

# Isotopic composition of dissolved inorganic carbon in bottled waters on the Slovene market

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## Abstract

This study investigates the stable isotopic composition of dissolved inorganic carbon (DIC), expressed as  $\delta^{13}\text{C}_{\text{DIC}}$ , in domestic and foreign bottled waters randomly collected on the Slovene market. All together 58 brands and 16 replicates were analysed. The  $\delta^{13}\text{C}_{\text{DIC}}$  values varied between  $-63.1\text{‰}$  and  $+1.0\text{‰}$  with an average of  $-12.3\text{‰}$ . Average  $\delta^{13}\text{C}_{\text{DIC}}$  values for naturally sparkling, artificially sparkling, still and flavoured waters were  $-3.3\text{‰}$ ,  $-36.5\text{‰}$ ,  $-10.0\text{‰}$  and  $-11.0\text{‰}$ , respectively. The lowest values are characteristic of artificial sparkling waters (minimum  $-63.1\text{‰}$ ) and can be attributed to injection of industrial  $\text{CO}_2$  during bottled water production. Therefore, determination of the isotopic composition of DIC can represent a useful analytical tool to distinguish between natural and artificially sparkling waters. Furthermore, the method used enabled determination of the various origins of still waters. From the bottled waters sampled it was possible to discern waters that originate from deeper aquifers, from aquifers in equilibrium with soil  $\text{CO}_2$ , or from aquifers with their recharge in a mountainous area. Finally,  $\delta^{13}\text{C}_{\text{DIC}}$  values of flavoured waters illustrate that isotopic fractionation occurs during the production process and that  $\delta^{13}\text{C}_{\text{DIC}}$  values in products of some producers have a large variation.

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## 1. Introduction

Carbon represents an important part of the dissolved species in water and in various food ingredients. Carbon distribution can be studied by analysis of the stable isotope ratio  $^{13}\text{C}/^{12}\text{C}$  and allows detection of the origin of dissolved carbon species. Carbon stable isotope analyses of the  $\text{CO}_2$  in food were first proposed for sparkling wines (Dunbar, 1982) and later fully developed for beer (Brooks et al., 2002), wines and other alcoholic drinks (Calderone, Nautet, Guillou, Reniero, & Blanch Cortes, 2005; Gonz ales-Martin, Gonz ales-P erez, & Marqu es-Macias, 1997; Martinelli et al., 2003). The idea of determination of the origin of  $\text{CO}_2$  in sparkling bottled waters was first devel-

oped by Hillaire-Marcel (1986) and applied and further developed for comparison of natural mineral waters and bottled waters by Redondo and Y elamos (2005).

Ordinary classification of bottled waters depends very much on the country's legislation and it is connected with traditions and the regulators' perception of the hydrological cycle as a source of water for bottling. Therefore, legislation regulating bottled water production and consumption differs considerably throughout the world. Stable carbon isotope analyses can be a very useful tool in controlling the origin of bottled water and how products are in agreement with legislation, especially European legislation, where various types of sparkling waters are defined (Anonymous, 1980).

In this study, the stable carbon isotopic composition of total dissolved inorganic carbon (DIC) in bottled waters available on the Slovene market in September 2004 was

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determined. The results obtained were used for a general overview of bottled water properties that are reflected in the isotopic composition of DIC and for examination of natural and production processes that can be traced by stable carbon isotopes in bottled waters.

## 2. Materials and methods

### 2.1. Methodological basis

Bottled waters originate from natural waters that are part of the hydrological cycle. During its circulation water dissolves various constituents of natural and anthropogenic origin. One of them is carbon that appears in inorganic and organic form. Usually the inorganic form of carbon prevails in groundwater, which is the main source of bottled waters. Its presence is a consequence of interactions between water, gaseous CO<sub>2</sub> and carbonate rocks.

DIC can be expressed as the sum of the concentrations of dissolved CO<sub>2</sub> (CO<sub>2aq</sub>), carbonic acid (H<sub>2</sub>CO<sub>3</sub>), bicarbonate (HCO<sub>3</sub><sup>-</sup>) and carbonate (CO<sub>3</sub><sup>2-</sup>). All these species constitute the carbonate system in dynamic equilibrium. The concentration of particular species depends mainly on pH, temperature and pressure (Dreybrodt, 1988). In natural systems the concentration of carbonic acid (H<sub>2</sub>CO<sub>3</sub>) is usually negligible, but it can be present in some flavoured bottled waters.

### 2.2. Sampling

Bottled waters commercially available from supermarkets in Ljubljana (Slovenia) and its vicinity were sampled. Collection of bottles was performed in two steps. In the first step a list of all brands of bottled waters available in large supermarkets was made. We believe that this procedure included nearly all brands available on the Slovene market. In the second step it was determined by chance selection which brands would be sampled as duplicated bottles, and for which brands samples would be repeated from the same bottle. According to the list of brands, bottles were then purchased in the shops. Bottles for each brand were randomly taken from the shop shelves. During the sampling no distinction was made between different types of waters. More details about sampling are given elsewhere (Brencic & Vreca, 2005).

Sampling for isotopic composition of dissolved inorganic carbon ( $\delta^{13}\text{C}_{\text{DIC}}$ ) was part of a larger sampling campaign reviewing the bottled waters available on the Slovene market. Each brand was analysed for chemical composition and stable isotopic composition of DIC, oxygen and hydrogen (Brencic & Vreca, 2005). Most brands were sold in 1.5 L plastic bottles; only 3 were sold in 1 L glass bottles. Altogether 58 brands were sampled: 15 foreign and 43 domestic brands. Duplication of bottles for nine particular brands was used for the determination of between-bottle variability of  $\delta^{13}\text{C}_{\text{DIC}}$  values. Duplicates of samples from

seven particular bottles were used for the control of within-bottle variability of  $\delta^{13}\text{C}_{\text{DIC}}$  values. For domestic brands the general hydrological conditions of the water resources used for production are known from the literature and based on our own hydrogeological knowledge. According to the available information, all sampled bottled waters used for production are groundwaters.

After purchasing was completed all bottles were taken to the laboratory of the Geological Survey of Slovenia where they were encoded. Only numbers identified samples. In the further process of analyses no information about brands was available to the analyst. pH, at 25 °C, was measured immediately after opening the bottle. Samples for  $\delta^{13}\text{C}_{\text{DIC}}$  determination were transferred to 12 mL glass ex-tainers and sent to the isotopic laboratory at the Jozef Stefan Institute where they were stored in a refrigerator prior to analysis.

### 2.3. $\delta^{13}\text{C}_{\text{DIC}}$ analyses

In all samples the isotopic composition of dissolved inorganic carbon ( $\delta^{13}\text{C}_{\text{DIC}}$ ) was determined on CO<sub>2</sub> collected after reaction of 0.5–5 mL of sample with 100% H<sub>3</sub>PO<sub>4</sub> on a continuous flow Europa 20–20 ANCA-TG stable isotope mass spectrometer. Samples were prepared in duplicate. In addition CO<sub>2</sub> collected after reaction of Na<sub>2</sub>CO<sub>3</sub> solution with 100% H<sub>3</sub>PO<sub>4</sub> was analysed with each set of samples. Results are expressed in standard delta notation ( $\delta$ ) as per ml (‰) deviation from the V-PDB standard as:

$$\delta^{13}\text{C} (\text{‰}) = \left( \frac{R_{\text{sample}}}{R_{\text{std}}} - 1 \right) \times 1000$$

where  $R_{\text{sample}}$  and  $R_{\text{std}}$  are <sup>13</sup>C/<sup>12</sup>C ratios of the sample and standard, respectively. Positive  $\delta^{13}\text{C}$  values mean a relative enrichment of the material in the heavy isotope, with respect to the standard, and negative  $\delta^{13}\text{C}$  values mean a lighter composition than the standard. Results are reported as the  $\delta^{13}\text{C}_{\text{DIC}}$  values of two duplicates (Tables 1–3). In a few cases only one value was obtained.

The mean sample repeatability was 0.1‰, but some analysed samples showed larger differences between duplicates (Tables 1–3). Most of these samples were flavoured waters that are characterised by lower dissolved inorganic carbon concentrations and lower pH (Brencic & Vreca, 2005). The mean value of 45 repeated measurements of Na<sub>2</sub>CO<sub>3</sub> solution was  $-10.6 \pm 0.1\text{‰}$ .

Analytical reproducibility was  $\pm 0.2\text{‰}$ , determined by repeated analyses of ISO-TOP reference CO<sub>2</sub> gas (Messer Griesheim, Krefeld, Germany) and working CO<sub>2</sub> gas calibrated to international reference gases (NIST RM8564 and RM8563).

### 2.4. Statistical analyses

Descriptive statistics were calculated for all samples and individual groups. Differences between samples were tested by one-way analysis of variance followed by the post hoc

Table 1  
Stable isotopic composition of dissolved inorganic carbon ( $\delta^{13}\text{C}_{\text{DIC}}$ ) in sparkling waters

Bottled by	Origin	Brand	CO <sub>2</sub> type	pH	$\delta^{13}\text{C}_{\text{DIC}}$ (‰)	
					Reading 1	Reading 2
Kolinska	Slovenia	Donat	Natural	6.44	1.2	0.8
Kolinska	Slovenia	Donat <sup>a</sup>	Natural	6.49	0.7	0.5
Kolinska	Slovenia	Tempel	Natural	5.49	-3.6	-3.5
Kolinska <sup>b</sup>	Slovenia	Tempel	Natural	5.49	-3.0	-3.3
Kolinska	Slovenia	Edina	Natural	5.24	-3.6	-3.9
Jamnica	Croatia	Jamnica	Artificial	6.02	-24.1	-24.2
Jamnica <sup>c</sup>	Croatia	Jamnica	Artificial	6.02	-24.6	-24.9
Radenska	Austria	Sicheldorfer Josefsquelle <sup>a</sup>	Natural	6.13	-10.2	-9.8
Bad Radgesburg	Austria	Long Life-1	Artificial	5.82	-33.1	-33.1
Bad Radgesburg	Austria	Long Life-2	Natural	5.94	-6.3	-6.4
Radenska	Slovenia	Classic <sup>a</sup>	Natural	5.99	-1.4	-1.4
Radenska	Slovenia	Classic	Natural	6.08	-0.5	-0.4
Radenska	Slovenia	Light-Miral	Natural	5.90	-1.4	-1.6
San Benedeto	Italy	Guizza	Natural	4.99	-7.0	-7.1
Tavina	Italy	Spar Sorgente Linda	Artificial	5.25	-51.8	
Sodavicarstvo Volk	Slovenia	Stirna	Artificial	5.00	-44.7	-44.6
Sodavicarstvo Volk <sup>c</sup>	Slovenia	Stirna	Artificial	5.00	-44.9	-44.9
Spinone al Lago	Italy	Primula	Artificial	5.06	-63.2	-63.0
Fonte S. Antonio	Italy	San Antonio	Artificial	4.67	-5.5	-5.4

<sup>a</sup> Glass bottles.

<sup>b</sup> Replicated bottle.

<sup>c</sup> Replicated sample from the bottle.

Table 2  
Stable isotopic composition of dissolved inorganic carbon ( $\delta^{13}\text{C}_{\text{DIC}}$ ) in still waters

Bottled by	Origin	Brand	pH	$\delta^{13}\text{C}_{\text{DIC}}$ (‰)	
				Reading 1	Reading 2
Radenska	Slovenia	Radin	7.27	-0.3	-0.2
Radenska <sup>a</sup>	Slovenia	Radin	7.27	-0.9	-0.7
Radenska	Slovenia	Izvir	6.93	-7.6	-7.2
Radenska	Slovenia	Iva	6.60	-7.6	-7.7
Radenska <sup>b</sup>	Slovenia	Iva	6.56	-8.2	-7.9
Radenska <sup>a</sup>	Slovenia	Iva	6.56	-8.1	-7.9
Vino Brezice	Slovenia	Bistra	7.39	-12.0	
Dana	Slovenia	Dana	7.24	-13.0	-12.7
Danone	France	Evian	7.18	-12.8	
Fructal	Slovenia	H <sub>2</sub> O	7.75	-10.5	-9.5
Jamnica	Croatia	Jana	7.43	-11.9	-12.0
Perne	Slovenia	Juliana	7.77	-9.4	-9.6
Lasko Brewery	Slovenia	Oda	7.58	-12.6	-12.2
Lasko Brewery <sup>b</sup>	Slovenia	Oda	7.69	-13.2	
Spinone al Lago	Italy	Primula	7.48	-8.6	-8.6
San Benedeto	Italy	Guizza Stilles	7.38	-9.7	-9.8
Fonte S. Antonio	Italy	San Antonio	7.76	-10.6	-10.2
Plastenka	Slovenia	Spar spring water	7.76	-11.8	-11.5
Plastenka	Slovenia	Spar spring water	7.78	-11.8	-11.9
Plastenka	Slovenia	Spar spring water	7.78	-11.7	-11.6
Plastenka	Slovenia	Spar table water	7.74	-11.9	-11.9
Plastenka	Slovenia	Ziva	7.74	-11.5	-11.7
Union Brewery <sup>b</sup>	Slovenia	Zala	7.36	-12.6	-12.3
Union Brewery <sup>a</sup>	Slovenia	Zala	7.36	-12.6	-12.7
Kolinska	Slovenia	Tiha	7.25	-12.5	-12.7

<sup>a</sup> Replicated sample from the bottle.

<sup>b</sup> Replicated bottle.

Tukey's least significance difference for an unequal number of samples at the 5% level of probability. Testing of the homogeneity of variance was performed by Hartley *F*-

max, Cochran *C* and Bartlett  $\chi^2$  tests (Scheffé, 1999). Tests were performed using the STATISTICA<sup>®</sup> 6.0 statistical package.

Table 3  
Stable isotopic composition of dissolved inorganic carbon ( $\delta^{13}\text{C}_{\text{DIC}}$ ) in flavoured waters

Bottled by	Origin	Brand	Flavour	pH	$\delta^{13}\text{C}_{\text{DIC}}$ (‰)	
					Reading 1	Reading 2
Vino Brezice	Slovenia	Active	Elderberry and lemon	3.94	-13.7	-13.7
Vino Brezice <sup>a</sup>	Slovenia	Active	Elderberry and lemon	3.93	-14.4	-14.6
Vino Brezice	Slovenia	Active	Fitness	3.73	-13.0	-13.9
Vino Brezice	Slovenia	Active	Guava and lime	3.90	-13.8	
Vino Brezice	Slovenia	Bistra	Apple	3.43	-12.9	-12.5
Vino Brezice	Slovenia	Bistra	Lemon	3.51	-12.7	-12.2
Vino Brezice	Slovenia	Mercator	Lemon	3.47	-12.6	-13.0
Vino Brezice <sup>a</sup>	Slovenia	Mercator	Lemon	3.47	-13.0	-12.6
Vino Brezice	Slovenia	Spar Active	Fitness	3.72	-12.3	-11.9
Vino Brezice	Slovenia	Spar Active	Apple	3.42	-12.5	-11.8
Vino Brezice	Slovenia	Spar Active	Orange	3.40	-13.9	-14.3
Dana	Slovenia	Dana	Apple	4.37	-7.4	-7.2
Dana <sup>b</sup>	Slovenia	Dana	Apple	4.37	-7.1	-7.1
Dana	Slovenia	Dana	Mango	4.24	-5.1	
Dana	Slovenia	Dana	Lime	4.26	-6.9	-7.2
Dana	Slovenia	Spar	Apple	4.58	-13.3	-13.7
Dana	Slovenia	Spar	Lime	4.07	-13.9	-13.6
Dana <sup>a</sup>	Slovenia	Spar	Lime	4.08	-13.9	-13.8
Union Brewery	Slovenia	Za	Lemon	3.19	-13.2	-13.2
Union Brewery <sup>a</sup>	Slovenia	Za	Lemon	3.19	-13.5	-13.1
Union Brewery	Slovenia	Za Life	Apple	3.43	-12.5	-12.7
Radenska	Slovenia	Izvir	Peach	3.53	-6.0	-5.9
Radenska	Slovenia	Izvir	Guava	3.49	-6.4	-6.5
Radenska	Slovenia	Izvir	Strawberry	3.45	-6.8	-6.4
Radenska	Slovenia	Izvir	Strawberry	3.45	-6.6	-6.7
Radenska	Slovenia	Izvir	Lemon and balm	3.37	-7.4	-7.1
Jamnica	Croatia	Jana	Strawberry and guava	3.23	-11.9	-12.0
Jamnica	Croatia	Jana	Lemon and lime	3.09	-12.1	-12.0
Perne	Slovenia	Juliana	Lemon	7.03	-9.8	-9.6
S.M.A	Slovenia	Har Di	Lemon	3.85	-12.4	-11.4

<sup>a</sup> Replicated bottle.

<sup>b</sup> Replicated sample from the bottle.

### 3. Results and discussion

#### 3.1. Classification of bottled waters

Measurements of  $\delta^{13}\text{C}_{\text{DIC}}$ , pH and the information on the bottle labels showed that in general the sampled waters can be divided into several groups. For further presentation and interpretation of the results, division of the data into three main groups and two subgroups was needed. Groups were defined as:

- (a) Sparkling waters – waters where dissolved gaseous  $\text{CO}_2$  is present.
  - (a.1) Natural sparkling waters – dissolved gaseous  $\text{CO}_2$  originating from the same aquifer as the water.
  - (a.2) Artificial sparkling waters – dissolved gaseous  $\text{CO}_2$  of artificial origin is present. The  $\text{CO}_2$  was added to the parent water during the production process.
- (b) Still waters – all waters without the presence of dissolved gaseous  $\text{CO}_2$  and without organic flavours introduced during production.

- (c) Flavoured waters – waters with organic flavours; mainly with different types of aromas and a small number amount of extracts.

The results of all  $\delta^{13}\text{C}_{\text{DIC}}$  vs. pH measurements are presented in Fig. 1, where the three main groups are clearly indicated;  $\delta^{13}\text{C}_{\text{DIC}}$  and pH data for different types of bottled waters are given in Tables 1–3. The average  $\delta^{13}\text{C}_{\text{DIC}}$  value of all samples is  $-12.3\text{‰}$  and the median value  $-11.7\text{‰}$  is very similar to the average. The minimum value of  $\delta^{13}\text{C}_{\text{DIC}}$  is  $-63.1\text{‰}$  and maximum value is  $+1.0\text{‰}$ . Descriptive statistics of  $\delta^{13}\text{C}_{\text{DIC}}$  values for the different groups of bottled water are given in Table 4. The range of  $64.1\text{‰}$  for all measured values is very large and not usually present in single natural systems. The average pH of all samples is 5.5, the same as the median. The minimum of pH is 3.1 and the maximum value 7.8.

Analysis of variance for  $\delta^{13}\text{C}_{\text{DIC}}$  values was made on four groups; natural and artificial sparkling waters, still waters and flavoured waters. The validity of alternative hypothesis showed that averages between groups were significantly different. The assumption of homogeneity of variance is violated; Hartley  $F$ -max 35.0, Cochran C

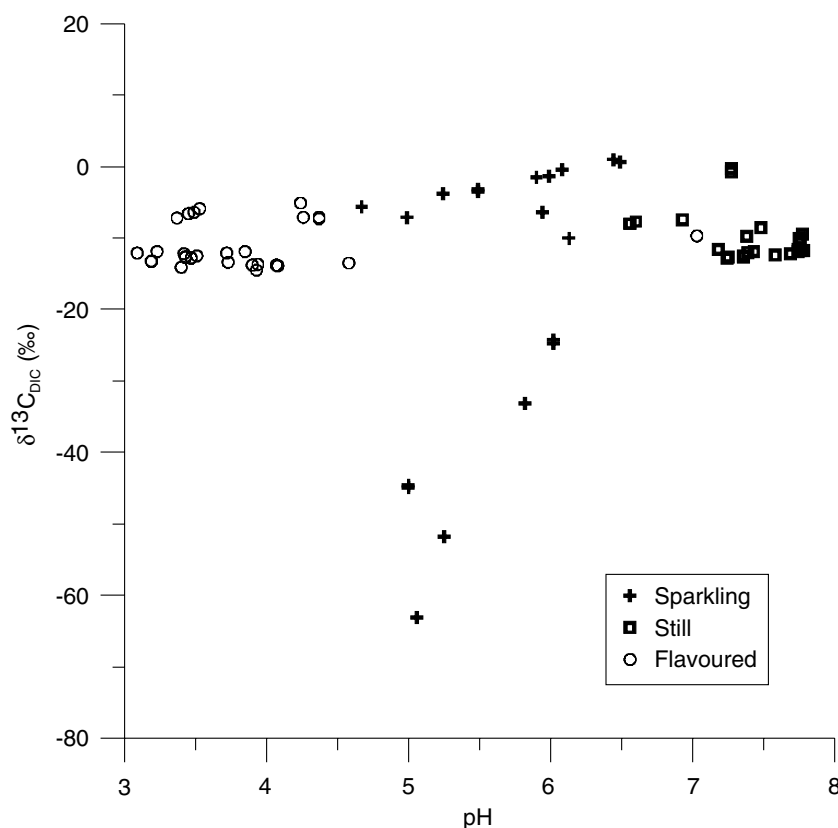


Fig. 1.  $\delta^{13}\text{C}_{\text{DIC}}$  and pH values from all samples divided according to the type of bottled water. Each symbol represents the mean of duplicate analyses (where available).

Table 4  
Descriptive statistics of  $\delta^{13}\text{C}_{\text{DIC}}$  for different types of bottled waters

	$\delta^{13}\text{C}_{\text{DIC}}$ (‰)					Range	N
	Average	Median	Minimum	Maximum			
All waters	-12.3	-11.8	-63.1	1.0	64.1	74	
Sparkling waters	-17.3	-6.4	-63.1	1.0	64.1	19	
Natural sparkling waters	-3.3	-3.2	-10.0	1.0	11.0	11	
Artificial sparkling waters	-36.5	-38.9	-63.1	-5.6	57.5	8	
Still waters	-10.0	-11.6	-12.8	-0.3	12.5	25	
Flavoured waters	-11.0	-12.4	-14.5	-5.1	9.4	30	

0.91, Bartlett  $\chi^2$  72.2 were calculated, respectively. The calculated probability for the validity of the zero hypothesis is very small with  $p \approx 10^{-15}$ . In spite of the homogeneity of variance violation, the post hoc test confirmed visual observation of Fig. 1 and Table 4 that different groupings of the samples existed. Tukey's least significance difference for an unequal number of samples at the  $p = 0.05$  level shows a statistically significant similarity between groups of natural sparkling waters and still waters, and between still and flavoured waters. The similarity between natural sparkling waters and flavoured waters is very close to the critical value of  $p = 0.05$ , being calculated as  $p = 0.03$ . The group of artificial sparkling waters shows a great difference from the other groups.

### 3.2. Sparkling waters

The range of  $\delta^{13}\text{C}_{\text{DIC}}$  values in sparkling waters is very large and identical to the range of whole set of samples (Table 4), meaning that the large range of  $\delta^{13}\text{C}_{\text{DIC}}$  values is a consequence of the range in the group of sparkling waters. However, Table 1 shows that the majority of  $\delta^{13}\text{C}_{\text{DIC}}$  values are positioned around  $-3\text{‰}$  and lie between  $-10.0\text{‰}$  and  $+1.0\text{‰}$ , though several samples are well below this range. The reason for such a large range and distribution of  $\delta^{13}\text{C}_{\text{DIC}}$  values is the very different origin of gaseous  $\text{CO}_2$  and DIC present in sparkling waters, which can be from air, geological processes and from artificial sources.

Natural sparkling waters are usually groundwater from deeper aquifers with moderate to high concentrations of total dissolved solids and dissolved gases, with CO<sub>2</sub> prevailing. These waters have deeper circulation, longer residence times and elevated temperatures in the aquifer. In deep aquifers the carbon mass balance is connected with rock–water interaction and consequently with a different isotopic fractionation than in the case of shallow aquifers. In nature this is reflected in  $\delta^{13}\text{C}_{\text{DIC}}$  and  $\delta^{13}\text{C}_{\text{CO}_2}$  values that are in the range between  $-8\text{‰}$  and  $+3\text{‰}$ . The CO<sub>2</sub> gas that originates from carbonate metamorphism has a similar isotopic composition as the parent rock, usually in the range around  $0 \pm 3\text{‰}$  (Schidlowski, Hayes, & Kaplan, 1983; Veizer & Hoefs, 1976), while the Earth's mantle emanates CO<sub>2</sub> with an isotopic composition between  $-4.7\text{‰}$  and  $-8\text{‰}$  (Barnes, Irwin, & White, 1978). Rare but possible emanation of CO<sub>2</sub> can also be connected with diagenesis of organic sediments in deep sedimentary basins and with metamorphosis of rocks with high organic content. The isotopic composition of such CO<sub>2</sub> is similar or lighter than its parent material, and less than  $-18\text{‰}$  (Winkler, 1984).

Extreme negative values of  $\delta^{13}\text{C}$  in bottled waters are a consequence of the artificial introduction of CO<sub>2</sub> into water (Redondo & Yèlamos, 2005). Industrial CO<sub>2</sub> has many applications and can be produced by various industrial procedures from different parent materials. This is the reason for the different  $\delta^{13}\text{C}$  values in industrial CO<sub>2</sub>. The production of CO<sub>2</sub> is relatively simple and inexpensive, and is very much connected with the availability of parent materials. Soft drinks companies may have their own gas generators. These autonomous plants produce CO<sub>2</sub> by combustion of liquid petroleum or desulphurised natural gas. CO<sub>2</sub> is the result of fuel combustion in power plants, but these emissions are not commonly recovered for CO<sub>2</sub> production. The main industrial source of CO<sub>2</sub> is that produced as a by-product of ammonia production in which H<sub>2</sub> is obtained by the oxidation of hydrocarbons. The second source of industrial CO<sub>2</sub> is oxidation of ethylene. Very pure CO<sub>2</sub> can be produced as a by-product of the fermentation of sugars and starches. (Redondo & Yèlamos, 2005) Historically CO<sub>2</sub> for the bottling industry was produced by the action of acid on limestone (Back, Landa, & Meeks, 1995) or on soda. Only a few cases are known where CO<sub>2</sub> is still produced from natural gas sources. One such case is that of Rogaska in Slovenia, the bottler of Donat mineral water, where CO<sub>2</sub> is produced from the surplus during the process of degassing mineral water.

Not very much is known about  $\delta^{13}\text{C}$  values of industrial CO<sub>2</sub> and how these values are connected with the production process. According to the authors' knowledge, no systematic study has been made on the isotopic composition of industrial CO<sub>2</sub>. In general the CO<sub>2</sub> produced has similar or lighter  $\delta^{13}\text{C}$  values to the parent material (Redondo & Yèlamos, 2005). For the combustion of fossil fuels  $\delta^{13}\text{C}$  values lie in the following ranges: petroleum from  $-25\text{‰}$  to  $-1\text{‰}$ ; natural gas from  $-75\text{‰}$  to  $-15\text{‰}$  (Calderone et al., 2005; Winkler, 1984). Coal  $\delta^{13}\text{C}$  values are from

$-30\text{‰}$  to  $-18\text{‰}$  (Degenes, 1969). It is reported that  $\delta^{13}\text{C}$  values of CO<sub>2</sub> from the manufacture of NH<sub>3</sub> is  $-32.4\text{‰}$  and from the combustion product of CO<sub>2</sub> + CH<sub>4</sub> is  $-36.1\text{‰}$  (González-Martin et al., 1997). According to Redondo and Yèlamos (2005), it is today difficult to find artificial CO<sub>2</sub> with  $\delta^{13}\text{C}$  values higher than  $-18\text{‰}$ , and according to their experience  $\delta^{13}\text{C}$  values in industrial CO<sub>2</sub> are not higher than  $-29\text{‰}$ .

The Slovene natural sparkling waters listed in Table 1 originate mainly from two large regional aquifer systems. In these aquifers similar hydrodynamic and thermodynamic conditions exist. The first group of samples are mineral waters from the Rogaska Slatina aquifer bottled by Kolinska, and the second group of samples are mineral waters from the Slovenske gorice mineral aquifer bottled by Radenska. In the waters bottled by Kolinska  $\delta^{13}\text{C}_{\text{DIC}}$  values are in the range between  $-3.8\text{‰}$  and  $+1.0\text{‰}$ . These values are in accordance with measurements reported for waters sampled in nature. For  $\delta^{13}\text{C}$  in CO<sub>2</sub> it was reported that values in mineral waters of the Rogaska area are in the interval between  $-6.5\text{‰}$  and  $-5.4\text{‰}$  and in DIC between  $-3.1\text{‰}$  and  $+3.3\text{‰}$  (Pezdic, 1997). In the sparkling waters bottled by Radenska  $\delta^{13}\text{C}_{\text{DIC}}$  values are in the range between  $-1.5\text{‰}$  and  $-0.5\text{‰}$  and are also in accordance with measurements reported for waters sampled in nature. For  $\delta^{13}\text{C}$  in CO<sub>2</sub> it was reported that values in mineral waters of the Slovenske gorice aquifer are in the interval between  $-6.0\text{‰}$  and  $-2.2\text{‰}$  and in DIC between  $-4.4\text{‰}$  and  $+4.2\text{‰}$  (Pezdic, Dolenc, Pirc, & Zizek, 1995). It can be concluded that  $\delta^{13}\text{C}_{\text{DIC}}$  values in these natural sparkling waters are in the same range as in the aquifers from which they are pumped out. It also follows that in this case the imprint of the production processes cannot be reflected in the  $\delta^{13}\text{C}_{\text{DIC}}$  values.

On the labels of the water brands Spar Sorgente Linda, Stirna and Primula it is clearly indicated that artificial CO<sub>2</sub> is added during the production process. The artificial origin of CO<sub>2</sub> in these sparkling waters is also clearly indicated by their very low  $\delta^{13}\text{C}_{\text{DIC}}$  values (Table 1), showing that CO<sub>2</sub> was probably produced by combustion of hydrocarbons. The San Antonio brand is also declared as sparkling water with artificial CO<sub>2</sub>, but  $\delta^{13}\text{C}_{\text{DIC}}$  values are very high compared to other artificial sparkling waters. The source of CO<sub>2</sub> in San Antonio is probably of geogenic origin but, according to the available results, it is not possible to distinguish whether it is produced from the action of acid on carbonate rocks or from natural CO<sub>2</sub> originating from emanations.

Among the waters that are declared as natural sparkling waters, low  $\delta^{13}\text{C}_{\text{DIC}}$  values were determined for the brands Long Life-1 and Jamnica. The Long Life brand originates from the area of Bad Radgesburg in Austria, on the border with Slovenia (Zettinigg, 1993). Under the name Long Life actually two brands are available on the market. To indicate the different type of brands with the same name we designated them as 1 and 2 respectively. According to the information written on the bottle label, brand Long

Life-1 is declared as a natural sparkling mineral water and Long Life-2 is declared as a natural moderately carbonated mineral water. The difference in CO<sub>2</sub> content is also seen from the pH values and it can be inferred that equilibrium conditions in the CaCO<sub>3</sub>–CO<sub>2</sub>–H<sub>2</sub>O system differ among the Long Life brands. It may be inferred from the literature without giving numbers (Goldbrunner, 1988) that CO<sub>2</sub> in the Radgesburg deep aquifer originates from Pliocene vulcanite. This means that  $\delta^{13}\text{C}_{\text{DIC}}$  values are typical of an inorganic CO<sub>2</sub> source, whether the interpretation of a volcanic origin is correct or not. The aquifer system from which the Long Life brands originate is similar to the system of the Slovenske gorice mineral aquifer where Radenska waters are captured. Therefore it can be expected that  $\delta^{13}\text{C}_{\text{DIC}}$  values would be similar. Values of  $\delta^{13}\text{C}_{\text{DIC}}$  for brand Long Life-2 are slightly lower than those in the Radenska system (Table 1). They are still in accordance with the expected origin of water from a deeper source. Values of brand Long Life-1 (Table 1) are much lower than the values expected in the proposed original aquifer, and therefore show that CO<sub>2</sub> in the bottle is probably of artificial origin.

We do not know the original  $\delta^{13}\text{C}_{\text{DIC}}$  values of the Jamnica aquifer. The only available information is that the  $\delta^{13}\text{C}_{\text{DIC}}$  values were measured and that the inorganic origin of CO<sub>2</sub> gas was proved (Veselic, 1977). The presumption of an inorganic origin of CO<sub>2</sub> can also be given based on the geology of the aquifer, since rocks of volcanic origin are positioned in the base. Based on values reported in the literature (Hoefs, 1997) for inorganic CO<sub>2</sub>, values of  $\delta^{13}\text{C}_{\text{DIC}}$  should be higher than  $-8\text{‰}$  and it can be speculated that values of  $\delta^{13}\text{C}_{\text{DIC}}$  in Jamnica (Table 1) are of artificial origin.

Sicheldorfer Josefsquelle mineral water is also a foreign brand. The original spring is positioned in Styria in the same aquifer as the springs of Radenska waters (Zettinigg, 1993). Theoretically it is possible that the CO<sub>2</sub> originates from the same aquifer as the water. It was reported that CO<sub>2</sub> from the Termal II aquifer positioned below some parts of the Styrian basin in Slovenia has an isotopic composition between  $-10.8\text{‰}$  and  $-7.8\text{‰}$  (Pezdic et al., 1995), which is similar to  $\delta^{13}\text{C}_{\text{DIC}}$  determined for Sicheldorfer Josefsquelle mineral water (Table 1). However, interpretation of the origin of CO<sub>2</sub> in the bottled water of Sicheldorfer Josefsquelle based only on the  $\delta^{13}\text{C}_{\text{DIC}}$  value obtained is not possible.

During the process of production of natural sparkling water the water pumped from boreholes in a deep aquifer is very often artificially degassed and the natural CO<sub>2</sub> is captured for later use. This process is performed with the aim of removing iron and manganese from the original groundwater solution (Kozinc, 2002). On reintroduction of CO<sub>2</sub> it can happen that the amount of original CO<sub>2</sub> gas is insufficient and CO<sub>2</sub> of artificial origin must be additionally introduced. Furthermore, addition of CO<sub>2</sub> can be used for pH adjustment. Mixing of CO<sub>2</sub> gas from different sources and pH adjustment can result in  $\delta^{13}\text{C}_{\text{DIC}}$  values

somewhere between the original from the aquifer and from the artificial source. Therefore, determination of DIC origin in sparkling waters without having precise information about the source aquifer and based only on  $\delta^{13}\text{C}_{\text{DIC}}$  values in the interval between  $-18\text{‰}$  and  $-8\text{‰}$  is problematic.

In the available literature reported  $\delta^{13}\text{C}_{\text{DIC}}$  values for artificially sparkling waters and for waters where industrial CO<sub>2</sub> is added are in the range between  $-21.9\text{‰}$  and  $-35.6\text{‰}$  (Redondo & Yèlamos, 2005), and one reported value of  $-54.15\text{‰}$  (Calderone et al., 2005). The values for the artificially sparkling waters Spar Sorgente Linda, Stirna and Primula given in Table 1 are not much different from the value reported by Calderone et al. (2005), but much lower than the values obtained for the Long Life-1 and Jamnica brands, which are similar to those reported by Redondo and Yèlamos (2005). All other sparkling waters sampled have higher  $\delta^{13}\text{C}_{\text{DIC}}$  values than waters of artificial origin reported in the literature, proving that their DIC is of natural origin or of an origin that could not be detected as artificial by  $\delta^{13}\text{C}_{\text{DIC}}$  measurements. Comparison of our results and values reported in the literature shows that the difference between artificial DIC originating from the combustion of organic compounds and DIC of natural origin can be detected by the method applied.

### 3.3. Still waters

According to our knowledge and the information on the bottle labels, all sampled still waters originate from groundwater. For the interpretation of  $\delta^{13}\text{C}_{\text{DIC}}$  values in bottled still waters knowledge of the carbon cycle in groundwater is needed. Groundwater from shallow non-carbonate aquifers is in equilibrium with soil CO<sub>2</sub> that originates from plants and their decomposition in soils (Clark & Fritz, 1997). Most plants use the C<sub>3</sub> or Calvin photosynthetic cycle and their  $\delta^{13}\text{C}$  values vary from  $-34$  to  $-24\text{‰}$ . (Guillou & Reniero, 1999; Hoefs, 1997) Fewer plants use the C<sub>4</sub> or Hatch–Slack photosynthetic cycle and their  $\delta^{13}\text{C}$  values vary from  $-19\text{‰}$  to  $-6\text{‰}$ . (Guillou & Reniero, 1999; Hoefs, 1997) The isotopic composition of soil CO<sub>2</sub> in a temperate climate where C<sub>3</sub> plants prevail is usually about  $-22\text{‰}$  (Redondo & Yèlamos, 2005). In carbonate aquifers the groundwater carbon chemistry is a result of complex interrelations between soil CO<sub>2</sub> and the rock–water interaction where carbon enters into solution from minerals such as calcite (CaCO<sub>3</sub>) and dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>). Most carbonate rocks originating from the marine environment have  $\delta^{13}\text{C}$  values between  $-2\text{‰}$  and  $+1\text{‰}$  (Clark & Fritz, 1997). In groundwater of temperate climates they produce  $\delta^{13}\text{C}_{\text{DIC}}$  values around  $-11\text{‰}$ . As a consequence, values of  $\delta^{13}\text{C}_{\text{DIC}}$  in shallow carbonate aquifers are between  $-11\text{‰}$  and  $-22\text{‰}$  (Redondo & Yèlamos, 2005). In colder climates and above the tree line in mountains of carbonate rocks where vegetation cover is minor, <sup>13</sup>C-enriched DIC indicates that DIC is mainly produced through dissolution of carbonates, while

interaction with soil CO<sub>2</sub> is less important. Consequently,  $\delta^{13}\text{C}_{\text{DIC}}$  values between  $-6\text{‰}$  and  $-4\text{‰}$  were observed in springs from high mountainous carbonate aquifers in Slovenia (Brencic, 1998). In surface waters and groundwater  $\delta^{13}\text{C}$  values in DIC and CO<sub>2</sub> are usually not lower than  $-20\text{‰}$  (Clark & Fritz, 1997).

Among still waters the highest  $\delta^{13}\text{C}_{\text{DIC}}$  values were found in Radin produced by Radenska (Table 2). These values are in accordance with the values measured in the sparkling waters of Radenska and in agreement with the available hydrogeological information about the aquifer. Radin is obtained from the same aquifer as other sparkling mineral waters from Radenska with a well of small CO<sub>2</sub> yield. The influence of groundwater with a deeper circulation is also evident in other Radenska waters. These waters are captured in shallow boreholes in an area where the supposed influences of mineral waters are smaller. Values of  $\delta^{13}\text{C}_{\text{DIC}}$  for these waters are between  $-8.0\text{‰}$  and  $-7.4\text{‰}$  and probably reflect mixing of shallow and deeper mineral waters in the aquifer.

Other samples of still waters can be divided into two subgroups, the first with  $\delta^{13}\text{C}_{\text{DIC}}$  values between  $-10.4\text{‰}$  and  $-8.6\text{‰}$  and the second below  $-11.6\text{‰}$ . In the first subgroup the following brands are present: Juliana, H<sub>2</sub>O, Primula, Guizza Stilles and San Antonio. The first two brands are domestic and the hydrogeological conditions of their recharge area are relatively well known. For foreign brands no hydrogeological information is accessible. The recharge area of the Juliana spring is in a dolomite aquifer in the mountains near the tree limit (Brencic, Budkovic, Ferjancic, & Poltnig, 1995). At a little lower altitude but still in the mountains is the recharge area of the H<sub>2</sub>O brand. Based on the interpretation of domestic brands in this group, we can suppose that the somewhat higher  $\delta^{13}\text{C}$  values of this group are the consequence of higher recharge areas in the mountains, where dissolution of carbonates represents the most important source of DIC.

The second subgroup of still waters has  $\delta^{13}\text{C}_{\text{DIC}}$  values between  $-12.8\text{‰}$  and  $-11.7\text{‰}$  with an average value of  $-12.1\text{‰}$ . These waters are in the majority and represent nearly 55% of all still waters. The average value is typical of aquifers with shallow groundwater circulation in equilibrium with CO<sub>2</sub> in soil (Clark & Fritz, 1997). The information available on the hydrogeological conditions in the recharge area of the water resources for the domestic brands Dana, Bistra, Oda, Zala and Tiha confirms this interpretation.

### 3.4. Flavoured waters

Not very much is known about  $\delta^{13}\text{C}$  values of DIC in flavoured waters. A comparison between flavoured and still waters by analysis of variance showed that the two groups are statistically similar. Comparison of the still waters that represent the basis for flavoured water production and flavoured waters from the same producer clearly showed that differences between the two types of waters exist. This discrepancy leads to the interpretation that  $\delta^{13}\text{C}_{\text{DIC}}$  values of

flavoured waters are the consequence of the production process and of the flavours in the water.

Differences between flavoured waters and still waters are shown in Fig. 1. The average value of  $\delta^{13}\text{C}_{\text{DIC}}$  values of flavoured waters is  $-11\text{‰}$  with the range between  $-14.5\text{‰}$  and  $-5.1\text{‰}$ . In general flavoured water has a relatively low pH, between 3.1 and 4.6, with an average value of 3.7. The only exception is Juliana lemon with a pH of 7.0.

The parent water of Radenska flavoured waters is Izvir still water (Table 3).  $\delta^{13}\text{C}_{\text{DIC}}$  values of Radenska are connected with pH and therefore isotopic fractionation probably occurs in relation to pH. In waters bottled by Dana two groups can be found (Table 3). Waters that are produced under their own brand name are probably based on Dana still water (Table 2). Flavoured waters surprisingly have a much higher  $\delta^{13}\text{C}_{\text{DIC}}$  than the parent water. Waters filled by Dana for the Spar supermarkets have lower  $\delta^{13}\text{C}_{\text{DIC}}$  values than Dana still water, but differences are much smaller than compared to their own brand (Table 3). According to information on the labels, they are probably filled with different parent water from the waters with the Dana brand name.

Flavoured waters from Vino Brezice comprise the majority of sampled brands (Table 3). The reason for this is that they are produced and sold for different groups of supermarkets under various brand names.  $\delta^{13}\text{C}_{\text{DIC}}$  values for this producer are in the range between  $-14.5\text{‰}$  and  $-12.1\text{‰}$  and show a negative trend with pH, in contrast to Radenska production, where the trend is slightly positive.

Based on the available results it is not possible to interpret the fractionation of carbon isotopes in flavoured waters. The scatter of  $\delta^{13}\text{C}_{\text{DIC}}$  values in flavoured waters differs among producers and within groups of waters from the same producer, contradicting Calderone et al. (2005) who supposed that  $\delta^{13}\text{C}$  values are stable in the beverages of a particular producer. Fractionation is not only related to pH change but probably also to the type of flavour and the production process. For further interpretation of  $\delta^{13}\text{C}_{\text{DIC}}$  in flavoured waters, an experimental study related to knowledge of the type of flavours and the parent water source is needed. The natural variability of  $\delta^{13}\text{C}_{\text{DIC}}$  values in the parent water should also be studied to see how this variability influences the variability of flavoured water.

## 4. Conclusion

The isotopic composition of DIC of bottled waters has no direct health implications, but they can prove very important as a quality control tool for market regulators and independent organizations. They can help in determination of the origin of bottled water, determination of the natural conditions of the parent water body and production process that takes water from its source through the production line into the bottle. All these processes influence the quality of bottled water and its health consequences for human metabolism. An important part of the bottled water market is advertising of the water source and its pur-



ity. Bottled water producers put a lot of effort into persuading consumers that their waters are from clean remote or deep sources and that their recharge areas are completely free from pollution. It was shown that  $\delta^{13}\text{C}_{\text{DIC}}$  analyses are a very useful tool to confirm this information. And last but not least,  $\delta^{13}\text{C}_{\text{DIC}}$  analyses can help in the assessment of how bottled water products agree with the classification of natural mineral waters defined by legislation.

Recent pollution of natural water bodies is very diverse and the total number of pollutants that can appear in waters is nearly infinite. Legislative demands require control only of a limited number of the most probable pollutants. With the available analytical methods it is impossible to control all pollutants. Therefore control of bottled water quality should also be indirect by inspection of the recharge zone.  $\delta^{13}\text{C}_{\text{DIC}}$  values can indicate various processes during the infiltration and flow of water through the water body and are useful for this purpose. In recharge zones, where some processes are more likely, for instance, shallow circulation of water under the surface, vulnerability to aquifer pollution is higher.

The bottled water market requires cheap products. This is the reason why regional brands of bottled waters prevail. According to origin the only exceptions are the bottled waters of some global brands that can reach higher prices. Very often some global brands use the same commercial name and labels for different waters that are of local origin. Due to the regional origin of the parent water, bottled waters on the local market reflect some common characteristics that are connected with the geological and hydrological conditions of the region and water availability. The characteristics of bottled waters on the market also indirectly reflect consumers' preferences and traditional use of water. These common characteristics are also reflected on the Slovene market where bottled waters of Slovenian origin and neighbouring countries in Central Europe, are present. For the average consumer in Central Europe, bottled water is pure and originates from a clean mountainous remote spring. The present research on bottled waters available on the Slovene market proves this is not the case. Bottled waters are of various origin; production and bottling processes are very different and show very distinct characteristics. Bottled waters have their sources in thermal and shallow aquifers, they are produced with artificial flavours and some are mixtures of different components. Differences among bottled waters according to the source can also be expected on other markets. Information about source characteristics are not obvious from the labels on bottles or from advertising, but can be identified by investigation of the isotopic composition of DIC, in combination with a knowledge of water chemistry, production procedures and the hydrological characteristics of the source area.

Further investigations about the characterisation of bottled waters through the isotopic composition of DIC is needed. The applied approach should be tested on bottled waters from a wider area and on waters that originate from

other sources. It will be useful to test not only groundwater sources but also bottled waters that originate from treated marine and surface waters.

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