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CARBON ISOTOPIC COMPOSITION OF FRESH GROUNDWATER IN THE TERRITORY OF BELARUS (IN THE CONTEXT OF ITS VULNERABILITY ESTIMATION)

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Abstract: Investigations of the distribution of the carbon isotopes (^{14}C, ^{13}C) at water intakes used for drinking water supply of Minsk (Quaternary and Upper Proterozoic aquifers complexes) and Gomel (Cretaceous and Paleogene aquifers) became the first stage of works aimed at the estimation of vulnerability of fresh groundwater aquifers in Belarus. The radiocarbon concentrations obtained and corrections for carbon stable isotopes were used to calculate the formal and corrected radiocarbon age (time of occurrence in an aquifer) of fresh groundwater of the studied aquifers. So, the most ancient radiocarbon age is characteristic of water samples from the Upper Proterozoic aquifer of Belarusian hydrogeological massif in the Minsk region (12,000-14,000 years). Fresh groundwater from the Cretaceous aquifer in the junction zone of the Pripyat artesian basin and Voronezh hydrogeological massif (Gomel region) show wider age range (7000-15,000 years). As aquifers of Belarus become younger, the groundwater isotope composition area comes more similar to the recent water area (II). An analysis of isotope ratios suggests (area I) that only a part of groundwater samples from Cenozoic aquifers (Paleogene and Quaternary Dnieper-Sozh horizon is found in the area of radioactive decay (this is more typical for water from Paleogene aquifer) and may corresponds to the actual time of its occurrence in an aquifer.

1. STATEMENT OF THE PROBLEM

Groundwater is the main source of drinking and industrial water supply in large cities of most European countries (Zektser, 2001), Belarus included. Diverse human economic activities cause considerable changes of conditions of formation and quality of groundwater resources, their depletion and pollution.

In this situation an estimation of groundwater (aquifer) vulnerability is quite important. The groundwater vulnerability means its capacity to resist negative natural and anthropogenic impact. Two approaches are distinguished when groundwater vulnerability is studied. The first one consists in an estimation of vulnerability without specific pollutant properties and features being considered (inherent vulnerability). The second approach suggests an assessment of protective features of a natural system as applied to a specific kind of pollution (specific vulnerability).

An estimation of inherent vulnerability groundwater vulnerability is based on analysis and processing of all hydrogeological data available (Goldberg and Gazda, 1984; Goldberg, 1987; Zektser, 2001) and obtaining isotope-geochemical parameters of used aquifers (Ferronsky *et al.*, 1984; Polyakov, 1991).

Results of several years' hydrogeological and isotope - geochemical studies carried out in various regions of the world testify that the important characteristic determining vulnerability of underground waters is the time for which water stays in an aquifer. This parameter serves in the certain measure as a measure of tightness of hydrogeological structures can vary while in service aquifer and is determined by the tritium and radiocarbon concentrations in groundwater.

A problem of radiocarbon supply into groundwater has been studied by many scientists (Münnich *et al.*, 1967; Pearson *et al.*, 1967 and 1974; Bondarenko,1983; Ferronsky *et al.*, 1984). The method of radiocarbon determination

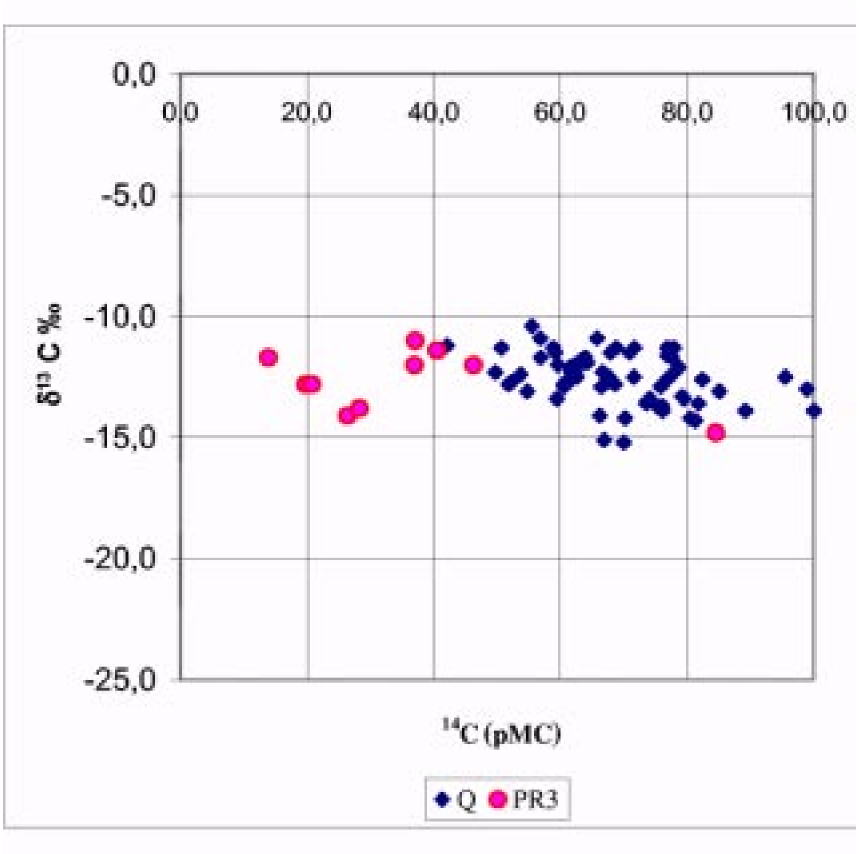

Fig. 1. *Relationship between the radiocarbon concentrations and carbon stable isotope composition in groundwater of the Belarussian hydrogeological massif (Minsk region). PR_3 – water from Upper Proterozoic aquifer. Q – water from Quaternary aquifer*

of groundwater age was elaborated by K.O. Münnich (1967). This method is based on the same assumptions that are made when dating solid organic samples (Libby, 1967). These assumptions are as follows:

1) radiocarbon concentration in water of a catchment area is known and invariable at lest within the time emberaced by the radiocarbon age scale (up to 50,000 years);
2) outside the catchment area radioactive carbon does not enter the groundwater carbonate system;
3) if the radiocarbon content of an aquifer decreases due to not only radioactive decay, but also because of some other processes, then the influence of these processes is taken into account by one means or another;
4) water flow from one aquifer to another can be neglected.

The fourth assumption is not observed in most cases in intensively used aquifers, that make possible groundwater contamination forecasting from isotope data. The local water recharge of aquifers and water flows from one aquifer to another actually occurs causing groundwater mixing. Therefore, an absolute hydrogeochronology can not be suggested from radiocarbon concentrations determined in groundwater. An age of groundwater means the average time of water stay in an aquifer (Polyakov and Seletsky, 1979; Vogel, 1967).

Investigations aimed at the age assessment of fresh groundwater which is of primary importance in drinking water supply started since 2000 at the Institute of Geological Sciences of the National Academy of Sciences of Belarus. Currently available methods that permit the correct determination of radiocarbon concentrations and carbon stable isotopes in groundwater have been adapted to conditions of drinking water intakes of Minsk (intermorainal Dnieper-Sozh and Upper-Proterozoic aquifer complexes) and Gomel (Palaeogenic, Turonian-Maastrichtian, Aptian-Lower Cenomanian and Oxfordian aquifers).

2. METHODS

To determine the carbon isotopic composition, $CaCO_3$ was precipitated from the studied groundwater, which holds the total carbon contained as dissolved compounds in water samples. A special procedure developed for calcium carbonate precipitation permits determination of optimum amounts of water samples and reagents with regard to the groundwater composition.

Radiocarbon concentrations were determined by scintillations in benzene (Mikhailov *et al.*, 2001). Synthesis of the latter from water samples was made with an installation which permits generating purest benzene in amounts sufficient for beta counting. ^{14}C beta particles were counted using a GUARDIAN ultralow background counter made by WALLAC. An active protection system used in this instrument allows a decrease of the background counting rate to 1.3 counts per minute, which increases the quality of analysis. To determine a ratio of carbon stable isotopes in carbonate precipitate a MI-1201 mass-spectrometer was used. This information was needed to make correct conclusions about the water stay in an aquifer that are possible only when ^{14}C and ^{13}C concentrations are available and considered simultaneously (Polyakov and Seletsky, 1979; Ferronsky *et al.*, 1984).

The time of stay of underground waters (radiocarbon age) in aquifer in terms of radiocarbon content, is calculated using the following formula: equality

$$t = 8268 \cdot ln \frac{-5.7 \cdot \delta^{13}C_t}{A_s} \qquad (2.1)$$

where $\delta^{13}C_t$ is isotope composition of stable carbon carbonate systems of water (‰ PDB), A_s - activity ^{14}C in sample

3. RESULTS AND DISCUSSION

In artesian basins where interbasin groundwater recharge and discharge areas (studied aquifers included) are of great importance the distribution of radioisotope concentrations depends on the water vertical migration through a poorly permeable bed and the aeration zone. However, proportions of horizontal and vertical flow water mixing and isotopic characteristics of an assumed function of the recharge zone and vertical flow water are of prime consideration. It should also be considered that water migration through the aeration zone and a poorly permeable bed can be small or insignificant. In the present case this is confirmed by a correlation dependence established between the radiocarbon concentrations and the above parameters. Interpretations of data obtained for aquifers and aquiferous complexes of the Minsk and Gomel water intakes was made in the routine way (Ferronsky *et al.*, 1984) – by analyzing $\delta^{13}C$ – ^{14}C pMC correlation plots (**Figs 1** and **2**). Two straight lines divide (Ferronsky *et al.*, 1984) the isotopic data field into three area as follow: I – area of radioactive decay; II – of recent water; III – "after thermonuclear epoch". The recent water will occur nearby the line of normal dilution model (^{14}C =85%, $\delta^{13}C$ = -15 ‰), "thermonuclear" water points - above this line, and groundwater corresponding to the actual time of its stay in an aquifer – below this line (^{14}C =100%, $\delta^{13}C$ = -25‰).

An analysis of carbon isotope ratios in groundwater samples from different age deposits permits an estimation of the general hydrogeological dynamics of fresh groundwater in the territory of Belarus.

In accordance with the carbon isotopic composition, groundwater from the Upper Proterozoic aquifer of the Belarussian hydrogeological massif (Minsk) and Cretaceous aquifers in the junction zone of the Voronezh hydrogeological massif and the Pripyat artesian basin (Gomel) is found in the radioactive decay field. This corresponds most likely to the actual time of water stay in aquifers. Radiocarbon concentrations obtained and corrected for the carbon stable isotope ratios were used to calculate the radiocarbon age of groundwater from these aquifers (**Fig. 3**). The most ancient radiocarbon age corresponds to water samples from the Upper Proterozoic aquifer of Minsk (12,000-14,000 years). Groundwater from the Cretaceous aquifer of Gomel shows the wider age range (7000-15,000 years). An appreciable variation of data is due to a different degree of water interaction with enclosing rocks involving carbonate material. A transformation of some portion of the enclosing rock carbonate material into a dissolved state causes a shift of the carbon isotopic composition relative to that determined in the primary material. This holds true for both stable isotopes, and radioactive carbon. An appreciable marginal difference in the radiocarbon age values also suggests a possible mixing of various age water. As rocks of the studied aquifers become younger, the groundwater isotopic composition comes close to the recent water area. Only a part of groundwater samples from Cenozoic (Palaeogene and Quaternary) aquifers is found in the normal radioactive decay field (**Figs 1** and **2**) and corresponds to the actual time of water stay in aquifers which is within 4000-5000 years. The major part of figurative dots representing the isotopic composition of groundwater from Cenozoic aquifers is found in the recent water area suggesting a high vulnerability of these aquifers due to vertical water migration. A location of several dots reflecting

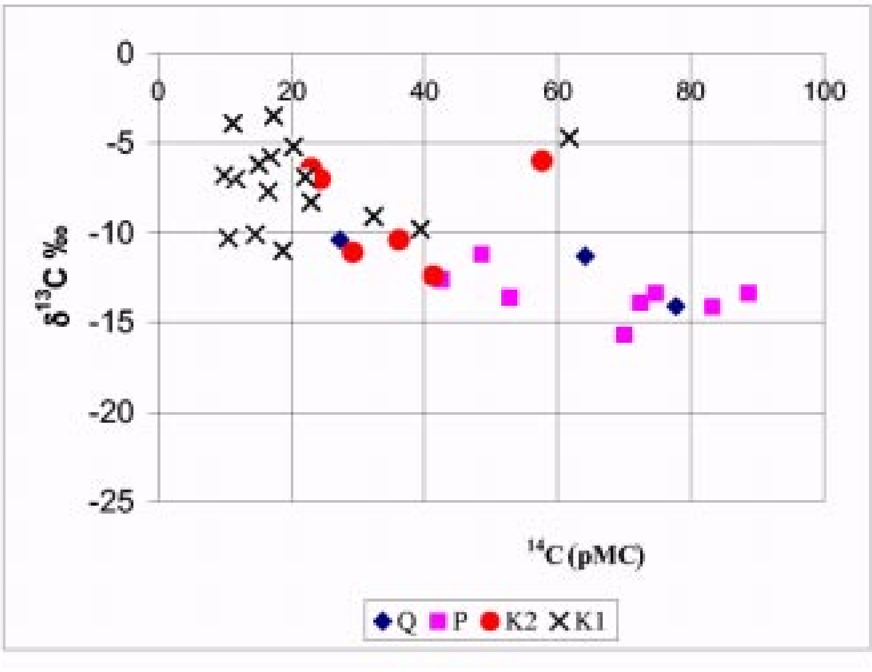

Fig. 2. *Relationship between the radiocarbon concentrations and carbon stable isotope composition in groundwater in the zone of junction of the Voronezh hydrogeological massif and Pripyat artesian basin (Gomel region).*
K_1, K_2 – water from Cretaceous aquifers;
P – water from Palaeogene aquifers;
Q – water from Quaternary aquifers

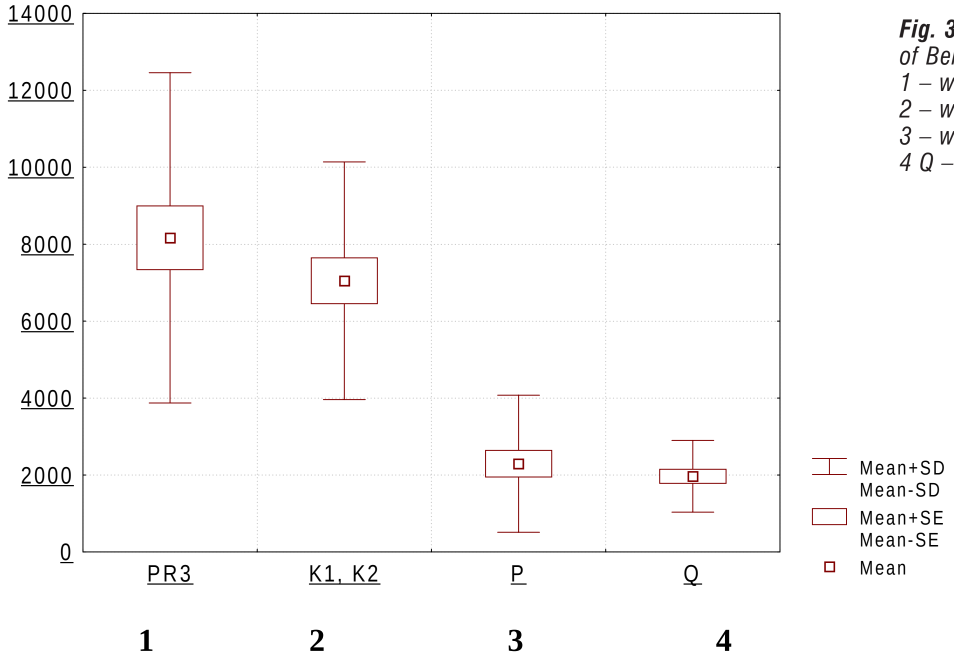

Fig. 3. *Distribution of radiocarbon age of Belarus fresh groundwater.*
1 – water from Cretaceous aquifers;
2 – water from Palaeogene aquifers;
3 – water from Upper Proterozoic aquifer;
4 Q – water from Quaternary aquifer

the isotopic composition of groundwater from Quaternary and Cretaceous deposits in the area III (see **Figs 1** and **2**) indicates an excessive (thermonuclear) carbon supply to hydrogeological systems within the past 40 years.

In conclusion it can be stated that the estimated time of water stay in the investigated aquifers is highly variable. This suggests that the vulnerability of aquifers (in the present case, inherent vulnerability is dealt with) is rather high, in particular, when the water isotopic composition is indicative of water transition to the "recent water" area, and even "after thermonuclear epoch" area.

Data presented in this paper are the important carbon isotopic-geochemical parameters obtained for fresh groundwater from aquifers that are the main source of industrial and drinking water supply. This information may serve as a ground for detailed studies within individual aquifers aimed at assessment of the inherent and specific vulnerability of fresh groundwater.

REFERENCES

Bondarenko G., 1983: *Forming of isotope content of carbonate natural water system*. Kiev: 152 (in Russian).

Ferronsky V., Polyakov V. and Romanov V., 1984: *Cosmogenic isotopes in Hydrosphere.* Moscow (in Russian).

Goldberg V., 1987: Interrelation between groundwater pollution and environment. *Leningrad*: 248 (in Russian).

Goldberg V. and Gazda S., 1984: Hydrogeological background for groundwater protection. *Nedra. Moscow*: 262 (in Russian).

Libby W.F., 1967: *History of radiocarbon dating. Radioactive dating and methods of low-level counting. Vienna IAEA.*

Mikhailov N., Kolkovsky V., Luchina G. and Pavlova I., 2003: Radiocarbon studies at the Institute of Geological Sciences of the National Academy of Sciences of Belarus (Methodical aspects). *Litasphera* 1(18). *Minsk*: 117-126 (in Russian).

Münnich K.O., RoetherW. and Thilo L., 1967: Dating of groundwater with tritium and «^{14}C. *Isotopes in hydrology. Vienna IAEA*.

Pearson F.I. and White D.E.,1967: Carbon-14 ages and flow rates of water in Carizzo Sand. Atascosa County, Texas. *Water Research. Fources* 3.

Pearson FJ. and Swarzenki W. V., 1974: ^{14}C evidence for the origin of arid region groundwater, North-Eastern province, Kenya. In: *Isotope techniques in ground water hydrology. Vienna II*.

Polyakov V. and Seletsky J., 1979: Natural factors influencing the accuracy of radiocarbon dating of groundwater, and means of factor determination. *Isotope studies of groundwater. Moscow*: 122-130 (in Russian).

Polyakov V., 1991: Application of isotope methods in assessing protection of groundwater from contamination. *Application of geophysical methods in environmental issues. Moscow* (in Russian).

Vogel I. C., 1967: Investigation of ground water flow with radiocarbon. *Isotopes in hydrology. Vienna: IAEA.*

Zektser I., 2001: Groundwater as a component of environment. *Nautchny Mir*. *Moscow*: 328 (in Russian).