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title: **The groundwater age and diluted in water helium distribution in the Lithuanian aquifers**

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INTRODUCTION

The interpretation of groundwater residence time in the artesian basins by radiocarbon data is complicated and apparent. The decrease of radiocarbon activities during time is conditioned not only by radioactive decay but also by geochemical processes in groundwater carbonate system, which regulated the carbon-14 activity of dissolved inorganic carbon in groundwater. Progress in regional studies of the delta carbon-14 values of the aquifers in Lithuania has been made by Banys et al. (1979), Juodkazis et al. (1995), Mažeika and Petrošius (1996), Mokrik and Mažeika (2002), Mokrik (2003), where the initial values of carbon-14 data were quoted via dilution factor (q) initiated as 0.75-0.85, which reflected a statistical index of carbonate dilution in the aquifer. In the some cases dilution factor was calculated using stable isotope carbon-13 data (Mokrik (2003), Mokrik et al. (2009).

The carbon isotopes composition of saturated zone should be a result of many factors – fractionation of dissolved carbon dioxide in the unsaturated "open" system condition, involve of the "dead" carbon during weathering and dissolution of carbonaceous minerals, fall from solution of re-precipitated carbon and other constituents, mixing of different age waters through leakage, decay of radioactive carbon-14 in flow system. These processes direct regulate the carbon-14 activities and complicate assessment of groundwater ages. The corrected age of groundwater was determined from the well-known decay equation (Clark and Fritz 1997):

$$t = -8267 \cdot \ln \frac{a^{14}C_{DIC}}{q \cdot a_0{}^{14}C} \quad (1)$$

where: t – is the age of groundwater; q – the dilution factor; $a_0{}^{14}C$ - the initial carbon-14 activity of water at the time of recharge; $a^{14}C_{DIC}$ - the measured groundwater activity of carbon-14.

This paper is resulted from encompasses the isotope-geochemical aspects of different correction methods used to estimate ages of groundwater in Lithuania. The isotopical-hydrogeochemical data in this study mainly are made in the Radiocarbon Laboratory of the Geological Institute of Lithuania.

AGE OF GROUNDWATER

The main problem to find an appropriate correction model of groundwater age is requirement to determine initial carbon-14 content and to draw the geochemical reactions through additional representative parameters as such as delta carbon-13 and tritium along the pathways from the recharge to discharge area. One of the simple modus to eliminating bombs related carbon-14 activities in DIC is to plot the tritium and carbon-14 values of samples on the diagram. The initial carbon-14 activities for different aquifers can be find from this versus plot, where the distribution curves hits the detection limit boundary of tritium. Whereas many samples has high tritium content, water in these wells water contains a large content of modern groundwater (<50 years old). The groundwater with the tritium –bearing water had so named "future" radiocarbon age uncertainty. Thus, the apparent radiocarbon age of groundwater will be adjusted. Below of the tritium detection boundary the groundwater carbon-14 activities should be exclude bomb outcomes in the infiltration recharge water. Tritium qualitative-quantitative age estimation in Lithuania based on the more 200 tritium bearing water samples shows, that groundwater with tritium activity below 2.5 TU have the lying depth interval 14-

125 meters and are recharged earlier as 450 years and is submodern (Mažeika and Petrošius 1996). To estimate of the initial carbon-14 activities of groundwater in the Lithuanian aquifer systems we are pick the tritium detection limit value equal to 2.5 TU (Figure 1). As shown in Figure 1, the initial carbon-14 activity for Devonian aquifers can be accepted as 50 pmC corresponding to the carbon-14 activities average except the Middle and Lower Frasnian aquifers, where the average activity is much lower – 10 pmC, because by evidence of large karst system with gypsiferous layers.

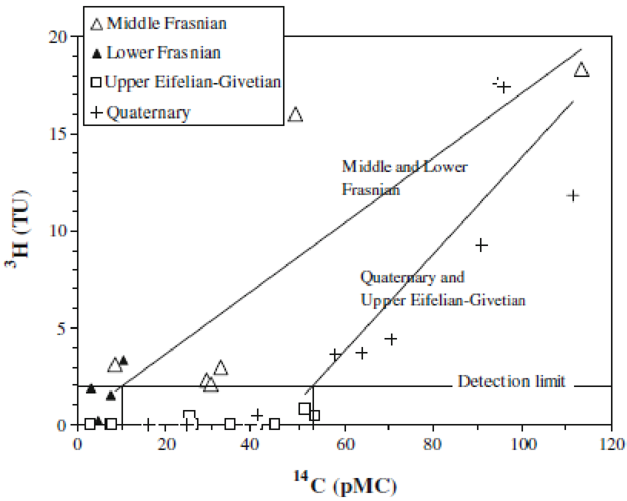

Figure 1. Relationship between 14C and tritium of studied groundwater (based on Mokrik et al. 2009).

The simple combined model regarding to delta carbon-13 and carbon-14 activities was earlier found and well-known:

$$a_0{}^{14}C = a^{14}C_{soil}\,\frac{\partial^{13}C_{DIC}}{\partial^{13}C_{soil}} \qquad (2)$$

Neglecting geochemical reactions, the age equation (1) is then modified:

$$t = 8267 \cdot \ln a^{14}C_{soil}\,\frac{\partial^{13}C_{DIC}}{\partial^{13}C_{soil}\,a^{14}C_{DIC}} \qquad (3)$$

Assume that carbon-14 activity value of soil is around 100% and delta carbon-13 value respectively -25‰, the formula (3) is:

$$t = 8267 \cdot \ln \frac{-4\partial^{13}C_{DIC}}{a^{14}C_{DIC}} \qquad (4)$$

Ferronsky et al. (1984) were recommended for a “close” aquifer system conditions use in equation (4) instead value -4 number of -5.7, because has recipient accordingly the carbon-14 activity value of recharge water 85 pmC and the delta carbon-13 value -14.9‰ respectively.

A groundwater corrected carbon-14 residence times in Lithuanian aquifers was calculated by the carbon mixing (Pearson and Hanshaw 1970; Mook 1976; Wigley 1976), matrix exchange (Fontes and Garnier. 1979, 1981), also according to Ferronsky et al. (1984) and equation (4) models (Figure 2).

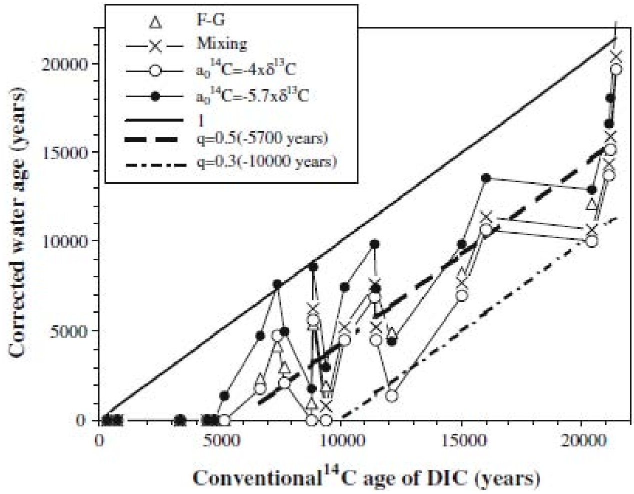

Figure 2. Comparison between age of 14C correction models for studied groundwater (based on Mokrik et al. 2009).

Good congruence were found between the delta carbon-13 mixing and Fontes-Garnier matrix exchange models whish correlated signally with tritium data to determine initial carbon-14 activities for groundwater or with the dilution factor equal to 0.4. Worthy of note, that easy for calculating formula (4) can give same a good confirmation to respect of geochemical models and indicates as viable method for correct dating. The delta carbon-13 values in the groundwater changes from -20.2 to 2.3‰ reflecting dissolution step of carbonates during regional movement of water along lateral downgradient and into depth. Thereof, these trend objectives are related with the rates of infiltrating, and groundwater ions activities in aqueous solution during water-rocks interaction.

For all analyzed groundwater samples the adjusted carbon-14 ages distribution by depth is demonstrated on *Figure 3*. Age versus depth diagram shows that the modern recharge water is spread for the Quaternary and Lower Frasnian aquifers from the several tens to 90 meters, for Middle Frasnian – from several to 24 meters and for the Upper Eifelian-Givetian aquifer 90-185 meters correspondingly. Along the downgradient flow path in the diapason of 40-250 meters the groundwater age increased progressively up to 20000÷25000 years BP, except many samples of the Middle Frasnian aquifer, where the old age of water considered with water-bearing rocks dedolomization adding much dead DIC near the surface. On the areas of groundwater upgradient flow the ages distribution along the depth have a reverse character, because by vertical leakage through tectonic lineaments and river valleys towards surface. Old ages in the rivers valleys and in vicinities of hydraulically permeable tectonic fractures has confirmed by geogenic helium anomalies locations (Mokrik 2003; Mokrik et al 2002).

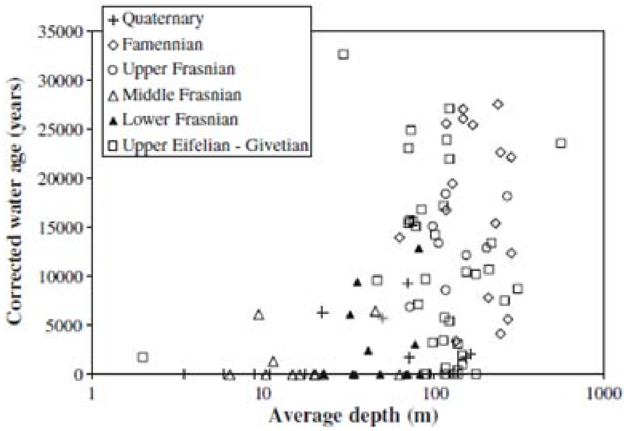

Figure 3. Groundwater corrected age distribution by average depth (based on Mokrik et al., 2009).

Most fresh groundwater of Ca-HCO_3 and Ca-Mg-HCO_3 facies resulted from the modern recharge water at highlands where aquifers is covered by Quaternary cover. The same type of groundwater occurred within the Quaternary aquifers. Thus, the aquifers groundwater chemical composition here is formed through downward percolation from the above lying Quaternary deposits, owing to short residence time that is substantially equal to modern. The radiocarbon age of Quaternary aquifer system and shallow aquifers groundwater at highlands of Lithuania is close to recent or essentially several hundred years old and consist about 30-50 pmC of modern meteoric carbon-14 activities.

The sodium bicarbonate groundwater facies of the aquifers forms at the intermediate depth (65-270 meters). In the Na-HCO_3 groundwater facies a high concentration of Na^+ might result from cation exchange with sodium rich clay minerals on the surface of interbedded clay layers occurrence within the aquifers. The time required for Na-HCO_3 facies formation ranges from 1681 to 10234 years BP. This groundwater facies for the Upper Eifelian-Givetian aquifer are transitional from the Ca-HCO_3 and Ca-Mg-HCO_3 types of facies to the chlorides type groundwater facies. The corrected radiocarbon age of sodium bicarbonate groundwater varies in range of 13905÷27436 years BP. The oldest water spread on the coast of Baltic Sea vicinities which are related by upward leakage of oldest groundwater through the discharge zones from the underlying deeper aquifer. The groundwater hydrochemical facies are outgoing from the carbon dioxide dilution in water and dissolution of carbonate minerals in the aquifers deposits. Most influence of carbon dioxide pressures ($10^{-1.2}$÷10^{-2} atm) are found in the Quaternary aquifer, which has equilibrated or supersaturated with calcite and dolomite. In the pre-Quaternary aquifers the carbon dioxide content derived from the Quaternary deposits decreases and the final CO_2 pressure come lower – 10^{-2}÷10^{-3} atm and is accompanied with increase of pH values and by positioning of the water samples on the dolomite stability field. These features were realized during correction of groundwater radiocarbon age modeling.

Deeper groundwater age of the Na-Cl facies is estimated only on the western part of the Lithuanian coast from the depth of 565 meters in the Upper Eifelian-Givetian aquifer, where the carbon-14 activity was 2.91 pmC, and corrected age form 23510 years BP.

The presence of the total helium in groundwater is a clear indication of a parent radioactive source in the crystalline basement and of intensive diffusion as through fractured zones in the basement and sedimentary bedrocks towards the shallow groundwater aquifers. The dissolved helium concentration in the groundwater was measured using the INGEM-1 equipment. Increased contents of it occur along faults near the Rapakivi granite massifs. The helium dissolved in the groundwater was found to vary considerably from $5 \cdot 10^{-5} \div 100 \cdot 10^{-5}$ ml/l in the low helium generating blocks to $100 \cdot 10^{-5} \div 60000 \cdot 10^{-5}$ ml/l along deep-seated faults. The maximum helium values are found in the groundwater samples taken from and near the basement. High values of helium, up to $50000 \cdot 10^{-5}$ ml/l, occur also in the groundwater of oil fields, because solubility of helium increases several times in oils. The dissolved in groundwater helium values decrease upwards from the basement surface. This suggests that Rapakivi massifs are important producers of helium in groundwater, and that faults penetrating from the basement are the active carriers of helium up to surface.

CONCLUSIONS

The investigation of isotopic geochemistry shows that obtained results can rarely be approached as true groundwater age. The decrease of radiocarbon activities during time is conditioned not only by radioactive decay but also by geochemical processes in groundwater carbonate system, which regulated the carbon-14 activity of dissolved inorganic carbon in groundwater. Geochemical models, which include carbon-13 data in their calculations, were used for the evaluation of these processes and for corrections of groundwater radiocarbon dating. Tritium data were also used for the motivation of this analysis. Obtained results show that initial activity of radiocarbon in groundwater of Lithuanian aquifer systems decreases approximately in half because of geochemical processes. In the active karstic matrixes the reservoir correction can reach up to 29 ky, where the groundwater age of aquifer system is approximately equal to modern or submodern. In the vicinities of hydrogeologically active tectonic fractures zones the groundwater radiocarbon age and dissolved helium values are maximally high. The high values of dissolved in groundwater helium content confirm leakages through the tectonic lineaments.

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