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Geochemical survey of Slovenian bottled waters

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ABSTRACT

The geochemistry of the major components and trace elements in Slovenian bottled water available on the market in 2004 and 2008 was studied. The waters were predominantly from the Radenska and Rogaška Slatina mineral water source region. In this paper, a comparison of two data sets from two time periods was performed based on the Kolmogorov–Smirnov independent two-sample test. The bottled waters in the data sets were in agreement with drinking water and mineral water standards. Discrepancies were only present for B and Ni in highly mineralised waters. Analyses of the labels on the bottle packaging showed that the analytical results were in general agreement with the values reported on the labels. At the same time, the values reported on the labels by the producers showed that the chemical compositions of products available on the market for longer time periods vary. Slovenian bottled waters are predominantly controlled by a $CaCO_3$–CO_2–H_2O system where Na, Cl^- and SO_4^{2-} are present as the major components, in different combinations.

1. Introduction

The consumption of bottled water is very often connected with old beliefs and traditions of healthy mineral springs (Back et al., 1995; Albu et al., 1997). In Slovenia, positioned in the border region between Central Europe and the Balkans in the south, a long tradition of mineral water usage for health and healing purposes exists. In the past, there were two large important water centres and many smaller ones. Links with the past usage of springs for health purposes can also be inferred from their names; Roman Resurgence is the name of the spring which is most often associated with health benefits. The oldest water centre known from the Middle Ages is the Rogaška healing resort in the eastern part of Slovenia. It was even appointed as the official water supplier for the royal court of the former Austrian Empire in Vienna (Režek, 1964). In the beginning of the nineteenth century, Rogaška resort began to develop rapidly and was known as one of the most important healing resorts in the Austrian Hungarian monarchy. In the second half of the nineteenth century they started the production of bottled waters, and in the middle of the twentieth century this production was completely developed (Leskovar, 1963) and still exists today. The second important water centre, based on mineral waters, is the Radenci healing resort in northeast Slovenia. Mineral springs were known to locals much earlier, before the development of the resort started in the late nineteenth century; bottling started and production was fully developed before World War II. In Radenci, the production of bottled water even expanded after World War II and in the former Yugoslavia the bottled water producer Radenska was the biggest soft drinks production enterprise in the state, with large volume being exported in other Central European countries with similar traditions in the usage of mineral waters. Across the country, there were also many other small bottled water producers with the mineral waters of total dissolved solids (TDS) higher than 1 g/L or high CO_2 concentrations (Šlebinger, 1932; Brenčič and Poltnig, 2008). However, due to the small production capacity and a small market, this type of production almost ceased before World War I.

From a geochemical point of view, Slovenian mineral waters have been studied by several authors since the beginning of modern science (Šlebinger, 1932). In several studies, some authors presented an overview of the mineral waters from the Slovenian territory (Kralj and Kralj, 2000; Gros, 2003; Kralj, 2004a,b). Thorough studies were presented for the Rogaška Slatina mineral water source region (e.g. Pezdič, 1997) and the Radenci mineral water source region (e.g. Pezdič et al., 1995). To the best of our knowledge, there is no systematic study currently available on the geochemistry of bottled waters available on the Slovenian market.

During 2004 and 2008, we sampled and geochemically interpreted bottled water originating from Slovenia and the geological structures in the near vicinity of the state border (Long Life and Sicheldorfer Josefsquelle in Austria and Jamnica and Jana in Croatia). Their locations are shown on Fig. 1. Many are defined as natural mineral waters according to EU and national legislation. The aim of this study was to (1) compare the data sets of two sampling campaigns of

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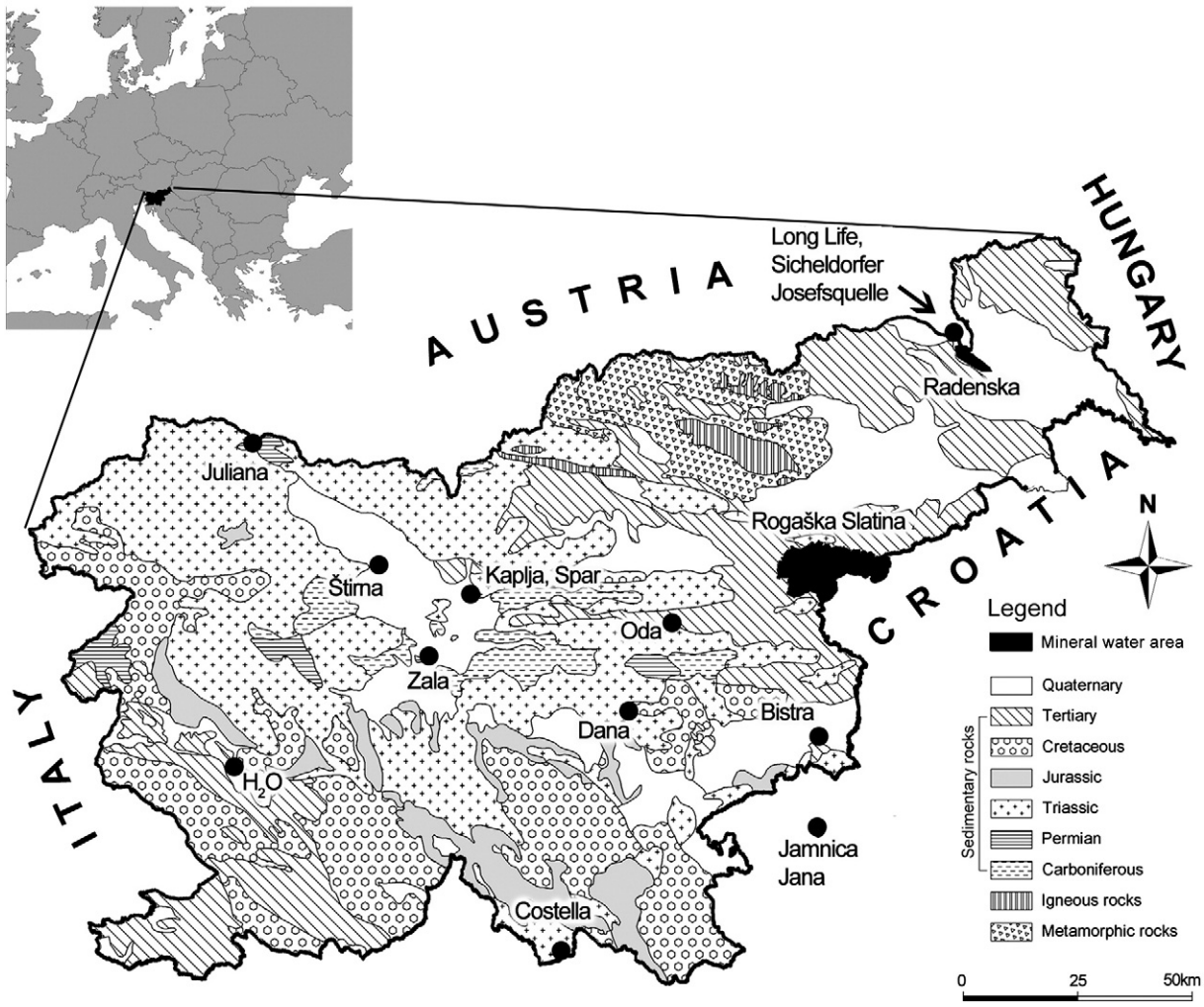

Fig. 1. Simplified geological map of Slovenia showing the location of the sources of bottled water.

Slovenian bottled waters available on the market; (2) determine the compliance of Slovenian bottled water with regulation demands; (3) compare the variability of analytical results reported on bottle labels and analytical results from the data set, and (4) define the basic geochemical characteristics of Slovenian bottled waters according to their places of origin.

2. Materials and methods

2.1. Geological settings

Nearly half of Slovenia is covered by Mesozoic carbonate and dolomite rocks forming large karstic and fissured aquifers of very high yields (Fig. 1). They are found in the southern and northwestern parts of the country. Other important and high yielding unconfined aquifers, which also represent the main drinking water resource in Slovenia, are porous aquifers positioned inside coarse carbonate sediments located inside larger pull-apart tectonic depressions. In the northeastern part, various sediments within the Pannonian basin from the Tertiary to the Quaternary are present, which form complex patterns of confined and unconfined aquifers. A more detailed description of the hydrogeological conditions is described elsewhere (Brenčič, 2010).

2.2. Sampling

The details for the September 2004 sampling campaign and sample preparation are given elsewhere (Brencic and Vreca, 2005). A second sampling campaign was performed between the 14th and 18th of January 2008. The sampling plan was devised and performed based on an internet survey which found 20 Slovenian brands of bottled water on the market. Sample bottles were purchased from two large stores in Ljubljana; only 13 brands were found on the shelves. The other 7 brands were not available at the time of purchasing or they had already been removed from the market. The sample bottles were packed into a cardboard box and sent via ordinary mail to the analytical laboratory. The locations of the bottled water brands sampled are given on Fig. 1. The positions of water sources for the producers Radenska and Droga Kolinska – Rogaška Slatina – are given as patches on the map. They use different local aquifers at various depths.

2.3. Accuracy and precision

The samples from the 2004 set underwent multi-elemental analysis at the ActivatedLab in Canada by inductively coupled plasma-mass spectrometry (ICP-MS). The concentration of SO_4^{2-} was determined by the SIST EN ISO 10304-1 method (ion chromatography – IC), F^- by the SIST EN ISO 10304-2 (IC) method, and HCO_3^- was determined by titration; these analyses were performed at the chemical laboratory of the Ljubljana waterworks, Slovenia. The concentrations of Cl^- were determined by IC at Joanneum Research, Institute of Water Resources Management, Graz, Austria. Trace element concentrations determined on certified reference solutions SRM1643e were used to evaluate the precision and accuracy; the results are reported in Table 1.