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COMPARISON OF THE ^{14}C ACTIVITY OF GROUNDWATER AND RECENT TUFA FROM KARST AREAS IN YUGOSLAVIA AND CZECHOSLOVAKIA

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ABSTRACT. ^{14}C activity of dissolved inorganic carbon (DIC) in water and in recent tufa samples in several karst areas of Yugoslavia and Czechoslovakia was measured. Groundwater from 11 karst springs were measured for their isotopic content (^{14}C, ^{3}H, ^{13}C), chemical composition (HCO_3^-, Ca^{2+}, Mg^{2+}) and physico-chemical properties (temperature, pH). Seasonal variations of the ^{14}C activity of DIC in two karst springs in Plitvice Lakes area, Yugoslavia, were measured systematically from 1979 – 1987. ^{14}C activity of recent tufa samples from several locations downstream were also measured. The activity of DIC in karst spring water in both countries ranged from 63–87 pMC, which is attributed to differences in geologic structure of the recharge area, topsoil thickness and composition. Grouping of ^{14}C activities of DIC ca $(82\pm4)\%$ is evident. Tritium activity at all the springs indicated short mean residence time (1–10 yr). Concentration of HCO_3^-, Ca^{2+} and Mg^{2+} in spring water varied with geomorphology. ^{14}C activity of streamwater and recent tufa increased downstream from karst springs due to the exchange between atmospheric CO_2 and DIC.

INTRODUCTION

Tufa formation has been systematically studied at Rudjer Bošković Institute during the past several years. An investigation of ^{14}C activity of tufa samples (Srdoč *et al,* 1980, 1983, 1987; Krajcar Bronić *et al,*1986) as well as measurements of physico-chemical properties of freshwater to determine the conditions for tufa formation (Srdoč *et al,* 1985) have been done in the karst area of the Plitvice National Park, Yugoslavia.

The main problem in ^{14}C dating of tufa deposits is determining initial ^{14}C activity. Water circulation in karst results in dissolution of soluble rock such as limestone, chalk and dolomite. The dissolution of rock depends on water temperature and its chemical composition, with the dominant role of dissolved CO_2 originating in a relatively thin layer of topsoil. The net result of this dissolution process, followed by an exchange of carbon between gaseous and liquid phases, is an unpredictable isotopic composition of dissolved inorganic carbon (DIC).

The aim of this work was 1) to compare ^{14}C activity of DIC in water and in recent tufa samples in 7 karst springs in Yugoslavia and 4 karst springs in Czechoslovakia, and 2) to compare physico-chemical conditions for tufa precipitation in the same areas.

SITE DESCRIPTIONS

Tufa and groundwater samples were collected in the Dinaric karst, a range stretching from Trieste in Italy to Montenegro in SE Yugoslavia (Fig 1A). Karst aquifers issuing at Crna Rijeka, Bijela Rijeka, Plitvica and Rječica springs (1–4, Fig 1A) represent the main sources feeding the Plitvice Lakes. In the valley of the Korana River and its tributaries, the Mesozoic bedrock is overlain by layers of Quaternary tufa. All these streams precipitate tufa from their waters. With the exception of Rječica, the streams' watersheds are in extremely karstic limestones with many sinkholes and poljes. Additional tufa deposits can be found downstream in Cretaceous limestones below the mouth of the Plitvica Creek into the Korana River.

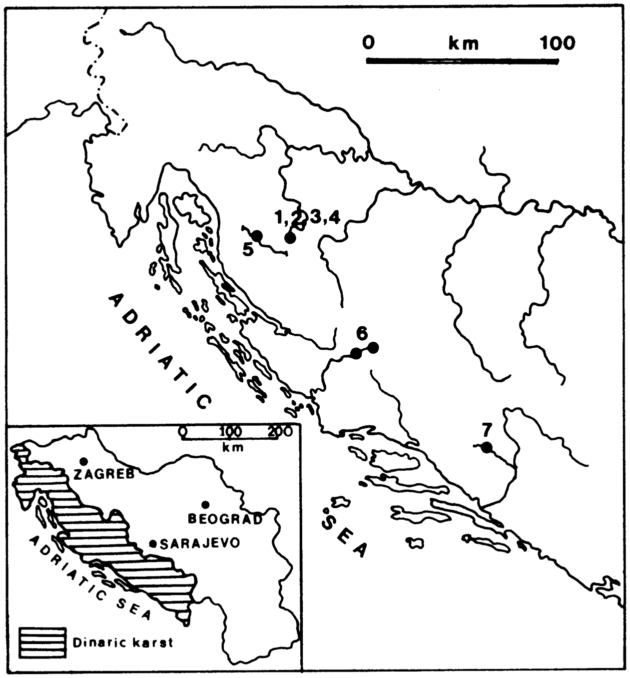

Fig 1A. Map showing sampling sites in the Dinaric karst of Yugoslavia: 1– Crna Rijeka, 2– Bijela Rijeka, 3– Plitvica, 4– Rječica, 5– Gacka, 6– Krčić, 7– Trebižat

Krčić (Fig 1A:6) flows along a valley in a karst area not far from Dinara Mountain, which gave the name, Dinaric karst. The riverbed is cut in dolomites and old tufa deposits were found on both sides of the Krčić River banks. Recent tufa was found ca 5km downstream from the spring.

The Trebižat River (Fig 1A:7) belongs to the Neretva River catchment area in the eastern part of the Dinaric karst. Its karst spring issues at the contact zone between flysch sediments and limestone bedrock. Only

Holocene tufa was found in the Kravice waterfall area, the main tufa depositing area of the Trebižat River.

Tufa and groundwater samples were collected at 3 locations in the Central Bohemian Karst and 1 in the Male Karpaty Mountains in western Slovakia, Czechoslovakia (Fig 1B). The sites in the Central Bohemian Karst are ca 25km SW of Prague close together along the Berounka River valley, the bottom of which is ca 210m asl.

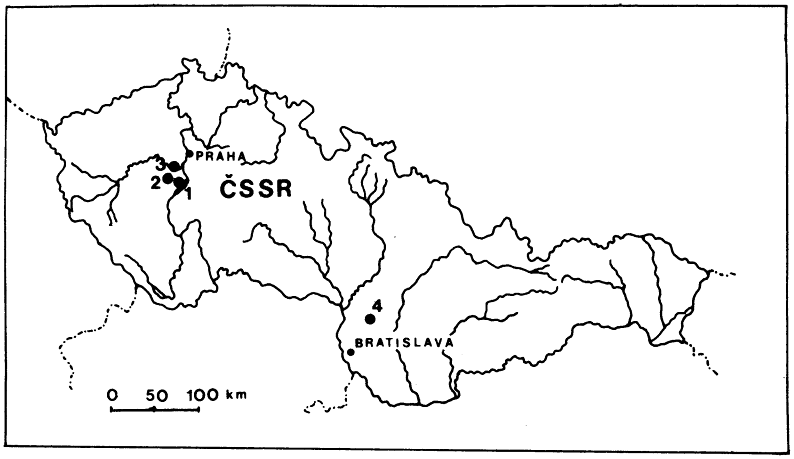

Fig 1B. Map showing sampling sites in Czechoslovakia: 1– Cisarska rokle, 2– Koda near Srbsko, 3– Sv Jan pod skalou, 4– Babina near Hradište

Cisarska rokle gorge (Fig 1B:1) is a short steep valley on the south bank of the Berounka River. Tufa has precipitated from a small stream which starts at a karst spring at the upper end of the ravine at ca 310m asl. Foam sinter and sandy tufa of Holocene age are preserved in partly eroded cascades. Fresh modern tufa is being precipitated in the stream bed at small cascades and on the surface of large Holocene deposits of tufa.

Koda (Fig 1B:2) is a short steep valley 1km NW of Cisarska rokle. Tufa has precipitated below a spring which is on the valley slope at ca 320m asl and forms cascades reaching 250m asl. The valley contains foam sinter and hard tufa.

Svaty Jan pod Skalou (Fig 1B:3) is a tufa cascade at a karst spring on the north bank of Kačak Creek, a tributary of the Berounka River. The deposit in the Male Karpaty Mountains (Fig 1B: 4) consists of alternating layers of porous tufa, sandy and foam sinter, and hard dense tufa.

All these tufa deposits were formed during the Holocene. The Svaty Jan pod Skalou deposit is from the Middle and Late Holocene to the Middle Ages (Kovanda, 1973).

TABLE 1

Isotopic and chemical analyses of groundwater from karst aquifers in Yugoslavia and Czechoslovakia*

YUGOSLAVIA

	ISOTOPIC ANALYSES					CHEMICAL ANALYSES							
	^{14}C activity (% modern)		$\delta^{13}C$	^3H**	MRT	t	pH	CO_2	HCO_3^-	Ca	Mg	I_{sat}†	
KARST AQUIFER	water	recent tufa	(‰ vs PDB)	(Bq/l)	(year)	(°C)		(mmol/l)	(mmol/l)	(mmol/l)	(mmol/l)	($CaCO_3$)	Comment
1. Crna Rijeka													
spring	63.0±4.0		−12.4±0.6	3.0	2	7.9	7.47	0.44	4.24	1.60	0.71	0.97	No tufa precipitation
3km downstream	85.0±1.0					8.5	8.0	0.15	4.19	1.60	0.66	2.74	Tufa precipitation
2. Bijela Rijeka													
spring	82.7±2.4		−12.4±0.4	4.1	4	7.5	7.46	0.53	4.87	1.46	1.17	0.99	No tufa precipitation
2km downstream		85.3±0.8				7.9	7.80	0.25	4.65	1.38	1.11	2.10	Tufa precipitation
3. Plitvica													
spring	82.5±0.9		−12.8±0.8	3.1	3	7.3	7.60	0.36	4.56	1.53	0.9	1.35	No tufa precipitation
3km downstream		86.8±0.7				7.3	8.20	0.08	4.56	1.43	0.93	5.89	Tufa precipitation
5km downstream		91.2±0.7				8.7	8.34	0.06	4.34	1.44	0.89	6.83	Tufa precipitation
4. Rječica													
1km downstream		80.0±0.9	−9.4±0.4										Tufa precipitation
3km downstream	88.8±0.9					10.4	8.1	0.12	5.38	1.50	1.46	5.61	Tufa precipitation
5. Gacka													
spring						9.4	7.3	0.72	4.89	1.25	1.32	0.65	No tufa precipitation
5km downstream						11.1	7.7	0.28	4.9	1.25	1.32	1.73	No tufa precipitation
15km downstream		82.9±1.1				13.2	8.3	0.06	4.34	1.98	0.31	10.40	Tufa precipitation
6. Krčić													
spring						8.7	7.6	0.24	3.15	1.36	0.26	0.89	No tufa precipitation
5km downstream		88.8±1.1					8.3	0.05	3.15	1.39	0.32	4.68	Tufa precipitation
7. Trebižat													
3km downstream		76.8±1.1				18.4	7.8	0.12	3.1	4.32	0.41	6.11	Tufa precipitation

TABLE 1, (continued)

CZECHOSLOVAKIA

	ISOTOPIC ANALYSES					CHEMICAL ANALYSES							
KARST AQUIFER	^{14}C activity (% modern) water	^{14}C activity (% modern) recent tufa	δ^{13}C (‰ vs PDB)	^{3}H** (Bq/l)	MRT (year)	t (°C)	pH	CO_2 (mmol/l)	HCO_3^- (mmol/l)	Ca (mmol/l)	Mg (mmol/l)	I_{sat}† ($CaCO_3$)	Comment
1. Cisarska rokle													
spring	78.7±1.2			4.7	7	9.7	7.35	0.76	5.78	3.3	0.7	2.30	No tufa precipitation
150m downstream		81.8±1.2	−9.27±0.4			9.2	8.02						Tufa precipitation
300m downstream		89.2±1.2	−7-12±0.4										Tufa precipitation
2. Koda near Srbsko													
spring	87.1±1.1			5.7	10	10.8	7.4	0.65	5.67	3.92	0.5	3.12	No tufa precipitation
300m downstream		91.9±1.3	−9.03±0.4			10.3	8.13	0.09	4.28	3.06	0.38	9.72	Tufa precipitation
3. Sv Jan pod skalou													
spring	82.8±1.1			5.5	9	11.1	7.30	0.76	5.35	3.62	0.58	2.18	No tufa precipitation
4. Babina near Hradište pod vratnom													
spring	76.4±1.1			1.7	1	10.6	7.55	0.44	5.45	1.76	1.32	1.89	No tufa precipitation

*Results of isotopic and chemical analyses of groundwater from aquifers Crna Rijeka, Bijela Rijeka and Plitvica represent the mean values over several years. Values for other aquifers represent single measurement.

**1σ error for all tritium measurements is 0.2 Bq/l.

†Saturation index of $CaCO_3$ (I_{sat}) is calculated according to Stumm and Morgan (1970):

$$I_{sat} = \frac{IAP}{K_C} = \frac{(Ca^{2+}) \cdot \gamma_{Ca} \cdot (HCO_3^-) \cdot \gamma_{HCO_3} \cdot K_2}{K_C \cdot (H^+)}$$

ISOTOPIC ANALYSES

The results of isotopic analyses which include ^{14}C, ^{3}H and ^{13}C concentration in water and in recent tufa are given in Table 1. Tritium activity in water was measured systematically at three karst springs (Crna Rijeka, Bijela Rijeka and Plitvica) from 1976–1987 (Fig 2). The mean residence time (MRT) of the spring waters was determined using tritium measurements and exponential model (Eriksson, 1962; Geyh, 1972) based on the assumption of a well-mixed aquifer. The MRT from 1–10 years was calculated for all the karst springs in the study.

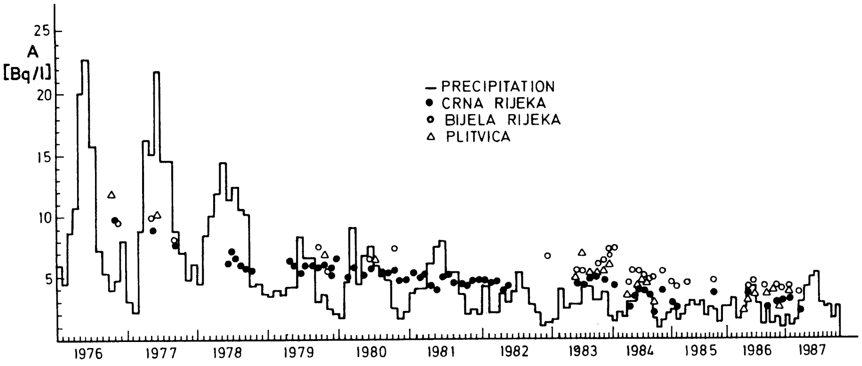

Fig 2. Tritium activity in precipitation at Zagreb and in three karst springs in the Plitvice Lakes, 1976–1987

The δ^{13}C values and the ^{14}C activity of DIC in spring waters and in recent tufa show the biogenic origin of tufa deposits. The more negative δ^{13}C values with respect to bedrock and ^{14}C activity ca 80 pMC result from the dissolution of bedrock limestone and dolomite by H_2CO_3 originating from decomposition of organic detritus and, more generally, from the soil zone.

^{14}C activity of groundwater and recent tufa was measured in different karst areas (Fig 1A, B). ^{14}C activity of DIC in water was measured systematically in two karst springs in Yugoslavia (Crna Rijeka and Bijela Rijeka) to determine seasonal variations of ^{14}C activity (Fig 3). We found a systematic difference in ^{14}C activity between these two karst springs. Crna Rijeka varied between 60–70%, and Bijela Rijeka between 75–87%, which can be a consequence of the different geological structures of the recharge areas and also of the reservoir itself.

The initial ^{14}C activity of these two karst springs was discussed in Krajcar Bronić *et al* (1986). The authors calculated initial groundwater activity using several models described in the literature (Fontes & Garnier, 1979; Mook, 1976; Eichinger, 1983; Tamers, 1970) and measured δ^{13}C values of DIC in groundwater and in soil CO_2 which sometimes gave unac-

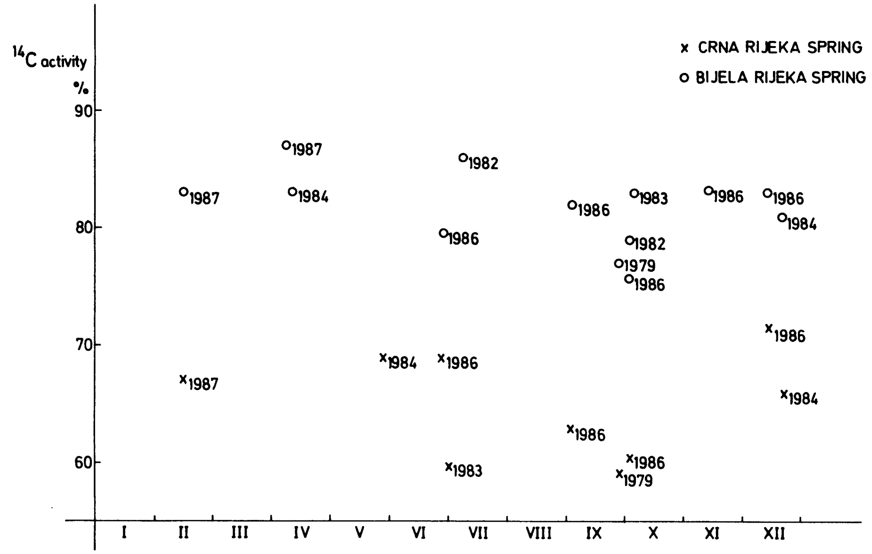

Fig 3. Seasonal variations of ^{14}C activity of DIC in water from two karst springs of the Plitvice Lakes

ceptable results due to an unpredictable fraction of atmospheric CO_2 in DIC. The measured groundwater activities in Crna Rijeka and Bijela Rijeka showed wide ^{14}C activity variations of ca 10% during one year, indicating an admixture of atmospheric CO_2 which varies between 10–40% of total DIC (Krajcar Bronić *et al*, 1986). The isotopic exchange between DIC and precipitated calcite is also possible (Mozeto *et al,* 1983) but when MRT of springwater is short (1–10 yr), and the contribution of atmospheric CO_2 to the DIC is significant, and when the recrystallization process does not take place, this exchange process can be neglected.

In Yugoslavia (Fig 1A: 1–4) and in Czechoslovakia (Fig 1B: 1,2) we measured ^{14}C activity of DIC in springwater and recent tufa downstream from the springs at various distances. As in our previous measurements in the Plitvice Lakes, we noticed increased ^{14}C activity downstream (Srdoč *et al*, 1986). Increased ^{14}C activity per unit distance is not the same in all the streams, which is dependent on the exchange process between atmospheric CO_2 and DIC.

CHEMICAL ANALYSES

We measured chemical composition and physico-chemical properties of water, using standard methods in aquatic chemistry to determine the conditions for calcite precipitation (Stumm & Morgan, 1970). Temperature, pH and very often alkalinity were measured *in situ,* whereas the rest of the measurements (concentration of Ca^{2+} and Mg^{2+}) were done in the laboratory. Total dissolved CO_2, ionic activity product (IAP) and $CaCO_3$ saturation index (I_{sat}) were calculated, using pH, alkalinity and temperature (see Table

1). All the karst aquifers lacked tufa precipitation at the springs because of the low saturation index of calcite. All the karst springs are characterized by a very high partial pressure of CO_2, and mainly the constant pH value, 7.3–7.6. The concentration of dissolved CO_2 drops rapidly downstream from the springs caused by rapid degassing of excessive CO_2 in springwater. This is followed by a quite constant partial pressure of CO_2 over the longest section of the river. The pH value depending directly on dissolved CO_2 concentration, increases downstream and, in the area of tufa precipitation, its value is above 8. The $CaCO_3$ saturation index also increases downstream from I_{sat} 1 in springs to even 10 in tufa precipitation area. In most of the karst areas, calcite starts to precipitate when the I_{sat} exceeds 2 to 3 (see Table 1).

CONCLUSIONS

The ^{14}C activity of DIC from 11 karst springs in Yugoslavia and Czechoslovakia varied from 63–87 pMC, which is attributed to geomorphological differences in the recharge areas. The attempt to correlate the geomorphology of the catchment area and its vegetation with the ^{14}C activity of groundwater having short residence time in karst failed to produce consistent results. It seems that the exchange between the atmospheric and/or soil CO_2 and dissolved CO_2 in groundwater in the cavernous karst underground plays a dominant role in the formation of isotopic composition of DIC in water.

The measured ^{14}C activities listed in Table 1 cannot be used as initial activities for old calcareous deposits because of contamination of recent DIC and tufa with bomb-produced ^{14}C. This problem has been discussed extensively elsewhere (Srdoč, 1986). All the karst aquifers in our study have a short MRT of groundwater (1–10 yr) according to tritium concentration measurements.

^{14}C activity of DIC and recent tufa increases downstream from karst springs as a result of exchange between atmospheric and dissolved CO_2.

Physico-chemical measurements show that the concentration of dissolved CO_2 drops rapidly downstream from karst springs, causing a corresponding increase of pH and $CaCO_3$ saturation index. In most of the karst areas, calcite starts to precipitate when the saturation index exceeds 2–3.

ACKNOWLEDGMENTS

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