MnHCO ₃) ⁺ , MnCO ₃ , (FeHCO ₃) ⁺ , | | | |
| | $Cu\Phi K$, $Cu(\Phi K)_2^{2-}$ Zn^{2+} , $(PbHCO_3)^+$, | $Fe(HCO_3)_2$, $FeCO_3$, $Fe_2(CO_3)_3$, Cu^{2+} , $(CuHCO_3)^+$, $CuCO_3$, | | | |
| | (PbOH) ⁺ , PbCO ₃ | (ZnHCO ₃) ⁺ , ZnCO ₃ , Pb ²⁺ , PbΦK | | | |
| South taiga | Na ⁺ , Mg ²⁺ , Ca ²⁺ , Mn ²⁺ , Fe ²⁺ , (FeOH) ²⁺ , | (MgHCO ₃) ⁺ , (CaHCO ₃) ⁺ , (MnHCO ₃) ⁺ , MnCO ₃ , (FeHCO ₃) ⁺ , | | | |
| | CuCO ₃ , Zn ²⁺ , (PbHCO ₃) ⁺ , (PbOH) ⁺ , PbCO ₃ | Fe(HCO ₃) ₂ , FeCO ₃ , Fe ₂ (CO ₃) ₃ , Cu ²⁺ , (CuHCO ₃) ⁺ , CuΦK, | | | |
| | | $Cu(\Phi K)_2^{2-}, CuOH^+, (ZnHCO_3)^+, ZnCO_3, Pb^{2+}$ | | | |
| Woodland | Na ⁺ , Mg ²⁺ , Ca ²⁺ , Mn ²⁺ , MnCO ₃ , Fe ²⁺ , | (MgHCO ₃) ⁺ , MgSO ₄ , (CaHCO ₃) ⁺ , CaCO ₃ , CaSO ₄ , | | | |
| Woodland | $(FeOH)^{2+}$, $Fe_2(CO_3)_3$, $CuCO_3$, Zn^{2+} , | (MnHCO ₃) ⁺ , MnSO ₄ , (FeHCO ₃) ⁺ , Fe(HCO ₃) ₂ , FeCO ₃ , Cu ²⁺ , | | | |
| grass | ZnCO ₃ , (PbOH) ⁺ , PbCO ₃ , (PbHCO ₃) ⁺ | (CuHCO3)+, CuOH+, (ZnHCO3)+, ZnSO4, Pb2+ | | | |

Note* major- 25 %; secondary – from 1 % to 25% of total content.

The results of water mineral - forming capacity are represented in table 4. Results analysis showed that groundwater formed in central taiga conditions generally are equilibrium to hematite, magnesite, kaolinite, quartz and sometimes with siderite. Water in south taiga territories comparable to the groundwater in the northern territories are equilibrium to a wide spectrum of carbonate and clay minerals. Besides previously mentioned minerals, groundwater of Quarternary and Paleogene deposits is equilibrium or practically equilibrium to goethite, calcium montmorillonite, siderite, calcite and aragonite.

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Groundwater of woodland grass and grassland is equilibrium to clay minerals (kaolinite, hydromica, Ca- and Mg-montmorillonite, and sometimes Na-montmorillonite), carbonates (often, calcite, aragonite, dolomite, siderite, strontianite, cerussite sometimes malachite), quartz and sulfites (almost always barite) (table 4).

| Landscape | Equilibrium (L > 0) | Practically equilibrium (0> L> -5) | Moderately unsaturated (-5> L> -10) | Unsaturated (-10 >L >-15) | |
|-------------------|---|---|---|--|--|
| Central taiga | | CaCO ₃ , CaCO ₃ aragonite, CaMg(CO ₃) ₂ , FeCO ₃ , MnCO ₃ , SrCO ₃ , BaSO ₄ | ZnCO ₃ , Cu ₂ CO ₃ (OH) ₂ , CaSO ₄ , CaSO _{4*} 2(H ₂ O), SrSO ₄ | BaCO ₃ , MgCO ₃ , PbSO ₄ | |
| South taiga | CaCO ₃ , CaCO ₃ aragonite, CaMg(CO ₃) ₂ | FeCO ₃ , MnCO ₃ , PbCO ₃ , SrCO ₃ , Cu ₂ CO ₃ (OH) ₂ , BaSO ₄ | BaCO ₃ , MgCO ₃ , ZnCO ₃ , CaSO ₄ , CaSO _{4*} 2(H ₂ O), SrSO ₄ | PbSO ₄ | |
| Woodland grass | CaCO ₃ , CaCO ₃ aragonite, CaMg(CO ₃) ₂ , PbCO ₃ , SrCO ₃ , FeCO ₃ , BaSO ₄ , SrSO ₄ | MnCO ₃ , ZnCO ₃ , Cu ₂ CO ₃ (OH) ₂ , CaSO ₄ , CaSO _{4*} 2(H ₂ O), PbSO ₄ | BaCO ₃ , MgCO ₃ | | |

Table 4. Saturation index (L) of groundwater to carbonate and sulfate minerals.

4. Conclusion

West Siberian territory is characterized by a variety of landscapes, climate and geomorphological conditions, which, in its turn, provides suitable conditions for different chemical groundwater types in hypegenesis zone of moderate climate and flat structures. This groundwater is equilibrium to different minerals.

From north to south, due to the influence of different horizontal landscape alterations, groundwater TDS increases, as well as chemical elements, furthering migration type evolution as complex compounds and expanding the secondary mineral equilibrium phase.

There are no problems concerning the drinking water quality in taiga conditions. Non-conventional water via appropriate simple water treatment methods could be easily converted be to the sanitary standards and regulations. In the grasslands of Western Siberia, with highly populated areas, the water of almost all water-bearing rocks, except for Quaternary alluvial deposits, often have components which exceeding total hardness and salinity, bromine, lithium, and sometimes sulfate, chloride, boron, strontium and barium content. Drinking water in taiga lands as groundwater contains high contents of iron, magnesium and organic compounds.

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