Underground water in Sukhodol Bay area (South Primorye)

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Abstract. The paper describes the specific chemical groundwater composition in Sukhodol Bay (eastern Ussuri Bay). The equilibrium between groundwater and carbonate-aluminosilicate minerals in water-bearing rocks was calculated. It was established that a fraction of the studied water was calcite saturated. However, dolomite and magnesium undersaturated groundwater is non-equilibrium with primary aluminosilicates.

1. Introduction

The significance of this research is relevant to the composition formation of highly calcium-chloride / calcium-sodium chloride concentrated water. In this case, this research was never conducted in the south Far East, Russia. However, groundwater occurrences with high salt concentration were found during prospect drilling of coal, hydrocarbon, limestone, mineral water, etc. [1].

The target of this research includes not only the investigation of the hydrogeochemical properties but also the evaluation of the highly-mineralized groundwater -primary rock-forming mineral equilibrium within Sukhodol Bay area (Figure1).

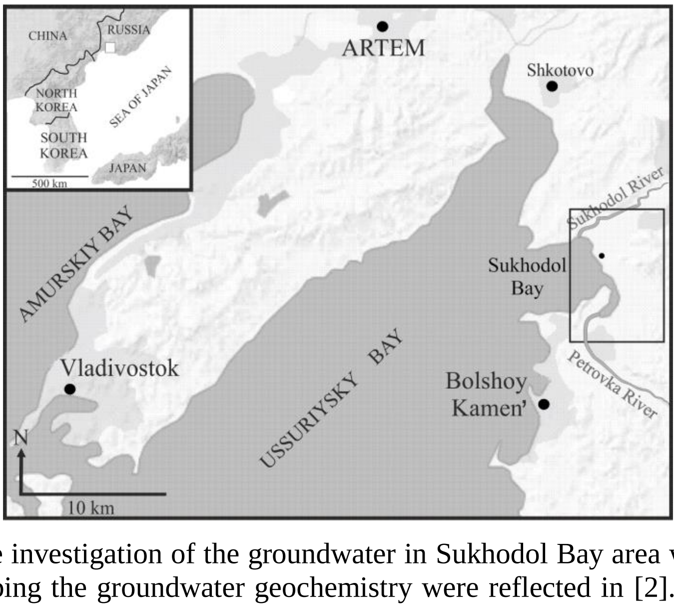

Figure 1. Map of study area.

The investigation of the groundwater in Sukhodol Bay area was launched in 2007. The first results describing the groundwater geochemistry were reflected in [2]. This paper embraces unique research data of the last few years (2014 and 2015) in chemical composition of groundwater and coastal marine water (150m from the well).

Macro-micro component analyses were conducted in the approved testing laboratory within the framework of Far East Geological Institute, Far Eastern Branch RAS. The major cations and anions were determined via ion chromatography liquid method (HPLC-10AVp, SHIMADZU). Bromine was analyzed in the Central approved chemical testing laboratory JSC "Primorgeology."

2. Geological background

Investigated area is located within Partisan depression, South Primorye trough (downside area Khanka massif) [3].

The most ancient formations within this region are Mid- Upper Triassic sediments embracing dark gray aleurolites with limestone-marl lenses and concretions, fine-grained sandstone and Ammonoidea layered. Upper Jurassic sediments include gray quartz-feldspar sandstones, sandstones with embedded coal lenses, limestone- siltstones. Cretaceous sediments are interlayered tuff siltstone, sandstone, weathered and weakly-fractured aleurolites, as well as fractured argillites. Recent sediments are found throughout the coastal area of Sukhodol estuary (liman) and subside to the coastline for about 500m. They are divided into two genetic types: (1) recent alluvial-marine sediments occurring immediately at subsurface and including dark gray fine-grained silt sand and peat bands The thickness is 1,5-6.0m. (2) alluvial Upper Quaternary sediments underlying alluvial-marine sediments embracing gravel with block masses and sand inclusions and sandy-clayey gravel boulders. The thickness is up to 10m.

3. Study area

The study area is characterized by complex hydrogeological conditions and varied hydrogeochemical cross-section. Hydrogeologically, the study area is located in the central part of South Primorye province, Primorye composite artesian basin. Based on the geological structure and hydrogeological conditions, the following aquifer types were defined:

1) Upper Quaternary aquifer – recent marine and alluvial-marine sediments (a-mQ_{III-IV}) are well-represented in Sukhodol bay mouth and embraces sands, sand loam and pebbles interbedded with silt. Static water level in wells is 1.3–1.7 m., well flow rates from 1.4 to 2.69 liter/sec., filtration coefficient – from 7.4 to 15.2 m/a day. Water here is predominately fresh, hydrocarbonate and hydrocarbonate chloride but, rarely calcium chloride or of mixed cation composition.

2) Upper Cretaceous aquifer- Korkian sediments. The hydrogeological conditions of this aquifer is associated with the litho-facies and structure-tectonic features of water-bearing rocks. Fault water is confined not only to zones of weathered Cretaceous rocks but also to zones of tectonic fracturing and intrusive contact disturbance. Static water level in wells is 0.8 m, well flow rates from 0.6–0.7 liter/sec. under depression level of 15–30 m. filtration coefficient for lithologically different rocks varies; for sandstones and conglomerates it is averagely 0.1–1.5 m/a day, but sometimes, 5–10 m/a day. Wells of up to 15m deep drilled at 0-500m from the coastal zone and 1km. from Sukhodol and Petrov Rivers revealed low-medium salt water (0.6–8.5 gr./liter); whereas drilled 15-300m wells revealed high calcium chloride sodium-calcium chloride mineralized water and brine water (20–110 gr/liter).

4. Results and discussion

Water chemical composition is described in table 1. The following types of water were studied: fresh, salt and brine water, as well as marine water. Based on the chemical water composition data depicted in table 1 and previous published data [2], three hydrogeochemical zones were identified in the cross-section:

1. fresh water with mineralization of up to 1 gr/liter, mixed anion-cation composition (calcium sulphide-hydrocarbonate, calcium-sodium chloride-hydrocarbonate). Non-artesian water extends to a depth of 15m. and is confined to Upper Quaternary-Recent marine and alluvial-marine sediments. Probably, there are traces of the water- marine sediment interaction in this zone;

2. calcium sodium-chloride brine water with mineralization of 50gr/liter was found in the depth interval of 15-250 m;

3. calcium chloride, calcium sodium and sodium-chloride salt water with mineralization of 27 to 35 gr/liter was found in the depth interval of 250-300m.

Brine and salt water zones (2 and 3) confined to Upper Cretaceous terrigenous sediments have pressure head (+1.4 m). Water-bearing rocks embrace aleurolites, tuff aleurolites, fine-grained sandstones and argillites. The difference between 2nd and 3rd zones involves mineralization and macro-micro component variations. These waters usually have high iron-manganese-strontium content. Bromine content is at the average value level of ocean water (Horns value – 67 mgr/liter) [4], iodine is not found.

Table 1. Chemical composition of studied waters.

Parameters	Measure-ment unit	Well № 2PR					Water from Sukhodol Bay
		Sample date					
		05.07.2014	15.02.2015	15.09.2015	17.09.2015	17.09.2015	15.09.2015
Sampling depth	m	250-300				0.5-10	
pH		7.42	6.89	7.1	7.42	7.43	6.6
Mineralization	g/l	35.0	31.8	35.5	33.9	0.62	5.9
HCO_3^-		0.015	0.016	0.017	0.0175	0.277	0.211
SO_4^{2-}		–	–	0.49	0.495	0.162	0.407
Cl^-		22.3	20.2	22.1	21.1	0.016	3.2
Ca^{2+}		9.5	9.4	9.6	9.5	0.12	0.095
Mg^{2+}		0.29	0.18	0.27	0.186	0.016	0.19
Na^+		3.0	2.02	3.0	2,6	0.026	1.8
K^+		0.007	0.005	0.007	0.003	0.005	0.063
Si		–	0,0026	0.003	0.004	0.015	–
Fe	ppm	1.07	0.95	1.35	1.24	0.08	0.8
Mn		5.37	4.93	52	7.37	0.0047	0.02
Br		–	–	64.2	58.5		9.11
Sr		204.8	171.5	206.8	248,1	0.732	–
Ba		0.37	0.4	0.5	0.59	0.09	0.0004
Li		1.5	3.5	3.5	1.93	0.011	0.002
Relationship between components							
Cl/Br		–	–	344	360	–	347
rNa/rCl		0.21	0.15	0.21	0.19	7.4	0.87
Ca/Cl		0.42	0.46	0.43	0.45	2.4	0.03
Formula of ion-salt composition		Cl/Na-Ca	Cl/Ca	Cl/Na-Ca	Cl/Ca	SO_4-HCO_3/Ca	Cl/Na

The marine water analysis from Sukhodol Bay revealed the fact that this water is of sodium chloride composition, having minimum pH value and total salt content, which, in its turn, is associated with the fresh water ingression from Sukhodol and Petrovks rivers into the bay (Figure 1), as well as the low bay depth.

The prevalence of this or that chemical element in the solution is not accidental and is governed by characteristic origin aspects and succeeding groundwater conversion in each specific case. For example, to determine the genesis of high-salinity water the Cl/Br, rNa/rCl, Ca/Cl coefficient ratio was applied [5].

Calculated genetic coefficient values of investigated water is listed in table 1. These calculations showed that high-salinity water as a consequence of low sodium content exhibits minimum coefficient value of rNa/rCl, while this ratio for marine water exhibits 0.87. The extent of water metamorphization can be inferred by the distinct increase of calcite content after brine burial. According to this ratio value these waters could be correlated to intensively metamorphosed ones.

The composition and salinity of water depends on numerous factors and processes, including the following major ones: composition of host rocks, geomorphological and landscape features, hydrodynamic conditions and others. Water exchange intensity is the main influence factor for high-salinity groundwater. Hydrogeologically, the formation of calcium chloride, sodium-calcium chloride high-salinity water is governed by the impeded water exchange, which, in its turn, reveals relatively low reservoir properties of Mesozoic Primorye rocks. This is also confirmed by previous data showing that the content value of tritium in water is less than 0.3 TE. This clearly demonstrates the aquifer integrity including brines, i.e. hindering its mixing with recent waters and water exchange.

To determine the formation conditions of high salinity groundwater chemical composition in the studied area equilibrium state of water to leading minerals in host rocks was calculated (Figures 2, 3).

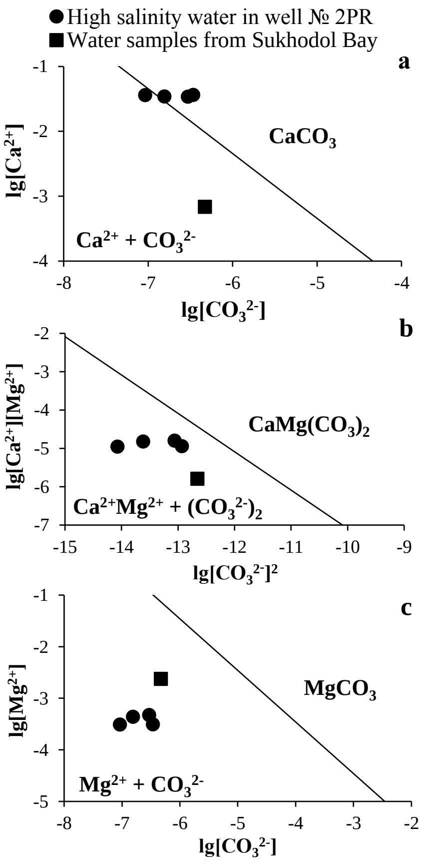

Figure 2. Water saturation intensity relative to (a) calcite, (b) dolomite, (c) magnesium

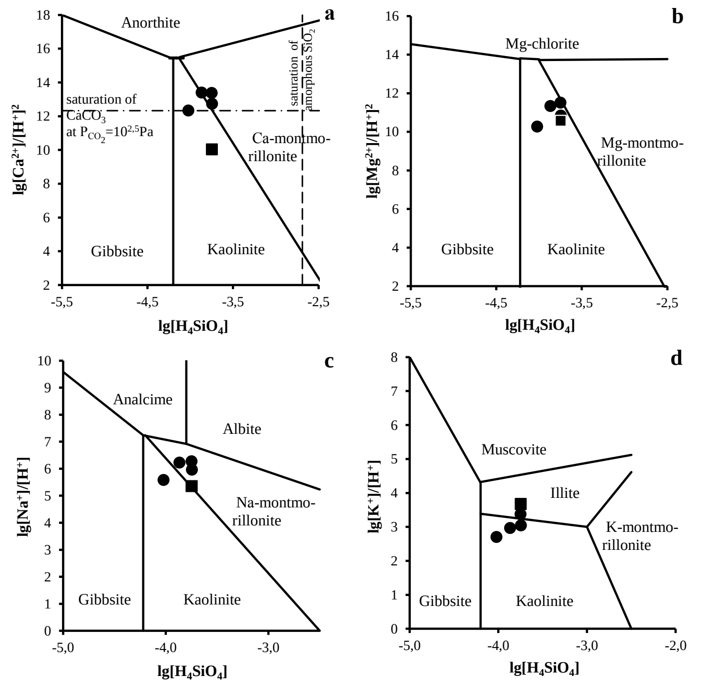

Figure 3. Diagrams of aluminosilicate mineral saturation intensity in water under standard conditions: (a) HCl-H_2O-Al_2O_3-CO_2-CaO-SiO_2 system; (b) HCl-H_2O-Al_2O_3-CO_2-MgO-SiO_2 system; (c) HCl-H_2O-Al_2O_3-CO_2-Na_2O-SiO_2 system and (d) HCl-H_2O-Al_2O_3-CO_2-K_2O-SiO_2 system. (Legend – Figure 2).

Component activity in aqueous-based solution is calculated via HydroGeo program [6]. The selection criterion identified the possible calculations of activity by applying Pitzer algorithm, designed high salinity water and brines.

In model matching the most common minerals from the studied cross-section were imported into the system (aluminosilicate minerals, calcite, dolomite, magnesium and others). Calculation of component activity was performed in standard (laboratory) conditions.

Thermodynamic calculations in determining the water to carbonate minerals equilibrium (Figure 2) revealed the fact that a portion of water is saturated with calcite, while other waters are undersaturated relative to dolomite and magnesium.

Despite the continuous interaction of investigated high salinity water with rocks, the equilibrium to primary aluminosilicate minerals was not observed. Simultaneously, there exists the water to kaolinite, illite, Ca- and Na montmorillonite equilibrium (Figure 3).

Mineralization, Ca, Na, Mg, K, Si content and pH value govern the equilibrium degree of high salinity water to aluminosilicate minerals. Secondary mineral formation (carbonates, clays, etc.) is the barrier in establishing the equilibrium with primary aluminosilicate minerals.

5. Conclusion

Based on hydrogeological and hydrogeochemical data the formation conditions of unique high salinity water in Primorye territory, located in the coastal area of Sukhodol Bay, were determined. It was established that hydrogeochemical water behavior is governed by sedimentation water and sedimentary rock interaction within slow water exchange zone. Analysis results showed that the high salinity groundwater -rock system preserves its equilibrium- non-equilibrium state, which, in its turn, is determined by the non-consistent interaction of its components, and, respectively, consistent evolution of groundwater composition.

Acknowledgments

The research was supported by Russian Foundation for Basic Research funding, project No. 15-35-50438

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