INCREASE OF ^{14}C ACTIVITY OF DISSOLVED INORGANIC CARBON ALONG A RIVER COURSE

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ABSTRACT. Results of measurements for 3 years (1981–1983) of ^{14}C activity of dissolved inorganic carbon (DIC) in water samples from the Korana River, as well as that of recent tufa and aquatic plants, showed that ^{14}C concentration increases from karst spring to the estuary. A model describing the increase of ^{14}C activity was developed assuming that the increase is due to the exchange of the dissolved CO_2 in stream water with atmospheric CO_2 and to dissolution of CO_2 from the decay of organic material and root respiration. It is possible to distinguish these two contributions by measuring the $\delta^{13}C$ values of DIC in water. As expected, our data show that the exchange process between atmospheric CO_2 and DIC dominates at rapids and waterfalls, while biologic contribution is much higher in lakes and along the lowland flow of the Korana River. Agreement between the calculated and the measured activities supports the proposed mechanisms of chemical and isotopic exchanges in stream waters.

INTRODUCTION

A comprehensive study of the Korana River catchment area involved systematic measurements of aquatic chemistry and isotope hydrology of surface and ground waters, as well as precipitation water. These measurements enabled us to construct a scheme of spatial and temporal distribution of stable and radioactive isotopes in the whole hydrologic cycle. The atmospheric and soil CO_2 activity, the tritium activity and the stable isotope content in precipitation served as input functions which made possible calculations of the initial ^{14}C groundwater activity, the mean residence time (MRT) of ground water and evaluation of the aquifer recharge periods (Krajcar-Bronić *et al*, 1986).

Measurements of ^{14}C activity of dissolved inorganic carbon (DIC) in springs and in stream water showed a systematic increase of ^{14}C activity along the water course which has been attributed to the influx of atmospheric CO_2 as well as to the contribution from terrestrial plants, through detrital decay and root respiration. A model based on the described processes was developed, which predicts fairly accurately the ^{14}C activity along the river course, using the experimentally–obtained coefficients for stream flow characteristics. Those coefficients are quite different for cascades, steady flow, etc, which is in accordance with the model concept.

Owing to the difference in ^{13}C content of terrestrial plants and of atmospheric CO_2 ($\delta^{13}C = -24$ to $-30\%_0$ and $-8\%_0$, respectively) it was possible to separate the contribution of each source of ^{14}C to the DIC activity.

[14]C and $\delta^{13}C$ samples were taken along the Korana River in NW Yugoslavia, which is free from industrial pollution and has a long record of aquatic chemistry measurements. From its springs to its mouth, the Korana River changes flow characteristics, from torrential rapids to steady lowland flow. Also, along a 15km section close to the springs the Korana River is intersected by numerous tufa barriers which dam 16 small lakes connected with waterfalls and cascades. Thus, a variety of stream flow modes were used to verify the proposed model of increasing the ^{14}C activity of DIC in surface waters.

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The described measurements and calculations of DIC activity in the Korana River served a twofold purpose: 1) to explain and define quantitatively the increase of DIC activity along the river course, and 2) to calculate the initial activity a_0 of of lake sediments and tufa deposits in a string of lakes and tufa barriers in the Plitvice National Park.

EXPERIMENTAL

Several kinds of samples were used to measure ^{14}C activity. The most reliable sample, although not always available, was $BaCO_3$ precipitated from ca 200L of water, using a routine procedure (IAEA, 1967). Less reliable were tufa, lake sediment, and aquatic plants, because of the inherent uncertainty in isotopic fractionation, bioturbation, microlocation, etc. Most of the recent samples consisted of precipitated DIC in the form of $BaCO_3$, whereas pre-bomb-test tufa and aquatic plants were obtained from Plitvice National Park and Pevalek collections (collected 1919–1937). Whenever possible, we compared the results on two or more kinds of materials, such as the DIC, recent aquatic plants, the surface layer of tufa, and the lake sediment collected in a trap. Very often, the ^{14}C activity at a particular location was within the statistical error of measurement for all kinds of samples. The largest deviation amounted to $\pm 2 - 2.5\%$ of modern activity.

Processing of carbonates and counting procedures have been described (Srdoč, Breyer & Sliepčević, 1971; Srdoč *et al*, 1979, 1982). The mass spectrometric analyses were done at Jožef Štefan Institute, Ljubljana, and Institut für Radiohydrometrie, Munich. The ^{14}C data are expressed in percent modern, using 0.95 of NBS oxalic acid activity as the modern standard. $\delta^{13}C$ values are relative to the PDB standard.

RESULTS

The results of ^{14}C activity, mass spectrometry, and aquatic chemistry measurements are shown in Figure 1 together with a schematic profile of the first 15km of the Korana River. A steady increase of ^{14}C activity of DIC in the downstream direction is quite evident, as opposed to the $\delta^{13}C$ values which reach a maximum after 15km of turbulent flow, followed by a decrease in the lowland area.

The concentration of DIC decreases sharply along the first 15km due to intensive lake sediment precipitation and tufa formation, followed by a slightly decreasing value in the lowland area. CO_2 concentration (or partial pressure) in water drops even more rapidly, eg, by a factor of 5 from karst springs to the confluence, reaching a steady value (0.05 ± 0.015 mmole/l) ca 4km downstream from the confluence (see Fig 1, sections 4 and 5).

The DIC balance is rather complex since it includes a rapid loss of CO_2 along the first few km of water course, followed by a substantial loss of carbon due to calcite precipitation in the next following 15km of river flow. Several smaller springs and tributaries bring highly mineralized water causing minor fluctuations in an otherwise constantly decreasing DIC concentration, as shown in Figure 1.
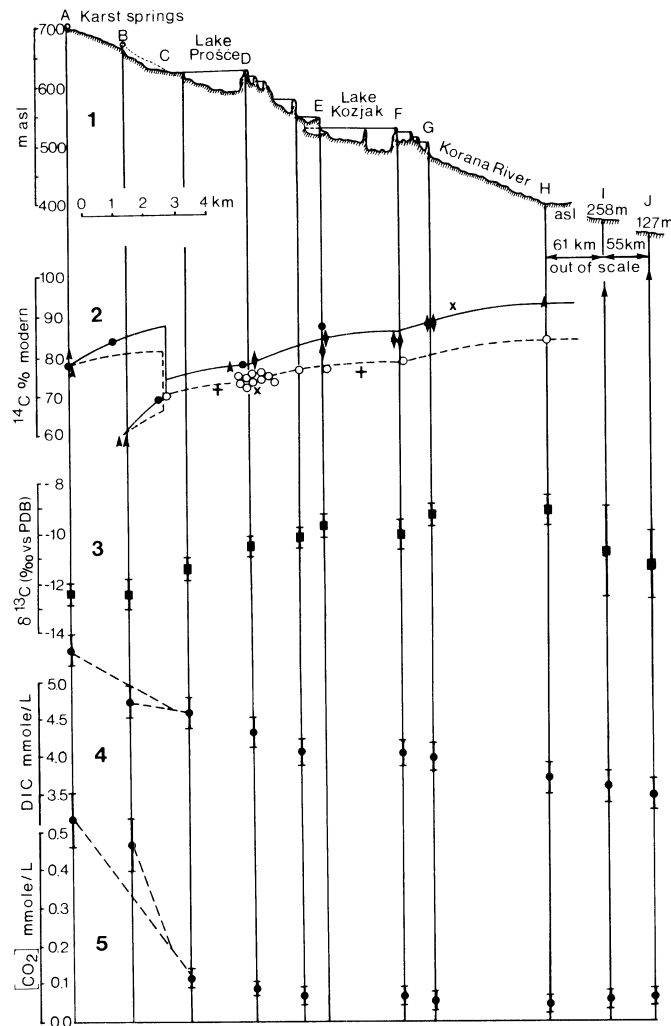
Fig 1. 1. The sketch of the riverbed profile. 2. The increase of ^{14}C activity along the water course; ● – recent tufa (1976–1983); ▲ – DIC in water; ♦ – carbonate precipitated on polyamide mats; O – tufa, before 1945; x – moss (*Cratoneurum commutatum*); + – top layer of lake sediments; —— – calculated activity (Eq 2), 1980–1983; ---- – calculated activity (Eq 2), before bomb tests (1945). 3. $\delta^{13}C$ content of DIC. 4. DIC, mmoles per liter. 5. CO_2 concentration, mmoles per liter.

The CO_2 balance is characterized by a *quasi* exponential drop caused by rapid degassing of excessive CO_2 in spring water. This is followed by a constant partial pressure of CO_2 over the longest section of the river and a slight increase of CO_2 pressure in the lowland area, caused by biogenic contribution, *ie*, decay of detritus and root respiration.

The DIC and CO_2 balances can be calculated by using data shown in Figure 1, or—more precisely—by using numerical data stored in our com-

puter memory,[1] since no analytical expression can describe the complexity of the system. On the contrary, ^{13}C and ^{14}C balances seem to be within the reach of analytical solutions, at least in the first approximation and with the help of numerical data shown in Figure 1. Since the aim of this work has been the calculation of ^{14}C activity and δ^{13}C content of DIC along the river, we have modified the conventional mass balance procedure to obtain the numerical values of ^{14}C activities and δ^{13}C content as functions of distance from the springs. Namely, the *specific activity* of DIC depends on the uptake of ^{14}C along the river course mainly from the atmosphere, which—in turn—depends on the difference in activity and partial pressure of CO_2 in both systems. The partial pressure and activity of CO_2 in the air is quite constant during the river water turnover, and so is the partial pressure of CO_2 in water along 93% of the Korana River flow. Therefore, for this section a relatively simple model describing the ^{14}C activity increase was developed assuming that the increase is due to the exchange of the dissolved CO_2 in stream water with atmospheric CO_2.

The differential increase of DIC activity $dA(aq)/d\ell$ should be proportional to the difference between the partial pressure of atmospheric CO_2, p(atm) multiplied by its ^{14}C activity, and the partial pressure of CO_2 in water, p(aq) at a given point ℓ multiplied by its ^{14}C activity:

$$\frac{d[p(aq)\,A(aq)]}{d\ell} = k\,[p(atm)\,A(atm) - p(aq)\,A(aq)] \qquad (1)$$

The coefficient k in Eq 1 is proportional to the exchange rate between the dissolved and the atmospheric CO_2 at the point ℓ. The equilibrium activity between all ionic species containing ^{14}C is attained rapidly in turbulent water, hence the sought DIC activity is equal to the ^{14}C activity of CO_2 in water, denoted by A(aq) in Eq 1 and 2. The solution of Eq 1 has a simple exponential form:

$$A(aq) = \frac{1}{p(aq)}\{A(atm)p(atm) - [A(atm)p(atm) - A_0(aq)p_0(aq)]\,e^{-k\Delta\ell}\} \quad (2)$$

for constant values of p(atm), p(aq), and the coefficient k over the river segment $\Delta\ell$. $A_0(aq)$ is the DIC ^{14}C activity at the starting point of the river segment and $\Delta\ell$ is the distance between the starting and the end point. Whereas the constant value of p(atm) is not questionable along the river course, the assumed constancy of p(aq) in water is valid only over a limited distance or under specific conditions. Only measurements of p(aq) in water can give an answer about its constant value in a given segment. The coefficient k is definitely a function of the stream flow mode and the value obtained by applying Eq 2 is the *average* value for that segment. The coefficient k reaches its highest value (0.635 km^{-1}) at the waterfalls where the intensive exchange between gaseous and dissolved CO_2 takes place. The lowest value of coefficient k (0.0016km^{-1}) was obtained for the lowland meandering flow of the Korana River. These results are in qualitative agreement with data obtained by Mook (1970).

[1] The data are available on request

Measurements of ^{13}C content of DIC in water, shown in Figure 1, indicated that at least two contributions to the DIC ^{14}C activity exist which cannot be resolved by analysis of ^{14}C data. Terrestrial plants and atmospheric CO_2 have the same ^{14}C activity; however, their ^{13}C contents are different, offering the possibility of distinguishing their relative contribution. A more complex model taking into account both ^{14}C and ^{13}C data was developed in the following way. The increase of ^{14}C activity is proportional to the difference between the partial pressure of atmospheric CO_2, p(atm) and p(aq) multiplied by the corresponding ^{14}C activities, as well as to the ^{14}C contribution from terrestrial plants. The change of $\delta^{13}C$ is proportional in the same way to the difference between $\delta^{13}C$ of atmospheric CO_2 and $\delta^{13}C$ of DIC as well as to the contribution of plants:

$$\frac{d[A(aq)\ p(aq)]}{d\ell} = k_1 \left\{ [A(atm) - 2\epsilon]p(atm) - A(aq)p(aq) \right\} \tag{3}$$

$$\frac{d[\delta(aq)\ p(aq)]}{d\ell} = k_1 \left\{ [\delta(atm) - \epsilon]p(atm) - \delta(aq)p(aq) \right\} \tag{4}$$

where δ stands for the corresponding $\delta^{13}C$ value. ^{14}C and ^{13}C contributions from terrestrial plants are proportional to the plant activity A_{pl} and their ^{13}C content, respectively:

$$\frac{dA(pl)}{d\ell} = k_2 A_{pl} \tag{5}$$

$$\frac{d\delta(pl)}{d\ell} = k_2\ \delta\ ^{13}C_{pl} \tag{6}$$

Coefficients k_1 and k_2 are proportional to the exchange rate of atmospheric and dissolved carbon dioxide and to the plant contribution, respectively. The fractionation factor ϵ between the gaseous CO_2 and bicarbonates is equal to $-9.6\permil$ at 10°C (Fontes, 1983). As in the previous case, Eq 3 and 4 can be solved for a constant difference in partial pressure of CO_2 between the liquid and the gaseous phase. The analytical solutions of Eq 3 and 4 are valid in the lowland area, whereas numerical methods have to be applied for regions of rapid changes of CO_2 partial pressure in water, using data from Figure 1.

Our measurements showed that $\delta^{13}C$ of plants in the area varies between $-26\permil$ and $-30\permil$ *vs* PDB (Krajcar-Bronić *et al*, 1986). These values are several per mil lower than the soil CO_2 values of Dörr and Münnich (1980). The mean value of $-28\permil$ was used for calculation. The $\delta^{13}C$ value of atmospheric CO_2 is equal to $-8\permil$ (Stuiver & Polach, 1977).

Coefficients k_1 and k_2 were calculated for segments along the water course having characteristic flow mode. As expected, the coefficients are different for each segment and the contribution of atmospheric *vs* biogenic CO_2 can be calculated for any particular river segment (Table 1).

It is reasonable to suppose that the coefficients are the same at least for the Holocene when climatic conditions and hydrology of the Plitvice lakes system did not change very much. Thus, by applying our model it is

TABLE 1

The increase of ^{14}C activity of DIC for various segments shown
in Figure 1 along the water course

River segment (Fig 1)	Length of segment (km)	[14]C activity increase (% per km)	Atmospheric CO_2 (%)	Biogenic CO_2 (%)
A–C Rapids	3.8	2.2	~98	<2
B–C Rapids	2.7	6.2	>99	~0.5
C–D Lake	2.0	2.0	~98	~2
D–E Rapids and waterfalls	1.8	4.3	>99	<1
E–F Lake	1.7	0.7	95	~5
F–G Waterfalls	1.0	2.3	~99	<1
G–H Rapids	4.7	1.5	>97	<3
H–I Lowland flow	61	0.06	36	64
I–J Lowland flow	55	0.05	23	77

possible to calculate the initial activity for any location along the water course (Fig 1), provided that ^{14}C activity of DIC in spring water has not been influenced by nuclear weapon test [14]C (Krajcar-Bronić *et al*, 1986). The obtained results are in quite good agreement with initial activities calculated independently from experimental results (Srdoč *et al*, 1986). Further, by knowing the ^{14}C activity of the atmospheric CO_2 in the last 30 years and assuming that the yearly growth of tufa is constant, it was possible to calculate the ^{14}C activity of tufa layers grown in this period. Several tufa samples grown during the last 30 years showed the ^{14}C activity in agreement with the calculated values.

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