Use of Subpermafrost Groundwater Resources for Drinking Water Supply in Yakutia

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Abstract. In central Yakutia, Russia, the use of subpermafrost water for domestic purposes is limited due to the elevated levels of lithium and some other elements. Based on a review of available data on well water chemistry, this study estimated lithium contents in groundwater of the southern Yakutian Artesian Basin. The highest concentrations of lithium were found to occur in subpermafrost water of the Lower Jurassic – Middle Cambrian aquifer system due to the presence of clay rocks. The ion exchange method was demonstrated experimentally to be capable of reducing lithium levels to the drinking water standard. A series of laboratory experiments performed by the author produced graphical curves of lithium removal from model solutions and natural subpermafrost waters. They also provided the kinetic and dynamic characteristics of the lithium removal process. In the course of the experimental studies on the subpermafrost water purification of casting by the ion exchange method, content of lithium reduced from 0.41 to 0.006 mg/L. The results of this study may be useful for developing subpermafrost water treatment schemes for drinking purposes.

1. Introduction
The problem of inadequate drinking water supply in the Republic of Sakha (Yakutia), Russia, associated with severe climatic conditions can be partially solved by adopting groundwater as an additional source of public water supply. Of the main groundwater types occurring in permafrost regions, subpermafrost aquifers are most widespread. The stable chemical composition, bacteriological purity, and natural protection from surficial contamination make them a promising source of domestic water supply. However, despite the large volume of subpermafrost water, its use for drinking purposes is limited due to the elevated levels of some elements, including lithium [1]. The maximum allowable level of lithium in drinking water set by the Russian regulatory authorities is 0.03 mg/L.

Lithium is widely distributed in the Earth's crust [2]. It only appears naturally in the form of compounds and occurs predominantly in acidic igneous and sedimentary rocks at an average level of 65 g/t [3, 4]. In the main types of sedimentary rocks, its concentration increases from 17.4 g/t in carbonate rocks and 29 g/t in sands to 54.7 g/t in clays and 65 g/t in shales, reaching a maximum of 183 g/t in alumina rocks [5]. Lithium occurs as a silicate, fluoride, and phosphate, as well as a chloride in solutions of different origin. The natural abundance of lithium in sea water is 0.17*10^-4% (0.17
mg/L) and 2.5*10^{-7}% (0.0025 mg/L) in river water [4, 6]. The highest levels of lithium in low-salinity groundwater range from hundredths to a few tenths of mg/L.

Micas are the most common lithium-bearing minerals, which alter to clay minerals by hypergenic processes [7]. In clay minerals, lithium is present as an isomorphic impurity; some part is adsorbed on the surface of clay minerals and thus can migrate into groundwater as the cation Li^+.

Lithium is known to have carcinogenic properties and to cause toxic effects, such as deterioration of renal function and disorders of the cardiovascular and central nervous systems [8, 9]. In the human body, it tends to accumulate in the thyroid gland and bone tissue [10-12]. Lithium has been used in clinical medicine to treat severe psychiatric disorders. However, despite proven effectiveness, its use in medical practice is limited due to numerous side effects [13].

The absence of proven methods of lithium removal from drinking water makes selection of treatment technologies applicable to subpermafrost groundwater difficult. The existing techniques of lithium extraction from solutions are specific to hydrometallurgy and inorganic chemistry and not appropriate for drinking water systems. Commonly, reverse osmosis, sorption and electrodialysis are utilized to recover lithium from aqueous solutions [14-17].

At present, reverse osmosis plants are widely used for water treatment. However, it is not effective against lithium and leads to significant production losses of water. Long-term experience of their operation in Yakutsk shows that the producers receive not more than 50% purified from the total volume of the selected water [18].

The purpose of this study is to develop a technology for removing lithium ions from Yakutia's subpermafrost groundwater that can be used in drinking water treatment systems.

2. Methods

This study investigated subpermafrost groundwater water samples from the Yakutian Artesian Basin having an initial lithium-ion concentration of 0.41 mg/L. To examine the effect of total water salinity, model solutions prepared by dissolving a lithium ion standard in distilled water to a lithium concentration of 0.5 mg/L were also studied.

Commercially available DowexTM HCR-S/S (Na) Cation Exchange Resin containing active sulfonic groups was used as a sorbent. The total exchange capacity of the cation exchange resin of this brand, corresponding to the number of active ion-exchange functional groups capable of being exchanged per unit volume, is 1.9 eq/L. The granulometric composition is characterized by grains of monospheric type, 0.6 to 0.8 mm in size.

Water chemical analysis was performed with a Kapel-104T capillary electrophoresis instrument following the standard procedure.

Lithium extraction curves were obtained at a constant temperature by the variable volume method. In a series of test tubes, 0.1 L of solution was added to different masses, mi, of the ion-exchange resin and left for 1 h and 24 h until equilibrium was reached.

The kinetics of lithium sorption was studied under static conditions with continuous stirring. One liter of solution was added to a series of cylinders each containing 50 g of ion exchange resin. The water was sampled at regular time intervals for measurement of current lithium concentrations.

Dynamic characteristics were studied using a laboratory filter column filled with 0.1 L of the ion exchange resin. The filtered natural subpermafrost water was sampled at regular volume intervals and measured for residual lithium concentration.

The recovery of lithium, S (%), from subpermafrost water samples and model solutions at a given time t was calculated as follows:

$$S = \frac{(C_0-C_t)}{C_0} \times 100\%$$

where $C_0$ is the initial concentration of lithium ions (mg/L); $C_t$ is the concentration of lithium ions at time t (mg/L).
3. Results and discussion
Although the level of lithium in subpermafrost water of the Yakutian Artesian Basin is low, it is several tens of times higher than the maximum concentrations set by drinking water regulations.

The use of ion exchange can be a way to remove lithium from water [19]. This method is based on the capability of ion exchangers to absorb positive or negative ions from a solution in exchange for an equivalent number of similarly charged ions.

Testing of the ion exchange method for water purification from lithium ions was carried out in the Laboratory of permafrost groundwater and geochemistry of the Melnikov Permafrost Institute of Siberian Branch of Russian Academy of Sciences.

During the purification process, lithium ions are replaced by sodium ions, as confirmed by a decrease in lithium ions and insignificant increase in sodium ions in the treated water [18].

3.1. Hydrochemical setting
Lithium in fresh subpermafrost groundwater water of the Yakutian Artesian Basin has been best studied in the Tuymaada Valley where the city of Yakutsk is located.

In most of the area, subpermafrost water occurs in the terrigeneous Lower Jurassic aquifer system. This system predominantly consists of sandstone, often with gravels and pebbles. Its lower part contains lenses and interbeds of conglomerates, while the upper part is interbedded with siltstone and argillite with some thin lenses of coal [20, 21]. Groundwater is a sodium chloride-bicarbonate type, with dissolved-solids concentrations varying from 0.7 to 1.9 g/L and lithium contents in the range of 0.15 to 0.55 mg/L.

In the southern part of the study area, the Lower Jurassic aquifer system is hydraulically connected to the Middle Cambrian aquifer system which consists of limestone interbedded with marl and dolomite. Groundwater in the Middle Cambrian rocks is generally sodium bicarbonate-sulfate, and to a lesser extent sodium chloride-bicarbonate, with dissolved-solids contents ranging from 1.1 to 2.6 g/L and lithium levels from 0.16 to 0.34 mg/L. Water in the wells producing from both the Lower Jurassic and Middle Cambrian aquifer systems is of the sodium sulfate-chloride-bicarbonate or sodium chloride-sulfate-bicarbonate type. The lithium content in groundwater varies widely, from 0.12 to 0.85 mg/L [18].

Wells in the northern part of Yakutsk penetrated the Middle and Upper Jurassic rocks below the depth of 380 m. The Middle Jurassic materials primarily consist of sandstone. Groundwater is sodium bicarbonate type, with dissolved-solids concentrations of 1.3-1.5 g/L and lithium contents of up to 0.3 mg/L.

3.2. Experimental results
After contacting subpermafrost water with Na-cation exchange resin, the lithium content decreased from 0.41 to 0.006 mg/L, which did not exceed the established maximum permissible concentrations for drinking water.

The content of the main cations in the natural subpermafrost water before and after the lithium removal experiments by the ion exchange method is shown in table 1.

| Cations, mg/L | Maximum contaminant level in drinking water | Initial water | Water after ion exchange |
|---------------|--------------------------------------------|---------------|--------------------------|
| Li⁺           | 0.03                                       | 0.41          | 0.006                    |
| Ca²⁺          | -                                          | 15.7          | 0.60                     |
| Mg²⁺          | 50                                         | 21.8          | 0.80                     |
| Sr²⁺          | 7                                          | 1.56          | 0.12                     |
| Na⁺           | 200                                        | 183.6         | 198.3                    |
It was established that during the ion exchange the sodium concentration is increased due to the retained hardness, lithium and strontium cations.

Thus, the replacement reactions of lithium ions with sodium ions on Na-cation exchange ion resin will be written as follows [1]:
in the molecular form:
\[ \text{NaR} + \text{LiCl} \rightarrow \text{LiR} + \text{NaCl}, \]
in the ionic form:
\[ \text{Na}^+\text{R}^{-} + \text{Li}^+ \rightarrow \text{Li}^+\text{R}^{-} + \text{Na}^+, \]
where R is a complex cationite radical not subject to dissolution in an aqueous medium.

The regeneration reaction of the Na-cation exchange resin in the molecular will have the form:
\[ \text{LiR} + \text{NaCl} \rightarrow \text{NaR} + \text{LiCl}. \]

The study of lithium sorption under static conditions has shown that increasing the amount of ion exchange resin increases the recovery of lithium up to 90% for natural groundwater samples and 99% for model solutions at a resin dose of 100 g/L and contact time of 24 h, as shown in the figures 1 and 2. The trend lines obtained from the experimental data are described by a logarithmic function with the coefficient of determination of 0.91 to 0.99.

The kinetic curve shown in figure 3 indicates that the rate of ion exchange is highest at the initial stage. The ion exchange equilibrium is reached within 15 minutes, but the most rapid exchange occurs during the first 5 minutes of phase contact.

Figure 4 shows the relationship between lithium recovery and treated water volume obtained from repeated cycles of passing subpermafrost water through the ion exchange column. The relationship is best described by a fourth degree polynomial with a R-squared value of 0.99. The maximum lithium uptake at the initial stage was 99%. Afterwards, lithium ions broke through in concentrations exceeding the drinking water standard due to the exhaustion of the resin. The exchange capacity of the resin is fully restored by regenerating it with a NaCl solution.
Figure 3. Kinetic curve of lithium sorption from natural subpermafrost water and model solutions.

Figure 4. Lithium recovery vs. filtrate volume of natural subpermafrost water.

4. Conclusion

Micas and clays may be the sources of lithium in subpermafrost groundwater. Elevated chloride levels in water appear to enhance leaching of lithium from rocks. This type of water is observed in the wells producing from the interconnected Lower Jurassic and Middle Cambrian aquifer systems. No clear correlation was found between lithium concentration and total dissolved solids or any major element.

If subpermafrost aquifers are planned to be used as alternative, or the only, sources of water supply, it will be necessary not only to conduct investigations to understand the hydrogeological and hydrochemical conditions, but also to undertake measures to improve water quality to the acceptable level.

In the course of conducting experiments under static conditions, it was established that the degree of extraction of lithium from natural subpermafrost waters and model solutions is more than 90%. When water was filtered on a model plant, the efficiency of lithium removal from natural subpermafrost water was 99%.

The results of this study demonstrate that ion exchange is an high effective and promising method for removing lithium ions from the Yakutian subpermafrost groundwater and thus can be used in the development of water treatment schemes [1].

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