

## ON THE INITIAL $^{14}\text{C}$ ACTIVITY OF KARST AQUIFERS WITH SHORT MEAN RESIDENCE TIME

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**ABSTRACT.** The  $^{14}\text{C}$  activity of total dissolved inorganic carbon (DIC) as well as tritium activity and stable isotope content ( $^{13}\text{C}$ ,  $^2\text{H}$ ,  $^{18}\text{O}$ ) of spring water were measured for 3 consecutive years at 3 karst springs that feed Plitvice Lakes, NW Yugoslavia. The constant chemical and stable isotope composition and temperature indicated well mixed aquifers. A very short mean residence time of underground water (2–5 yr) was determined by tritium activity measurements. Measured  $^{14}\text{C}$  activities of 3 karst springs varied from 60.0% to 82.5%. The measured  $^{14}\text{C}$  activities were compared with calculated  $^{14}\text{C}$  activities based on various models using measured values of  $^{14}\text{C}$  activity of soil at different depths and  $^{13}\text{C}$  content of limestone, plants, and soils from the recharge area. Our measurements indicate that recharge systems in karst aquifers are open to the atmosphere. The atmospheric  $\text{CO}_2$  contributes to the  $^{13}\text{C}$  content and the  $^{14}\text{C}$  activity of ground water to an estimated extent which varies between 10 and 40% of DIC.

### INTRODUCTION

Plitvice Lakes in northwest Yugoslavia are fed by three main and several minor springs. Measurements of  $^{14}\text{C}$  activity of ground water were made to determine the initial activity of carbonate deposits as well as to compare the measured and the calculated values of groundwater activity  $a_0$ . Measurements of temperature, pH,  $\text{HCO}_3^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{CO}_2$  concentrations, as well as  $^3\text{H}$  activity and stable isotope content in spring water have been performed monthly for three consecutive years.  $^{14}\text{C}$  activity of spring water was measured less frequently due to the tedious procedure which involved processing of ca 200L of spring water per  $^{14}\text{C}$  analysis. The  $^{14}\text{C}$  activity of ground water in karst areas does not reflect its age, which is very short compared to the half-life of  $^{14}\text{C}$ . Instead, the  $^{14}\text{C}$  activity of ground water in the investigated area depends on the processes in topsoil and along the recharge paths which contribute to the  $^{14}\text{C}$  activity and  $^{13}\text{C}$  content of the dissolved bicarbonates. The applicability of several models published in the literature was tested by using the experimentally obtained values of  $^{14}\text{C}$  and  $^{13}\text{C}$  concentration in ground water, soil, limestone, and plants.

### EXPERIMENTAL RESULTS

Each of three major springs that feed the Plitvice Lakes is characterized by very constant temperature and chemical composition. The difference in temperature between the three springs is  $<1^\circ\text{C}$  and the spread is  $\pm 0.15^\circ\text{C}$  for each spring throughout the year. Departures occur in spring and fall at high waters after intensive snow melting and heavy rains. Another characteristic feature is an almost ideal equilibrium of calcium carbonate solution ( $I_{\text{sat}} \approx 1.0$ ) and a very high partial pressure of  $\text{CO}_2$ . No calcium carbonate or dolomite precipitation at karst springs was observed.  $\text{CO}_2$  partial pressure drops rapidly within several hundred meters from the karst springs, causing a corresponding increase of pH. No changes of other constituents were observed in the karst spring area. Chemical composition of spring water is given in Table 1.

TABLE 1

The mean temperature, pH, and concentration of major ionic species of springs which feed the Plitvice Lakes

Spring	t (°C)	pH	HCO <sub>3</sub> <sup>-</sup> (mmole/l)	CO <sub>2</sub> (mmole/l)	Ca <sup>2+</sup> (mmole/l)	Mg <sup>2+</sup> (mmole/l)
Crna rijeka	7.9	7.47	4.24	0.44	1.60	0.71
Bijela rijeka	7.5	7.46	4.87	0.53	1.46	1.17
Plitvica	7.3	7.60	4.56	0.36	1.53	0.90

The chemical composition of each spring water is slightly different reflecting the geologic composition of the recharge area. The spread of measured values presented in Table 1 is within analytic error.

Stable isotope contents ( $\delta^2\text{H}$ ,  $\delta^{18}\text{O}$ ) were measured in precipitation and in spring waters. Although  $\delta^2\text{H}$  of precipitation varies during the year between  $-115\text{‰}$  and  $-20\text{‰}$  and  $\delta^{18}\text{O}$  between  $-14.5\text{‰}$  and  $-4\text{‰}$ , yearly variations in spring waters are considerably lower. Mean values of stable isotope content in precipitation and in springs are very similar, indicating that both winter and summer precipitation contributes to the recharge and that contributions for several years are well mixed in the aquifers.

The  $^3\text{H}$  concentration in spring waters was measured monthly. No seasonal variations were observed. The mean residence time (MRT) was determined using the exponential model (Eriksson, 1962; Geyh, 1972) which is based on the assumption of a well-mixed aquifer. The MRT of 2, 4 and 3 years were calculated for Crna rijeka, Bijela rijeka, and Plitvica, respectively.

To verify the validity of several proposed models for groundwater age calculation the  $^{14}\text{C}$  activity and  $\delta^{13}\text{C}$  of limestone, plants, and soil at various depths in the recharge area were measured. The DIC was precipitated from water as  $\text{BaCO}_3$  at  $\text{pH} > 8$ .  $^{14}\text{C}$  activity and  $\delta^{13}\text{C}$  content of DIC were measured using standard procedures. The  $^{14}\text{C}$  activity of spring waters differs for the three karst springs. It is quite constant for Bijela rijeka and Plitvica, while Crna rijeka spring shows seasonal variations from the prevailing 60% up to 70%. Carbon isotope data are presented in Table 2.

#### MODELS

Several theoretical models for groundwater  $^{14}\text{C}$  activity are published in the literature. Tamers' chemical mixing model (Tamers, 1967; Tamers & Scharpenseel, 1970) is based on the assumption that half of bicarbonate is derived from biogenic  $\text{CO}_2$  and the other half from bedrock carbonates. The fraction of the carbon of biogenic origin in the total dissolved carbon gives the initial activity of the DIC. Pearson's isotope mixing model (Pearson & Hanshaw, 1970) is based on the calculation which takes into account  $\delta^{13}\text{C}$  of each species (soil  $\text{CO}_2$ , solid carbonate and DIC). The models developed by Tamers and Pearson do not take into account the isotopic exchange between the soil  $\text{CO}_2$  and DIC. The approach of Mook (1976) was to calculate the isotope mass balance at each step of chemical and isotopic exchange processes. As a result, one obtains Tamers' equation corrected by

TABLE 2  
 $^{14}\text{C}$  activity and  $\delta^{13}\text{C}$  of spring waters, soil, and plants in Plitvice National Park

Sample	$a_0$ <sup>14</sup> C (%)	$\delta^{13}\text{C}$ (‰ vs PDB)
	Spring water*	
Crna rijeka	63.0 ± 4.0	-12.4 ± 0.6
Bijela rijeka	82.7 ± 2.4	-12.4 ± 0.4
Plitvica	82.5 ± 0.9	-12.8 ± 0.8
	Limestone**	
Bedrock	0.0 ± 0.4	-0.5 ± 0.2
	Plants**	
Twigs ( <i>Salix cinerea</i> ) (1979)	130.3 ± 0.9	-27.5 ± 0.2
Grass (1984)	121.3 ± 0.8	-27.2 ± 0.2
Leaves ( <i>Fagus silvatica</i> ) (1979)	134.6 ± 0.8	-30.0 ± 0.2
Twigs ( <i>Fagus silvatica</i> ) (1984)	121.9 ± 0.8	-28.1 ± 0.2
	Soil**	
Surface	119.4 ± 0.7	-27.6 ± 0.2
0-10cm	102.0 ± 0.7	—
15-30cm	91.3 ± 0.7	—
50-75cm	80.0 ± 0.6	—

\* Mean values over a 5-yr period

\*\*Single measurements

a term for isotopic exchange. The model of Fontes and Garnier (1979) assumes that the reaction of gaseous  $\text{CO}_2$  and solid carbonate in aquatic medium is accompanied by an isotopic exchange in a closed system. According to the model proposed by Eichinger (1983) the initial activity can be obtained from Tamers' formula corrected by the carbon exchange factor that includes  $\delta^{13}\text{C}$  values.

Results of calculations based on the above cited models using the data from Table 2 are presented in Table 3. The mean  $\delta^{13}\text{C}$  value of soil  $\text{CO}_2$  of -28‰ and the  $^{14}\text{C}$  activity of gaseous soil  $\text{CO}_2$  of 100% were used (Srdoč *et al.*, 1977; Thorstenson *et al.*, 1983).

It is obvious that the calculated  $a_0$  values based on various models and the experimental  $a_0$  values are not in accordance. The models of Pearson, Mook, Fontes and Garnier, and Eichinger, which are partly based on  $\delta^{13}\text{C}$  values, cannot simply be applied, because from  $\delta^{13}\text{C}$  (soil  $\text{CO}_2$ ) of -28‰ and  $\delta^{13}\text{C}$  (carbonate) of -0.50‰, the  $\text{HCO}_3^-$  content of the water should have  $\delta^{13}\text{C} = -13.75\text{‰}$  at the most, which is already more negative than  $\delta^{13}\text{C}$

TABLE 3  
 Comparison of ground water  $^{14}\text{C}$  activity obtained using various models with experimental data

Spring	$a_0$ (experimental)	$a_0$ (Tamers)	$a_0$ (Pearson)	$a_0$ (Mook)	$a_0$ (Fontes- Garnier)	$a_0$ (Eichinger)
Crna rijeka	63.0	54.7	43.3	13.0	35.0	44.0
Bijela rijeka	82.7	54.9	43.4	16.0	36.0	45.0
Plitvica	82.5	54.2	44.5	16.0	36.0	45.0

TABLE 4  
The percentages of atmospheric CO<sub>2</sub> in DIC of 3 karst springs, calculated on the basis of various models

Spring	Mook	Models		Eq 3
		Fontes-Garnier	Eichinger	
Crna rijeka	16.5	19.3	18.2	11.0
Bijela rijeka	17.0	24.2	29.1	37.0
Plitvica	17.6	25.3	31.3	37.5

(DIC). The conclusion must be that the mixing of soil CO<sub>2</sub> with atmospheric CO<sub>2</sub> through porous karst brings about an exchange of carbon isotopes, increasing the <sup>14</sup>C activity and the <sup>13</sup>C content of ground water.

An estimated contribution of atmospheric CO<sub>2</sub> to the DIC of karst ground waters can be calculated using models that take into account the isotopic fractionation. By inserting measured δ<sup>13</sup>C values and <sup>14</sup>C activities from Table 2 in equations describing these models, we inferred that the contribution of atmospheric CO<sub>2</sub> to the DIC is significant, as shown in Table 4. In addition, our measurements of chemical and isotopic composition of ground water and the <sup>14</sup>C activity of atmospheric CO<sub>2</sub> enabled us to calculate the percentage of atmospheric CO<sub>2</sub> in the DIC of ground water. Owing to the very short mean residence time (MRT) of karst ground water, no decay of <sup>14</sup>C affects the calculation of the proportion of atmospheric CO<sub>2</sub> in DIC. Starting with the basic equation for inactive bedrock carbonate dissolution by soil CO<sub>2</sub>:



one arrives at the well-known chemical (Tamers) equation for the <sup>14</sup>C activity of DIC:

$$a_T = a_s \frac{[\text{H}_2\text{CO}_3^*] + \frac{1}{2} [\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3^*] + [\text{HCO}_3^-]} \quad (2)$$

where  $a_s$  denotes the soil CO<sub>2</sub> activity, which is close to 1. The fraction  $f$  of atmospheric CO<sub>2</sub> in DIC which entered an aquifer through exchange between gaseous and liquid phases is given by:

$$f = \frac{a_{\text{gw}} - a_T}{a_{\text{atm}} - a_T} \quad (3)$$

where  $a_{\text{gw}}$  is the measured ground water activity,  $a_T$  is calculated <sup>14</sup>C activity based on Tamers model (Eq 2), and  $a_{\text{atm}}$  is the <sup>14</sup>C activity of atmospheric CO<sub>2</sub>. The contribution of soil CO<sub>2</sub> in the exchange process after dissolution of carbonates is neglected in this calculation. An equation similar to Eq 3 was derived to calculate the contribution of atmospheric CO<sub>2</sub> based on the <sup>13</sup>C content of DIC, soil, and atmospheric CO<sub>2</sub>, taking into account the isotopic fractionation factor. The calculated data using δ<sup>13</sup>C values listed in Table 2 support our assumption that soil CO<sub>2</sub> does not play an important role in the gas/liquid phase exchange process.

Before man's interference with natural  $^{14}\text{C}$  balance, Eq 3 could be reduced to:

$$f = \frac{a_{\text{gw}} - a_{\text{T}}}{1 - a_{\text{T}}} \quad (4)$$

since the atmospheric  $\text{CO}_2$  activity fluctuated close to unity. The calculation of  $f$  which takes into account the Suess effect and especially the bomb-produced  $^{14}\text{C}$  is more complex and requires the knowledge of  $^{14}\text{C}$  input function over several MRT.

In case of a very short MRT (eg, 1–3 yr) an approximate solution of Eq 3 can be obtained by inserting the mean value of atmospheric  $\text{CO}_2$  activity over 1 MRT period. The fraction  $f$  of atmospheric  $\text{CO}_2$  in DIC of 3 karst springs thus obtained is shown in Table 4.

#### CONCLUSION

The calculation of the initial groundwater activity  $a_0$  using several models described in the literature and measured  $\delta^{13}\text{C}$  values of DIC in ground water and of soil  $\text{CO}_2$  gives sometimes unacceptable results due to an unpredictable fraction of atmospheric  $\text{CO}_2$  in DIC. The measured groundwater activities in a relatively small area of northwest Yugoslav Karst showed a wide range of  $a_0$ , from 60% to 85% indicating an admixture of atmospheric  $\text{CO}_2$  ranging from 11 to 38% of total DIC.

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