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# ANALYSIS OF THE RADIOGENIC CARBON-14 RECORD OF GROUNDWATER AT THE ZLATNA POST-MINING SITE (ROMANIA)

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**Abstract:** Groundwater samples from a post-mining environment of a gold deposit in Romania (Zlatna mining site, Apuseni Mountains) were analysed for carbon isotopes in order to estimate the age, recharge conditions and flow transit velocities. Three distinct types of groundwater have been considered: springs, domestic wells and mine water. The previous stable isotope results ($^{2}H/^{1}H$ and $^{18}O/^{16}O$) showed that the recharge source of the groundwater is local meteoric water. All obtained per cent modern carbon (pMC) values are less than 100% which indicates old groundwater or mixture of old groundwaters and modern water coming from precipitation. The distribution of pMC data clearly shows an increasing trend from 40.86% in mine water to values as high as 93% in phreatic water sampled in domestic well. Springs show an intermediate position with pMC values varying from 54.03% to 79.41%. Mean calibrated date vary from 6065 BC to 2553 BC in mine water, from 3754 BC to 186 AC in springs, and from 563 AC to 1354 AC in phreatic water. Non-renewable paleo-waters could not be recognized in the study area. Correlation between pMC values and $\delta^{18}O$ values of groundwater allowed to recognize inputs from the late-glacial (Younger Dryas) recharge in the case of mine water and several springs, as well as contributions from modern precipitation in the case of other springs and phreatic water sampled in domestic wells. Using radiocarbon dating for pairs of sampling points allowed the calculation of flow transit velocities of groundwater. For the groundwater sampled in springs we obtained a mean flow transit velocity of 2.4 m/year.

**Keywords:** C-isotopes, groundwater, radiocarbon dating, post-mining, Zlatna, Apuseni Mountains

## 1. INTRODUCTION

The present work is the first radiogenic $^{14}C$ study performed on the groundwater system at the Zlatna mining site. In combination with our previous results (Papp et al,. 2017, 2020), the carbon isotopes data allowed us to estimate the age, recharge conditions, and flow transit velocities of studied groundwater sources.

Radiocarbon dating of dissolved inorganic carbon (DIC) in groundwater has a large application in hydrology, representing the main dating tool for ages covering time spans from a few thousand years up to 40,000 years (Geyh, 2000). Information on groundwater age is required to address aspects such as recharge rates and mechanisms, resource renewability, flow rate estimation in aquifers, and vulnerability to pollution.

Radioactive $^{14}C$ is produced in the atmosphere via the interaction of $N_2$ with cosmic rays and has a half-life of 5730 years. The direct dating of groundwater based on the measured $^{14}C$ activity was first introduced by Münnich (1957, 1968). The calculation of $^{14}C$ ages may be complicated, and sometimes uncertain, because the decrease in $^{14}C$ activity due to radioactive decay can be distorted during subsequent storage in the aquifer by the superimposed influence of hydro-chemical reactions, geo-hydraulic mixing, and physical processes. Other uncertainties in dating can occur if groundwater DIC is derived from a mixture of sources (Clark & Fritz, 1997). For example, if a large proportion of DIC is derived from the dissolution of $^{14}C$-free carbonate minerals, the $^{14}C$ originating from the atmosphere or soil zone will be significantly diluted. Additionally, groundwaters recharged post 1950 may have anomalously high $^{14}C$ activities due to the $^{14}C$ produced during atmospheric nuclear tests.

A number of models based on both major ion and stable carbon isotope geochemistry have been

proposed to correct apparent $^{14}C$ ages (e.g. Mook, 1976; Reardon & Fritz, 1978; Fontes & Garnier, 1979; Han & Plummer, 2016). A computer program (NETPATH) has been developed (Plummer et al., 1994) to simulate the progressive changes in carbon isotope geochemistry along the groundwater flow path based on the prevailing hydro-chemical conditions.

Used in conjunction with $^{3}H$, $^{14}C$ data may also be used to study mixing in shallow aquifers (e.g. Atkinson et al., 2014). $^{3}H$ has a significantly shorter half-life (12.33 years) and there is negligible change to $^{3}H$ activities other than decay. Therefore, $^{3}H$ provides an excellent tool for detecting the presence of recent groundwater (with residence times of up to 100 years) (Vogel et al., 1974) that might alter the calculation of $^{14}C$ ages if not considered.

In recent years, the interest in radiocarbon dating of dissolved inorganic carbon in aquifers from the Carpathian area has been enhanced with the goal of better constraining the groundwater flow and recharge conditions (Făurescu et al., 2011, 2015; Bojar et al., 2020). Radiocarbon measurements have been also performed on river water from the Romanian sector of the Danube River (Făurescu et al., 2009; Varlam et al., 2010). To date, no radiocarbon data are reported for mine water in Romania.

## 2. GEOLOGICAL BACKGROUND

The Zlatna mining site, situated in the South Apuseni (Metaliferi Mountains), is part of the gold-rich district known as the "Golden Quadrilateral", which is one of the most intensely mined regions of Romania.

The South Apuseni Mountains began to operate as a geosyncline area in the Alpine cycle. Large masses of ophiolites were emplaced at the beginning of its evolution. Ophiolitic magmatism manifested from the Middle Jurassic to the Lower Cretaceous with some periods of calm (Ianovici et al., 1976). In the study area, ophiolites outcrop in the western and southwestern part (Fig. 1).

The sedimentary cover starts with Upper Jurassic – Hauterivian deposits consisting of reef limestones. The subsequent Cenomanian - Lower Turonian suite has a predominated pelitic detrital character (Borcoş et al., 1981; Ianovici et al., 1976). Sedimentation conditions changed in the entire area of the South Apuseni during the Turonian tectonic events. Thus, in the south-eastern part of the Metaliferi Mountains, the Upper Cretaceous sedimentary rocks, consisting mainly of sandstones and shales, form molasse deposits. The overlying Badenian formations lie unconformably and include the Fața Băii conglomerates, the Almaşu Mare gravels, and the Late Badenian volcanogenic sedimentary formation. In its upper part, globigerina tufaceous marls, andesite breccia, and sandstone are also found.

Neogene volcanism in the Apuseni Mountains, Badenian - Pliocene in age, is the last stage of the Alpine magmatogenesis (Ianovici et al., 1976). In the Metaliferi Mountains it was controlled by the regional geodynamic evolution of the Carpathian orogen and the Pannonian basin during the Cenozoic. This evolution consisted of subduction and collision of the European and Moesian plates with the Alcapa and Tisia blocks, initiating a subsequent extensional regime, which was driven by the translation and clockwise rotation of the Tisia block. The extensional regime led to the uplifting and decompression of the asthenosphere, causing the melting of its upper part and of the lower crust (Seghedi et al,. 2004). The volcanic activity had two main stages at 14.6 – 10.8 Ma and 9.3 – 7.4 Ma, respectively (Roșu et al., 2004).

In the Zlatna area, the Neogene magmatism had a calc-alkaline character with an obvious evolution trend towards adackite (Seghedi et al., 2007). The first eruptions of rhyolites and amphibole andesites, which occur in alternation with the Badenian sedimentary deposits belonging to the Fața Băii conglomerates, are considered the oldest products of the Neogene magmatism (Roșu et al., 2004; Seghedi et al., 2011). The main petrographic types are quartz andesite with amphibole and pyroxene, and quartz andesite with amphibole and biotite. Basalt andesites also occurred at the end of the volcanic activity.

The polymetallic mineralization from Zlatna is related to the Neogene calc-alkaline magmatism and comprises Au +/– Ag, Cu, Pb, and Zn in varying amounts. It was extracted in two mines: Haneş and Stănija. The main adit from which the Haneş mine was developed (Haneş – Larga adit) is 2.5 km in length. Mining works opened dozens of gold veins at a height of 170 m. At the Stănija mine the main adit is the Podul Ionului adit which extends over a length of about 4 km and opened lenticular Au veins hosted by basic rocks. At depth, the veins are linked to porphyry-copper mineralisation, which was not sufficiently explored. Mining operations at both mines completely ceased in 2007. Several adits (e. g. Toți Sfinții and 23 August) were closed prior to this date. The mine openings are currently secured, but significant amount of acid mine drainage persists to discharge into the surface water system.

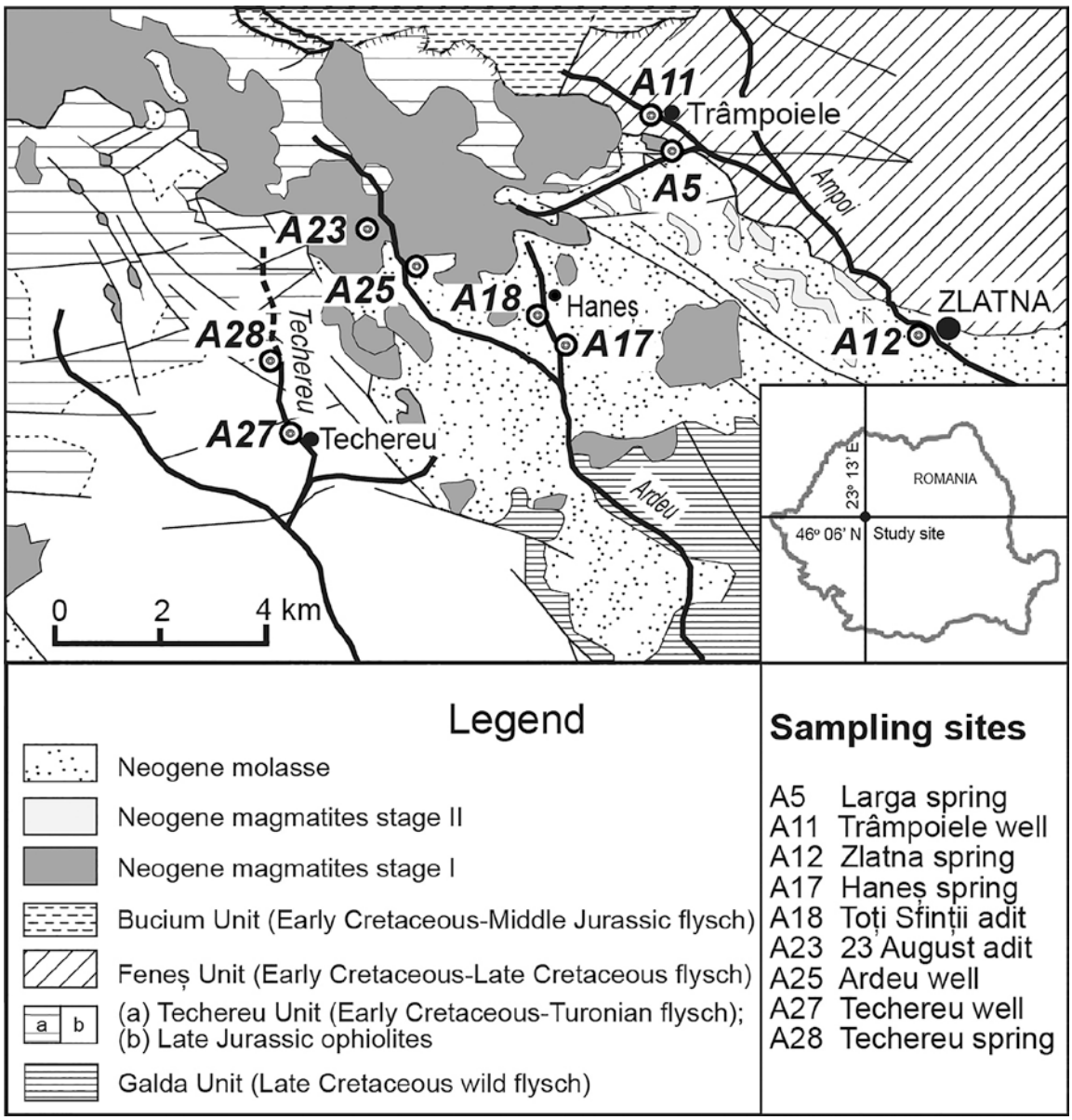


Figure 1. Simplified geological map of the Zlatna mining site showing the location of the 9 sampling sites. The map is redrawn after the Geological map of Romania scale 1:50,000, sheet 74C-Zlatna.

In the study area, elevation ranges between 420 m and 1100 m. The density of the hydrographical network is about 1 km/km$^2$. The Ampoi River, the Ardeu stream, and the Techereu stream are the main collectors. The area is a medium-rain area (~ 600 mm/year). The average annual temperature is 10.5°C, with a maximum monthly average of 28°C during summer, and minimum monthly average of –5°C during winter.

### 3. SAMPLE COLLECTION

Water sampling for carbon isotopes analyses was conducted at and around the Haneș and Stănija mine sites in November 2015. Three sampling zones, which correspond to the drainage basins of the main collectors in the area, were considered for the present study. These zones are: Trâmpoiele – Zlatna, Haneș – Ardeu, and Techereu. We chose for sampling 2 sources of mine water (neutral, pH > 6), 4 natural springs, and 3 representative domestic wells (phreatic water). Figure 1 shows sample locations in relation to geological and hydrological site features.

The springs and the domestic wells are representative for each sampling zones: the springs A5 and A12 and the domestic well A11 for the Trâmpoiele – Zlatna zone, the spring A17 and the domestic well A25 for the Haneș – Ardeu, and the spring A28 and the domestic well A27 for the Techereu zone. The selected domestic wells are currently in use for household purposes. The water level in the domestic wells decreased drastically during the summer months. The flow rate of the springs is relatively constant over the year, but low.

Mine water was sampled at the mine openings. The A18 water sample was collected at the Toți Sfinții adit (Haneș mine), and the A23 sample at the 23 August adit (Stănija mine). Other samples of mine water (acidic, pH < 6) could not be considered for the present study because of the low carbonate content. The relative abundance of dissolved inorganic carbon speciation is a function of pH.

From each site unfiltered and unpreserved water was collected in 500 ml bottles. Samples were kept cold and dark and transported immediately to the laboratory facilities to avoid contamination in field conditions.

## 3. ANALYTICAL TECHNIQUES

Using a calibrated Hanna HI9828 portable multiparameter meter, the following parameters were measured in the field for each water source: pH, temperature, and total dissolved solids (TDS).

Radiocarbon analyses in dissolved inorganic carbon were performed at the Horia Hulubei National Institute for Research and Development in Physics and Nuclear Engineering - Department of Tandem Accelerators (Bucharest) immediately after the samples were collected. The DIC was precipitated as $BaCO_3$ from the collected water samples using $BaCl_2$.

The result of the analysis is reported in Modern Carbon Percentage (pMC). Conventional pMC is calculated relative to the international standard NIST Oxalic Acid (SRM 4990C), so that 74.59% of its activity is the reference of modern $^{14}C$ activity. Percentage of Modern Carbon is corrected for isotopic fractionation using the $\delta^{13}C$ parameter calculated with reference to the VPDB standard. $^{13}C$ was measured using an isotope ratio mass spectrometer (IRMS) and is expressed as permil (‰) relative to standard.

Calibration of the results was done using the INTCAL13 data base (Talma & Vogel, 1993; Reimer et al., 2013). In order to convert pMC into $^{14}C$ calendar age the OxCal 4.4.4. (2021) software (Bronk Ramsey, 2009) was used. The software uses Bayesian modelling based on radiocarbon measurements and information from the $^{14}C$ calibration curves.

## 4. RESULTS AND DISCUSSION

### 4.1. Characterization and age of the water samples

The measured isotope ratios, pMC and associated $\pm 1\sigma(\%)$ are presented in Table 1. The values of pH, temperature, and total dissolved solids measured in the field are also shown. Table 1 also includes hydrogen and oxygen isotopes data for the same water samples (Papp et al., 2017) that are used in the interpretation of the current results.

Groundwater (springs and wells) is characterized by neutral pH (~ 7.5) and TDS values ranging between 215 and 337 mg/l. The slightly higher TDS values displayed by Techereu well (A27) is due to the infiltration of polluted waters from the nearby Techereu stream into the phreatic water. The two samples of mine water display characteristics of neutralized AMD (neutral pH (>7) and TDS values similar to other sources of groundwater (313 mg/l to 394 mb/l)). Such mine water only interacts with host rock in abandoned mining works and does not come into direct contact with mineralization.

The springs and the domestic wells in this study are characterized by similar $\delta^2H$ (-70.1‰ to -60.0‰) and $\delta^{18}O$ (-10.2‰ to -9.3‰) values. Mine water is characterized by slightly lower $\delta^2H$ and $\delta^{18}O$ values ($\delta^2H$ ~ -72‰; $\delta^{18}O$ <-10‰). Linear correlation between the two parameters, as previously shown (Papp et al., 2017), attested to the fact that all water sources (springs, domestic wells, and mine water) belong to the meteoric cycle. For mine water, snowmelt and high-altitude precipitations was suggested as the main source of recharge.

The $\delta^{13}C$ values clearly separate the mine water (-1.4‰ and -5.8‰) from other groundwater sources (-9.8‰ to -16.1‰). In groundwater, most of the isotopic variation in $\delta^{13}C$ of DIC is caused by water-rock interaction occurring in shallow recharge areas, or geochemical reactions in the aquifer (e.g. Geyh, 2000 and literature there in). Higher values of $\delta^{13}C$ typically occur due to isotope fractionation between soil gas $CO_2$ and $HCO_3^-$ in recharge water and/or to isotope dilution from dissolution of carbonates in rocks that are enriched in $^{13}C$ (Vogel et al., 1970; Tamers, 1975; Mook, 1976). However, in practice, although the scatter of the initial $\delta^{13}C$ values encountered in recharge areas is usually not accurately known, this is of significantly less magnitude than the global ranges (Fontes & Garnier, 1979; Phillips et al., 1989; Geyh, 2000; Plummer & Sprinkle, 2001).

The distribution of pMC data plotted in Figure 2 clearly shows an increasing trend from 40.86% in mine water (A18) to values as high as 93% in phreatic water sampled in domestic well (A25). The corresponding ages are presented in Table 1. Calculations indicate that mine water from Toți Sfinții adit (A18) is the oldest having an age of 7879

Table 1. Stable isotope data ($\delta^2H$, $\delta^{18}O$ and $\delta^{13}C$), per cent modern carbon (pMC) and radiocarbon ages for different water sources from the Zlatna mining site. pH, temperature, and total dissolved solids (TDS) values measured onsite are also displayed.

| Sample | pH | t (°C) | TDS (mg/l) | $\delta^2H^*$ (‰) (VSMOW) | $\delta^{18}O^*$ (‰) (VSMOW) | $\delta^{13}C$ (‰) (VPDB) | pMC (%) | 1σ (%) | Uncorrected age (years BP) | Calibrated date (median) |
|---|---|---|---|---|---|---|---|---|---|---|
| **A5** | 7.0 | 10 | 337 | -68.0 | -9.8 | -9.8 | 54.03 | 0.65 | 5507 | 3754 BC |
| **A11** | 7.1 | 11 | 215 | -66.4 | -9.7 | -9.9 | 89.39 | 0.49 | 819 | 1139 AC |
| **A12** | 7.7 | 9 | 226 | -61.0 | -9.0 | -13.4 | 79.41 | 0.76 | 1576 | 186 AC |
| **A17** | 7.6 | 10 | 133 | -70.1 | -10.2 | -14.9 | 61.25 | 0.77 | 4193 | 2426 BC |
| **A18** | 7.3 | 11 | 394 | -71.8 | -10.4 | -1.4 | 40.86 | 0.83 | 7879 | 6065 BC |
| **A23** | 7.9 | 9 | 313 | -71.8 | -10.6 | -5.8 | 60.67 | 0.77 | 4185 | 2553 BC |
| **A25** | 7.7 | 10 | 330 | -65.2 | -9.4 | -16.1 | 93.00 | 0.57 | 552 | 1354 AC |
| **A27** | 7.6 | 11 | 566 | -67.6 | -9.8 | -10.6 | 82.76 | 0.31 | 1435 | 563 AC |
| **A28** | 7.7 | 11 | 238 | -67.1 | -9.3 | -15.1 | 74.31 | 0.95 | 2168 | 514 BC |

* Data from Papp et al. (2017); Calibrated date was obtained using the OxCal v.4.4.4. (2021) software (Bronk Ramsey, 2009).

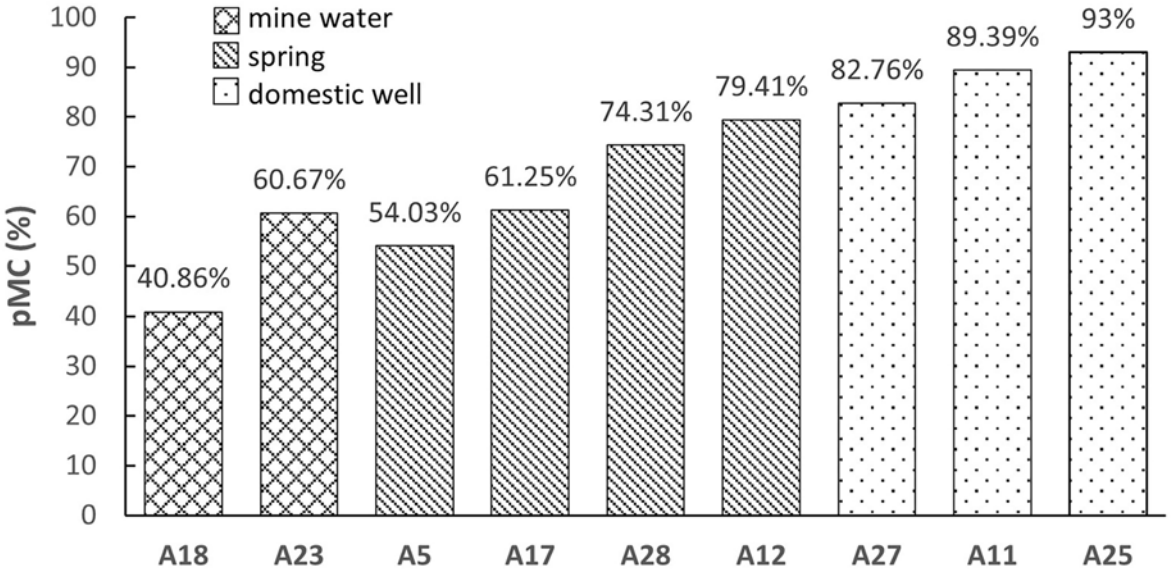

Figure 2. Distribution of the pMC (%) in different types of groundwater from the Zlatna mining site.

years BP. The mine water from the 23 adit (A23) is much younger (4185 years BP). Two of the springs (A5 and A17) display similar ages (5507 years BP and 4193 years BP, respectively) while for the other two springs (A12 and A28) we obtained slightly younger ages. Phreatic water sampled in domestic wells is younger than 1400 years BP. The calibrated date intervals and the median date for each sample was obtained using the OxCal v.4.4.4. (2021) software (Bronk Ramsey, 2009) and are displayed in Figure 3.

### 4.2. Age significance and correlation with stable isotopes data

Interpretation of groundwater ages obtained by radiocarbon dating should always be done with caution because of the many uncertainties in determining the initial $^{14}C$ content of dissolved carbon in recharge areas and in accounting for the many chemicals and physical processes that alter the $^{14}C$ content along flow paths. Several adjustment models have been developed over the years in order to refine the radiocarbon age calculations of DIC in groundwater. Basically, all adjustment models address two aspects: (i) definition of the $^{14}C$ content in the recharge zone where water becomes isolated from the modern $^{14}C$ reservoir, and (ii) adjustment of this initial $^{14}C$ value for chemical reactions occurring along the flow path. These models involve a good knowledge of aquifers and recharge areas from a hydrogeological and geochemical point of view. Carbonate mineral dissolution is often accompanied by other secondary processes such as sulphate reduction, dolomite dissolution, Ca/Na ion exchange, $CO_2$ gas dissolution and isotope exchange between soil CO2, calcite and DIC during recharge. Some models use adjustments in a closed system, while others are based on partially open system calculations. Most of these models were discussed by Fontes & Garnier (1979), Fontes (1992), and Kalin (2000). Although differences in ages between models may occur (e.g. Făurescu et al., 2015), they are of less significance than the global ranges.

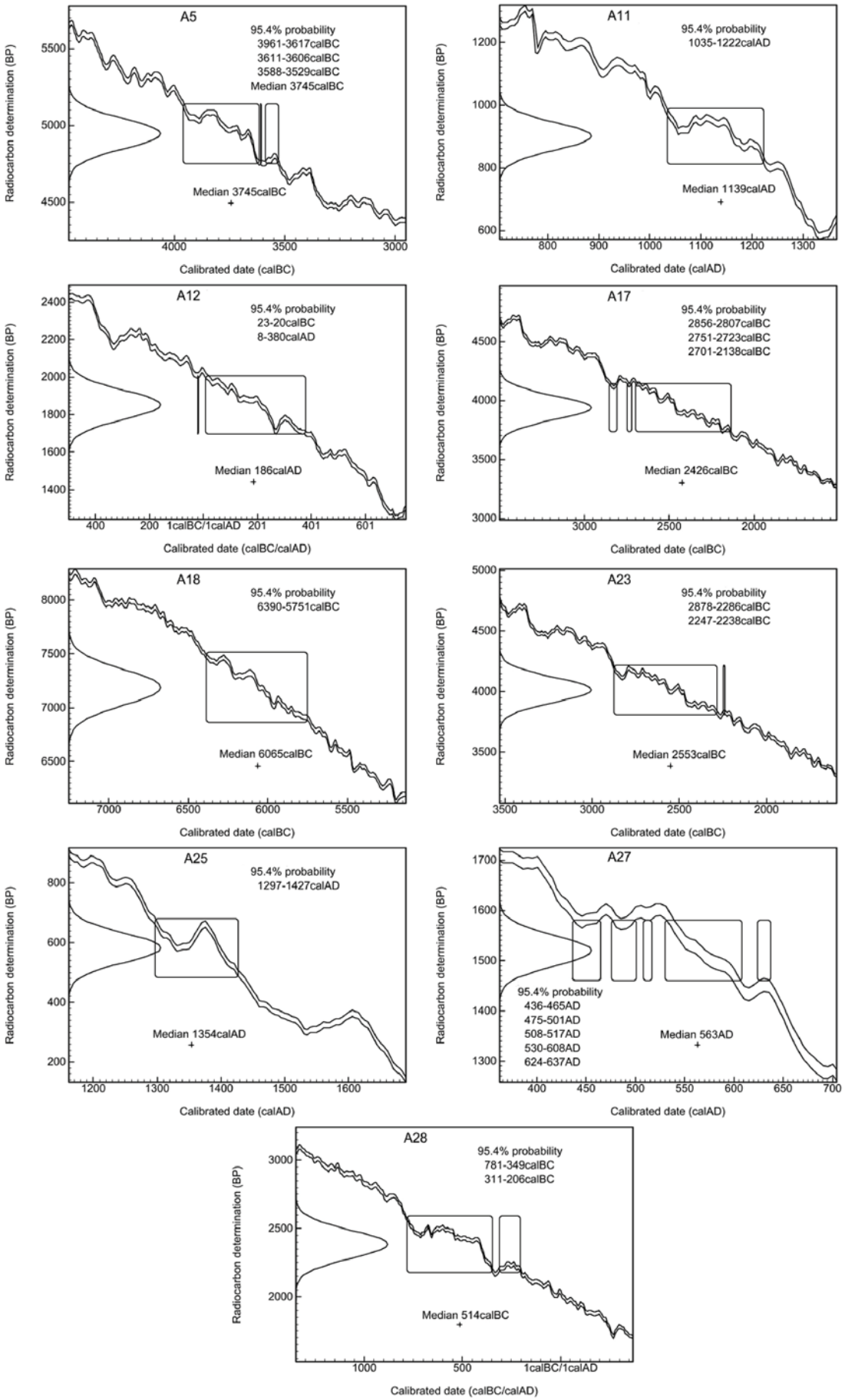


Figure 3. Multiple plots of calibrated date (BC/AC) using radiocarbon determination (BP) of groundwater samples.

Due to the uncertainties that might be introduced by using one model or another and by the selection of initial $^{14}C$ values, here we discuss the $^{14}C$ records in groundwater in terms of per cent modern carbon (pMC). The calibrated ages must be seen as approximations.

The pMC values of all samples are under 100%, which means that they are old (pre-modern) groundwaters or mixture of old (pre-modern) groundwaters and modern water coming from precipitation. Non-renewable paleo-waters could not be recognized in the study area. The pMC values of phreatic water sampled in wells (pMC > 80%) associated with relatively low $\delta^{13}C$ values (< -10‰) are typical values for an open system (Plummer & Glynn, 2013).

Mine water samples display the lowest pMC values (between 40.86% and 60.67%) suggesting they are the oldest. It is also possible for the low pMC values in mine water to be a consequence of pH removal of $^{14}C$ (Boylan et al., 2017). Even though the sampled mine water is currently neutral water (pH ~ 7), $^{14}C$ removal could take place when it was in contact with the mineralization and had an acidic character. The pMC values in springs vary between 54.03% and 74.31% and overlap partially the pMC values in mine water suggesting underground connections. Phreatic water sampled in domestic wells is characterized by the highest pMC values (> 82%). If $\delta^2H$ and $\delta^{18}O$ data and their seasonal variation are taken into consideration then high pMC values are an indication that all domestic wells are influenced by modern precipitations.

Although there is no statistically significant correlation (r=0.6) between pMC values and $\delta^{18}O$ values, it can be noticed that samples that are more depleted in $^{18}O$ display lower pMC values (< 62%) (Figure 4). Because of the linear relationship between the $\delta^{18}O$ and $\delta^2H$, analogous correlation is obtained between pMC values and $\delta^2H$ values. For the sample group consisting of mine waters and springs A5 and A17, we may consider some input from the late-glacial (Younger Dryas) recharge which is characterized by lower $\delta^2H$ and $\delta^{18}O$ values (Rozanski et al., 1997) than the present meteoric water. Younger Dryas represents the last major period of aquifer refill (Bath et al., 1979; Awaleh et al., 2020). The age of the Younger Dryas is around 12,900 to 11,700 years BP (Pillans & Gibbard, 2012). Similar finding implying the Younger Dryas event is described by Bojar et al. (2020) for a hydrological system in Quaternary clastic deposits in the South Carpathian Mountains.

In the case of mine water, low $\delta^{18}O$ values and high $\delta^{13}C$ values in the Younger Dryas could reflect low air temperatures and dominance of carbonates-derived carbon from the poorly vegetated catchment.

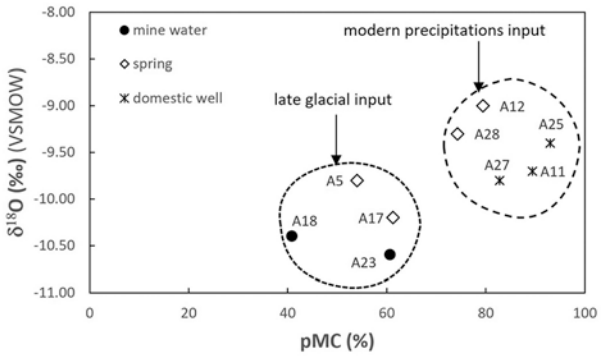


Figure 4. The relationship between pMC (%) and $\delta^{18}O$ for different types of groundwater at the Zlatna mining site.

### 4.3. Estimation of groundwater flow transit velocity

Despite the fact that radiocarbon age values should be used with caution, they can provide helpful information for estimating mean flow transit velocity of underground water (Bhandary et al., 2015; Făurescu et al., 2015; Cartwright et al., 2020). Mean transit velocity is obtained from the relative values of radiocarbon age for two sources located on the flow pathway of groundwater. For this calculation we considered the mean values of calibrated date (Table 1), the linear distances between them measured on map, as well as the difference in their altitude. We performed this calculation for all sampled springs. The resulted flow transit velocities are displayed in Table 2.

Table 2. Flow transit velocities of groundwater

| Springs | Mean age difference (years) | Distance between sources (m) | Altitude difference (m) | Flow transit velocity (m/year) |
|---|---|---|---|---|
| A5-A17 | 1328 | 4690 | 136 | 3.5 |
| A5-A28 | 3240 | 8908 | 15 | 2.7 |
| A5-A12 | 3940 | 3634 | 83 | 0.9 |
| A17-A28 | 1912 | 4454 | 151 | 2.3 |
| A17-A12 | 2612 | 6836 | 219 | 2.6 |
| **Mean flow transit velocity** | | | | **2.4** |

The estimated mean flow transit velocity is about 2.4 m/year. This value is a normal value for aquifers located in fractured andesites and sedimentary detrital rocks with medium to high permeability and is comparable to other groundwater velocities obtained using the same procedure for

aquifers in Romania (Făurescu et al., 2015).

Groundwater flow transit velocity is mainly controlled by permeability of the rocks, as well as by the layout of different flow pathways. Higher flow rates are obtained in the case of mine waters due to the mining network. For the phreatic water sampled in domestic wells such calculations are less relevant due to the direct connection to surface water.

## 5. CONCLUSIONS

Three distinct types of groundwater have been considered: springs, domestic wells and mine water. The previous stable isotope results ($^{2}H/^{1}H$ and $^{18}O/^{16}O$) showed that the recharge source of the groundwater (springs, domestic wells, and mine water) is local meteoric water. The $^{14}C$ content of dissolved inorganic carbon in all three types of groundwater showed that they are old groundwaters or mixture of old groundwaters and modern water coming from precipitation. No paleo-waters could be recognized in the study area.

The distribution of pMC data clearly shows an increasing trend from 40.86% in mine water to values as high as 93% in phreatic water sampled in domestic well. Springs show an intermediate position with pMC values varying from 54.03% to 79.41%. Mean calibrated ages vary from 6065 BC to 2553 BC in mine water, from 3754 BC to 186 AC in springs, and from 563 AC to 1354 AC in phreatic water.

Correlation between pMC values and $\delta^{18}O$ values of groundwater separates the studied sources in two groups. For the group consisting of mine waters and two springs (A5 and A17) some inputs from the late-glacial (Younger Dryas) recharge may be considered. For the second group consisting of two other springs and domestic wells, contributions from modern precipitation are taken into account.

Although radiocarbon ages themselves are only estimated, the relative values for pairs of sampling points allow the calculation of flow transit velocities of groundwater. For the groundwater sampled in springs, a mean flow transit velocity of 2.4 m/year was obtained.

Further radiogenic studies using tritium could allow a better constrain of the contribution of modern precipitation to the recharge budget of groundwater. This is an important factor when planning local water supplies.

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