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# Tracing groundwater recharge conditions based on environmental isotopes and noble gases, Lom depression, Bulgaria

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ABSTRACT

*Study region:* Lom depression, Bulgaria.

*Study focus:* A multi-tracer investigation was applied to identify the recharge conditions and isotope hydrological character of four aquifers in the Lom depression (Northwest Bulgaria) using environmental isotopes ($\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C$, $^{3}H$, $^{14}C$) and noble gases. The radiocarbon age model of Ingerson and Pearson was used to estimate the mean residence time of groundwater samples from four aquifers (Dacian, Pontian, Meotian, Sarmatian). Our study focuses on the study of recharge conditions and provides an additional information to hydrodynamic understanding of the four aquifers.

*New hydrological insights for the region:* The mean residence time of groundwater samples represent the last twelve thousand years. In addition to a recently recharged groundwater sample, some samples represent the early Holocene and samples closely correspond to the late Pleistocene or the transition time between the early Holocene – late Pleistocene. The lower noble-gas recharge temperature values may indicate that the recharge occurred during the Late Glacial–Holocene climatic transition. These data can also be used to verify the existence of paleowater from the Pontian and Sarmatian aquifers on a trend of the mean residence time of older water heading north away from the study area. Besides the paleoclimatological investigation, it was determined that the Pontian aquifer has no hydraulic connection with the Danube River. The sandy layers and lenses forming the Dacian aquifer are apparently hydraulically isolated and therefore have high degree of heterogeneity.

## 1. Introduction

In the past several decades, there has been increasing concern for global water resources as influenced by climate change. This concern has motivated studies that examine the effects of climate change on the water cycle and their specific impacts on aquifers at regional and local scales (Aeschbach-Hertig and Gleeson, 2012). Groundwater is critical to water supply, irrigation and industry. Further assessment of its sustainability in response to future changes requires the better knowledge about hydrological features and

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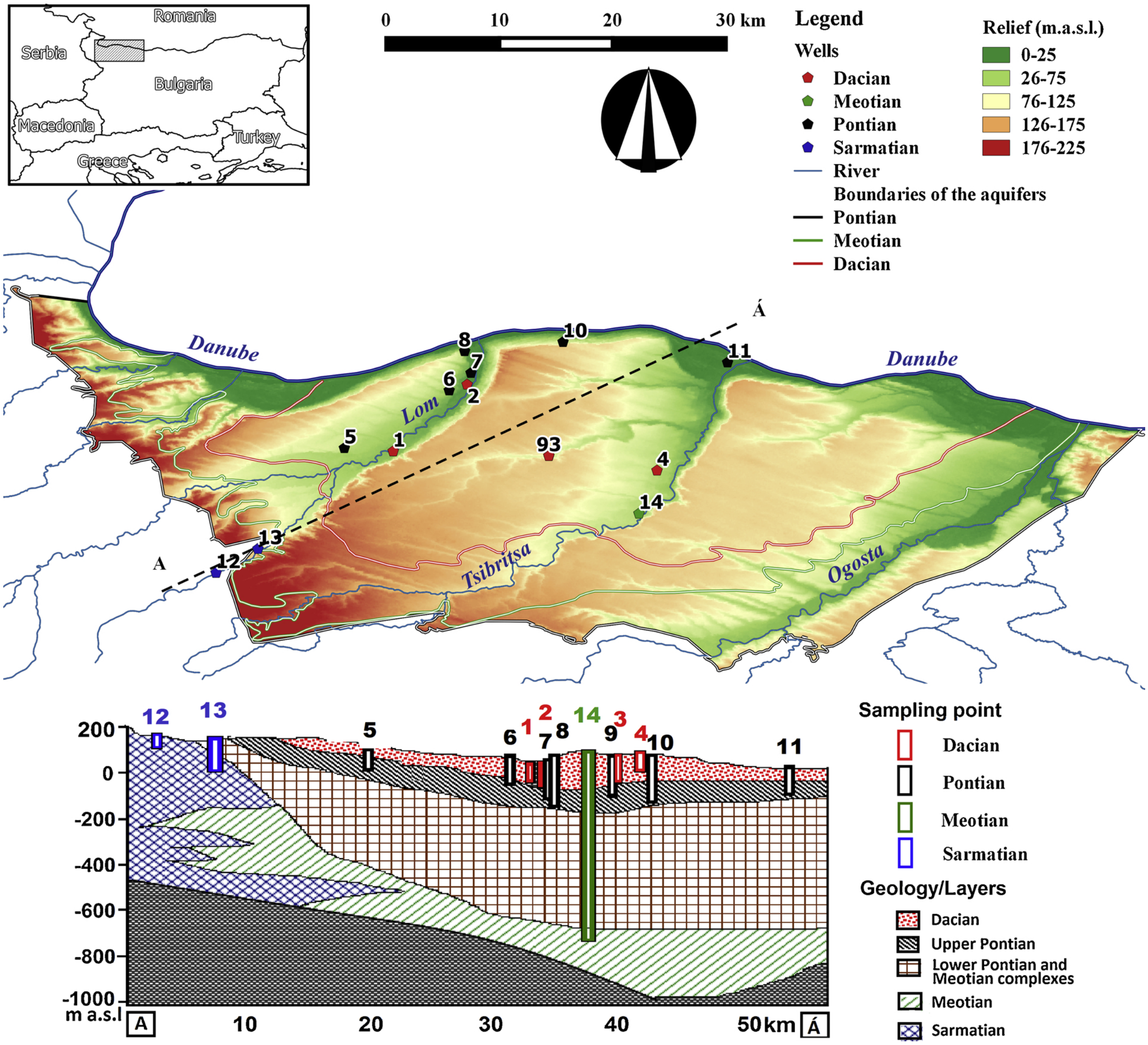



**Fig. 1.** Schematic cross section of the studied area is plotted from A to Á. The pentagon marks symbolize the locations of sampling points and their colors sign the aquifers. Lines on the topographic map show the extensions of the aquifers and the assumed depth of the aquifers in the cross section.

processes as well as climate-driven changes in specific aquifers.

Environmental isotope hydrology is a powerful tool in discovering the origin of water and the characterization of aquifer conditions. Using environmental tracers (isotopes, noble gases, etc.), groundwater recharge conditions such as mean residence time (MRT) and climatic influences at the time of recharge can be determined (Fontes, 1980; Clark and Fritz, 1997; Sarkar et al., 2017; Joshi et al., 2018). MRT values are usually estimated by the radiocarbon content of the water (Stute and Deak, 1989; Stute and Schlosser, 1993; Aeschbach-Hertig et al., 1999; Klump et al., 2007; Varsányi et al., 2011). A direct quantitative method using the temperature dependence of noble gas solubility in water allows the reconstruction of past mean annual temperatures.

In this study, a multi-tracer investigation was carried out for a multilayered aquifer system in the Lom depression in Bulgaria, which combines hydrochemical data, environmental isotopes ($\delta^{18}O$, $\delta^{2}H$, $\delta^{13}C$, $^{3}H$, $^{14}C$) and noble gases in order to reconstruct the recharge conditions and identify the isotopic character of this system. Although such isotopic hydrological studies exist for Bulgaria, the data coverage is poor and general knowledge is still scarce (Rank et al., 1985; Pulido-Bosch et al., 1999; Magro et al., 2010; Machkova et al., 2014, as well as unpublished data).

The aim of this first sampling campaign was to examine the aquifers of the Lom depression from a paleoclimatological point of view, and to use this information for late Pleistocene and Holocene paleoclimate reconstruction. Our study focuses on the study of recharge conditions and aiming to provide an additional information to hydrodynamic understanding of the four aquifers.

## 2. Study area

The study area is located in Northwest Bulgaria within the Danubian Plain and covers about 2500 $km^2$ (Fig. 1). From a geological point of view, this is the Lom depression (the most outstanding tectonic feature in Northwest Bulgaria), and from a hydrogeological point of view, this is the Lom artesian basin (part of the North Bulgarian artesian basin).

The climate of the study area is a fully-humid warm temperate zone with hot summers according to the Köppen-Geiger climate classification (Cfa). The recharge area belongs to the fully-humid warm temperate zone with warm summers (Cfb) (Peel et al., 2007). According to observations, the mean annual rainfall varies from 546 to 677 mm. The average air temperature on the Danubian Plain is 11.4 °C.

The study area is bounded on the North by the Danube River and its tributaries – the Lom River and the Tsibritsa River flow from the south within the study area. The relief of the interfluvial areas is flat, with altitudes up to about 150–200 m above sea level. In general, the relief is inclined slightly to the north and northeast towards the Danube River, with the lowest altitudes at about 30 m. The main drainage artery of the region is the Danube River.

### 2.1. Geology

From a geological point of view, the Lom depression is located in the western part of the Moesian plate and is mainly filled by Neogene sediments (*Archar Formation, the Meotian – Lower Pontian sediments*, *Brusartsi Formation*) and Quaternary deposits (Kojumdgieva, Popov, 1988). The *Archar Formation* ($N_1p$) mainly consists of well-sorted sand. *The Meotian – Lower Pontian sediments* that occur in the central part of the Lom depression are mainly built of clay. The *Brusartsi Formation* ($N_2$) mostly consists of clay with sandy lenses. All Neogene layers dip toward the northeast. *Quaternary sediments* are widespread in the region and were deposited under a variety of sedimentary environments, including: alluvial, fluvial, and aeolian (loess) origins.

### 2.2. Hydrogeological characterization

Hydrogeological conditions in the study area are mostly determined by geological factors. The main hydrogeological structure here is the Lom artesian basin (Yovchev, Ryzhova, 1962), coinciding with the tectonic unit of the Lom depression. This basin is an upper part of the North Bulgarian artesian region - the largest hydrogeological structure in Bulgaria, with well-expressed hydrodynamic, hydrochemical and hydrogeothermal zonality both in vertical and in horizontal directions (Antonov, Danchev, 1980).There is a multilayered aquifer system in these formations, in which five hydrogeological units can be distinguished (Table 1, Fig. 1).

The uppermost *Quaternary aquifer* is associated with alluvial sediments (in the Danube lowlands and river valleys), Early Pleistocene fluvial and fan deposits, and loess deposits. The most permeable Quaternary sediments are alluvial deposits (gravels and sands, with intercalations of clays), with discordant layering relations in comparing to the older formations, both aquiferous and low permeable.

The object of the study is groundwater formed in Neozoic strata. They sink from the western, southern and eastern periphery to the central northern part of the study area. Based on lithostratigraphic features of the sediments, the most important hydrogeological units (HGU) can be distinguished (Table 1).

*The Dacian-Romanian complex (DRA, Dacian aquifer)*, which is fully contained within the *Brusartsi Formation* (Table 1), is located at the upper part of Neozoic sediments. From a hydrogeological point of view, it is rather heterogeneous. The formation mainly consists of clay interspersed with sandy lenses with thickness from 0.5 to 20 m. Most of the lenses are completely isolated, and some of them are interconnected. The sandy lenses at the top of the *Brusartsi Formation* receive recharge from fluvial Early Pleistocene deposits (boulders, gravel and coarse-grained sands). The local groundwater discharge occurs through springs on the slopes of the Danube River and its tributaries. Some artesian wells have been established, providing a continuous discharge to the surface. Regionally, the Dacian-Romanian complex is an aquiclude, with coal layers at the bottom. The hydraulic conductivity of individual sand lenses is in the range of 0.64 to 2.1 m/d (Benderev et al., 2010; Stoyanov, 2019).

*The Upper-Pontian aquifer* (UPA, Pontian aquifer) covers an area of 1700 $km^2$ and it is the most essential aquifer in the study area. It is important for water supply to settlements (by a large number of wells) and therefore it is quite well investigated (Benderev et al., 2010; Stoyanov, 2019). The aquifer is related to sediments of the *Archar Formation* (Table 1) with total thickness of about 80–100 m. It is built of different grained sands, locally with intercalations of clayey sands.

The hydraulic conductivity of the aquifer is relatively high but varies in the fraction of sand, related to the paleogeographic environment during sedimentation. In the western parts of the study area, near the town of Lom, the Upper-Pontian deposits are rather coarse with transmissivity from a few hundred to over 2000 $m^2/d$ (Benderev et al., 2010). To the east, finer-grained sands are deposited, leading to a reduction of transmissivity values (from 40 to155 $m^2/d$). At the eastern edge, the transmissivity is about 20 $m^2/d$. Locally, a highly permeable zone is identified near the village of Valchedram, with transmissivity around 750 $m^2/d$.

Outcropping zones of the aquiferous *Archar Formation*, as well as the areas where it is covered only by the loess deposits, are located on the peripheral parts of the Lom depression (Fig. 2). It is in these peripheral parts that the main recharge of the Upper-Pontian aquifer occurs. Due to flat relief and widespread loess cover, the surface outflow is relatively slow and the rainwater infiltrates into the loess complex as groundwater recharge into the aquifers, which generates baseflow of the rivers or outflow through springs.

The aquiferous sandy layers dip to the central parts of the depression, where they are covered by sediments of the *Brusartsi Formation*. Most clayey deposits in the lower part of the last formation play the role of a regional aquiclude separating the two

**Table 1**
Lithostratigraphic and hydrogeological units in the study area (after Kojumdgieva and Popov, 1988; Nakov et al., 2001; Ivanov et al., 2002; Yaneva and Ognjanova-Rumenova, 2012; Yovchev and Ryzhova, 1962; Benderev et al., 2010).

| Formation | Age | Thickness | Lithological description | Hydrogeological unit |
|---|---|---|---|---|
| Brusartsi | Late Pontian-Romanian | from 40-50 to 120-140 m locally | gray pure and sandy clay with intercalations of sand and locally strata of lignite coal in the area of Lom | Dacian - Romanian complex (DRC) |
| Archar | Late Pontian | from 20-30 to 100-120 m | sand with intercalations of clay | Upper-Pontian aquifer (UPA) |
| Smirnenski | Maeotian-Pontian | up to 500-550 m in the area of the Lom depression | alternation of predominantly claystone and sandstone. The sandstone content decreases to the north | Maeotian – Lower Pontian aquitard |
| Florentin | Chersonian | 70-80 m; the top of the formation is usually eroded | varved calcareous claystone with rare layers of dolomitic limestone and limestone | |
| Furen | Late Bessarabian/ Early Chersonian | 15-550 m | limestone with local reef development | Sarmatian aquifer |
| Krivodol | Volhynian/ Bessarabian | from 20 to 150-200 m and more | gray-blue calcareous claystone with intercalations of clayey limestone | Sarmatian aquitard |
| Deleina | Badenian | 50-200 m | limy clays | |

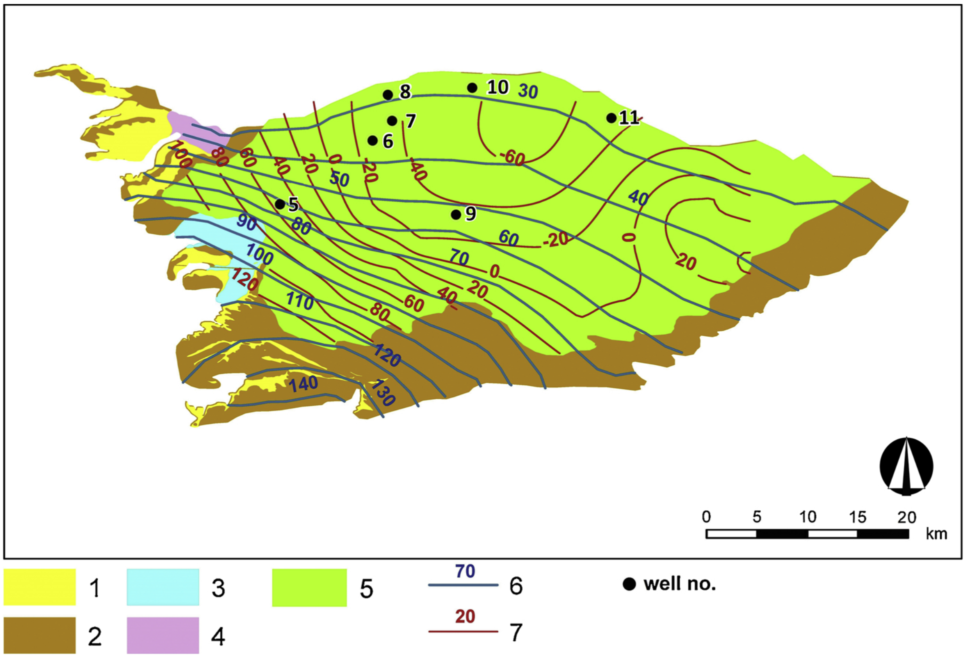



**Fig. 2.** Zoning of the Pontian aquifer: 1 - zone of outcrops of the aquifer; 2 - zone where the aquifer is covered by the Loess Formation; 3 – zone of aquifer recharge through alluvial sediments; 4 - discharge zone of the aquifer into the Archar-Orsoya lowland; 5 - zone where the aquifer is covered by low permeable sediments and the aquifer is confined; 6 - groundwater table elevation m asl, 7 - top of the Archar Formation.

hydrogeological units: DRA and UPA. The general direction of the groundwater flow is to the north. The aquifer is confined in its inner part with a hydraulic pressure head of between 40 and 80 m. The hydrodynamic features of UPA presented in Fig. 2 are derived both from observations and groundwater modeling results (Benderev et al., 2010; Stoyanov, 2019).

The drainage of UPA occurs into alluvial deposits of the Danube River at the western and eastern edges of the aquifer. One part of the groundwater probably flows north towards Romania, where the sandy fraction in the Dacian-Romanian sediments prevails (Enciu, 2009).

The Upper Pontian aquifer overlays the *Meotian – Lower-Pontian aquiclude (MLPA)*. The latter is mainly made up of the clayey sediments of the Smirnenski and Florentin Formations (Table 1), with intercalations of aquiferous sandstones and dolomitic limestones in the first and the second formations respectively.

Outside the areas covered by the *Archar Formation*, these clayey formations are covered by loess deposits and outcrop only in river valleys. Data on the spatial position of the MLPA is mainly based on boreholes for oil and gas exploration. There are only a few drillings with available hydrogeological information and these are mainly in areas where the aquifer is relatively shallow. The aquiferous sandy and carbonate layers within MLPA are confined with difficult water exchange, except for of its outcropping zones.

The Meotian – Lower-Pontian sediments are underlain by those of Sarmatian age (Fig. 1) that refer to various lithostratigraphic units with complex spatial relationships due to Facies changes (Cheshitev and Filipov, 1989a, b). These units have been studied in more details outside the study area. Within the scope of the Lom depression, there is information only on their lithological composition based on deep boreholes. The most permeable is limestone of the *Furen Formation* (Table 1), forming the *Sarmatian aquifer (SA)*. In outcropping zones, it is karstified with transmissivity up to 220 $m^2$/d. Sarmatian sediments of the *Krivodol and Delein Formations* consist of clays with enhanced carbonate content form the *Sarmatian aquiclude* (Table 1).

As a whole, in the study area the Sarmatian aquifer is confined, with delayed water exchange. In the present study, attention is mainly focused on the northern zones, where the Sarmatian sediments dip downwards (Filipov, 1995; Haydutov, 1995), with transition from unconfined to confined conditions.

## 3. Methods

Groundwater sampling was conducted in October, 2016. Four water samples were taken from the Dacian aquifer and seven from the Pontian aquifer, as well as two from the Sarmatian aquifer and one groundwater sample from the Meotian aquifer (see Table 1). The sampling points are shown on the map and the cross-section (Fig. 1). For artesian wells and pumping station, the groundwater samples were collected directly at the well heads after the boreholes/wells had been primed. Three types of wells were identified and sampled: artesian wells, water supply wells and observation wells (Table 2). The artesian wells flow continuously. The samples from the water supply wells were taken during exploitation periods, and the two observation wells were primed to remove more than three volumes of the water before sampling.

The groundwater temperature, pH, electrical conductivity, alkalinity, as well as redox potential were measured in situ in the field.

**Table 2**
Chemical components of the groundwater samples collected during the field campaign held in October, 2016; (ORP: oxidation-reduction redox potential; COD: chemical oxygen demand).

| well no. | well name | well type | depth (m) | HGU | T (°C) | pH | ORP (mV) | EC (µS/cm) | $Na^+$ (mg/l) | $K^+$ (mg/l) | $Ca^{2+}$ (mg/l) | $Mg^{2+}$ (mg/l) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | S. Mahala | artesian well | 64 | DRA | 14.5 | 6.7 | 64 | 484 | 19.9 | 1.6 | 69.2 | 12.9 |
| 2 | Fishfarm | water supply well | 60 | DRA | 16.4 | 7.3 | −14 | 1031 | 53.3 | 3 | 139.5 | 31.2 |
| 3 | Komoshtitsa pumped | artesian well | 120 | DRA | 15.4 | 7 | −65 | 731 | 48.7 | 0.9 | 84.8 | 21.5 |
| 4 | Valchedram | water supply well | 80 | DRA | 15.9 | 7.2 | −11 | 632 | 41.5 | 1 | 81.4 | 14.4 |
| 5 | Vasilovtsi | water supply well | 75 | UPA | 13 | 7.5 | 177 | 510 | 11.8 | 1.5 | 67.6 | 13.3 |
| 6 | Agroinvest | observation well | 106 | UPA | 15.4 | 7.6 | 73 | 812 | 50.5 | 1.9 | 113.4 | 25.9 |
| 7 | RUA | water supply well | 114 | UPA | 15.8 | 7.8 | −18 | 788 | 56.7 | 1.9 | 81.4 | 16.3 |
| 8 | Hospital | water supply well | 180 | UPA | 14.8 | 7.5 | 124 | 844 | 44.6 | 1.7 | 109.8 | 31.2 |
| 9 | Komoshtitsa deep | observation well | 220 | UPA | 13.7 | 7.6 | 203 | 840 | 55.1 | 1.1 | 89.2 | 33.3 |
| 10 | Dolno Linevo | water supply well | 200 | UPA | 16.5 | 7.1 | −27 | 832 | 38 | 1.5 | 98.2 | 29.3 |
| 11 | Dolni Tsibar | artesian well | 150 | UPA | 14.6 | 6.3 | −10 | 1135 | 103.5 | 2.4 | 93.2 | 22.8 |
| 12 | Bukovets | artesian well | 40 | SA | 12.9 | 6.9 | 23 | 800 | 28.7 | 1.4 | 122.9 | 20.9 |
| 13 | Smirnenski | water supply well | 120 | SA | 15.3 | 7 | 43 | 632 | 33.8 | 2 | 78.3 | 20.8 |
| 14 | Cherni Vrah | artesian well | 819 | MLPA | 13.9 | 6.8 | 232 | 722 | 43.6 | 1.3 | 106.3 | 21.6 |

| well no. | $NH_4^+$ (mg/l) | $Cl^-$ (mg/l) | $HCO_3^-$ (mg/l) | $SO_4^{2-}$(mg/l) | $NO_3^-$(mg/l) | $NO_2^-$ (mg/l) | $PO_4^{3-}$ (mg/l) | $F^-$ (mg/l) | COD (mg/l) | TOC (mg/l) | Ca/Mg molar ratio | $SO_4+HCO_3$/ Ca + Mg (meq/meq) | $SO_4$/Ca molar ratio |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 0.1 | 5.1 | 301.9 | 19 | 0.3 | 0.1 | < 0.5 | 0.3 | 1 | 0.4 | 3.2 | 1.2 | 0.1 |
| 2 | 1.7 | 22 | 550.5 | 109.6 | 0.3 | 0.1 | < 0.5 | 0.2 | 4.2 | 3.6 | 2.7 | 1.2 | 0.3 |
| 3 | 0.1 | 10 | 438 | 33 | 0.3 | 0.1 | < 0.5 | 0.2 | 0.8 | 0.4 | 2.4 | 1.3 | 0.2 |
| 4 | 0.2 | 8.7 | 378.8 | 27 | 0.3 | 0.1 | < 0.5 | 0.1 | 0.7 | 0.4 | 3.4 | 1.3 | 0.1 |
| 5 | < 0.05 | 9.6 | 224.9 | 35 | 31 | < 0.05 | < 0.5 | 0.3 | < 0.5 | 0.6 | 3.1 | 1 | 0.2 |
| 6 | 1.1 | 24 | 420.2 | 62 | 8.6 | 0.2 | 0.7 | 0.1 | 1.2 | 1.3 | 2.7 | 1 | 0.2 |
| 7 | 2.6 | 63 | 372.9 | 0.9 | 0.3 | 0.1 | < 0.5 | 0.2 | 1.5 | 0.5 | 3 | 1.1 | 0 |
| 8 | 1.3 | 25 | 544.9 | 19 | 0.4 | 0.1 | < 0.5 | 0.2 | 0.6 | 0.6 | 2.1 | 1.2 | 0.1 |
| 9 | < 0.05 | 4.4 | 541.6 | 14 | 17 | < 0.05 | < 0.5 | 0.5 | < 0.5 | 0.4 | 1.6 | 1.3 | 0.1 |
| 10 | 1.6 | 19 | 494.2 | 16 | 0.4 | 0.1 | < 0.5 | 0.2 | 1.2 | 0.8 | 2 | 1.2 | 0.1 |
| 11 | 5.5 | 172.7 | 396.6 | 4.1 | 0.3 | 0.2 | < 0.5 | 0.3 | 2.4 | 0.5 | 2.5 | 1 | 0 |
| 12 | < 0.05 | 16 | 461.7 | 57 | 0.4 | 0.1 | < 0.5 | 0.5 | < 0.5 | 0.6 | 3.6 | 1.1 | 0.2 |
| 13 | 0.2 | 9.1 | 369.9 | 41 | 0.3 | < 0.05 | < 0.5 | 0.3 | 0.5 | 0.5 | 2.3 | 1.2 | 0.2 |
| 14 | < 0.05 | 3.5 | 476.5 | 9.8 | 6 | 0.1 | < 0.5 | 0.3 | 0.6 | 0.3 | 3 | 1.1 | 0 |

The $HCO_3^-$, $Cl^-$, $NO_3^-$, $NO_2^-$, $F^-$, $PO_4^{3-}$, $SO_4^{2-}$, $Ca^{2+}$, $K^+$, $Na^+$, $Mg^{2+}$, and $NH_4^+$ analyses were conducted at the ICER laboratory, Debrecen, Hungary. The anions were measured by ion chromatography and trace elements by MP-AES (microwave plasma atom emission spectrometer), additionally $NH_4^+$ was determined by spectrophotometry. The COD (chemical oxygen demand) of the water samples was determined by titration, while the TOC (total organic carbon) by high temperature catalytic oxidation with infrared detection.

Stable isotopic analyses of water and dissolved inorganic carbon (DIC) from the water samples were carried out with an automated GASBENCH II sample preparation device attached to a Thermo Finnigan Delta$^{PLUS}$ XP mass spectrometer (Vodila et al., 2011). Hydrogen and oxygen isotopes of the groundwater, as well as carbon and oxygen isotopes of carbonate samples were analyzed and then expressed as $\delta^2H$, $\delta^{18}O$, and $\delta^{13}C$ values relative to V-PDB for $\delta^{13}C$ and V-SMOW for $\delta^2H$ and $\delta^{18}O$, following the equation: $\delta = (R_{sample}/R_{standard}-1)*1000$, where R is the $^2H/H$, $^{18}O/^{16}O$ or $^{13}C/^{12}C$ ratio in the sample or in the international standard. The precision of the measurements is better than ± 0.15 ‰ for $\delta^{18}O$ and ± 2 ‰ for $\delta^2H$, and ± 0.1 ‰ for $\delta^{13}C$.

The $^{14}C$ content in the dissolved inorganic carbon (DIC) from the groundwater samples were measured using accelerator mass spectrometry (EnvironMICADAS AMS). No preservatives were used, but samples were stored in dark and cold conditions. DIC content of the groundwater sample was degassed as $CO_2$ with addition of phosphoric acid (85%) in vacuum sealed gas reaction vessels at 75 °C for 2 h (Molnár et al., 2013a). The carbon-dioxide samples were cleaned in a cryogenic gas extraction line and converted into graphite for AMS analyses. The $^{14}C$ results were corrected for decay of the standard and for isotope fractionation using on-line $^{13}C$ measurements on the AMS (Molnár et al., 2013b).

Noble gas and tritium measurements were performed by a VG5400 noble gas mass spectrometer (Fisons Instruments). The groundwater samples for dissolved noble gases were stored in copper tubes sealed by stainless-steel pinch-off clamps. The mass spectrometer has an automated extraction and purification system for degassing noble gases from water samples and after the sample passes through this system the mass spectrometer measures the noble gas concentrations as well as $^3He/^4He$ isotope ratios (Papp et al., 2012). The tritium concentrations were measured using the $^3He$ ingrowth method with a detection limit of 0.012 tritium units (TU) or better, and the accuracy is 2.4% for TU between 1 and 20 (Palcsu et al., 2010).

## 4. Results and discussion

### *4.1. Hydrogeochemistry*

Chemical parameters of the 14 samples are summarized in Table 2. Shallow and deep wells were sampled: there are water samples from the Dacian aquifer with depths between 60–120 m and from the Pontian aquifer from depths between 75–225 m, and one sample from the Meotian aquifer at a depth of 819 m. The temperature of the groundwater from the Dacian aquifer was between 14.5 and 16.4 °C and the water samples from the Pontian aquifer was in the range 13.0–16.5 °C. The aquifers are generally characterized by neutral pH values (6.27–7.84).

In terms of dissolved anions, $HCO_3^-$ dominates in the waters followed by $SO_4^{2-}$ and then $Cl^-$. In case of dissolved cations the dominant ion is $Ca^{2+}$ followed by $Mg^{2+}$. The Ca-$HCO_3$ water type is dominant in all aquifers except for the RUA well which is of Ca-Na-$HCO_3$ type and for Dolni Tsibar, which has Ca-Na-$HCO_3$-Cl chemistry.

It can be seen that moving away from the recharge zone, the dissolved solids become slightly higher along the prevailing flow lines (Fig. 1, Table 2). A study of possible water-rock interaction processes which control the groundwater chemistry is necessary to understand the basic geochemical characteristics and processes of an aquifer. Possible carbonate dissolution processes can be determined based on the Ca/Mg molar ratio. In this case, the Ca/Mg ratio of the samples is in the range from 1.6 to 3.6 (Table 2), where the ratio between 1 and 2 is attributed to calcite dissolution and a ratio higher than 2 is typical for the contribution of calcite rich minerals (Katz et al., 1997). Probable ion-exchange processes can be characterized by an equivalent ratio of Ca + Mg versus $SO_4 + HCO_3$ of groundwater samples, which values are between 1.0 and 1.3 (Table 2) and this indicates that ion exchange can occur in the area and suggests dissolution of carbonate and gypsum (Fisher and Mullican, 1997). This molar ratio is appropriate for estimating the contribution of gypsum, calcite and dolomite to the water composition, although the $SO_4$/Ca molar ratio of groundwater samples ranges between 0 and 0.3 (Table 2) may confirm the lack of gypsum dissolution. For a better illustration of the chemical character of the groundwater, ions are plotted in a Piper diagram (Fig. 3).

### *4.2. The stable oxygen and hydrogen isotope composition of samples*

The stable isotopic values of groundwater samples from all the studied aquifers vary between -9.82 ‰ and -14.24 ‰ for $\delta^{18}O$, and between -68.7 ‰ and -103.1 ‰ for $\delta^2H$ (Fig. 4). The samples from the Dacian aquifer display less variability between -10.44 ‰ and -12.44 ‰ for $\delta^{18}O$, and -72.4 ‰ to -89.6 ‰ for $\delta^2H$. The GMWL (Global Meteoric Water Line) shows the average relationship between the hydrogen and oxygen isotope ratios in precipitation, which is expressed as a worldwide average $\delta^2H = 8*\delta^{18}O + 10$ (Craig, 1961). Although there is no measured stable isotope composition of precipitation in the area, the recent precipitation at Ramnicu Valcea, Romania (GNIP station of IAEA) located 150 km northeast of the research area can be considered representative for the Danubian Plain. Monthly $\delta^{18}O$ values in regional precipitation are -2.5 ‰ to -15.0 ‰ and -23.6 to -111.0 for $\delta^{18}O$ and $\delta^2H$, respectively. The prevailing winds for the study area are from west and northwest and seasonally from south. Generally, west-east or south-north transport of air masses over Bulgaria prevails. Zonal circulation has a larger influence on precipitation in Bulgaria compared to meridional circulation (Nojarov, 2017). Some prominent local geographical features including the Black Sea in the east, and Carpathian Mountains and Balkan Mountains to the north and west, contribute to the evolution of air masses (Knight et al.,

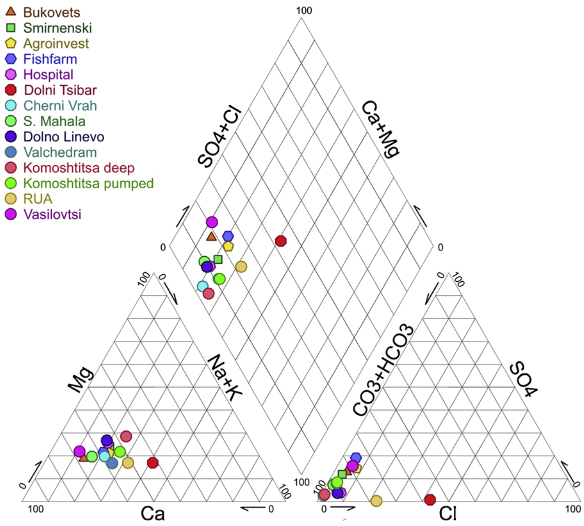



**Fig. 3.** Piper diagram of the groundwater samples.

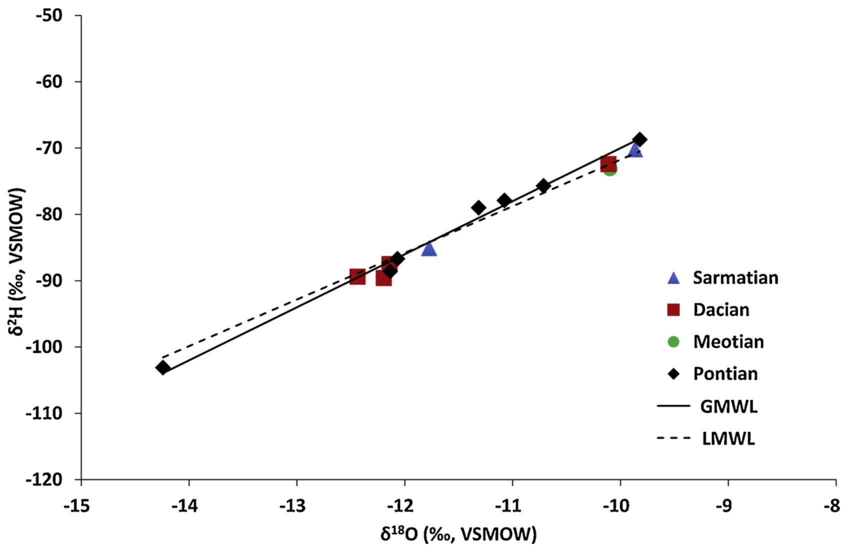



**Fig. 4.** $\delta^2$H versus $\delta^{18}$O values of groundwater investigated in this study as compared to the GMWL and LMWL.

2004). According to the stable isotope data for Ramnicu Valcea precipitation, the LMWL (Local Meteoric Water Line) can be calculated and gives a regional average $\delta^2H = 7.03*\delta^{18}O-1.44$ and the hydrogen and oxygen isotope distributions are correlated for meteoric waters, thus these data reflect a meteoric origin for groundwater samples.

### 4.3. *Water mean residence time*

To better understand water transport in a multilayered aquifer system, the residence time of groundwater can be a useful tool. Tritium, radiocarbon, noble gases and stable isotopes can be used both for age dating as tracers in groundwater systems. These environmental isotopic tracers can be used to estimate residence time, and to determine environmental conditions upon recharge.

#### 4.3.1. *Tritium*

As tritium is a radioactive isotope with a short half-life of 12.32 years (Lucas and Unterweger, 2000), it can be used to identify modern recharge. Natural tritium is produced in the atmosphere due to nuclear reactions between galactic cosmic rays and atmospheric gases. The tritium concentration in precipitation is representative of the atmosphere and is about 10 TU in Central Europe. The average value in Debrecen, Hungary is 11.3 TU (Palcsu et al., 2018) and 11.66 TU in Râmnicu Vâlcea, Romania (Varlam et al., 2013). Our tritium results are shown in Table 3. Most of the groundwater samples showed very low tritium concentrations (lower than 0.02 for RUA, Valchedram, Komoshtitsa pumped, Cherni Vrah, Dolno Linevo, Hospital, S. Mahala, Komoshtitsa deep, Dolni

**Table 3**
Isotope data of sampled points with modelled mean residence time of waters using Ingerson and Pearson (1964) model.

| well no. | well name | $^{14}C$ pMC | $^{3}H$ (TU) | $\delta^{13}C$ (‰, VPDB) | $\delta^{2}H$ (‰, VSMOW) | $\delta^{18}O$ (‰, VSMOW) | pH | $\varepsilon^{13}C_{HCO3-CO2(g)}$ | $\delta^{13}C_{soil}$ | $A_0$ | Ingerson and Pearson (yr BP) | aquifer |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | S. Mahala | 63.18 ( ± 0.22) | 0.014 ( ± 0.003) | −14.75 | −72.4 | −10.11 | 6.67 | −9.11 | −15.89 | 91.49 | 3061 | Dacian |
| 2 | Fishfarm | 53.11 ( ± 0.19) | 1.232 ( ± 0.025) | −13.11 | −87.5 | −12.14 | 7.34 | −8.89 | −16.11 | 80.21 | 3409 | Dacian |
| 3 | Komoshtitsa pumped | 29.15 ( ± 0.19) | 0.003 ( ± 0.005) | −13.42 | −89.6 | −12.2 | 7 | −9.00 | −16.00 | 82.73 | 8622 | Dacian |
| 4 | Valchedram | 23.67 ( ± 0.14) | 0 ( ± 0.005) | −13.32 | −89.4 | −12.44 | 7.23 | −8.95 | −16.05 | 81.78 | 10249 | Dacian |
| 5 | Vasilovtsi | 98.6 ( ± 0.28) | 6.818 ( ± 0.057) | −12.86 | −68.7 | −9.82 | 7.5 | −9.28 | −15.72 | 80.64 | −1663 | Pontian |
| 6 | Agroinvest | 23.85 ( ± 0.13) | 0.150 ( ± 0.005) | −11.9 | −103.1 | −14.24 | 7.61 | −9.00 | −16.00 | 73.36 | 9288 | Pontian |
| 7 | RUA | 33.61 ( ± 0.16) | 0 ( ± 0.020) | −14.51 | −88.6 | −12.14 | 7.84 | −8.96 | −16.04 | 89.16 | 8065 | Pontian |
| 8 | Hospital | 46.15 ( ± 0.18) | 0.009 ( ± 0.007) | −13.65 | −77.9 | −11.08 | 7.46 | −9.07 | −15.93 | 84.53 | 5004 | Pontian |
| 9 | Komoshtitsa deep | 63.68 ( ± 0.20) | 0.015 ( ± 0.005) | −10.6 | −75.7 | −10.71 | 7.6 | −9.20 | −15.80 | 66.17 | 316 | Pontian |
| 10 | Dolno Linevo | 39.83 ( ± 0.17) | 0.008 ( ± 0.005) | −15 | −79 | −11.32 | 7.13 | −8.88 | −16.12 | 91.74 | 6897 | Pontian |
| 11 | Dolni Tsibar | 20.83 ( ± 0.12) | 0.016 ( ± 0.004) | −13.93 | −86.7 | −12.07 | 6.27 | −9.10 | −15.90 | 86.34 | 11756 | Pontian |
| 12 | Bukovets | 46.95 ( ± 0.18) | 0.986 ( ± 0.020) | −12.21 | −70.2 | −9.87 | 6.91 | −9.29 | −15.71 | 76.67 | 4055 | Sarmatian |
| 13 | Smirnenski | 15.94 ( ± 0.11) | 0.107 ( ± 0.007) | −10.92 | −85.1 | −11.77 | 6.96 | −9.01 | −15.99 | 67.36 | 11917 | Sarmatian |
| 14 | Cherni Vrah | 60.37 ( ± 0.20) | 0.006 ( ± 0.004) | −14.59 | −73.1 | −10.1 | 6.84 | −9.18 | −15.82 | 90.91 | 3384 | Meotian |

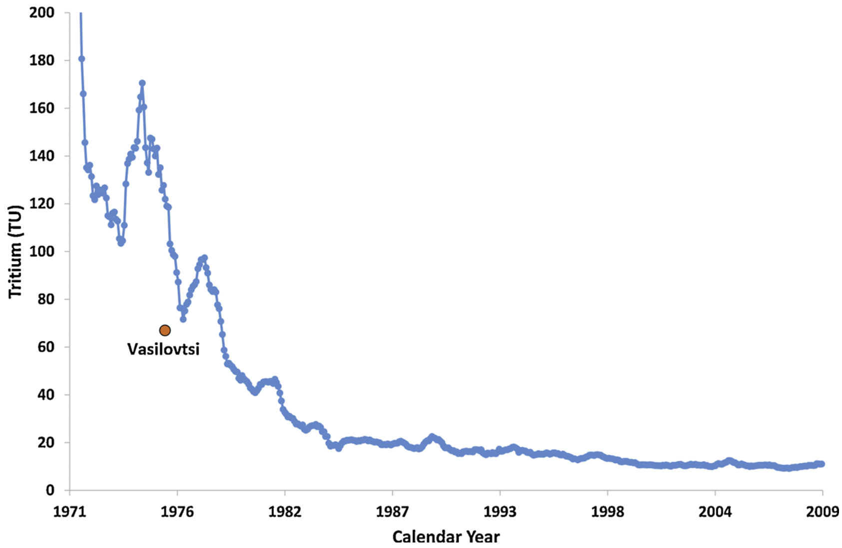



**Fig. 5.** The yearly $^3H$ concentrations in precipitation from 1961 to 2009 in Vienna, Austria (IAEA/WMO (2009)) with the calculated initial tritium content of Vasilovtsi by the time of recharge.

Tsibar). Groundwater from the Vasilovtsi well had the highest tritium content of 6.8 TU (indicating modern recharge), followed by Fishfarm with a value of 1.23 TU and Bukovets with a value of 0.99 TU. There are two wells with a value in the range of 0.1-0.15 TU (Smirnenski, Agroinvest). The measureable tritium in Smirnenski well along with the lowest radiocarbon content (15.94 pMC) attracts attention and suggests mixing with recent water. This mixing process could have occurred due to a malfunction of the well or from a well with multiple screen depths, or from leakage. Assuming this sample represents aquifer water, we infer that the Sarmatian aquifer is affected by mixing between recent and old groundwater. A similar observation was made by Joshi et al., 2018 with regards to the isotopic signature of the groundwater from aquifers of NW India. This is a reasonable interpretation as the recharge zone is located nearby.

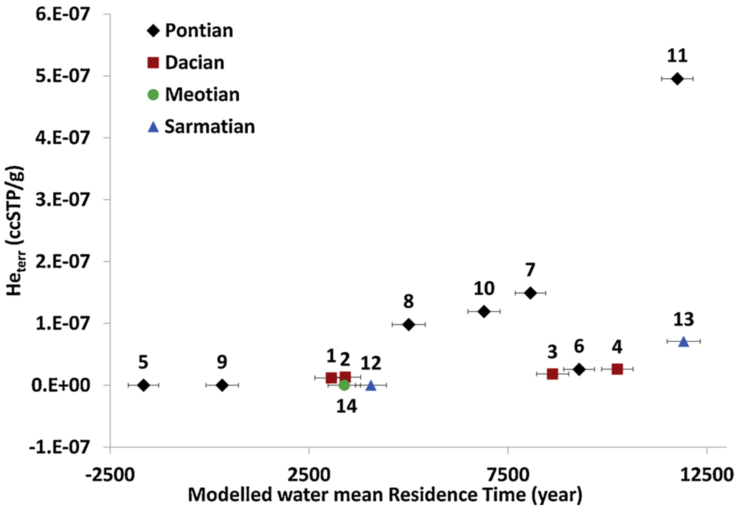
Since groundwater from the Vasilovtsi well has the highest tritium concentration, it is worth calculating the $^3H/^3He$ age of groundwater. Although dissolved $^3He$ in groundwater may have several origins, the $^3H/^3He$ age of Vasilovtsi can be calculated and more precise groundwater residence time can be estimated. The tritiogenic $^3He$ concentration is calculated by subtracting from the measured helium content that amount due to atmospheric solubility, excess air and radiogenic production (Schlosser et al., 1989). Based on these calculations, the tritiogenic $^3He$ is 60.1 TU and the $^3H/^3He$ age is calculated to be 40.6 ± 0.7 years. According to the calculations and tritium recovery curve of precipitation in Vienna (Fig. 5), the initial tritium concentration at the time of recharge was 66.9 ± 2.9 TU, and the decay from the time of the mid 1960s and mid-1970s "bomb" peak this peak provides a reference point for determining groundwater residence time. The samples were taken in 2016 and a $^3H/^3He$ age of ˜40 years implies the recharge events could have occurred around 1976 (Fig. 5).

### *4.3.2. Modelled radiocarbon ages*

In groundwater, the DIC (dissolved inorganic carbon) results from $CO_{2(aq)} + HCO_3^- + CO_3^{2-}$ which are dissolved in the recharge water, and these contain atmospheric $^{14}C$. This is a useful tool for dating groundwater, and is measured in dissolved inorganic/organic carbon. For estimation of groundwater residence time, we use the radiocarbon model of Ingerson and Pearson (1964). This method produces similar ages to a variety of other methods (Ingerson and Pearson, 1964; Fontes and Garnier, 1979; Mook, 1980; Salem et al., 1980; Plummer and Glynn, 2013). To calculate the apparent age of the groundwater (in years), the following equation can be used:

$$t = 8267 \ln (A_0/A_t)$$

To estimate the residence time of groundwater, the initial $^{14}C$ content ($A_0$) of DIC in groundwater at the recharge zone must be evaluated. Here the Vasilovtsi well can be used as representative for initial $^{14}C$ content, based on the $^3H/^3He$ age and the measured $^{14}C$ content which is 98.6 pMC. This is somewhat higher based on the groundwater recharge that can have occurred during the last 50 years and is therefore likely to contain a component of bomb derived $^{14}C$. The results of the Ingerson and Pearson model (1964) are given in Table 3. In this model, a dilution factor (q) is used to estimate $A_0$, according to the equation: $q = (\delta^{13}C_{DIC} - \delta^{13}C_{carb})/(\delta^{13}C_{soil} - \delta^{13}C_{carb})$. Here, $\delta^{13}C_{DIC}$ is the measured $\delta^{13}C$ in groundwater, and $\delta^{13}C_{carb}$ is the $\delta^{13}C$ value of the dissolved carbonate which is usually 0 ‰. The $\delta^{13}C_{soil}$ term is the $\delta^{13}C$ value of the $CO_2$ in the soil, which depends on the plants growing there (in temperate zone: $C_3$), $C_3$ plants are about -25 ‰ (Table 3). An enrichment factor was used to calculate q because the soil can be enriched in $^{13}C$ based on equilibrium exchange processes between soil $CO_2$ and DIC at increasing pH. The dilution factor (q) can be calculated based on the equation: $q = (\delta^{13}C_{DIC} - \delta^{13}C_{carb})/((\delta^{13}C_{soil} + \varepsilon^{13}C_{DIC\text{-}CO2(soil)}) - \delta^{13}C_{carb})$ where the $\varepsilon^{13}C_{DIC\text{-}CO2(soil)}$ depends on pH following the $\delta^{13}C$




| well no. | well name |
|---|---|
| 1 | S. Mahala |
| 2 | Fishfarm |
| 3 | Komoshtitsa pumped |
| 4 | Valchedram |
| 5 | Vasilovtsi |
| 6 | Agroinvest |
| 7 | RUA |
| 8 | Hospital |
| 9 | Komoshtitsa deep |
| 10 | Dolno Linevo |
| 11 | Dolni Tsibar |
| 12 | Bukovets |
| 13 | Smirnenski |
| 14 | Cherni Vrah |

**Fig. 6.** Terrigenous helium concentration in groundwater concerning different aquifers in respect to groundwater age (yr BP).

mixing model of Pearson (1965) and Pearson and Hanshaw (1970), see $\delta^{13}C$ correction (Table 3). The error in the corrected ages was derived by propagating the errors of the independent elements in the dilution factor equation, including errors for measured radiocarbon content and $\delta\ ^{13}C$ values of DIC, pH, and alkalinity are the measurement errors. The corrected ages are reported with one sigma error.

The $^{14}C$ content of the groundwater samples range from 15.9 pMC to 98.6 pMC (Table 3, Fig.1). These data suggest that three aquifers of four might contain waters recharged during the early Holocene - late Pleistocene (Pontian, Dacian, Sarmatian). There are two wells in the Pontian aquifer (Dolni Tsibar, 20.83 ± 0.12 pMC; Agroinvest, 23.85 ± 0.13 pMC) with low radiocarbon content. The wells near the area of Agroinvest are characterized by higher radiocarbon content, moving away from the well (in any direction) the radiocarbon content is increasing. In the Dacian aquifer, there is only one well, the Valchedram, which might show late Pleistocene recharge given the level of 23.7 pMC. In the Sarmatian aquifer, the oldest water was obtained from all samples with 15.94 pMC for the Smirnenski well. This is of interest, because the distance between Bukovets and Smirnenki is less than 5 km although the screen depth of Smirnenski well is 100 m deeper, so this difference may be related to another flow path.

The age of the groundwater is the mean water residence time in the aquifer of each individual groundwater sample. This was calculated from the average of ages derived from the various radiocarbon models. The uncertainty associated with residence times is obtained as the standard deviation of ages from the different models, and then this average age is consistently used in the following interpretations. The $^{3}H/^{3}He$ age determination showed the most recently-recharged sample was Vasilovtsi from the Pontian aquifer (Fig. 5). A number of samples appear to be recharged during the late Holocene (Komoshtitsa deep, S. Mahala, CherniVrah, Fishfarm, Bukovets) with ages between 3000 and 4000 calibrated years before present (yr BP) (Fig. 6). In addition, there are samples with ages between 5000–6800 yr BP (Hospital, Dolno Linevo) from the Pontian aquifer. Furthermore, there are groundwater samples with residence time between 8000-9300 yr, which represents the early Holocene (RUA, Komoshtitsa pumped, Agroinvest) (Fig. 6). Samples with ages between 10 000–12 000 yr BP (Valchedram, DolniTsibar, Smirnenski) closely correspond to the late Pleistocene or the early Holocene – late Pleistocene transition.

#### *4.3.3. Terrigenous helium accumulation*

Terrestrial $^{4}He$ ($^{4}He_{terr}$) can be used to classify groundwaters with longer mean residence times (Solomon, 2000). It is used especially when characterizing the old fractions in groundwater that have experienced mixing. Modelled water mean residence times plotted versus $^{4}He_{terr}$ content identify groundwater samples with relatively long residence times that contain excess $^{4}He_{terr}$ (Fig. 6), likely incurred during the early Holocene – late Pleistocene climatic transition. We observe a tendency of increased terrigenic helium contents in older groundwater from the Pontian aquifer and in the Sminenski sample (Fig. 6).

#### *4.3.4. Hydrogeological aspects*

The correct interpretation of the results requires the exact location of the boreholes sampled. Some of the boreholes correspond to the deeper confined zone of the aquifer, and others to the outcrops of the aquiferous formations. Considering the groundwater properties of the aquifers and corresponding boreholes, the following hydrogeological settings can be defined.

*4.3.4.1. Sarmatian.* One of the boreholes (Bukovets) is located within the outcrops of the aquifer, and the second one (Smirnenski) is below the local erosion base (Fig. 1). The covered (confined) part of the aquifer is generally characterized by very slow water exchange. This is mainly observed at the village of Smirenenski. The groundwater residence time for the borehole in the village of Smirnenski shows weak water exchange and the highest groundwater age, possibly due to the influence of deeper water.

*4.3.4.2. Meotian.* Relatively younger groundwater compared to other waters indicates a probable connection between the Smirnenski Formation sandy layers with the outcropping sands of the Pontian aquifer (Fig. 1).

*4.3.4.3. Dacian.* A specific feature of this aquifer complex are sandy lenses and layers that vary in thickness, location in depth, and hydraulic conductivity values (depending of the sandy content). The wide range of groundwater age in two neighboring boreholes close to the village of Komoshtitsa (300 yr BP and 8600 yr BP) indicates poor hydraulic connection between different lenses and layers as well as different recharge and discharge conditions. This significant difference also suggests the absence of a hydraulic connection in this area between the waters of Dacian and underlying Pontian aquifers.

*4.3.4.4. Pontian.* The numerous samples of the Pontian aquifer (7 samples) demonstrate groundwater ages that range from about 300 to 11 700 yr BP. One exception is the water sample from the borehole in the village of Vasilovtsi, where water can be considered to be modern. In this area, the Pontian aquifer is relatively shallow and could have a direct connection with the river passing near the village at lower elevation. The highest values (from about 8000 to 11 700 yr BP) are common in the central part of the aquifer, with a reduced age near the town of Lom (to 5000 yr BP). This phenomenon could be explained by significantly higher hydraulic conductivity values in this area. A second possibility could be intensive groundwater exploitation near to the town of Lom.

The various samples taken from the Pontian aquifer were analyzed for possible interrelations between parameters determined from individual groundwater samples. The most indicative parameter is thought to be the groundwater age. Increasing groundwater age is associated with increasing concentrations of $Na^+$, $K^+$, $Cl^-$ concentrations and increasing electrical conductivity of water. Moreover, an increase nitrite $NO_2^-$ and ammonium $NH_4^+$ contents is registered along with increasing of COD (chemical oxygen demand) in these water samples. Conversely, the redox potential and nitrate $NO_3^-$ show evident decrease with the increasing groundwater age.

### *4.4. Noble gas temperature and paleoclimate reconstruction*

The concentrations of noble gases are suitable indicators to estimate the groundwater recharge temperature. The noble gas concentrations of Ne, Ar, Kr and Xe are derived from the atmosphere and after their dissolution into the water their concentrations do not change along the flow path since they take part neither in chemical nor biological processes. The interpretation of noble gas concentrations in groundwater requires inverse modelling, which can determine reliable noble gas solubility or recharge temperature (NGT). This requires a correction for excess air and a model proposed to determine its formation. The closed system equilibration model of gas partitioning was used in this study (Aeschbach-Hertig et al., 1999). Noble gas results are shown in Table 4 and the uncertainty of the noble gas temperature determination is about ± 0.6 °C.

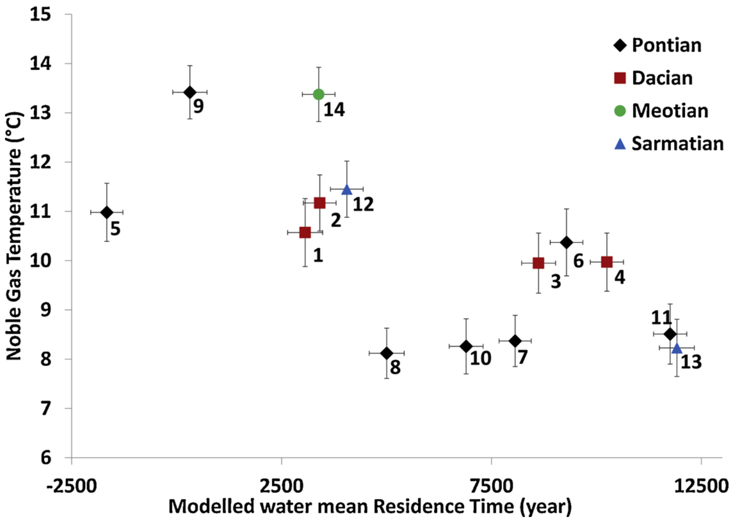
We already noted that the average air temperature in the Danubian Plain is 11.4 °C. Water temperature near in the recharge area (Vasilovtsi) is 13 °C, as measured in the field, which may reflect ground temperature. The noble gas temperatures measured vary between 8.1 °C and 13.4 °C (Table 4). NGTs of the Dacian aquifer vary between 9.95 °C and 11.17 °C although the NGTs from the Pontian aquifer shows higher variability 8.1 °C to 13.4 °C.

Somewhat lower NGT values in the Smirnenski, Dolni Tsibar and Valchedram wells presumably indicate recharge during the glacial-Holocene transition (Fig. 7). A likely admixture of recent groundwater to glacial water is conceivable due to the low radiocarbon content with measureable tritium in a water sample from the Smirnenski well, and a minimal tritium content in the Dolni Tsibar well.

The waters from the Sarmatian and Pontian aquifers are presumed to have recharged during late glacial times, or to have incorporated glacial water that result in NGT somewhat lower than groundwater from the mid and late Holocene (Fig. 7). These groundwater samples are characterized by NGTs of about 8.3 °C, whereas the late Holocene waters have NGTs around 12 °C, which is

**Table 4**
Noble gas results and calculated noble gas temperature (°C) data of groundwater samples and their fit to the CE-model.

| well no. | well name | He (ccSTP/g) | Ne (ccSTP/g) | Ar (ccSTP/g) | Kr (ccSTP/g) | Xe (ccSTP/g) | R/Ra | NGT (°C) | ± ΔT (°C) | $X^2$ | p (%) | $^4He_{terr}$ (ccSTP/g) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | S. Mahala | 7.58E-08 | 2.69E-07 | 4.33E-04 | 9.55E-08 | 1.33E-08 | 0.84 | 10.57 | 0.69 | 0.03 | 86.8 | (1.19 ± 0.15)E-08 |
| 2 | Fishfarm | 7.23E-08 | 2.44E-07 | 3.96E-04 | 8.85E-08 | 1.27E-08 | 0.78 | 11.17 | 0.57 | 0.63 | 42.6 | (1.31 ± 0.14)E-08 |
| 3 | Komoshtitsa pumped | 1.47E-07 | 4.93E-07 | 5.37E-04 | 1.08E-07 | 1.44E-08 | 0.77 | 9.95 | 0.61 | 0.04 | 84.6 | (1.82 ± 0.30)E-08 |
| 4 | Valchedram | 9.36E-08 | 2.79E-07 | 4.32E-04 | 9.53E-08 | 1.35E-08 | 0.69 | 9.97 | 0.59 | 0.18 | 67.1 | (2.62 ± 0.16)E-08 |
| 5 | Vasilovtsi | 6.45E-08 | 2.74E-07 | 4.17E-04 | 9.25E-08 | 1.29E-08 | 2.70 | 10.98 | 0.59 | 0 | 94.5 | (0.00 ± 0.15)E+00 |
| 6 | Agroinvest | 1.02E-07 | 3.16E-07 | 4.67E-04 | 9.97E-08 | 1.37E-08 | 0.68 | 10.37 | 0.68 | 0.17 | 68.3 | (2.58 ± 0.18)E-08 |
| 7 | RUA | 2.12E-07 | 2.59E-07 | 4.22E-04 | 9.57E-08 | 1.40E-08 | 0.28 | 8.38 | 0.52 | 0.93 | 32.7 | (1.49 ± 0.25)E-07 |
| 8 | Hospital | 1.61E-07 | 2.59E-07 | 4.24E-04 | 9.72E-08 | 1.41E-08 | 0.37 | 8.13 | 0.51 | 0.08 | 76.9 | (9.81 ± 0.20)E-08 |
| 9 | Komoshtitsa deep | 7.48E-08 | 3.67E-07 | 4.20E-04 | 8.91E-08 | 1.21E-08 | 0.94 | 13.42 | 0.54 | 0.05 | 82.6 | 0.00( ± 1.84E-09) |
| 10 | Dolno Linevo | 1.81E-07 | 2.63E-07 | 4.34E-04 | 9.85E-08 | 1.41E-08 | 0.33 | 8.25 | 0.56 | 0.05 | 82.4 | (1.19 ± 0.02)E-07 |
| 11 | Dolni Tsibar | 5.57E-07 | 2.61E-07 | 4.39E-04 | 9.82E-08 | 1.41E-08 | 0.13 | 8.51 | 0.61 | 0.57 | 45.2 | (4.95 ± 0.06)E-07 |
| 12 | Bukovets | 5.29E-08 | 2.40E-07 | 3.85E-04 | 8.70E-08 | 1.22E-08 | 1.00 | 11.27 | 0.57 | 0.18 | 87.4 | 0.00( ± 1.29E-09) |
| 13 | Smirnenski | 1.33E-07 | 2.62E-07 | 4.30E-04 | 9.76E-08 | 1.38E-08 | 0.45 | 8.23 | 0.58 | 0.01 | 91.4 | (7.08 ± 0.18)E-08 |
| 14 | Cherni Vrah | 8.04E-08 | 2.23E-07 | 4.21E-04 | 8.91E-08 | 1.21E-08 | 0.89 | 13.37 | 0.55 | 0.04 | 84.9 | 0.00( ± 1.89E-09) |




| well no. | well name |
|---|---|
| 1 | S. Mahala |
| 2 | Fishfarm |
| 3 | Komoshtitsa pumped |
| 4 | Valchedram |
| 5 | Vasilovtsi |
| 6 | Agroinvest |
| 7 | RUA |
| 8 | Hospital |
| 9 | Komoshtitsa deep |
| 10 | Dolno Linevo |
| 11 | Dolni Tsibar |
| 12 | Bukovets |
| 13 | Smirnenski |
| 14 | Cherni Vrah |

**Fig. 7.** Noble gas temperatures vs. modelled water mean residence time (year) with errors (standard deviation of modelled ages).

similar to the mean annual air temperature of 11.4 °C so the largest temperature change observed is about 3.7 °C. These recharge temperature differences might represent the transition time between these two periods. This transition period can be also observed in the stable isotope data, where the groundwater with larger residence times has more negative $\delta^2H$ and $\delta^{18}O$ values, suggesting the groundwater recharge occurred during the Late Glacial–Holocene climatic transition period (Table 3, Fig. 8).

Paleoclimate reconstruction studies in Europe based on dissolved noble gases in groundwater have shown higher temperature differences between the Holocene and glacial periods, for example 5–7 °C in the Bohemian Cretaceous Basin (Corcho Alvarado et al., 2013) and at least 5 °C in the Glatt Valley, Switzerland (Beyerle et al., 1998). In the Pannonian Basin, the warming after the last glacial maximum (LGM) reached a temperature of 9.1 °C (Varsányi et al., 2011) and this temperature in the Ledo-Paniselian Aquifer is 9.5 °C (Blaser et al., 2010). Comparing these NGT values in Europe, the temperature differences obtained here appear to be too low. Comparable observations were made for a Jurassic limestone aquifer in Poland, where the NGT was 2–3.5 °C lower than recent recharge groundwater (Osenbrück et al., 1993). Assuming some mixing with recent waters, these noble gas temperatures could reflect either mixing, or a transition phase between the two climatic periods. The lower NGT difference between the colder and warmer recharge waters can be explained as that the mean residence times do not reflect groundwater recharged at the LGM, i.e. the groundwater at the oldest part of the aquifer does not reflect glacial temperatures.

## 5. Conclusion

This study presents a hydrogeological and palaeoclimatic interpretation for the Lom depression, Northwest Bulgaria. A multi-tracer approach is presented to reconstruct the recharge temperature and identify isotopic hydrological character of the aquifers using the environmental isotopes: $\delta^{18}O$, $\delta^2H$, $\delta^{13}C$, $^3H$, $^{14}C$, and noble gases. The stable isotope results show that the recharge sources of the groundwater studied are local meteoric water. For a groundwater sample from the Vasilovtsi well, the $^3H/^3He$ groundwater age of 40.6 ± 0.7 years was confirmed. Tritium content in deep groundwater with low radiocarbon content was determined for three

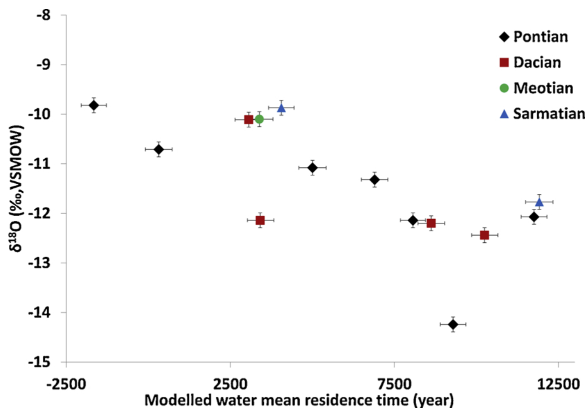



**Fig. 8.** Modelled water mean residence time (year) (standard deviation of modelled ages) against stable oxygen isotopes ( ± 0.2 ‰).

wells. The presence of tritium can be attributed to mixing process between old and recent waters due either to overexploitation or leakage in the well. The Ingerson and Pearson radiocarbon model was used to estimate mean residence times taking into account chemical and isotope hydrological parameters to achieve precise groundwater ages from the $^{14}C$ content of dissolved inorganic carbon. Modelled groundwater residence times fall within the last twelve thousand years, with samples from the early Holocene with ages between 8000–9300 yr BP (RUA, Komoshtitsa pumped, Agroinvest) and older waters that date to between 10 000–12 000 yr BP (Valchedram, Dolni Tsibar, Smirnenski), from the late Pleistocene or the transition time between the Holocene and Pleistocene.

The noble gas results provide quantitative information on the temperature of recharge and qualitative information on the time of recharge. They make it conceivable to estimate the climatic conditions under which the recharge took place and to confirm the time of recharge. Values of 3–4 °C lower NGT for Smirnenski, Dolni Tsibar and Valchedram presumably indicate that the recharge occurred during the glacial-Holocene transition. An admixture of recent Holocene groundwater to glacial water is likely due to the low radiocarbon content in presence of some tritium in water sample from Smirnenski well, and a low tritium content for the Dolni Tsibar well.

The results of this study significantly change our previous knowledge about the hydrodynamics of the Lom Basin. In particular, we have shown that the Pontian aquifer has no hydraulic connection to the Danube River.The sandy layers and lenses forming the Dacian aquifer are apparently hydraulically isolated and therefore have high degree of heterogeneity.

## Acknowledgement

We are grateful for the help of Prof. A.J. Timothy Jull for the English revision and for his constructive comments. The research was supported by the European Union and the State of Hungary, co-financed by the European Regional Development Fund in the project of GINOP-2.3.2-15-2016-00009 'ICER'.

## Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.ejrh.2019.100611.

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