Geologos 28, 3 (2022): 179–189
https://doi.org/10.14746/logos.2022.28.3.0001

Calibrated geochemical ages of the Baltic Artesian Basin groundwater

Vytautas Samalavičius*, Jurga Arustienė

Institute of Geosciences at Vilnius University, Čiurlionio Street 21/27, 03101 Vilnius, Lithuania
e-mail addresses: vytautas.samalavicius@chgf.vu.lt, jurga.arustiene@chgf.vu.lt
* corresponding author

Abstract

For the present study, geochemical ages were derived from radiocarbon and radiokrypton age calibration with groundwater chemical contents (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, HCO_3^-). Geochemical ages may fill the dating gap (40–150 ka) between the isotope techniques mentioned. A case study of groundwater in the Baltic Artesian Basin has involved geochemical age calibration, data filtering (such as regional subdivision of the basin for more accurate results) and geochemical dating of groundwater of unknown age. Various approaches to interpretations of geochemical age results could be used. Bicarbonate and sulphate are sensitive to the hydrochemical environment and should be omitted from geochemical age calculations. Modern fresh groundwater samples should also be excluded from calibration in order to obtain more reliable trend lines. Calcium-sodium cation exchange occurs in deep aquifers and may be used for geochemical age determination of fossil groundwater.

Key words: groundwater dating, isotope geochemistry, radiocarbon, radiokrypton

1. Introduction

Dating of groundwater by the use of radioactive isotope techniques has limitations due to a number of factors. For example, a particular isotope can be used only for a certain dating range; therefore, multiple isotopes are applied for obtaining groundwater age. Tritium and krypton-85 are used for an age range <50 a, argon-39 covers 50–1,000 a, radiocarbon (^{14}C) 4–40 ka, chlorine-39 0.1–1 Ma and radiokrypton (^{81}Kr) is applied for the 0.15–1.5 Ma range (Winsberg, 1956; IAEA, 2013; Atkinson et al., 2014; Mace et al., 2017). Conventional helium and helium isotopic dating techniques have been broadly used as continuous and linear dating methods (Ciężkowski et al., 1992; Zuber et al., 1995, 1997; Kotowski and Najman, 2015). However, in the latest research where helium dating techniques were compared to krypton-81 and modelled ages reveal that uncertainties may be huge due to the geological settings of a particular site or basin (Mokrik et al., 2021). An obvious problem occurs in dating gaps between various isotopic techniques; direct measurement of these gaps is often impossible. Moreover, dating in a particular range is not necessarily accurate. Radiocarbon in groundwater is often contaminated with carbonate rock dissolution or organic carbon, resulting in older and younger ages, respectively (IAEA, 2013). Radiokrypton diffusion through aquitards may also distort dating results (IAEA, 2013). Moreover, recent studies have brought evidence that underground radiokrypton generation may be significant (Purtschert et al., 2021). Various methods were put forward to resolve this problem, such as coupling multiple dating techniques, numerical modelling, a study of groundwater origin using its isotope geochemistry and noble gas content, groundwater mixing models, anomaly research, etc. (Sturchio et al., 2004, 2014; Bethke and Johnson, 2008; IAEA, 2013; Torgersen and Stute, 2013; Gerber et al., 2017; Matsumoto et al., 2018; Mokrik et al., 2021). In spite of advances in analytical methods, the dating of old fossil groundwater with radiokrypton may not be sufficient for extremely old (>1.3 Ma) groundwater (Gerber et al., 2017). These problems are especially important for regional-scale hydrosphere evolution and groundwater circulation studies. The lack of necessary groundwater age data in shallow, intermediate and deep aquifers could distort interpretations of results on the origin, source and processes that occurred in forming isotope geochemistry contents.

Geochemical age calculation could obtain an unknown sample residence time, expand the existing data set of ages, or support a previously established age. Chemical characteristics deduced as age were studied mainly in the same flow system, for example, in aquifers (Edmunds and Smedley, 2000; Edmunds et al., 2003)). Reactive and nonreactive categories of hydrochemical substances could be distinguished (Edmunds and Smedley, 2000). Reactive parameters include cations (Na^+, K^+, Mg^{2+}, Ca^{2+}), $\delta^{13}C$; nonreactive – halides (Cl^-, Br^-, I^-) chlorine-36 and noble gases (Edmunds and Smedley, 2000). Groundwater quality parameters (Na^+, NO_3^-, PO_4^{3-}, HCO_3^-, F^-, etc.) were analysed according to tritium age in New Zealand (Morgenstern and Daughney, 2012). Trace element (Li, Mo, Rb, Mn, Cs) calibration with groundwater age was suggested as an alternative for major ionic contents that reach the solubility limit (Edmunds and Smedley, 2000; Edmunds et al., 2003).

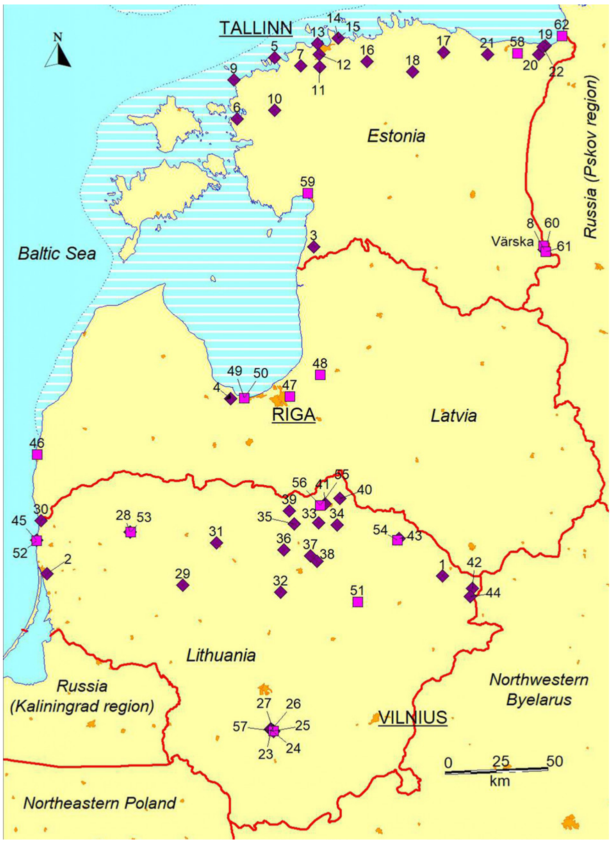

Fig. 1. Map with dated groundwater sites. Green diamonds – radiokrypton-dated groundwater, purple diamonds – radiocarbon. Pink squares represent geochemically dated groundwater.

The Baltic Artesian Basin (BAB) is a good example of two problems in groundwater age determination that have been outlined previously: the dating gap (^{14}C–^{81}Kr) and stagnant brines (age >^{81}Kr). Studies of groundwater age in this region have involved tritium monitoring of modern groundwater in the Quaternary aquifer system. A gradient method was developed to resolve the lack of initial tritium age and a numerical modelling application for estimating hydraulic age and comparison to tritium age (Štuopis et al., 2012; Mokrik et al., 2014; Samalavičius and Mokrik, 2016). Radiocarbon dating of anomalous Pleistocene time groundwater in northern Estonia was executed to understand its origin and effect of seawater intrusion during exploitation and modern groundwater leakage through buried valleys (Banys et al., 1979; Raidla et al., 2012; Pärn et al., 2018, 2019). A case study of Lithuania's mineral groundwater located in Birštonas, where brine water recharges into the freshwater aquifer area, involved radiocarbon dating (Zuzevicius et al., 2007). Radiocarbon age data were obtained for the new Visaginas Nuclear Power Plant construction site for better groundwater circulation characterisation (Mažeika et al., 2013). Middle–Upper Devonian aquifer system groundwater in Lithuania was dated with radiocarbon to evaluate the dolomitisation effect on ^{14}C values, to correct age by the Fontes-Garnier matrix exchange model and dilution factors derived from tritium and carbon-13 data (Mokrik et al., 2009). Valuable krypton-81 data were obtained from seven intermediate to deep wells in the BAB (Gerber et al., 2017; Vaikmäe et al., 2020). Groundwater age was calculated for these, with the exception of two samples which were above the detection limit (Genčiai and Riga) and older than 1,300 ka. The age of the Riga site was corrected using a brine-glacial-modern groundwater mixing model, estimating a residence time of >1,279 ka. Data from publications which include radiocarbon or radiokrypton age records of the BAB were taken to develop a data set that has been used for the present study (Apendix 1; Fig. 1). The main objectives of the present note are to use groundwater age data to connect and fill a gap between ^{14}C and ^{81}Kr dating ranges (40–150 ka) and extrapolate radiokrypton age above the detection limit of >1,300 ka. A major dissolved ion content was used to calibrate ^{14}C and ^{81}Kr ages. Trendline equations obtained were then applied to calculate groundwater age derived from chemical composition – geochemical age.

2. Hydrogeology and geology of the Baltic Artesian Basin

The BAB is a sedimentary basin with multiple aquifers and aquitards located in the area of Lithuania, Latvia, Estonia, north-east Poland, the north-west range of Belarus, Russia (Pskov and Kaliningrad regions) and a significant part of the Baltic Sea (Fig. 2). The sedimentary cover overlies a crystalline basement. The total area of the BAB is 426,000 km^2 (Delina et al., 2012). The depth of the sedimentary basin varies from a few dozen metres to ~5 km in the southern part of the basin (Mokrik, 2003). Water-bearing aquifers are of different ages and include: Cambrian–Vendian Cm-V (partly subdivided into V_2gd [Gdov], V_2vr [Voronka]), Ordovician–Cambrian O-Cm, Devonian D_{2-1}, D_2, D_3, Permian–Devonian P_2-D_3, Triassic T_1, Jurassic J_3-J_1, Cretaceous K_2cm-K_1, K_2 and a multi-layered Quaternary aquifer system. Major regional aquitards confine groundwater to three zones: active exchange (depth <360 m), delayed (360–1,850 m) and stagnant (>1,850 m) (Mokrik, 2003).

Tectonic faults transecting the BAB act as highways for groundwater migration between aquifers

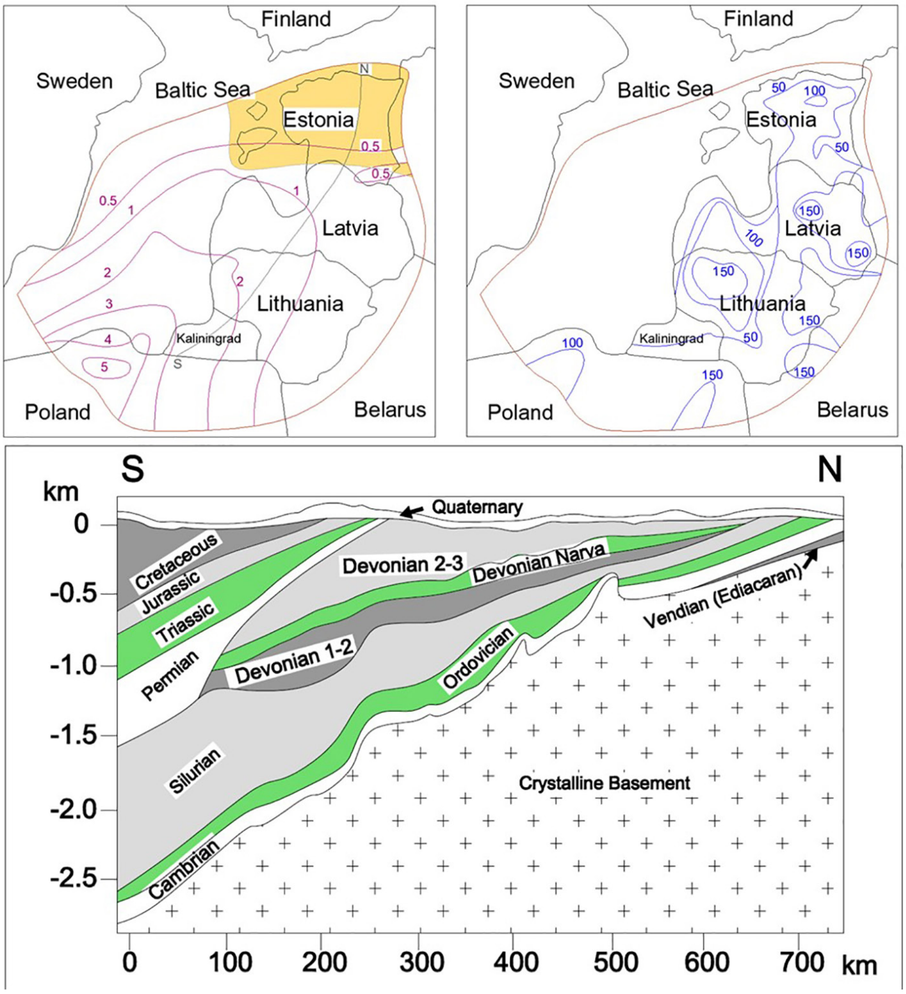

Fig. 2. Location of the Baltic Artesian Basin (BAB); dotted lines represent the depth (in metres) of the crystalline basement below sea level. The Estonian Homocline is hatched in yellow, blue lines represent the piesometric level of Quaternary groundwater. Longitudal cross section of the BAB. (after Juodkazis, 1980; Virbulis et al., 2013; Pärn et al., 2016; Samalavičius, 2022).

as well as prevent (in case of vertical dislocation) lateral groundwater flow; therefore, hydrogeological subbasins can be derived (Delina et al., 2012). For example, the Estonia Homocline could be considered as a subbasin separate from the rest of the BAB. Intermediate depth (300–800 m) aquifer groundwater flows from the south are limited by a fault zone in southern Estonia (Mokrik, 2003). In Figure 2 it can be seen that the uplift of the crystalline basement transects the O, Cm and Vendian levels. Groundwater isotope geochemistry in Estonia is distinct from other localities within the BAB. Stable isotope content is depleted (**$\delta^{18}O$** is found down to -23‰), mainly due to cold climate-induced processes which occurred during the Pleistocene (Mokrik and Vaikmäe, 1988; Yezhova et al., 1996; Mokrik, 1997;; Vaikmäe et al., 2001; Raidla et al., 2012, 2019b; Babre et al., 2016; Sterckx et al., 2017, 2018; Pärn et al., 2019; Mokrik and Samalavičius, 2022; Samalavičius and Mokrik, 2021; Samalavičius, 2022). The groundwater in aquifers in Lithuania and Latvia is above $\delta^{18}O$ −14‰ (Delina et al., 2012).

Freshwater originates from precipitation, mainly recharging aquifers in the highlands of the BAB. The southeastern boundary of the basin is the main recharge areas for shallow freshwater. A few local recharge areas have also been observed in the highlands of Lithuania and Latvia (piezometric head > 150 m) (Fig. 2). Groundwater flow in shallow aquifers discharges into the Baltic Sea floor and major river valleys. Stagnant groundwater flows from the deepest parts of the BAB towards the periphery (Mokrik, 2003).

The groundwater of the BAB has previously been classified, systematised and published using the following parameters: alteration degree $(Na+Cl)/HCO_3$, Na/Cl ratio, hydrochemical type, TDS and aquifer depth (Mokrik, 1996, 1997, 2003). Precipitation acts as the main recharge source for shallow groundwater. Carbonate mineral dissolution takes place in freshwater aquifers, where the solubility limit causes TDS to be <1 g/L, and forming Ca-Mg-HCO_3 type, with anomalous exception of the Na-HCO_3 facies. Stagnant groundwater TDS is up to 400 g/L (Mokrik, 2003). Accordingly, the groundwater facies of deep and intermediate aquifers usually are Ca-Na-Cl or Na-Cl (Mokrik, 1997, 2003). Sulphate-type groundwater is found in Lithuania's karst region (Juodkazis and Mikalauskas, 1994;; Paukstys and Narbutas, 1996; Paukstys et al., 1999; Juodkazis, 2003; Mokrik, 2003) and in Latvia (Levins et al., 1998; Delina et al., 2012; Babre et al., 2016) being mostly associated with sulphate mineral deposits. Despite the common background values of groundwater composition, multiple anomalies are observed as well (Samalavičius, 2022). In the major aquifer systems, pore flow predominates. However, some discharges occur near hydraulically active tectonic faults. These are places where brackish groundwater anomalies occur in the BAB (Samalavičius, 2022).

3. Methods

A data set of 45 groundwater samples was compiled out of previous peer-reviewed research in Lithuania, Latvia and Estonia (Zuzevicius et al., 2007; Mokrik et al., 2009; Raidla et al., 2012; Gerber et al., 2017; Vaikmäe et al., 2020). We have used previously published data to make calculations of geochemical ages. The Baltic Artesian Basin was selected for our case study into the possibility of obtaining age values from raw chemical data. Criteria for data entries were major ion content combined with estimated age either with radiocarbon or radiokrypton technique. An uncorrected radiocarbon age was used in the present study so as to arrive at a consistent data set from multiple sources. In most cases, trace element data were insufficient; therefore, only major ion content was analysed.

All major ions (Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, HCO_3^-) and TDS are expressed in mg/L plotted against groundwater age (ka) in each sample. Trend lines were fitted for each chemical parameter. A similar approach was presented by Edmunds and Smedley (2000) and Edmunds et al. (2003). Linear equations appear to be suited best for logarithmic data plots. An extrapolation of separate radiocarbon and radiokrypton trends appeared ineffective for geochemical age estimates in a ^{14}C-^{81}Kr dating gap (Fig. 4). These trends did not intersect at any point. A similar graph was created for the entire data set of BAB groundwater, including both ^{14}C and ^{81}Kr in one series (Fig. 3). The trendline passed through the ^{14}C and ^{81}Kr dating gap, but showed rather low R^2 values (<0.7). Due to anomalous groundwater found in the Estonia homocline, it was separated into a subbasin. Data were reanalysed and divided into two major regions: Lithuania-Latvia (LT-LV) and Estonia (ES) (Fig. 3). The results revealed a higher correlation for the separate trends and clear separation of ES and LT-LV groundwater. As mentioned above, Estonia's groundwater was formed under cold-climate conditions and had $\delta^{18}O$ values in the range −23 to −12 ‰. In contrast, Lithuania – Latvia groundwater is more isotopically enriched, with oxygen-18 varying −12 to −4‰. It was concluded that most of the nonreactive ions are best suited for geochemical age determination; therefore, bicarbonate and sulphate were eliminated from further calculations. It was also suggested that low TDS samples should be excluded from the analysis on account of the high variation of radiocarbon age, which distorts the results. Arbitrary criteria were applied to filter data: sodium and chloride > 100

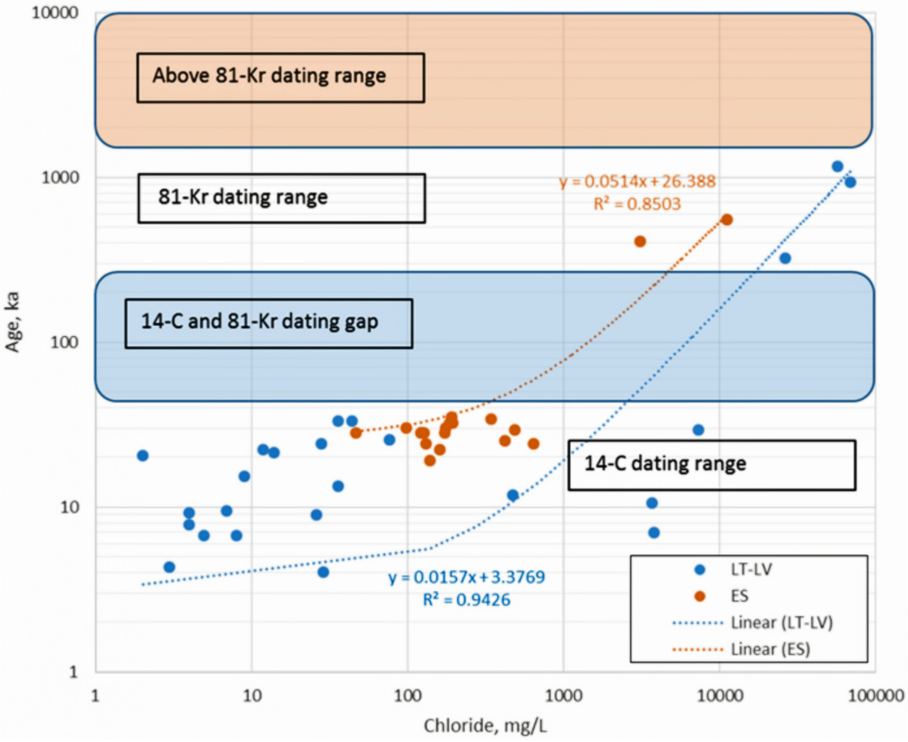

Fig. 3. Chloride geochemical age trendlines calibrated with linked radiokrypton and radiocarbon in Lithuania-Latvia and Estonia (without arbitrary criterium chloride > 100 mg/L).

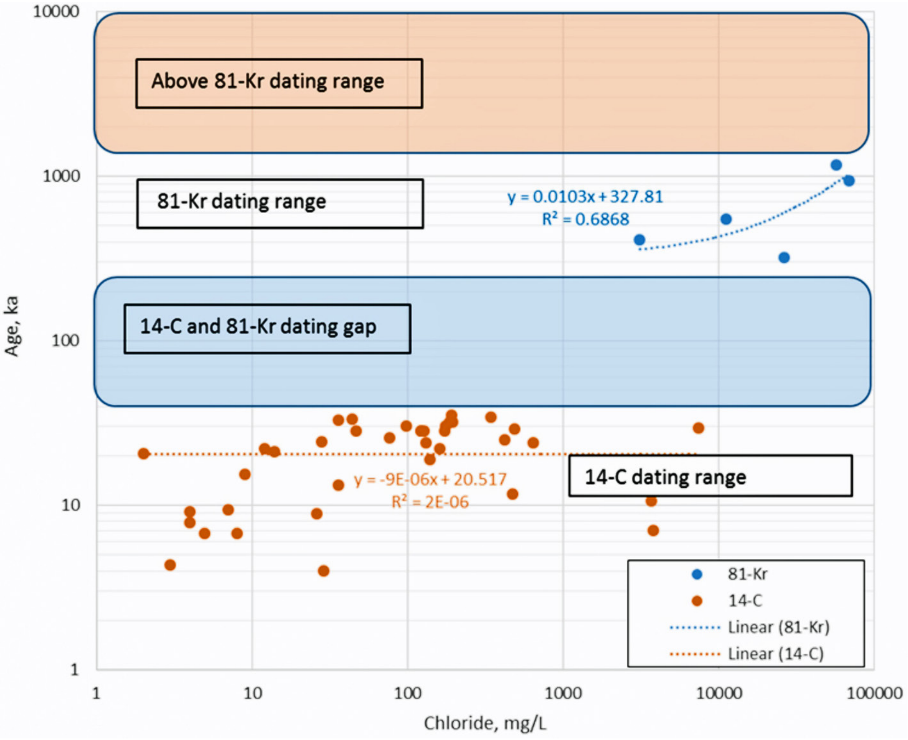

Fig. 4. Separate radiokrypton- and radiocarbon-calibrated chloride geochemical age trendlines (without arbitrary criterium chloride > 100 mg/L).

mg/L in LT-LV; calcium > 200 mg/L in LT-LV and > 50 mg/L in ES; TDS > 1,000 mg/L in LT-LV and > 500 mg/L in ES. The arbitrary criteria are based on the flow regime classification of the BAB. Average freshwater chemical composition is well known in this basin (Juodkazis and Mikalauskas, 1994). Ionic content that is significantly above the average maximum values is considered to represent outliers. The arbitrary criteria are very close to the average maximum values. A deep brine and active exchange shallow groundwater flow interact and mix in the delayed zone (Mokrik, 2003). In these parts, hydrochemical anomalies where brackish groundwater is formed from binary mixing might occur (Samalavičius, 2022). Newly filtered data were analysed–trendlines, equations and R^2 were obtained (Tables 1, 2).

An additional set (17 samples) of neither radiocarbon- nor radiokrypton-dated groundwater chemistry were collected from the data base (Appendix) (Vaikmäe et al., 2020). The samples were selected to represent shallow, intermediate and deep groundwater of the BAB. These units are the depth intervals of active exchange, delayed and stagnant groundwater. Equations obtained from ^{14}C and ^{81}Kr connecting trendlines were applied to estimate the geochemical age of unknown samples for Estonia and Lithuania-Latvia (Tables 1, 2). Two average geochemical age values for each site were calculated: from all major ions (Average 1), from filtered data with criteria defined as mentioned above – average 2 (Fig. 5, 6). Negative age values of groundwater results from mathematical equations obtained in the present study. In case the geochemical parameter value is too low (close to the dating gap's lower limit), the age equation results in negative age. Groundwater cannot be negative aged; therefore, such results are excluded from average calculations.

4. Results and discussion

Estonian samples for which geochemical ages were determined fall into a ^{14}C and ^{81}Kr dating gap or slightly overlap the radiocarbon range (Table 1; Fig. 5). Correlation of trendlines, R^2 is above 0.7 for all ions. These samples are from the southern part of the Estonia Homocline from a depth of >200 metres. A comparison of average values (Average 1 and 2) reveals that unfiltered data (Average 1) tend to result in younger geochemical ages obtained and *vice versa* (Fig. 5). Geochemical age calculated using different major ion contents differs up to two times. Radiocarbon-dated freshwater should be eliminated from geochemical age calculation. The increase of brackish groundwater Na, Ca, Cl, and Mg concentration is due to brine leakage through aquifers or other hydraulic connections such as faults. A portion of old brine leads to increased salinity and residence time accordingly. Groundwater age in the delayed zone should generally be in the dating gap because of the binary mixing of the two end members. Therefore, ^{14}C and ^{81}Kr calibration with dissolved ions should be applied to selectively picked radiocarbon-dated groundwater, which is affected by the brine discharge into shallow freshwater.

A peculiar case has been observed at the Värska site, where the average geochemical age was determined in O-Cm (97 ka) and Cmln (77 ka) levels and radiokrypton age (548 ka) in Cm-V aquifer groundwater. There seems to be a hydrochemical inversion: groundwater from the Cmln level is slightly less saline and therefore geochemically younger than the overlying O-Cm. This layer acts as an aquitard between the O-Cm and Cm-V levels; thus, groundwater should be less mobile and older. The geochemical age estimate, in this case, could be strongly affected by processes that occurred during the Pleistocene glaciations: cryogenic alteration and glacial meltwater intrusion. The cryogenic processes influenced groundwater in Estonia to be isolated from the rest of the BAB. The freshwater found in this area (especially the Cm-V and O-Cm aquifers) is depleted with $\boldsymbol{\delta}^{18}$O and is ten fold older, as based on radiocarbon (20–30 ka), than the rest of the BAB at the same depth (50–300 m). (Mokrik and Vaikmäe, 1988; Yezhova et al., 1996; Mokrik, 1997; Vaikmäe et al., 2001; Raidla et al., 2012, 2019a; Babre et al., 2016; Sterckx et al., 2017, 2018; Pärn et al., 2019; Mokrik et al., 2021; Samalavičius, 2022; Mokrik and Samalavičius, 2022). This, of course, has an influence on results of geochemical ages. Cryogenic brine rejection, which took place under cold-climate conditions, may increase salinity in the groundwater and; therefore, leads to errors in geochemical ages, making it seemingly older. However, the same process is likely to affect the brine member as well. In such case, the trend is corrected according to binary mixing which takes place in the Estonia Homocline. The radiocarbon and radiokrypton ages are valid for Estonian groundwater and can be used for geochemical age determination as long as it separated from the rest of the BAB.

Unknown groundwater geochemical ages for Lithuania and Latvia cover samples that are in radiocarbon to radiokrypton dating ranges, including the gap between them (Fig. 6; Table 2). Linear trendline fit was applied in these calculations, with R^2 above or close to 0.9. It is necessary to mention that correlation does not signify reliable results be-

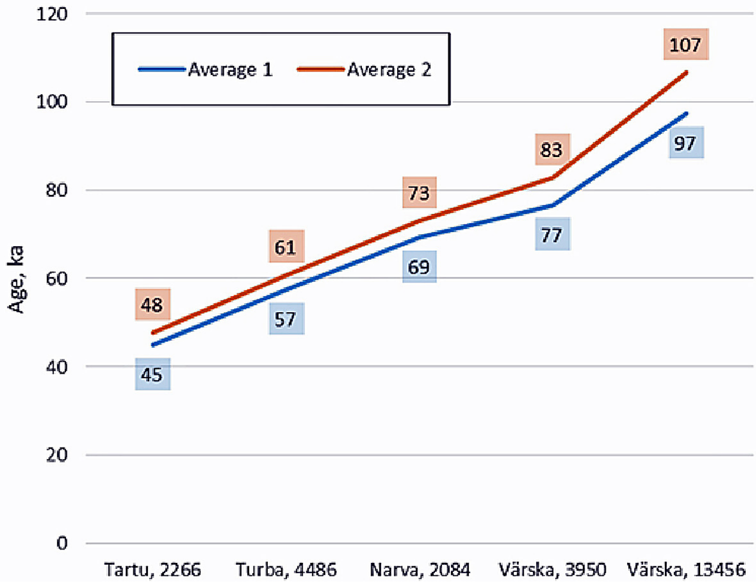

Fig. 5. Average geochemical age calculated for sites in Estonia.

Table 1. Geochemical age (ka) calculated using chloride, calcium, potassium, magnesium, sodium and TDS for sites in Estonia

			Geochemical age, ka								
Well no./ Fig. 1 no.	Sampling point	Well depth (m)	Cl	Ca	Ca >50 mg/L	K	Mg	Na	Na >100 mg/L	TDS	TDS >500 mg/L
2266/58	Tartu	280	47	37	51	31	44	51	58	31	55
4486/59	Turba	455	63	36	50	45	47	79	86	37	75
2084/62	Narva	211	82	44	57	49	53	99	105	42	91
3950/60	Värska	500	77	66	79	92	68	86	93	41	88
13456/61	Värska	470	98	90	102	144	87	100	106	46	103
Age equation			0.0514x + 26.388	0.5621x + 16.608	0.5446x + 30.961	7.8852x − 29.757	1.4892x + 20.157	0.1087x + 24.51	0.1068x + 32.316	0.0317x + 19.515	0.0311x + 27.653
R square value			0.85	0.74	0.71	0.92	0.78	0.87	0.85	0.86	0.84

cause of the uneven distribution of data on plots. This problem could be potentially resolved by applying similar geochemical age calculations using more isotopes for age determinations or hydrogeological modelling. More than two clusters could be deduced based on such methodology and benefit for finding better trendline fit (for example, nonlinear distribution). The other approach would be to collect more radiokrypton data. It would be strategically relevant to gain dating results of 100–200 ka-old groundwater to have a more even distribution of age values in the radiokrypton dating range. Geochemical age estimates in the present study may suggest the Likenai, Telsiai, Rokiskis and Palanga sites (Fig. 6).

A comparison of average values shows contrasting results in comparison to the Estonia subbasin (Fig. 5). Cases where groundwater with lower salinity values is excluded show younger groundwater in Lithuania and Latvia; this proves that the BAB should be subdivided into regions based on the sedimentary cover and on structural features of the crystalline basement.

Geochemical age varies ~two times depending on different major ions. The ^{14}C and ^{81}Kr calibration trend equations are likely to be unfit for use in radiocarbon dating range due to a lot of negative geochemical age values in lower salinity (<7 g/L) groundwater (Table 2). In contrast, samples from the radiokrypton dating range show a consistent geochemical age (i.e., Riga, Likėnai-Aukštaitija, Anykščiai, Palanga and Birštonas). The case of Riga could be used to evaluate the geochemical age determination technique. The radiokrypton-deduced age is >1,300 ka (above detection limit), but a correction model made on brine-glacial-meteoric water mixing reveals an age of >1,279 ka (Gerber et al., 2017). Comparing this date with geochemical ages obtained reveal closely similar results, especially in the case of calcium, calcium>200 mg/L, sodium and sodium >100 mg/L. This is an important observation because sodium-calcium ion exchange occurs in deep aquifers bearing fossil groundwater in the transition from Na-Cl to Ca-Cl groundwater chemical type (Mokrik, 2003). The sodium and calcium exchange may be applied in other geochemical age investigations when more relevant data will be collected from deep aquifers of the BAB.

Table 2. Geochemical age (ka) calculated using chloride, calcium, potassium, magnesium, sodium and TDS for sites in Lithuania and Latvia.

			Geochemical age, ka										
Well no./ Fig. 1 no.	Sampling point	Well depth (m)	Cl	Cl >100 mg/L	Ca	Ca >200 mg/L	K	Mg	Na	Na >100 mg/L	TDS	TDS >1000 mg/L
2647/ 46	Liepāja	58.1	32	−18	25	−41	45	49	25	−31	29	−22
1489/ 48	Inčukalns	365	27	−24	29	−37	44	29	23	−34	26	−26
50199/ 49	Jūrmala, Vaivari	400	48	−2	74	11	86	78	29	−27	47	−2
50210/ 50	Jūrmala, Vaivari	540	109	63	114	55	120	154	85	33	104	58
12350/ 51	Anykščiai	360	156	113	143	87	207	172	201	157	196	155
47543/ 52	Palanga	522	193	153	306	263	411	201	193	148	214	175
26418/ 53	Telsiai	715	4	−48	22	−45	34	24	1	−57	8	−44
11978/ 56	Likėnai Likėnai	434	39	−11	107	48	88	58	48	−7	62	13
4913/ 57	Birštonas	300	452	428	711	702	176	649	369	337	453	428
12349/ 54	Rokiskis, Vaiva	440	29	−22	103	43	113	60	27	−30	50	0
21965/ 55	Likėnai Aukštaitija	1011	1096	1113	1172	1200	647	1122	1089	1108	1095	1110
50194/ 47	Rīga, Gaiļezers	1027	1117	1135	1257	1292	689	1016	1207	1235	1141	1160
Age equation			0.0157x + 3.3765	0.0167x − 49.029	0.1519x − 10.054	0.1644x − 78.992	2.1022x − 0.8041	0.4186x − 8.2173	0.0336x − 1.7952	0.036x − 60.142	0.0096x − 4.3805	0.0102x − 57.58
R square value			0.94	0.93	0.97	0.97	0.97	0.96	0.91	0.89	0.94	0.93

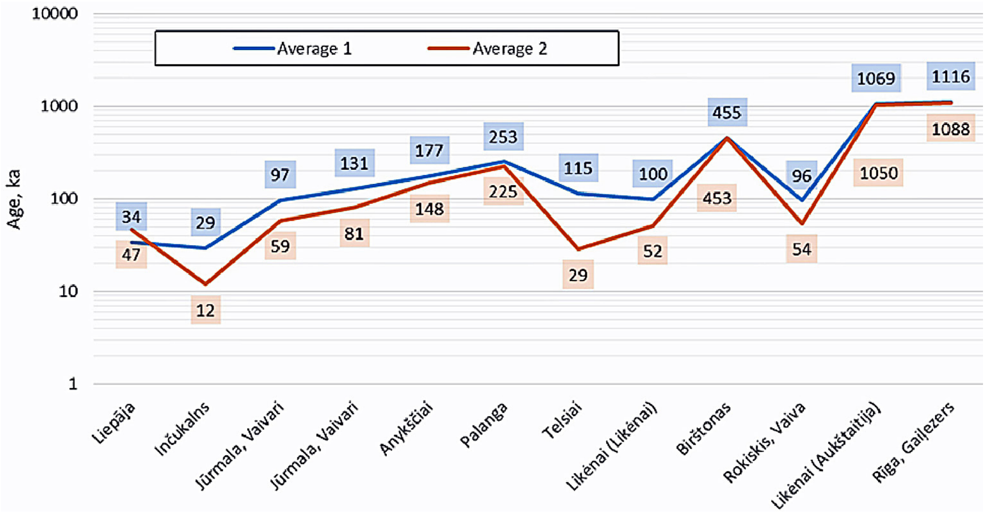

Fig. 6. Average geochemical age calculated for sites in Lithuania and Latvia.

5. Conclusions

Geochemical ages could be used for two main purposes: firstly, to date groundwater that falls within the conventional isotope ^{14}C and ^{81}Kr dating gap and, secondly, to extrapolate ages above the radiokrypton dating range. The initial methodical preparation for geochemical calculation should exclude modern freshwater data, because these can significantly distort the results. Chemical parameters such as sulphate or bicarbonate are not suited for geochemical age determination because of sensitivity to the geochemical environment, pH and Eh.

Geochemical ages determined in the Estonia Homocline area were found to vary from 31 to 144 ka, which completely covers the ^{14}C-^{81}Kr dating gap. In the rest of the BAB, geochemical age varies between 1 and 702 ka in intermediate depth aquifers (down to 1 km depth) and 647 to 1,292 ka in deep aquifers (> 1 km). The parameters which fit the geochemical dating best are: chloride, potassium, magnesium and sodium. The groundwater of age in the ^{14}C and ^{81}Kr dating gap forms mainly from the binary mixing of freshwater and brine. Therefore, these parameters are best suited for geochemical dating (saline groundwater type). Sodium and calcium ion exchange occurring in aquifers bearing fossil groundwater are suitable for dating old groundwater, which cannot be dated with radiokrypton (>1,300 ka). Both ^{14}C-^{81}Kr trends could be used for this purpose. Additional radiokrypton-calibrated groundwater chemistry values are necessary for a more accurate trendline interpolation. More tracers (tritium, CFC's, argon-39, etc.) could be introduced in a similar analysis to classify and date the groundwater of the BAB in more dating ranges (and gaps accordingly), thus expanding the age record.

Appendix is available in digital version of the article: http://www.geologos.com.pl/

References

Atkinson, A.P., Cartwright, I., Gilfedder, B.S., Cendón, D.I., Unland, N.P. & Hofmann, H., 2014. Using 14C and 3H to understand groundwater flow and recharge in an aquifer window. *Hydrology and Earth System Sciences* 18, 4951–4964.

Babre, A., Kalvāns, A., Popovs, K., Retiķe, I., Dēliņa, A., Vaikmäe, R. & Martma, T., 2016. Pleistocene age paleo-groundwater inferred from water-stable isotope values in the central part of the Baltic Artesian Basin. *Isotopes in Environmental and Health Studies* 52, 706–725.

Banys, J., Juodkazis, V. & Mokrik, R., 1979. Regional regularities of radiocarbon distribution in groundwaters of the Baltic artesian basin. *Water Resources* 6, 243–248 (in Russian).

Bethke, C.M. & Johnson, T. M., 2008. Groundwater age and groundwater age dating. *Annual Review of Earth and Planetary Sciences* 36, 121–152.

Ciężkowski, W., Gröning, M., Leśniak, P.M., Weise, S.M. & Zuber, A., 1992. Origin and age of thermal waters in Cieplice Spa, Sudeten, Poland, inferred from isotope, chemical and noble gas data. *Journal of Hydrology* 140, 89–117.

Delina, A., Kalvans, A., Saks, T., Bethers, U. & Valdis, V., 2012. *Highlights of groundwater research in the Baltic Artesian Basin*. University of Latvia, Riga, 156 pp.

Edmunds, W.M. & Smedley, P.L., 2000. Residence time indicators in groundwater: The East Midlands Triassic sandstone aquifer. *Applied Geochemistry* 15, 737–752.

Edmunds, W.M., Guendouz, A.H., Mamou, A., Moulla, A., Shand, P. & Zouari, K., 2003. Groundwater evolution in the Continental Intercalaire aquifer of southern Algeria and Tunisia: Trace element and isotopic indicators. *Applied Geochemistry* 18, 805–822.

Gerber, C., Vaikmäe, R., Aeschbach, W., Babre, A., Jiang, W., Leuenberger, M., Lu, Z.T., Mokrik, R., Müller, P., Raidla, V., Saks, T., Waber, H.N., Weissbach, T., Zappala, J.C. & Purtschert, R., 2017. Using 81Kr and noble gases to characterize and date groundwater and brines in the Baltic Artesian Basin on the one-million-year timescale. *Geochimica et Cosmochimica Acta* 205, 187–210.

IAEA, 2013. *Isotope methods for dating old groundwater*. IAEA, Vienna, 376 pp.

Juodkazis, V., 1980. *Formation and consumption of the groundwater resources of Baltic States*. Academy of Science, Vilnius, 176 pp. [in Russian]

Juodkazis, V., 2003. *Regional hydrogeology foundations*. Vilnius University Publishing House, Vilnius, 171 pp. [in Lithuanian]

Juodkazis, V. & Mikalauskas, V., 1994. *Groundwater*. [in:] Grigelis, A. & Kadūnas, V. (Eds): Geology of Lithuania. Science & Encyclopedia Publishing House, Vilnius, 334–398 [in Lithuanian]

Kotowski, T. & Najman, J., 2015. Results of the determination of He in Cenozoic aquifers using the GC method. *Ground Water* 53, suppl. 1, 47–55.

Levins, I., Levina, N. & Gavena, I., 1998. *Latvian groundwater resources*. State Geological Survey, Riga, 24 pp. [in Latvian]

Mace, E., Aalseth, C., Brandenberger, J., Day, A., Hoppe, E., Humble, P., Keillor, M., Kulongoski, J., Overman, C., Panisko, M., Seifert, A., White, S., Wilcox Freeburg, E. & Williams, R., 2017. Methods for using argon-39 to age-date groundwater using ultra-low-background proportional counting. *Applied Radiation and Isotopes* 126, 9–12.

Matsumoto, T., Chen, Z., Wei, W., Yang, G.M., Hu, S.M. & Zhang, X., 2018. Application of combined 81Kr and 4He chronometers to the dating of old groundwater in a tectonically active region of the North China Plain. *Earth and Planetary Science Letters* 493, 208–217.

Mažeika, J., Martma, T., Petrošius, R., Jakimavičiūtė-Maselienė, V. & Skuratovič, Z., 2013. Radiocarbon and other environmental isotopes in the groundwater of the sites for a planned new nuclear power. *Radiocarbon* 55, 951–962.

Mokrik, R., 1996. Pecularities of the formation of the isotopic composition of underground waters on the southern slope of the Baltic shield. *Geologija* 19, 16–25.

Mokrik, R., 1997. *The palaeohydrogeology of the Baltic Basin. Vendian and Cambrian*. Tartu University Press, 138 pp.

Mokrik, R., 2003. *The paleohydrogeology of the Baltic basin*. Vilnius University Publishing House, Vilnius, 333 pp. [in Lithuanian]

Mokrik, R. & Samalavičius, V., 2022. Interpretation of the anomalous groundwater chemistry and 234U/238U activity ratio disequilibrium in the northern part of the Baltic region. *Lithuanian Journal of Physics* 62, 21–43.

Mokrik, R. & Vaikmäe, R., 1988. *Paleohydrogeological aspects of Cm-V groundwater isotope content formation in Baltic region*. in: Isotope geochemistry research in Baltic and Belarus, pp. 133–143 [in Russian]

Mokrik, R., Juodkazis, V., Štuopis, A. & Mažeika, J., 2014. Isotope geochemistry and modelling of the multi-aquifer system in the eastern part of Lithuania. *Hydrogeology Journal* 22, 925–941.

Mokrik, R., Mažeika, J., Baublyte, A. & Martma, T., 2009. The groundwater age in the Middle-Upper Devonian aquifer system, Lithuania. *Hydrogeology Journal* 17, 871–889.

Mokrik, R., Samalavičius, V., Bujanauskas, M. & Gregorauskas, M., 2021. Environmental isotopes and noble gas ages of the deep groundwater with coupled flow modelling in the Baltic artesian basin. *Lithuanian Journal of Physics* 61, 53–65.

Morgenstern, U. & Daughney, C.J., 2012. Groundwater age for identification of baseline groundwater quality and impacts of land-use intensification - The National Groundwater Monitoring Programme of New Zealand. *Hydrogeology Journal* 456–457, 79–93.

Pärn, J., Raidla, V., Vaikmäe, R., Martma, T., Ivask, J., Mokrik, R. & Erg, K., 2016. The recharge of glacial meltwater and its influence on the geochemical evolution of groundwater in the Ordovician-Cambrian aquifer system, northern part of the Baltic Artesian Basin. *Applied Geochemistry* 72, 125–135.

Pärn, J., Affolter, S., Ivask, J., Johnson, S., Kirsimäe, K., Leuenberger, M., Martma, T., Raidla, V., Schloemer, S., Sepp, H., Vaikmäe, R. & Walraevens, K., 2018. Redox zonation and organic matter oxidation in palaeogroundwater of glacial origin from the Baltic Artesian Basin. *Chemical Geology* 488, 149–161.

Pärn, J., Walraevens, K., van Camp, M., Raidla, V., Aeschbach, W., Friedrich, R., Ivask, J., Kaup, E., Martma, T., Mažeika, J., Mokrik, R., Weissbach, T. & Vaikmäe, R., 2019. Dating of glacial palaeogroundwater in the Ordovician-Cambrian aquifer system, northern Baltic Artesian Basin. *Applied Geochemistry* 102, 64–76.

Paukstys, B. & Narbutas, V., 1996. Gypsum karst of the Baltic republics. *International Journal of Speleology* 25, 279–284.

Paukstys, B., Cooper, A.H. & Arustiene, J., 1999. Planning for gypsum geohazards in Lithuania and England. *Engineering Geology* 52, 93–103.

Purtschert, R., Yokochi, R., Jiang, W., Lu, Z.T., Mueller, P., Zappala, J., van Heerden, E., Cason, E., Lau, M., Kieft, T.L., Gerber, C., Brennwald, M.S. & Onstott, T.C., 2021. Underground production of 81Kr detected in subsurface fluids. *Geochimica et Cosmochimica Acta* 295, 65–79.

Raidla, V., Kirsimäe, K., Vaikmäe, R., Kaup, E. & Martma, T., 2012. Carbon isotope systematics of the Cambrian-Vendian aquifer system in the northern Baltic Basin: Implications to the age and evolution of groundwater. *Applied Geochemistry* 27, 2042–2052.

Raidla, V., Pärn, J., Aeschbach, W., Czuppon, G., Ivask, J., Kiisk, M., Mokrik, R., Samalavičius, V., Suursoo, S., Tarros, S. & Weissbach, T., 2019a. Intrusion of saline water into a coastal aquifer containing palaeogroundwater in the Viimsi Peninsula in Estonia. *Geosciences* 47, 9010047.

Raidla, V., Pärn, J., Schloemer, S., Aeschbach, W., Czuppon, G., Ivask, J., Marandi, A., Sepp, H., Vaikmäe, R. & Kirsimäe, K., 2019b. Origin and formation of methane in groundwater of glacial origin from the Cambrian-Vendian aquifer system in Estonia. *Geochimica et Cosmochimica Acta* 251, 247–264.

Samalavičius, V., 2022. *The groundwater isotope-geochemistry anomalies formation features in The Baltic Artesian Basin*. Vilnius University, 152 pp.

Samalavičius, V. & Mokrik, R., 2016. Tritium activity trend formation in groundwater of Quaternary aquifer system, south-eastern Lithuania. *Geologija. Geografija* 2, 173–181.

Samalavičius, V. & Mokrik, R., 2021. *Noble gas characteristics of the Baltic Artesian Basin groundwater*. [in:] Bioateitis, gamtos ir gyvybės mokslų perspektyvos, 46 pp. (in Lithuanian)

Sterckx, A., Lemieux, J.M. & Vaikmäe, R., 2017. Representing glaciations and subglacial processes in hydrogeological models: A numerical investigation. *Geofluids* 2017, 4598902.

Sterckx, A., Lemieux, J.-M. & Vaikmäe, R., 2018. Assessment of paleo-recharge under the Fennoscandian Ice Sheet and its impact on regional groundwater flow in the northern Baltic Artesian Basin using a numerical model. *Hydrogeology Journal* 26, 2793–2810.

Štuopis, A., Juodkazis, V. & Mokrik, R., 2012. The Quaternary aquifer system flow model by chemical and tritium isotope data: Case of south-east Lithuania. *Baltica* 25, 91–98.

Sturchio, N.C., Du, X., Purtschert, R., Lehmann, B.E., Sultan, M., Patterson, L.J., Lu, Z.-T., Müller, P., Bigler, T., Bailey, K., O'Connor, T.P., Young, L., Lorenzo, R., Becker, R., el Alfy, Z., el Kaliouby, B., Dawood, Y. & Abdallah, A.M.A., 2004. One million year old groundwater in the Sahara revealed by krypton-81 and chlorine-36. *Geophysical Research Letters* 31, 019234.

Sturchio, N.C., Kuhlman, K.L., Yokochi, R., Probst, P.C., Jiang, W., Lu, Z.T., Mueller, P. & Yang, G.M., 2014. Krypton-81 in groundwater of the Culebra Dolomite near the Waste Isolation Pilot Plant, New Mexico. *Journal of Contaminant Hydrology* 160, 12–20.

Torgersen, T. & Stute, M., 2013. *Helium (and other noble gases) as a tool for the understanding long time-scale groundwater transport*. [in:] Isotope methods for dating old groundwater. International Atomic Energy Agency, Vienna, 376.

Vaikmäe, R., Vallner, L., Loosli, H.H., Blaser, P.C. & Juillard-Tardent, M., 2001. Palaeogroundwater of glacial origin in the Cambrian-Vendian aquifer of northern Estonia. *Geological Society, London, Special Publications* 189, 17–27.

Vaikmäe, R., Martma, T., Ivask, J., Kaup, E., Raidla, V., Rajamäe, R., Vallner, L., Mokrik, R., Samalavičius, V., Kalvāns, A., Babre, A., Marandi, A., Hints, O. & Pärn, J., 2020. *Baltic groundwater isotope-geochemistry database*. https://doi.org/10.15152/GEO.488.

Virbulis, J., Bethers, U., Saks, T., Sennikovs, J. & Timuhins, A., 2013. Hydrogeological model of the Baltic Artesian Basin. *Hydrogeology Journal* 21, 845–862.

Winsberg, L., 1956. The production of chlorine-39 in the lower atmosphere by cosmic radiation. *Geochimica et Cosmochimica Acta* 9, 183–189

Yezhova, M., Polyakov, V., Tkachenko, A., Savitski, L. & Belkina, V., 1996. Paleowaters of North Estonia and their influence on changes of resources and quality of fresh groundwaters of large coastal water supplies. *Geology* 19, 37–40.

Zuber, A., Weise, S.M., Osenbrück, K., Grabczak, J. & Ciężkowski, W., 1995. Age and recharge area of thermal waters in Lądek Spa (Sudeten, Poland) deduced from environmental isotope and noble gas data. *Applied Geochemistry* 167, 327–349.

Zuber, A., Weise, S.M., Osenbriick, K. & Mateńko, T., 1997. Origin and age of saline waters in Busko Spa (Southern Poland) determined by isotope, noble gas and hydrochemical methods: evidence of interglacial and pre-Quaternary warm climate recharges. *Applied Geochemistry* 12, 643–660.

Zuzevičius, A., Mažeika, J. & Baltrūnas, V., 2007. A model of brakish groundwater formation in the Nemunas River Valley. *Geologija* 60, 63–75.

Manuscript submitted: 3 July 2022
Revision accepted: 23 October 2022