Estimation of uranium migration parameters in sandstone aquifers

A.I. Malov

Institute of Environmental Problems of the North at the Ural Branch of the Russian Academy of Sciences, 23 Severnoy Dviny Emb., Arkhangelsk, 163061, Russia

ABSTRACT

The chemical composition and isotopes of carbon and uranium were investigated in groundwater samples that were collected from 16 wells and 2 sources in the Northern Dvina Basin, Northwest Russia. Across the dataset, the temperatures in the groundwater ranged from 3.6 to 6.9 °C, the pH ranged from 7.6 to 9.0, the Eh ranged from −137 to +128 mV, the total dissolved solids (TDS) ranged from 209 to 22,000 mg L^{-1}, and the dissolved oxygen (DO) ranged from 0 to 9.9 ppm. The ^{14}C activity ranged from 0 to 69.96 ± 0.69 percent modern carbon (pmC). The uranium content in the groundwater ranged from 0.006 to 16 ppb, and the ^{234}U:^{238}U activity ratio ranged from 1.35 ± 0.21 to 8.61 ± 1.35. The uranium concentration and ^{234}U:^{238}U activity ratio increased from the recharge area to the redox barrier; behind the barrier, the uranium content is minimal. The results were systematized by creating a conceptual model of the Northern Dvina Basin's hydrogeological system. The use of uranium isotope dating in conjunction with radiocarbon dating allowed the determination of important water—rock interaction parameters, such as the dissolution rate:recoil loss factor ratio R_d:p (a^{-1}) and the uranium retardation factor:recoil loss factor ratio R:p in the aquifer. The ^{14}C age of the water was estimated to be between modern and >35,000 years. The ^{234}U—^{238}U age of the water was estimated to be between 260 and 582,000 years. The R_d:p ratio decreases with increasing groundwater residence time in the aquifer from n × 10^{-5} to n × 10^{-7} a^{-1}. This finding is observed because the TDS increases in that direction from 0.2 to 9 g L^{-1}, and accordingly, the mineral saturation indices increase. Relatively high values of R:p (200—1000) characterize aquifers in sandy—clayey sediments from the Late Pleistocene and the deepest parts of the Vendian strata. In samples from the sandstones of the upper part of the Vendian strata, the R:p value is ~24, i.e., sorption processes are expressed more weakly, and uranium is possibly desorbed from the sediments. Overall, these results provide a better understanding of the evolution of uranium isotopes in groundwater systems.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

The radioactivity of groundwater contributes significantly to the total radioactivity of the environment. Isotopes of uranium primarily determine the radiological suitability of groundwater for drinking purposes. Based on the recommendations of the World Health Organization (2011), the provisional guideline ^{238}U content is 0.030 mg L^{-1} (chemical aspects), which corresponds to an alpha activity of approximately 0.4 Bq L^{-1}. However, groundwater also contains ^{234}U isotopes with activities exceeding that of ^{238}U due to the recoil of ^{234}Th and preferential leaching of ^{234}U compared to ^{238}U (Cherdyntsev, 1955; Rosholt et al., 1963; Kigoshi, 1971). The ^{234}U:^{238}U activity ratio can reach 10 and more, and the

gross alpha activity increases by the same factor. The screening levels for drinking water, below which no further action is required, are 0.5 Bq L^{-1} for gross alpha activity. The guidance level of ^{234}U is 1 Bq L^{-1} (radiological aspect).

Uranium almost completely transfers into the groundwater from water-bearing sediments via cracks and pores, through which water moves from recharge to discharge areas. The oxidizing parts of aquifer are usually characterized by increasing ^{238}U content over the groundwater residence time; behind the redox barrier, the uranium content is minimal. The redox barrier is characterized by the highest ^{234}U:^{238}U activity ratios (Osmond and Cowart, 1976; Tricca et al., 2000).

Thus, evaluating the prospects of using fresh and mineral groundwater requires knowledge about the redox conditions in the aquifer and the parameters that determine migration of uranium.

The transport of uranium in solution is reasonably well

described with a standard advection−dispersion−exchange formulation

$$\Delta time = advection + weathering + recoil + desorption$$
$$+ production - precipitation - decay - adsorption$$

(Porcelli, 2008; Maher et al., 2004; Ivanovich et al., 1991). Among the many factors, the main ones are.

- t − Groundwater residence time in the aquifer (time),
- v − Groundwater flow velocity (advection),
- R_d − Dissolution rate (weathering − precipitation),
- R − Retardation factor (adsorption − desorption),
- p − Recoil loss factor (recoil + production), and
- λ_4 − Decay constants for ^{234}U (decay).

Suitable equations were derived by Andrews and Kay (1978), Fröhlich and Gellermann (1987), Ivanovich et al. (1991), and Porcelli (2008) to provide a $^{234}U-^{238}U$ dating method for groundwater under oxidizing conditions. However, the values of R, R_d (a^{-1}) and p needed to be determined. In turn, the recoil loss factor value p depends on the SSA (specific surface area). The published SSA values in sandy aquifers range from $0.9-1.8$ m^2 kg^{-1} (Andreas and Kay, 1983) to $330-390$ m^2 kg^{-1} (Maher et al., 2006). Accordingly, the ranges of R and R_d can be calculated using these formulas. Therefore, we consider it more appropriate to show R, R_d and p in the form of their ratios: R_d:p (a^{-1}), R:p and R_d:R (a^{-1}) (see Supplementary Information). This paper analyzes the possibility of combining radiocarbon and uranium-isotope methods to estimate these parameters, using the North Dvina Basin in Northwest Russia (Fig. 1) as an example.

We used the flow piston model (Münnich, 1957, 1968) to estimate the ^{14}C residence time of groundwater in an aquifer. This model assumes uniform groundwater movement along a flow line without considering the diffusion and dispersion of solutes. This model takes into account both carbon isotopic exchanges dominated by gaseous CO_2 in the unsaturated zone and carbon isotopic exchanges dominated by solid carbonate minerals in the saturated zone (Han and Plummer, 2013; Mook, 1976) (see Supplementary Information).

We also used the advective transport model (Porcelli, 2008) to estimate the R_d:p under oxidizing conditions for uranium. We used a simple model of the down-flow radioactive decay of ^{234}U excess in solution (Ivanovich et al., 1991) to estimate the $^{234}U-^{238}U$ residence time of groundwater under reducing conditions for uranium (see Supplementary Information).

2. Overview and geological structure

The Northern Dvina Basin represents an onshore continuation of the Dvina Bay (White Sea) and extends from the Dvina Estuary (White Sea) in the west to the Pinega River mouth in the southeast (Fig. 1a). The present-day basin is a sea-facing depression composed of sequences with different ages, namely, the Middle Carboniferous (Moscovian) carbonate-terrigenous (C_2), Upper Devonian−Lower Carboniferous terrigenous (D_3-C_1), and Vendian (Ediacaran) Padun (Vpd) and Mezen (Vmz) Formations (Fig. 1b). The basin is largely filled with clayey sediments from the Mikulinian interglacial (mIIImk) Boreal sea. The clays are underlain by a 10 to 15 m-thick sequence of loams from the Moskovian moraine (gIIms). The underlying Vendian terrigenous sequence ($600-700$ m) is composed of alternating sandstones, siltstones, and mudstones. The Mikulinian clays are overlain by a 10 to 15 m-thick sequence of Valdaian glaciation (gIIIvd) sediments, which are

largely represented by moraine boulder loams with local fluvioglacial and glaciolacustrine sands. The valley of the Northern Dvina River is filled with Upper Pleistocene and Holocene (QIII−IV) sandy−clayey sediments.

The upper part of the Vendian aquifer in the central part of the basin is characterized by inverse zonality and decreasing groundwater mineralization from 29 to 12 g L^{-1} (Fig. 1b). This pattern is primarily caused by the freshening of groundwater due to the long-term existence of terrestrial conditions in the Mesozoic and Cenozoic. The desalination of groundwater ceased after the Mikulino Sea's transgression ~130 ka ago (Lisitsyn, 2010). Subsequently, the upper part of the Vendian aquifer began to receive saline interstitial water, which was squeezed out under the load of the Valdai glacier from Mikulinian interglacial marine clays. After the formation of the Northern Dvina River valley due to the erosional activity of water that flowed from the melting glacier, the valley cut the Mikulinian clayey sequence almost up to its base. Saline water from the aquifer sediments of the terrigenous Padun Formation began to flow into the river valley and were replaced later by freshwater from the recharge area (Fig. 1b).

More information about the hydrogeological conditions of the Northern Dvina Basin has been described by Malov (2013).

3. Material and methods

3.1. Sample description and preparation

Nineteen water samples were collected in April 2012 and 2014; Fig. 1 depicts the study site and the sampling locations. Samples Ks and Kss were obtained from springs, while samples Kw, Il and 8q were collected from a well and represent groundwater from a Late Pleistocene sandy aquifer. The remaining samples consist of groundwater obtained from boreholes and represent groundwater from Vendian siltstone and sandstone aquifers.

All the water samples were filtered through 0.45 μm acetate cellulose in the field. The solutions filtered for cation and trace element analyses were acidified with double-distilled HNO_3 (pH < 2); the samples for anion analysis and ^{14}C were not acidified.

3.2. Analytical procedures

The water temperature, pH, Eh, and DO were measured in the field using portable HANNA instruments with uncertainties of 0.1 °C, 0.05 pH units, 0.1 mV, and 5%, respectively, representing a coverage factor k = 2. The calcium, magnesium, sodium, and potassium concentrations were determined with an uncertainty of 1−2% by using an atomic absorption spectrometer (AAS) (Perkin−Elmer 5100 PC). The alkalinity was measured by potentiometric titration with HCl by an automated titrator (Metrohm 716 DMS Titrino) using the Gran method (detection limit 10^{-5} M, uncertainty at ≥0.5 mmol L^{-1} 1−3%, at <0.5 mmol L^{-1} 7%, representing a coverage factor k = 2). The major anion concentrations (Cl^-, SO_4^{2-}) were measured by ion chromatography (HPLC, Dionex ICS 2000) with an uncertainty of 2%, representing a coverage factor k = 2. The total dissolved uranium was determined without preconcentration by inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 7500ce) at GET, Toulouse. A good agreement (≤10%) between the measured and certified uranium concentrations in a certified river water sample (SLRS-5) was achieved.

The uranium isotopes in the groundwater were determined in accordance with Malyshev et al. (1999), as also described by Fröhlich (2013). The spectrometric detection of alpha particles was performed using an alpha spectrometer ("Progress-alpha", uncertainty 10−20%, representing a coverage factor k = 2). The measurement uncertainties for uranium are reported individually