Tritium activity trend formation in groundwater of Quaternary aquifer system, south-eastern Lithuania

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Radioactive decay and mixing leads to tritium activity decrease in groundwater. In south-eastern Lithuania, the unconfined layer and precipitation water tritium activity decrease rate is dominated by radioactive decay for the period of 1980–2013. Confined aquifers are vastly affected by mixing; therefore, it is hard to predicted tritium activity values. To achieve it, the monitoring type of sampling must be applied in order to calculate tritium activity gradient value. Moreover, gradient values in different sampling points along the water pathway must be similar. It is a necessary condition when comparing theoretical decay curves with actually calculated. Only the shallowest confined aquifer (*ag II–III md-gr*) in this study met these conditions. An additional method for modelled data interpretation was *tritium peak analysis*. According to the modelled tritium peak, a few possible dating water age alternatives exist. The data analysis suggests that no certain water age could be determined. The *tritium peak analysis* could be a helpful method to gain more comprehensive and valuable hydrogeological information.

Keywords: tritium activity (*aT*), tritium gradient ($T_{grad.}$), groundwater dating, Quaternary aquifer system, south-eastern Lithuania

INTRODUCTION

The largest part of tritium in groundwater is anthropogenic in origin. The source of tritium is thermonuclear bomb testing in the upper atmosphere during 1954–1964 period (Clark, Fritz, 1997). In the atmosphere, tritium is being oxidized forming tritium water (THO or ^{3}HHO) (Canadian Nuclear Safety Commission, 2009). Therefore, tritium does not participate during chemical reactions and is introduced into the global hydrological cycle. As anthropogenic tritium spreads globally, precipitation constantly recharges groundwater, thus ^{3}H could be used as a tracer. At present, groundwater dating using tritium is hardly possible, because initial tritium activity values usually exist just for short time intervals. In addition, water mixing strongly affects the tritium signal. Groundwater age could only be a matter of agreement because old water constantly mixes with younger thus accurate age cannot be determined. Interpretation of tracer data includes box models such as the piston flow model (PFM), exponential model (EM), linear model (LM) and various mixed type models (Kinzelbachet et al., 2002; Maloszewski, Zuber, 1996). Each of these models has strict limitations and incorporates a few parameters. In the piston flow model, there is an assumption that there are no flow lines with different transient times. Hydrodynamic dispersion and molecular diffusion are being neglected in PFM (Maloszewski, Zuber, 1996). Exponential model approximation involves distribution of transient times. Initial concentration of the tracer is calculated as mass of the injected tracer diluted in the volume of the whole

system. According to this model no mixing occurs between flow lines. The only location for mixing is at the sampling point. The mean transit time is the only parameter of EM (Kinzelbachet et al., 2002; Maloszewski, Zuber, 1996). The linear model is similar to the exponential model – no mixing takes place between flow lines. The flow lines have the same velocity, but linearly increasing flow time (Maloszewski, Zuber, 1996). Due to small tritium values in samples, these models cause considerable uncertainties. In case of dating groundwater which has small (<15 TU) tritium values, water turns out to be older than it is determined by other modelling methods (Mokrik et al., 2012). Tritium activity values which are below the background concentrations usually means that groundwater is older than 60 years and no hydrogen bomb tritium is present in the aquifer. Despite the recharge of modern water, tritium values could be low if the model has a big dispersion parameter (Maloszewski, Zuber, 1996). Thus the mean water age alone is not sufficient for groundwater dating and describing the formation process. Moreover, lack of data itself makes it hard to interpret and calculate precise tritium trend formation during time.

In this study tritium was considered to be a tracer. Several different tritium peak analysis alternatives are presented in this article along with the gradient method. It could be used to describe the past and future tritium activity of a specific aquifer.

The studied cross-section includes one unconfined and five confined aquifers. These aquifers were formed during Quaternary chronostratigraphical events: Dzūkija–Dainava (Waalian interglacial, *ag II dz-dn*), Dainava–Žemaitija (Holsteinian interglacial, *ag II dn-žm*), Žemaitija–Medininkai (Drenthian-Warthian interglacial, *ag II žm-md*), Medininkai–Grūda (Eemian-Middle Weichselian interglacial/interstadial, *ag II-III md-gr*), Grūda–Baltija (Upper Weichselian interstadial, *ag III gr-bl*) (Mokrik et al., 2012). Two aquifers were added to other, more significant in amount, aquifers: locally spread *ag III bl-gr* and *ag II dz-dn* stratons combined with, respectively, *ag II-III md-gr* and *ag II žm-dn* (Mokrik et al., 2012). The shallowest confined aquifer is *ag II-III md-gr*, the second one is *ag II žm-md* and the third is *ag II dn-žm* which are separated with semi-permeable aquitards. The cross-section represents the full path of groundwater from recharge to discharge areas (Mokrik et al., 2012). The numbering starts with the first aquifer and proceeds from the recharge area: *ag II-III md-gr* – 1–4 points, *ag II žm-md* – 5–7 points, *ag II dn-žm* – 8–11 points. Additional sample points (12–20) were taken in the year 2013 from wells located near the earlier ones (Tables 3, 4). The *ag II-III md-gr* aquifer spreads locally, but is linked hydraulically to the entire groundwater path. Its area covers 8,570 km² (Fig. 1).
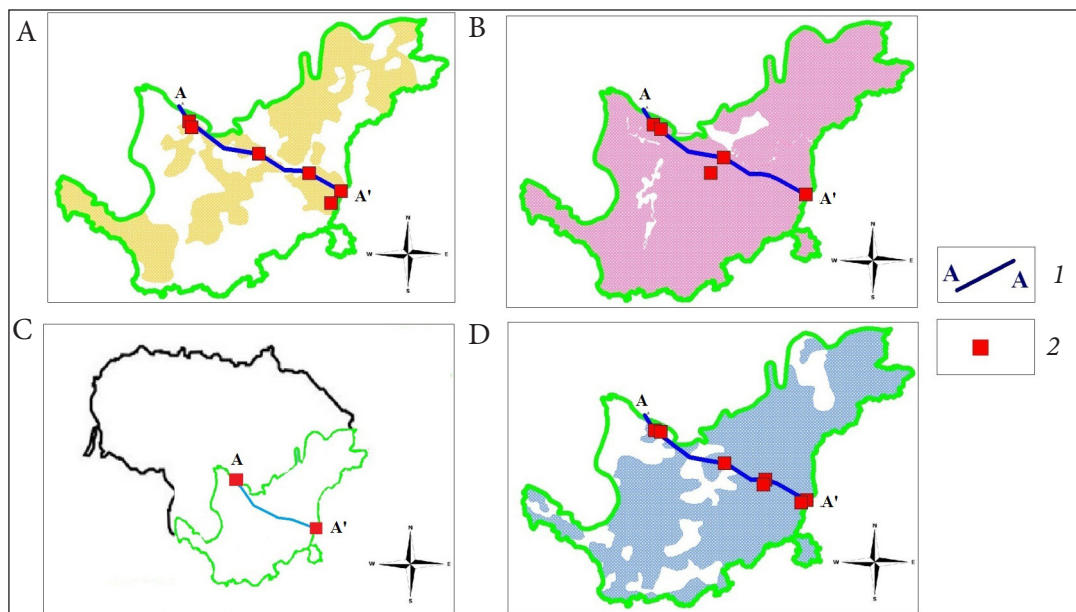

Fig. 1. Locations of aquifers (Mokrik et al., 2012): **A** – Medininkai–Grūda (*ag II-III md-gr*), **B** – Žemaitija–Medininkai (*ag II žm-md*), **C** – south-eastern Lithuania Quaternary aquifer system, **D** – Dainava–Žemaitija (*ag II žm-dn*). *1 – cross-section line, 2 – sampling sites*

Aquifers *ag II žm-md* (15,600 km²) and *ag II dn-žm* (12,360 km²) spread along almost the entire south-eastern Lithuania region (Fig. 1) (Mokrik et al., 2012). Hydrogeological stratons represented in cross-section are schematized to solid layers, ignoring disruptions (Fig. 2).

The hydrogeological structure strongly depends on ground surface relief. Lowlands descend and reach *ag II žm-md* aquifer. Vilnius is located in such a situation. The *ag II-III md-gr* and *ag II žm-md* aquifers exist in Vilnius, but due to a complicated situation, these layers were approximated into one, including an unconfined layer (Figs. 1, 2). The segments of landscape from Vilnius to Vievis are wavy, altitude amplitude is up to 50 m. The other section (Vievis–Kaunas) of the landscape descends evenly. Land surface (aquifers analogically) descends in distal direction from the recharge area. This situation determines water flow direction and hydraulic head gradient. All aquifers are above sea level, so they discharge into the basins of Neris and Nemunas rivers.

METHODS

During fieldworks, samples for tritium analysis were selected only from constantly exploitable wells. Water was extracted using submersible pumps for about 15 min before sampling. Samples were stored in 1 litre (PET) bottles.

Tritium analysis was done at Nature Research Centre, Laboratory of Nuclear Geophysics and Radioecology, using a liquid scintillation counting spectrometer Tri-Carb 3170 Tr/Sl, previously enriching the samples (Mažeika, 2007).

Tritium trend analysis is a complex process based on statistical data of global and Lithuanian tendencies through time, correlation of measured and theoretical results. Using earlier research and available databases, a graph was compiled (Fig. 3). It included tritium activity changes during the period 1980–2012. The graph includes unconfined and three confined aquifers, precipitation in Ottawa (Canada), Vienna (Austria) and Ignalina (Lithuania) (Mokrik, Mažeika, 2006;
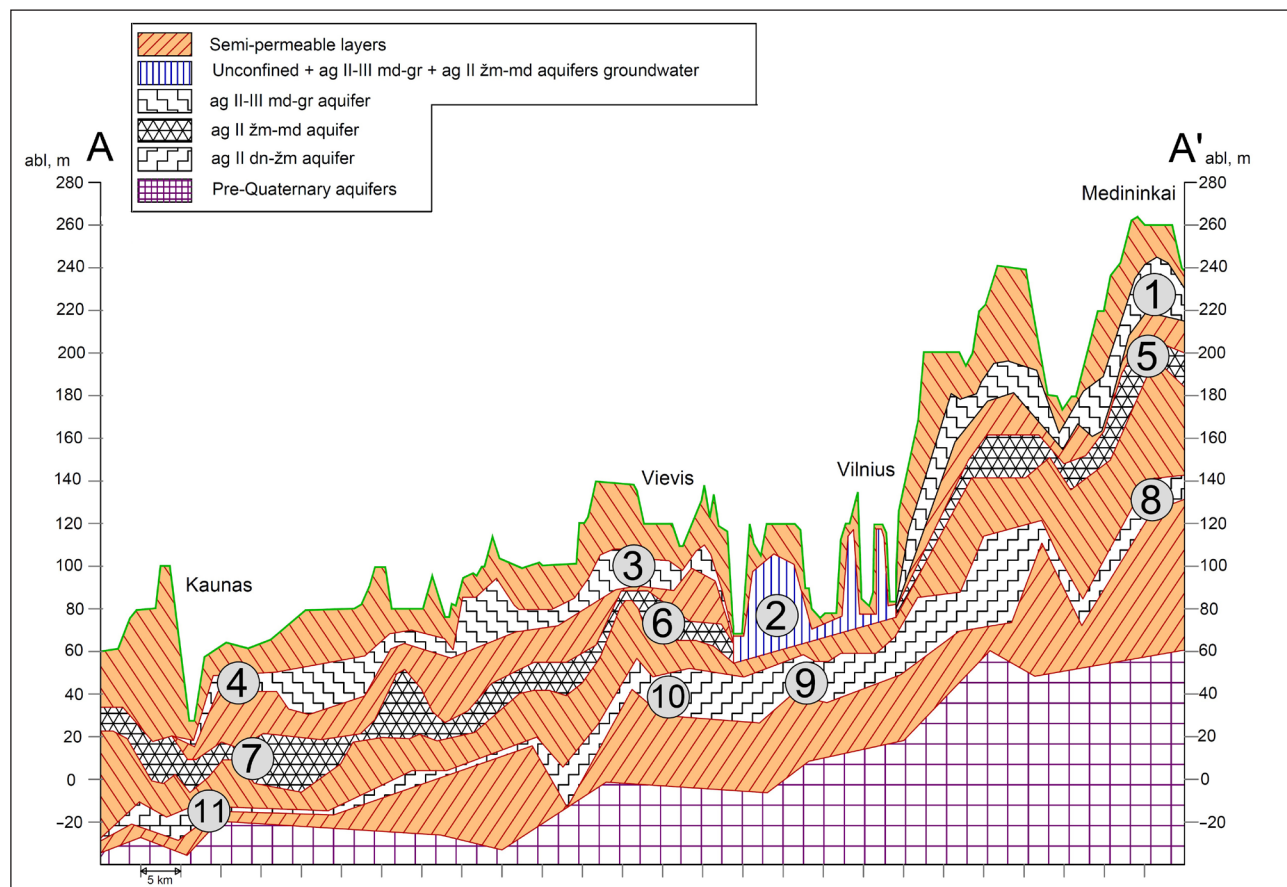

Fig. 2. A-A' cross-section of schematized hydrogeological stratons. Vertically – altitude in meters, horizontal steps – distance (1 step – 5 kilometres). The sampling sites indicated by numbers in filled dots
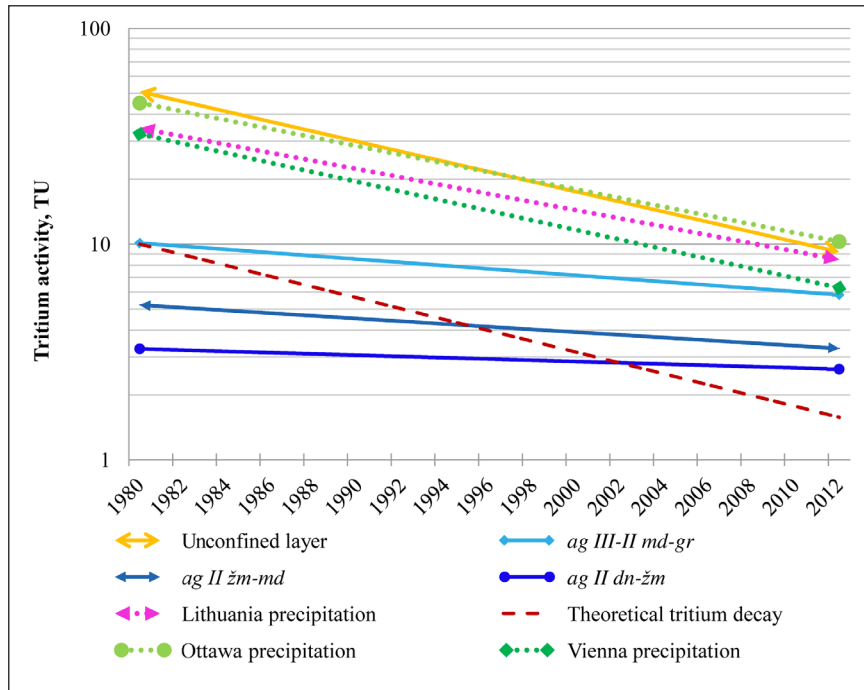
Fig. 3. Tritium activity decrease in precipitation and groundwater exponential trend lines during the period of 1980–2012 (Juodkazis et al., 1995; Clark, Fritz, 1997; Petrošius, 1990)

Juodkazis, Mažeika, Petrošius, 1995; Clark, Fritz, 1997; Petrošius, 1990).

The tritium volumetric activity trend in precipitation, after thermonuclear device detonation, shows cumulative increase of concentration in the atmosphere until 1964–1965. Later, rapid decrease is observed. It could happen due to planetary air mass dilution and dispersion until the year 1980. Since then, tritium activity decrease tendency in precipitation is based on the radioactive decay process (activity less than 100 TU). It will stop when the background, natural tritium activity, level will be reached. Therefore, after 1980 precipitation and unconfined groundwater tritium activity trends must be identical.

Tritium peak analysis in groundwater before 1980 needs either actual values from 1953 or modelling data. Modelling results show anthropogenic tritium peaks in different aquifers (Fig. 4). Every peak, because of its specific shape, needs individual analysis. It is a more appropriate way to describe groundwater behaviour than groundwater dating. A few possible alternatives are presented in this study: start residence time, peak formation time and others. It shows that no real groundwater age could be specified.

Peak analysis, after it reaches its maximum, could be accomplished using the gradient method. Theoretical tritium decay gradient curves were created using different initial tritium activity ($aT_0 = 30, 40, 50, 60, 70$ TU). To determine tritium decrease gradient in the aquifer at least a few sampling points must be selected. Two (or preferably more) separate measurements in one sampling point at different time is necessary for gradient calculation. Similar gradients in separate sampling points could mean that all aquifer water is in equilibrium with precipitation. The *ag II-III md-gr* aquifer satisfies this condition. Gradient value of Medininkai–Grūda aquifer was applied on the graph with theoretical gradient curves (Fig. 5). Using the best fitting theoretical curve, tritium activity can be predicted for the future (until background value) or reconstructed for the past (until maximum titium activity) in a specific aquifer. t – time, aT – tritium activity, $\alpha_0 T$ – initial tritium activity, $T_{grad.}$ – tritium gradient in time:

$$T_{grad.} = \frac{\alpha_0 T - \alpha_t T}{t} \tag{1}$$

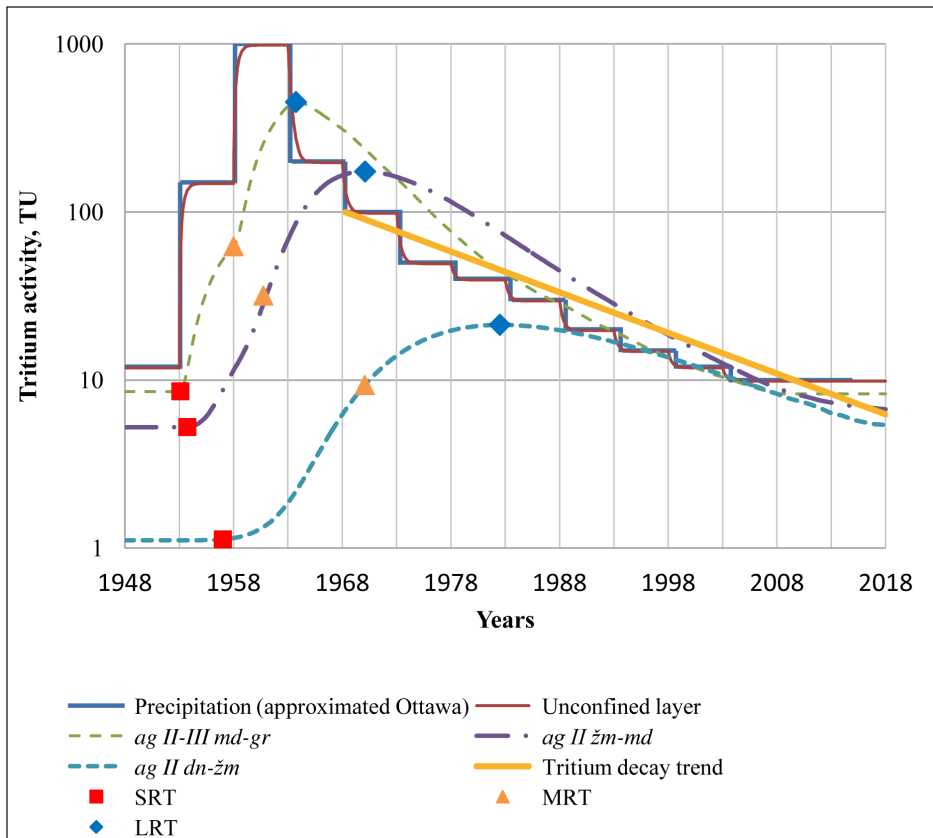$$aT = \alpha_0 T \times e^{-t/17.93} \tag{2}$$

Fig. 4. Modelling results of tritium activity alteration during the period of 1948–2018 – example of Medininkai
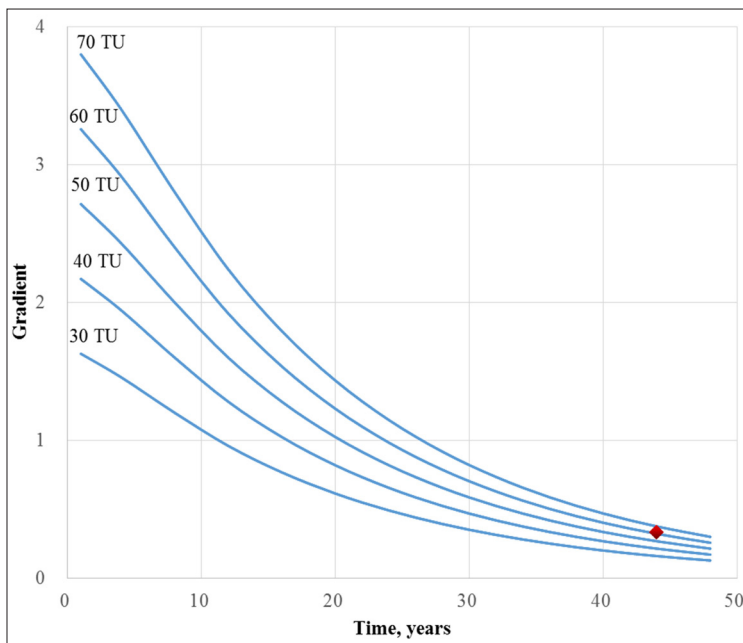

Fig. 5. Tritium decay gradient in time (step – 4 years) compared to the measured and calculated gradient value of *ag II-III md-gr* aquifer. Labels represent initial tritium activity values for gradient calculation

DISCUSSION

Decrease of tritium activity in the aquifer depends on two main factors: isotopic decay and mixing. Figure 3 shows approximate trends of tritium activity in precipitation (Ottawa, Vienna and Vilnius) and in groundwater (three confined and one unconfined layers). Trends represent average values of tritium activity based on statistical data collected since 1980. Precipitation trends inclination, in comparison with the radioactive decay line, are similar. It means that activity decrease rate is mainly determined by tritium decay in the atmosphere. Absolute activity values are

different (Ottawa – highest tritium activity, Vienna – lowest, and Vilnius is in the middle). This inequality could come from heterogenic tritium distribution in the atmosphere. It led to differences in precipitation water activity around the globe. Unconfined layer groundwater activity trend shows an inclination similar to the radioactive decay line, but absolute values are greater than in precipitation. Accumulation of tritium in unconfined aquifer groundwater appeared because the circulation rate in the hydrogeosphere is much slower than in the atmosphere. A significant drop in tritium concentration in the atmosphere occurred because of global air mass mixing and dilution (before year 1980) (Clark, Fritz, 1997). Groundwater in the unconfined layer is equilibrated with precipitation; tritium decrease rate is determined by radioactive decay. The unconfined aquifer is recharged with modern (<60 years) water. Confined aquifers tritium activity trend inclination is smaller (according to the ordinate axis). It means that tritium reached the aquifers, but equilibrium with precipitation did not settle. Absolute tritium activity values decrease according to the depth of the aquifer. However, Fig. 3 represents statistical data of all south-eastern Lithuania regions and in some places confined aquifers can be equilibrated with precipitation, for example, recharge area (Fig. 4). The modelling results of tritium activity of the Quaternary system in south-eastern Lithuania are shown in Fig. 4, period of 1955–2014. Pre cipitation is represented in green line and modelled using Ottawa precipitation trend. Unconfined layer groundwater reacts to precipitation almost instantly (about 1 year delay). Confined

aquifers tritium activity peaks come later. Analyzing the tritium signal as a tracer makes more logical and accurate conclusions than dating. Tritium peak in every aquifer could be described using such parameters as (Table 1):

• start residence time (SRT) – time from beginning of tracer injection to peak formation start,

• middle residence time (MRT) – time from beginning of tracer injection to peak formation halfway,

• largest (maximum) residence time (LRT) – time from beginning of tracer injection to peak formation end,

• peak formation time (PFT) – time from peak formation start to its maximum value,

PFT = LRT – SRT,

• background "prebomb" tritium activity – value of natural tritium activity in groundwater.

SRT, MRT, LRT and PFT present different stages of peak formation, but no certain water age could be determined. Since groundwater is being recharged by precipitation constantly, mixing makes accurate dating impossible. The modelled values of "prebomb" tritium activity in the aquifer are considered to be a baseline of peaks (Fig. 4). It gives a possibility to determine the quantity of anthropogenic tritium in the aquifer at a specific moment of time. These parameters could be used to gain more detailed hydrogeological information about groundwater circulation, recharge and discharge peculiarities. For example, SRT shows minimal flow time from precipitation event to recharge of the aquifer in a particular location, LRT would accordingly represent maximum flow time,

Table 1. **Peak description parameters based on the modelling results**

Location	Aquifer	SRT*, y	MRT, y	LRT, y	PFT, y	"Prebomb" tritium activity, TU
Medininkai	*gr-md*	1	5	11	10	8.5
	md-žm	2	8	15	13	5.1
	žm-dn	7	17	30	23	1.1
Vilnius	*gr-md*	2	13	25	23	3.5
	md-žm					
	žm-dn	9	18	32	23	0.8
Vievis	*gr-md*	8	30	53	45	0.4
	md-žm	17	35	54	37	0.2
	žm-dn	24	17	55	31	0.05
Kaunas	*gr-md*	1	5	10	9	6
	md-žm	5	19	34	29	0.1
	žm-dn	–	–	–	–	<0.0001

* SRT – start residence time, MRT – middle residence time, LRT – largest residence time, PFT – peak formation time.

PFT could be a parameter of water circulation in the aquifer itself (avoiding time necessary for water to reach the aquifer). These parameters are analogical to tracer experiment data, so theoretically aquifer parameters (such as effective porosity) could be calculated. Additional data would be required for this procedure.

Equilibrium between precipitation and groundwater in the aquifer could be identified comparing theoretical and measured tritium values. It requires a few (at least two) measurements at a particular point of a specific aquifer. Examples of sampling are shown in Table 2. Additional sampling points located near the cross-section are presented in Table 3.

An example of aquifer *ag II-III md-gr* shows parallel decrease rate (gradient) which leads to the conclusion that equilibrium between this aquifer and precipitation became prevalent. Radioactive decay factor dominates the decrease rate of tritium activity in Medininkai-Grūda aquifer. Using equation 2, theoretical tritium activity values for year 2012 were calculated using the measured value of 2008 as initial tritium activity and taking a four-year decay period. Results are presented in Table 4. Theoretical values resemble actual, in the range of uncertainties of measuring procedure.

At least two, separate in time, samples must be taken and analyzed in one location (sampling point). The gradient was calculated using equation 1. The calculated gradient values are presented in Table 2. The gradient values of *ag II-III md-gr* aquifer are similar. The tritium activity gradient

Table 3. **Additional tritium activity values measured in 2013 near the cross-section**

Well No.	Well depth, m	Location	³H volumetric activity, TU
ag II-III md-gr			2013
40000/12	30	Medininkai	6.9
44346/13	30	Vilnius*	2.9
27850/14	20	Kaunas	<0.2
ag II žm-md			
41638/15	60	Medininkai	7.0
37232/16	117	Vievis	<0.2
29331/17	87	Kaunas	1.6
ag II dn-žm			
44345/19	45	Vilnius	0.9
4951/20	120	Kaunas	2.2

values of a*g II žm-md* and *ag II dn-žm* aquifers are different along the groundwater path. The graph (Fig. 4) with theoretical decay gradient curves was plotted using initial tritium activities (30, 40, 50, 60, 70 TU). The starting point in time is year 1963 when maximum tritium values were detected in precipitation. The actual tritium gradient point is placed on theoretical curves depending on time elapsed after tritium peak in precipitation. Aquifer *ag II-III md-gr* coincides with the theoretical curve of initial activity value 60 TU. Following this curve it is possible to forecast how tritium concentration changed in a specific aquifer during time. However, the theoretical curve represents only decay. Mixing along with recharge time was not taken

Table 2. **Tritium activity values measured in 2008 and 2012 along the cross-section**

Well No.	Well depth, m	Location	³H volumetric activity, TU		Gradient, TU/year
ag II-III md-gr			2008	2012	
955/1	37.5	Medininkai	7.5	6.2	0.325
28809/2	23.7	Vilnius	10.2	9.1	0.275
29708/3	25.0	Vievis	5.5	4.1	0.350
30000/4	32.0	Kaunas	7.3	6.1	0.300
ag II žm-md				Average	0.313
42169/5	76.0	Medininkai	8.5	8.3	0.050
6442/6	64.0	Vievis	2.6	1.7	0.225
43515/7	60.0	Kaunas	2.3	<0.1	0.575
ag II dn-žm				Average	0.285
4121/8	130.0	Medininkai	<2	<0.1	0.000
28811/9	51.0	Vilnius	4.4	2.1	0.575
6446/10	93.0	Vievis	<2	<0.1	0.500
25940/11	98.0	Kaunas	<2	2.5	−0.125
				Average	0.238

Table 4. The *ag II-III md-gr* aquifer groundwater tritium data compared to tritium decay values (2008 – initial activity, period – 4 years)

			^{3}H volumetric activity, TU			
Well No.	Well depth, m	Location	2008 measured	2012 theoretical	2012 measured	Uncertainty, ±
Medininkai–Grūda						
955/1	37.5	Medininkai	7.5	6.1	6.2	0.4
28809/2	23.7	Vilnius	10.2	8.2	9.1	0.6
29708/3	25	Vievis	5.5	4.4	4.1	0.3
30000/4	32	Kaunas	7.3	5.9	6.1	0.4

into account. Uncertainty depends on the time of prediction: the longer time the bigger uncertainty. This method requires additional information like statistical or modelling data. It could show the period when radioactive decay is a dominant factor in tritium decrease rate.

CONCLUSIONS

1. The statistical data of tritium activity analysis revealed that the unconfined layer of groundwater of south-eastern Lithuania is in equilibration with precipitation while confined aquifers are not (period 1980–2012).

2. At some specific points of Medininkai–Vilnius–Vievis–Kaunas cross-section, aquifer *ag II-III md-gr,* groundwater tritium activity gradients show that the main factor of gradient decrease rate is radioactive decay. That enables to apply the gradient method and calculate initial tritium activity in the aquifer 42 years ago. Initial tritium activity Medininkai–Grūda is 60 TU.

3. The modelled tritium activity peaks in Medininkai recharge area could serve as an example of several dating possibilities. It leads to the conclusion that no certain water age could be determined. A more appropriate way is *tritium peak analysis* using these parameters (residence and peak formation time).

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PIETRYČIŲ LIETUVOS KVARTERO VANDENINGOJO KOMPLEKSO POŽEMINIO VANDENS TRIČIO AKTYVUMO TRENDO FORMAVIMASIS

S a n t r a u k a

Dėl XX a. antroje pusėje vykdytų termobranduolinių užtaisų bandymų į atmosferą pateko dideli kiekiai tričio, todėl išaugo ^{3}H koncentracija hidrosferoje. Šiuo metu tričio aktyvumas požeminiame vandenyje yra pasiekęs natūralias fonines reikšmes – antropogeninio ^{3}H signalas yra beveik išnykęs.

Atlikus tričio aktyvumo trendo analizę paaiškėjo, kad Pietryčių Lietuvos gruntinio vandens ^{3}H aktyvumas ir jo pokyčiai atitinka kritulių vandenį. Spūdiniuose sluoksniuose tričio aktyvumas yra veikiamas maišymosi. Pagrindinė problema analizuojant tričio signalą ir datuojant vandenį yra pradinių koncentracijų verčių trūkumas. Šias vertes galima apskaičiuoti naudojantis esamo signalo pokyčiu bėgant laikui, pasitelkus gradientų metodą. Įvertinant gradientą turi būti žinomos mažiausia dvi ^{3}H aktyvumo vertės, nustatytos viename taške, bet skirtingu laiku. Apskaičiuotos gradiento vertės taip pat turi sutapti keliose paėmimo vietose tiriamajame sluoksnyje. Šios sąlygos yra tenkinamos tik pirmame (*ag II-III md-gr*) spūdiniame sluoksnyje, kuriame pasiekta pusiausvyra tarp maitinančio gruntinio ir sluoksnyje esančio vandens.

Tričio aktyvumo smailės analizė yra siūloma kaip modeliavimo rezultatų interpretavimo metodas. Vykstant nuolatiniam seno ir naujai patenkančio vandens maišymuisi, datavimas tampa sąlyginis ir atitinka sutartinį, vidutinį vandens amžių. Remiantis modeliuotu tričio aktyvumo kitimo grafiku parodoma, kad egzistuoja keli variantai, kuriais galima nusakyti vandens amžių. Tai suteikia išsamesnę ir detalesnę hidrogeologinę informaciją.

Raktažodžiai: tričio aktyvumas (*aT*), tričio gradientas (*T$_{grad.}$*), požeminio vandens amžiaus nustatymas, kvartero vandeningas kompleksas, Pietryčių Lietuva