Journal of Geochemical Exploration 107 (2010) 305–316

Contents lists available at ScienceDirect

Journal of Geochemical Exploration

journal homepage: www.elsevier.com/locate/jgeoexp

Investigation of the hydrogeochemistry of some bottled mineral waters in Hungary

Ubul Fugedi, Laszlo Kuti, Gyozo Jordan *, Barbara Kerek

Geological Institute of Hungary, H-1143 Budapest, Stefánia út 14. Hungary

ARTICLE INFO

Article history:
Received 9 March 2010
Accepted 20 October 2010
Available online 5 November 2010

Keywords:
Mineral water
Statistical analysis
Water quality
Pannonian Basin
Hungary

ABSTRACT

Bottled drinking water constitutes a significant part of total water consumption in developed countries and national and EU legislation regulates their market production. In the framework of an international project carried out by the EuroGeoSurveys Geochemistry Expert Group 36 bottled waters were obtained from public markets in Hungary in order to determine their hydrogeochemical composition. The objective of this study is to investigate the possible relationship between groundwater aquifer lithology and the processed and marketed bottled waters, and to develop a classification of bottled waters, based on their dissolved mineral content. Analytical results of this study are compared with the composition shown on bottle labels, and with archive hydrochemical data from the producing wells. Results show that, while processing of original groundwater, such as oxygen addition, iron or hydrogen-sulphide removal can significantly alter water composition, bottled water composition can be used for selection of sites for detailed hydrogeochemical and hydrogeological characterization. A simple and useful classification of bottled water quality is also presented that is based on natural groups of sampled waters derived by means of statistical data analysis methods.

1. Introduction

Bottled drinking water production has steadily increased in the last few decades in industrialised countries, and the global consumption of bottled water reached 154 billion litres in 2004, up 57% from the 98 billion litres consumed five years earlier (Arnold, 2006). It is the most dynamic sector of all the food and beverage industry: consumption in the world increases by an average of 12% each year, in spite of its excessively high price compared to tap water. The per capita consumption of bottled water in the European Union varies enormously from one country to another with the average consumption at 105 l per year which is about 25% of the total drinking water consumption in Europe. 85% of total bottled water consumption is mineral water, followed by spring water (12%) and table water (3%) (Kay-Shuttleworth, 2009). In Hungary, since the transition to market economy in 1990, mineral water consumption has boomed from 3.7 l/person in 1991 to 110 l/person in 2009. Among the reasons for this increase are the lack of good quality potable tap water (piped water) in some regions, like large urban areas, or in the natural arsenic contaminated aquifers of the Great Hungarian Plain, as well as the easy market availability of a large selection of bottled waters with different composition and taste, and the marketing pressure of advertising by multi-national companies. There are, however, differences among the countries, both in the consumed bottled water quantities and in the quality preferences. Finland has the lowest consumption level with 16 l a year per inhabitant, and Italy has the highest at just under 200 l a year per inhabitant (Italy is the world leader in bottled water consumption, too). In terms of water quality, sparkling (CO_2 gaseous) water is preferred to still water in Hungary, as is in Germany, Austria and Czechia, while still water is favoured in France, Italy and Spain. In terms of market selection, there are 45–50 different brands of bottled mineral water available on the market in Hungary alone (Hungarian Mineral Water Association and Product Council, 2009), while in Germany there are more than 500 brands.

In order to protect drinking water, one of the most fundamental natural resources, the European Union (EU) introduced stringent regulations for water quality control, and for the management of water resources (Directive 2000/60/EC). Due to the huge consumed quantities, and large number of marketed brands, the EU specifically regulates the quality standards of bottled waters (Directive 80/777/EEC; Directive 96/70/EC). There are, however, different legal classifications and health standards for bottled waters in some countries. According to EU Directive 80/777/EC, "natural mineral water" is water that is microbiologically wholesome, "originating in an underground water table or deposit and emerging from a spring tapped at one or more natural or bore exits". Treatment of mineral water is restricted to removal of unstable elements, such as iron and sulphur compounds. In Hungary, for example, legislation designates natural groundwaters as 'drinking water', 'mineral water' and 'medicinal water', based on the maximum admissible concentration of certain components (drinking water), on its subsurface origin and bottling at the location of extraction

* Corresponding author. Geological Institute of Hungary (MAFI), Stefania ut 14, Budapest 1143, Hungary. Tel.: +36 1 251 0999; fax: +36 1 251 0703.
E-mail address: jordan@mafi.hu (G. Jordan).

0375-6742/$ – see front matter
doi:10.1016/j.gexplo.2010.10.011

(mineral water), and based on proven positive health effect (medicinal water) (Government Decree 201/2001; Government Decree 65/2004).

Bottled mineral waters are derived from groundwater aquifers and, therefore, their chemical composition is originally defined by geochemical water-rock interaction processes. In fact, some of their unique composition features, such as elevated carbon dioxide (CO_2), hydrogen sulphide (H_2S), sulphate (SO_4^{2-}), iron and high salt content are specific to the geological and hydrogeological position of the exploited springs and producing wells. However, these naturally occurring waters are often chemically processed before bottling in order to adjust to market needs. Processing can include de-gassing or just the addition of CO_2 gas, removal of iron to improve flavour, removal of reducing hydrogen sulphide for better consumption experience, etc. Manipulation of carbon dioxide content changes pH, removal of iron by precipitation can co-precipitate several trace elements, and the removal of reducing hydrogen sulphide increases Eh of the mineral water. The final bottled water product can have, therefore, little resemblance to the original groundwater composition.

Nevertheless, Misund et al. (1999) found a traceable link between bottled water composition and aquifer lithology in 66 European bottled waters. Groselj et al. (2008) used neural networks to arrive at the same conclusion. The natural mineral content of bottled waters originating from water-rock interaction in the exploited groundwater aquifers has been the subject of numerous studies, too (Garzon and Eisenberg, 1998; Ikem et al., 2002; Fiket et al., 2007; Kochubovski et al., 2007). Others, like Chiarenzelli and Pominville (2008) and Saleh et al. (2008), went further and evaluated the chemical, microbial and physical composition of commercial bottled waters for health considerations.

In this study, 36 randomly selected bottled waters were obtained from the public market and their hydrochemical composition was determined. The objective of this study is to investigate the link between the composition of marketed bottled water products and their geological–geochemical origin. Another aim of the study is to develop a classification of bottled waters, based on their dissolved mineral content. The laboratory analysis results are compared to archive hydrochemical data from the producing wells, and also compared to the chemical composition reported on bottle labels. When available, gaseous and non-gaseous varieties of marketed waters are compared in order to estimate the impact of water processing. It is not the objective of this study to evaluate or to compare the studied waters' drinking quality by any means, and neither to characterise bottled waters available on the market. Rather, the present study is a preliminary methodological investigation of the limitations and possibilities of using bottled waters for mapping the geochemistry of groundwater.

2. Study area

Hungary is situated in the Pannonian Basin surrounded by the Carpathian Mountains chain. Convergent motion between the African and European plates in the Alpine period (Late Jurassic–Neogene) resulted in the southerly subduction of the European plate under the Pannonian continental fragment between the two continents. This led to the formation of calcalkaline volcanic arcs (Inner-Carpathian Volcanic Belt) during the Eocene in the north, while the emergence of the Alpine-Carpathian chains, and the fast thermal sinking of the Pannonian fore-arc basin, led to the accumulation of very thick (often 6–7000 m; Fig. 1) marine and then fluvial clastic sedimentary sequences over the Palaeozoic and Mezozoic basement (Fig. 2) (Trunko, 1996). Some parts of the basement remained in elevated position exposing the dominantly Mesozoic carbonates (mostly limestone) of the closing Thethys Sea (Fodor et al., 2005). Besides the important carbonate groundwater aquifers, the majority of groundwater resources are stored in the thick clastic porous water reservoirs (Figs. 1 and 2). The country is rich in water resources, including mineralised and thermal waters, due to the high thermal gradient under the thin crust of the Pannonian Basin. Somlai et al. (2002) investigated the Ra content while Szanto et al. (2008) studied stable isotopes of Hungarian bottled waters. They both concluded that there exists a traceable link between the studied bottled water composition and aquifer lithology.

3. Materials and methods

3.1. Sampling, analysis and datasets

In order to characterise the composition of the studied bottled waters, three independent data sources were used: (1) laboratory analysis of bottled waters purchased from the public market carried out by the Federal Institute for Geosciences and Natural Resources (BGR) ('BGR Dataset'), (2) the chemical composition reported on bottle labels ('Bottle Dataset'), and (3) archive hydrochemical data from the producing wells in the National Borehole Database of the Geological Institute of Hungary ('MAFI Dataset'). The present study is based on the new BGR Dataset, and the two other datasets are used only for comparison.

The BGR Dataset was generated from 36 different brands of commercially available bottled waters, purchased from supermarkets in Budapest during 2009 (Table 1). When available, the smaller 0.5 l bottles were preferred to the larger bottles. Also, when available, the sparkling, still and medium varieties of the same water product were purchased (Table 1). In total, 51 bottles were purchased and sent to the BGR laboratory for analysis. The bottled waters were purchased within a period of 3 weeks, and they were transported to Germany either personally or by freight mail.

The mineral water bottles were first opened in the laboratory and a 100 cm^3 plastic beaker was filled with mineral water. The cap was then loosely replaced on the mineral water bottle, and the bottle was degassed for about 20 min in an ultrasound bath. The electrical conductivity and pH of the mineral water in the beaker were measured. After degassing, 25 cm^3 were withdrawn from the mineral water bottle for the bicarbonate titration. A 250 cm^3 HDPE bottle was rinsed with the degassed mineral water and then filled with the mineral water. The anions were determined by ion chromatography and ammonium ion was determined by a photometric method using the water in the HDPE bottle. A 125 cm^3 FLPE bottle was rinsed with the degassed bottled water and then filled with the bottled water. In the clean room, 1.5 cm^3 ultrapure 69% HNO_3 was added and the bottle shaken. The main cations were determined by ICP-OES and the trace elements by ICP-QMS. The ICP-QMS analyses were made using 13 cm^3 PP tubes (Sarstedt) with LDPE stoppers. This database is uniform and homogeneous due to the use of a single analytical method under well-controlled conditions of a single laboratory. The following parameters were determined: Ag, Al, As, B, Ba, Be, Bi, Cd, Ce, Co, Cr, Cs, Cu, Dy, Er, Eu, Fe, Ga, Gd, Ge, Hf, Hg, Ho, I, K, La, Li, Lu, Mg, Mn, Mo, Na, Nb, Nd, Ni, Pb, Pr, Rb, Sb, Sc, Se, Sm, Sn, Ta, Tb, Te, Th, Ti, Tl, Tm, U, V, W, Y, Yb, Zn, Zr, Br, HCO_3, Cl, F, NH_4, NO_2, NO_3, PO_4, SO_4, SiO_2, pH, electrical conductivity and total alkalinity.

Eight bottled waters (Ave, Fonyódi, Ferenc József, Hunyadi János, Bükkszéki Salvus, Germán Aqua, Parádi I., Mira), because of their unusual high salt content, were purchased a second time and sent to BGR for re-analysis.

More details about the analytical methods, quality control results, and re-analysis of bottled waters with unusually high values is found in Reimann and Birke (2010) and Birke et al. (2010).

The Bottle Dataset was very simply generated from the chemical composition displayed on bottle labels. The name of the 36 producing wells, if recorded, was also added to the database, together with the gas content of the water as sparkling (blue cap), still (pink cap) and medium (green cap). Information about bottle materials, such as plastic (PET) or glass bottle, bottle colour, and the plastic or metal cap was also included in the database. It is noted that the chemical composition on bottle labels