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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 $\delta^{13}C_{DIC}$, in domestic and foreign bottled waters randomly collected on the Slovene market. All together 58 brands and 16 replicates were analysed. The $\delta^{13}C_{DIC}$ values varied between −63.1‰ and +1.0‰ with an average of −12.3‰. Average $\delta^{13}C_{DIC}$ values for naturally sparkling, artificially sparkling, still and flavoured waters were −3.3‰, −36.5‰, −10.0‰ and −11.0‰, respectively. The lowest values are characteristic of artificial sparkling waters (minimum −63.1‰) and can be attributed to injection of industrial 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 CO_2, or from aquifers with their recharge in a mountainous area. Finally, $\delta^{13}C_{DIC}$ values of flavoured waters illustrate that isotopic fractionation occurs during the production process and that $\delta^{13}C_{DIC}$ values in products of some producers have a large variation.

Keywords: Sparkling water; Still water; Flavoured water; Carbon-13; Dissolved inorganic carbon

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 $^{13}C/^{12}C$ and allows detection of the origin of dissolved carbon species. Carbon stable isotope analyses of the 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, Naulet, Guillou, Reniero, & Blanch Cortes, 2005; Gonzáles-Martin, Gonzáles-Pérez, & Marqués-Macias, 1997; Martinelli et al., 2003). The idea of determination of the origin of CO_2 in sparkling bottled waters was first developed by Hillaire-Marcel (1986) and applied and further developed for comparison of natural mineral waters and bottled waters by Redondo and Yèlamos (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_2 and carbonate rocks.

DIC can be expressed as the sum of the concentrations of dissolved CO_2 (CO_{2aq}), carbonic acid (H_2CO_3), bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}). 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_2CO_3) 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 ($\delta^{13}C_{DIC}$) 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 $\delta^{13}C_{DIC}$ values. Duplicates of samples from seven particular bottles were used for the control of within-bottle variability of $\delta^{13}C_{DIC}$ 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 $\delta^{13}C_{DIC}$ determination were transferred to 12 mL glass exetainers and sent to the isotopic laboratory at the Jozef Stefan Institute where they were stored in a refrigerator prior to analysis.

2.3. $\delta^{13}C_{DIC}$ analyses

In all samples the isotopic composition of dissolved inorganic carbon ($\delta^{13}C_{DIC}$) was determined on CO_2 collected after reaction of 0.5–5 mL of sample with 100% H_3PO_4 on a continuous flow Europa 20–20 ANCA-TG stable isotope mass spectrometer. Samples were prepared in duplicate. In addition CO_2 collected after reaction of Na_2CO_3 solution with 100% H_3PO_4 was analysed with each set of samples. Results are expressed in standard delta notation (δ) as per ml (‰) deviation from the V-PDB standard as:

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

where R_{sample} and R_{std} are $^{13}C/^{12}C$ ratios of the sample and standard, respectively. Positive $\delta^{13}C$ values mean a relative enrichment of the material in the heavy isotope, with respect to the standard, and negative $\delta^{13}C$ values mean a lighter composition than the standard. Results are reported as the $\delta^{13}C_{DIC}$ 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_2CO_3 solution was -10.6 ± 0.1‰.

Analytical reproducibility was ±0.2‰, determined by repeated analyses of ISO-TOP reference CO_2 gas (Messer Griesheim, Krefeld, Germany) and working CO_2 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