Applicability study of deuterium excess in bottled water life cycle analyses

Uporabnost devterijevega presežka v analizi življenjskega kroga embaliranih vod

Mihael BRENČIČ[1,2] & Polona VREČA[3]

[1]Department of Geology, Faculty of Natural Sciences and Engineering, University of Ljubljana, Aškerčeva c. 12, SI–1000 Ljubljana, Slovenia; e-mail: mihael.brencic@ntf.uni-lj.si
[2]Geological Survey of Slovenia, Dimičeva ulica 14, SI–1000 Ljubljana, Slovenia
[3]Jožef Stefan Institute, Jamova cesta 39, SI–1000 Ljubljana, Slovenia; e-mail: polona.vreca@ijs.si

Abstract

Paper explores the possible use of *d*-excess in the investigation of bottled water. Based on the data set from Brencic and Vreca's paper (2006). Identification of sources and production processes of bottled waters by stable hydrogen and oxygen isotope ratios, *d*-excess values were statistically analysed and compared among different bottled water groups and different bottlers. The bottled water life cycle in relation to *d*-excess values was also theoretically identified. Descriptive statistics and one-way ANOVA showed no significant differences among the groups. Differences were detected in the shape of empirical distributions. Groups of still and flavoured waters have similar shapes, but sparkling waters differed to the others. Two distinctive groups of bottlers could be discerned. The first group is represented by bottlers with a high range of *d*-excess (from 7.7 ‰ to 18.6 ‰ with average of 12.0 ‰) exploring waters originating from the aquifers rich in highly mineralised groundwater and relatively high concentrations of CO_2 gas. The second group is represented by bottlers using groundwater from relatively shallow aquifers. Their *d*-excess values have characteristics similar to the local precipitation (from 7.8 ‰ to 14.3 ‰ with average of 10.3 ‰). More frequent sampling and better knowledge of production phases are needed to improve usage of isotope fingerprint for authentication of bottled waters.

Izvleček

Članek obravnava možnost uporabe devterijevega presežka pri raziskavah embaliranih vod. Delo temelji na podatkih o izotopski sestavi vod, ki so bili objavljeni v članku Brencic in Vreca (2006). Vrednosti devterijevega presežka so bile analizirane statistično in primerjane med različnimi skupinami embaliranih vod ter med različnimi polnilci. V okviru analize je bil teoretično identificiran življenjski cikel embaliranih vod. Opisne statistike in analiza variance – ANOVA so pokazale, da med skupinami ni značilnih razlik, razlike pa so bile opažene v oblikah empiričnih porazdelitev. Skupine naravnih vod in aromatiziranih vod imajo podobno obliko empiričnih porazdelitev, medtem ko je za gazirane vode drugačna. Znotraj slednjih lahko ločimo dve skupini. Prva skupina je sestavljena iz vod polnilcev z visokim razponom vrednosti devterijevega presežka (od 7,7 ‰ do 18,6 ‰ in povprečjem 12,0 ‰). Te vode izvirajo iz vodonosnikov bogatih z mineraliziranimi vodami in relativno visokimi koncentracijami plina CO_2. Drugo skupino predstavljajo vode polnilcev, ki uporabljajo vodo iz relativno plitvih vodonosnikov, vrednosti devterijevega presežka pa so podobne povprečnim vrednostim lokalnih padavin (od 7,8 ‰ do 14,3 ‰ in povprečjem 10,3 ‰). Za učinkovitejšo ugotavljanje skladnosti ustekleničenih vod s pomočjo izotopske sestave je potrebno izvesti pogostejša vzorčenja in izboljšati znanje o proizvodnih procesih.

Introduction

In climatic and hydrology studies, deuterium excess (*d*-excess; Dansgaard, 1964) has proven to be a useful parameter. It characterises the deviation of a stable hydrogen and oxygen isotopic composition in precipitation from an average global composition and reflects the origin of the moisture source as well as the condensation and evaporation processes in the hydrological cycle. Based on these properties it is supposed that *d*-excess can also be used to track the history of bottled water. The latter is a product of the food industry, however, it originates in the hydrological cycle and its isotopic characteristics reflect different paths through the environment. The isotopic composition of water in nature is the consequence of different fractionation processes; the same can be expected of bottled water where, besides the variability of isotopic composition in the parent water body, production processes and the interaction of bottles with the surrounding

environment can also influence the isotopic fingerprint. Stable hydrogen and oxygen analyses of bottled water have already been applied to study its origin and the influences of production processes on its composition (Chesson et al., 2010; Dotsika et al., 2010; Rangarajan et al., 2011; Kim et al., 2012; Godoy et al., 2012; Raco et al., 2013). They can be regarded as an authentication tool where two investigative approaches can be used; that from hydrology and the other from food analysis. Application of stable isotope analysis in hydrology is widely used for the detection of water circulation history through the hydrological cycle, while in food analysis stable isotopes are mainly used for quality control and determination of artificial food ingredients that are chemically identical to natural ones (Brencic & Vreca, 2007).

According to the author's best knowledge no systematic study of d-excess in bottled water is available in the literature. The main intention of this paper is therefore to explore the possible use of d-excess in the investigation of bottled water. In this study, based on the already available data set (Brencic & Vreca, 2006), we (1) performed a statistical analysis of calculated d-excess from the available set of data and compared d-excess values among different bottled water groups, (2) compared the variability of d-excess values for different bottlers producing several different brands of bottled water, and (3) theoretically identified the bottled water life cycle in relation to d-excess. Final conclusions were then reached based on these results and recommendations for further work with d-excess in relation to bottled water presented.

Methods

Methodological basis

Deuterium excess is defined as d-excess$=\delta^2$H$-8\delta^{18}$O (Dansgaard, 1964) where δ^2H and δ^{18}O are the isotopic compositions of water molecules. It has shown potential in climatic studies for tracing past and present precipitation processes. It is also a measure of the relative proportions of δ^2H and δ^{18}O in water and can be visually depicted as an index of the deviation from the global meteoric water line (GMWL; Craig, 1961) in the 2D space defined by the coordinates δ^2H and δ^{18}O (Fig. 1). In natural conditions, d-excess correlates with physical conditions such as humidity, air temperature and water temperature (Fröhlich et al., 2001; Gat, 2010) and the chemical status of water. Influences of the same parameters are also expected in bottled water.

During circulation through the hydrological cycle, the isotopic composition of water changes as a consequence of equilibrium, diffusion and kinetic fractionation. These processes are well reflected in the δ^2H and δ^{18}O diagram (Fig. 1). The
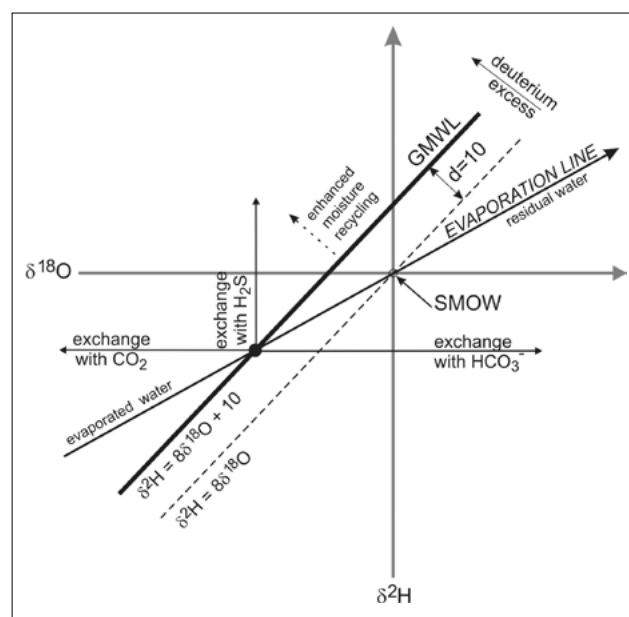

Fig. 1. Processes influencing the isotopic composition of water reflected in the δ^2H and δ^{18}O diagram (modified from Schotter et al., 1996; Fröhlich et al., 2001; Gat, 2010).

processes in the atmospheric part of the water cycle, from evaporation from the ocean surface to cloud condensation and precipitation, are well elucidated by the Craig and Gordon (Gat, 2010) model. Equilibrium fractionation and kinetic effects are reflected in the slope of the GMWL with a value of 8 (Fig. 1). During the equilibrium isotope fractionation in the hydrological cycle from ocean source water to water in another compartment (e.g. clouds) the isotopic composition changes along the line. Based on the Craig and Gordon (Gat, 2010) model, the assumption of evaporation taking place into the atmosphere of 75 % humidity above the ocean accounts for a d-excess value of 10 ‰ (Fig. 1) in atmospheric moisture which confirms the world average for meteoric waters (Gat, 2010). Both the slope of the GMWL and the global d-excess value justified Dansgaard's (1964) definition. In higher saturation states of the atmosphere above the ocean, d-excess is lower; therefore, some paleo-groundwaters show lower d-excess values than present groundwater (Gat, 2010).

If additional transport and fractionation processes are present during such a process, d-excess differs from that of the liquid vapour transition under equilibrium conditions. In the natural environment, such waters are positioned on the line with a slope reduced relative to the equilibrium line of the GMWL (Gat, 2010). The isotopic composition of residual water from evaporation is positioned along the line below the GMWL (Fig. 1) and evaporated water is positioned above the GMWL. Deviations in water isotopic composition from the equilibrium line have also been reported from the exposure and evaporation experiments on sample containers (Stewart, 1981; Rozanski & Rzepka, 1991; Rozanski & Chmura, 2008), thereby showing that

a stable isotopic composition of bottled water can be subject to change during its storage.

In deep and extensive aquifers, geochemical processes can also influence the isotopic composition of water. In mineral and thermomineral waters, aquifers might exchange with CO_2 and H_2S (CLARK & FRITZ, 1997). Exchange with CO_2 (BECK et al., 2005) and changes in the $CaCO_3 - CO_2 - H_2O$ system appear during the production processes and can influence the isotopic composition of bottled water (Fig. 1). If oxygen is exchanged for CO_2 the isotopic composition of $\delta^{18}O$ in water will shift to the left and if exchanged for HCO_3^- it will shift to the right (BECK et al., 2005). In highly reduced environments, exchange with H_2S shifts the isotopic composition of the parent water in a predominantly vertical direction. In the presence of hydrated minerals in the aquifer matrix, the shift of the water fingerprint is also possible. A combination of all these processes is likely in deep-seated aquifers, and the direction of the shift in isotopic composition is oblique to the equilibrium line depending on the predominant process. Consequently, all these changes can be reflected in changes in d-excess values.

Sampling

Sampling was performed based on a consistent sampling plan where all waters and products advertised as waters available on the Slovenian market in September 2004 were collected (BRENCIC & VRECA, 2006). The data set presents a statistically consistent and representative sample of bottled waters available on the Slovenian market at the time of sampling. By the data set overall characteristics of bottled waters on the market are presented therein.

Isotopic analyses

The details of stable isotope analyses are given elsewhere (BRENCIC & VRECA, 2006). The results are expressed in standard delta notation (δ) as per mil (‰) deviation from the standard V-SMOW for δ^2H and $\delta^{18}O$ as:

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

where $^Y X$ is ^{18}O or ^2H and R_{sample} and R_{std} are $^{18}O/^{16}O$ or $^2H/^1H$ ratios of the sample and standard, respectively. The measurement reproducibility of duplicates was better than ±0.05 ‰ for $\delta^{18}O$ and ±1 ‰ for δ^2H.

Analytical uncertainty $u(d)$ of d-excess for routine measurements was estimated (FRÖHLICH et al., 2001) as:

$$u(d) = \sqrt{u(\delta^2H)^2 + 8u(\delta^{18}O)^2}$$

In our case d-excess uncertainty $u(d)$ was 1.01 ‰.

Statistical analyses

Descriptive statistics, kernel density estimates with empirical distribution diagrams, the Anderson–Darling goodness of fit test for normal distribution and outlier detection, and analysis of variance (ANOVA) were used.

Empirical distribution functions (EDF) were used to analyse the exploratory data to detect the overall shape and symmetry of the empirical data distribution as well as any spurious observations in the data set.

In a classical statistical analysis, the empirical distribution of the data is usually represented by a histogram. Alternative graphical representations include the kernel density approach (REISS & THOMAS, 1997), which tries to mimic the hypothetical probability density function of the limit distribution. According to this method, the probability density $g_b(x,k(x))$ for particular data is estimated as:

$$g_b(x,k(x)) = \frac{1}{N_b} k \left(\frac{x - x_i}{b} \right)$$

where $k(x)$ is the kernel such that:

$$\int k(y)dy = 1$$

and where b is the bandwidth where $b>0$ and N_b is number of data inside of bandwidth interval. The Epanechnikov kernel was used:

$$k(x) = \frac{3}{4}(1 - x^2) \qquad I(-1 \leq x \geq 1)$$

In summing the single terms, one gets the kernel density:

$$f_{N,b}(x) = \sum_{i \leq N} g_b(x,k(x)) = \frac{1}{Nb} \sum_{i \leq N} k \left(\frac{x - x_i}{b} \right)$$

Based on the trial and error procedures on different data sets we arbitrarily chose a bandwidth of $b=2.592$.

BRENČIČ & VREČA (2010) have already illustrated that the empirical distribution of δ^2H and $\delta^{18}O$ from the Slovenian market can be modelled with a normal (Gaussian) distribution. The normal probability model fit of δ^2H is nearly perfect with the Kolmogorov–Smirnov statistic $d_{max} = 0.05$, which confirms a good fit at the 5% significance level. For the empirical distribution of $\delta^{18}O$ the normal distribution model can be also used (Kolmogorov–Smirnov statistic $d_{max} = 0.08$); however, the visual inspection of the EDF showed larger discrepancies from the straight line in the probability scale diagram than in the case of δ^2H (BRENČIČ & VREČA, 2010). Based on these findings it is also supposed that the EDF of d-excess as a linear combination of both parameters can be modelled with the normal distribution model.

Contrary to the previous normality assessment of $\delta^2 H$ and $\delta^{18}O$ (BRENČIČ & VREČA, 2010) the EDF in this study were tested with Anderson–Darling goodness of fit statistics A^2 according to the theory presented by STEPHENS (1986). In comparison to Kolmogorov–Smirnov statistics d_{max} Anderson–Darling A^2 is characterized by higher power and easier procedure for determining the exact significance level. The null hypothesis H_0 is valid when the random sample $X_1, \ldots, X_n$ comes from a normal distribution $N(\mu, \sigma)$ and where both parameters μ and σ of N are unknown. Defined as *Case 3* test, the μ and σ parameters were estimated with the method of moments (average and variance, respectively) from the data set under the consideration. A significance level p of A^2 was calculated with the help of empirical equations (STEPHENS, 1986). Statistics A^2 is defined as:

$$A^2 = -n - \frac{1}{n}\sum_i \left[(2i-1)\ln Z_i + (2n+1-2i\ln(1-Z_i)\right]$$

where

n – number of data in the data set

i – rank of data

Z_i – probability integral transformation with parameters μ and σ

An outlier observation is datapoint that seems to deviate markedly from other members of the data set in which it occurs. The definition of the outlier depends on the scope of the data investigation. In this study, outliers are those data at the lower or upper tails that are the reason for the deviation of EDF from the normal probability model. For the detection of outlier statistics A^2 sensitive to lower and upper tails was used. Based on the visual inspection of EDF possible outliers were identified at its lower and upper tails. Statistics A^2 was calculated by excluding supposed outliers step by step from the EDF. Calculated A^2 values were compared at every step. When calculated A^2 stabilised after excluding several data from the tails of EDF this was a criterion that no influences on the normality model are present from the tail parts of EDF.

The normal distribution of data is also an assumption in ANOVA. Differences between the d-excess values in the groups of bottled waters were tested by one-way ANOVA, followed by Tukey's post-hoc significance difference at the 5% level of probability. The null hypothesis of ANOVA suggested that the means of all groups are equal. The probability p for the validity of the null hypothesis was calculated.

ANOVA was calculated using the STATISTICA® 6.0 statistical package. Kernel density estimates were calculated with the program $X_T R_E M_E S$ (REISS & THOMAS, 1997). Anderson–Darling goodness of fit test was calculated with macro procedures written in a spreadsheet program.

Results and discussion

The analytical results of oxygen ($\delta^{18}O$) and hydrogen ($\delta^2 H$) isotopic composition have already been published (BRENCIC & VRECA, 2006). Calculated d-excess values are given in Tables 1, 2, and 3 for sparkling, still and flavoured waters, respectively. In Table 1, the column with CO_2-type classification (BRENCIC & VRECA, 2007) is included to discern waters where artificial CO_2 gas is introduced during the production process and waters originating from deeper aquifers. Bottler locations are illustrated in Figure 2, but bottled water originating from Italy and Switzerland is not shown.

Statistical analyses

Basic d-excess descriptive statistics of different bottled waters for different groups are given in Table 4 and the distribution of datapoints for the whole data set are illustrated in Figure 3. The lowest d-excess value 6.4 ‰ is observed in flavoured water and the highest 18.6 ‰ in natural sparkling waters. Except for natural sparkling waters average values among groups are similar and median values indicate that the EDF of particular groups are slightly asymmetrical. These can be confirmed with the inspection of box plot diagrams (Fig. 3) and the distributional illustrations presented in Figures 4, 5a, and 5b.

Owing to diverse possible influences on the d-excess values of bottled water it is expected that in the EDF of the whole data set some outliers are present. It can be hypothesised that d-excess outliers reflect special circumstances at the source or in production. In the upper tail of EDF outliers (Fig. 4), this can be interpreted as a consequence of natural conditions in the aquifers. In the lower tail of EDF outliers (Fig. 4), this could be an indicator of the influences of the production processes on the isotopic composition of water. Based on the Anderson–Darling A^2 statistics criteria in the upper tail of the data sets only two real vivid outlier values can be detected. These are d-excess values of 18.6 ‰ and 17.4 ‰ and are both obtained for water brand Donat-Mg™ (Table 1). By removing these values from the EDF A^2 becomes 0.47 and the zero hypothesis is significant at the level of $p=0.25$. If we remove further d-excess values (14.6 ‰, 14.3 ‰, and 14.0 ‰) from the upper tail of the EDF, A^2 drops from 0.42 to 0.39 and the significance level p rises from 0.31 to 0.38. When removing consecutive d-excess values A^2 starts to rise and p starts to drop. By removing values only in the lower tail of the EDF A^2 steadily grows and the p value drops. This indicates that these values are part of a supposed normally distributed population of d-excess values. The combination of removing values from the EDF at both tails simultaneously does not provide better results than just removing values at the upper tail. We conclude that only Donat-Mg™ represents a vivid outlier in the whole data set. According to the available information from the literature (PEZDIČ, 1997) those values can be interpreted as outliers showing natural conditions in the parent aquifer.

Table 1. *d*-excess values in sparkling waters

Bottled by	Origin	Brand	CO$_2$ type (BRENCIC & VRECA, 2007)	*d*-excess (‰)
Kolinska	Slovenia	Donat Mg™	natural	18.6
Kolinska	Slovenia	Donat Mg™ (G)	natural	17.4
Kolinska	Slovenia	Tempel™	natural	12.5
Kolinska	Slovenia	Tempel™ (B)	natural	13.1
Kolinska	Slovenia	Edina™	natural	12.5
Radenska	Austria	Sicheldorfer Josefsquelle™ (G)	natural	7.7
Bad Radgesburg	Austria	Long life™ – 2	natural	9.6
Radenska	Slovenia	Classic™ (G)	natural	12.0
Radenska	Slovenia	Classic™	natural	10.5
Radenska	Slovenia	Light Miral™	natural	9.9
San Benedeto	Italy	Guizza™	natural	7.8
Bad Radgesburg	Austria	Long life™ - 1	artificial	13.6
Jamnica	Croatia	Jamnica™	artificial	6.8
Jamnica	Croatia	Jamnica™ (S)	artificial	6.7
Tavina	Italy	Spar Sorgente Linda™	artificial	7.9
Sodavičarstvo Volk	Slovenia	Štirna™	artificial	12.9
Sodavičarstvo Volk	Slovenia	Štirna™ (S)	artificial	13.8
Spinone al Lago	Italy	Primula™	artificial	9.7
Fonte S. Antonio	Italy	San Antonio™	artificial	10.8

(G) – glass bottle; (B) – replicated bottle; (S) – replicated sample from the bottle

Table 2. *d*-excess values in still waters

Bottled by	Origin	Brand	*d*-excess (‰)
Radenska	Slovenia	Radin™	7.8
Radenska	Slovenia	Radin™ (S)	9.5
Radenska	Slovenia	Izvir™	9.7
Radenska	Slovenia	Iva™	8.1
Radenska	Slovenia	Iva™ (B)	10.0
Radenska	Slovenia	Iva™ (S)	8.0
Vino Brežice	Slovenia	Bistra™	9.6
Dana	Slovenia	Dana™	10.2
Danone	France	Evian™	8.1
Fructal	Slovenia	H2O™	14.3
Jamnica	Croatia	Jana™	10.8
Perne	Slovenia	Juliana™	12.2
Lasko Brewery	Slovenia	Oda™	11.8
Lasko Brewery	Slovenia	Oda™ (B)	11.3
Spinone al Lago	Italy	Primula™	11.0
San Benedeto	Italy	Guizza Silles™	8.9
Fonte S. Antonio	Italy	San Antonio™	13.1
Plastenka	Slovenia	Spar spring water™	10.2
Plastenka	Slovenia	Spar spring water™ (B)	9.1
Plastenka	Slovenia	Spar spring water™ (S)	9.7
Plastenka	Slovenia	Spar table water™	9.7
Plastenka	Slovenia	Živa™	11.4
Union Brewery	Slovenia	Zala™	10.0
Union Brewery	Slovenia	Zala™ (S)	11.4
Kolinska	Slovenia	Tiha™	10.9
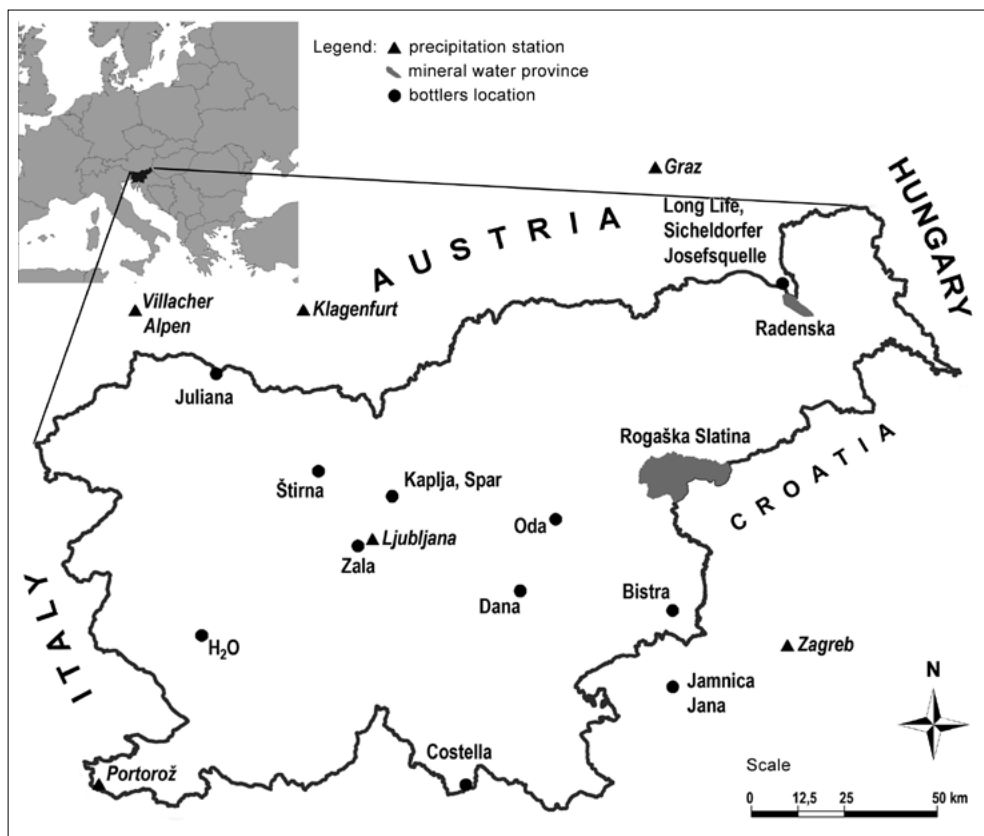
In Table 5, the results of the normality test with Anderson–Darling statistics A^2 are illustrated. In all groups, the significance level p of the null hypothesis is higher than the usual significance level of $p=0.05$. The only exception is the whole data set consisting of all groups indicating that outliers are present. In Figure 4, the EDF and cumulative kernel densities with the normal (Gaussian) theoretical model with parameters estimated from the whole data set are represented on the probability scale diagram. The EDF shows that data fluctuates around the straight line of the normal model and that the amplitude of fluctuation is relatively small, except at the tails. The lower tail does not influence the kernel density estimate, which is close to the normal model. The situation is different at the upper tail where outliers are the reason for the distinctive deviation from the normal model.

This relative irregularity of the kernel density estimates is more clearly seen in Figures 5a and 5b. Kernel density estimates in the frequency mode (Fig. 5a) are represented with the weight that represents a particular group's share in the whole data set. The kernel density for the whole data set represents the sum of particular groups, and the kernel density for sparkling water represents the sum of natural and artificial sparkling water. The distributions of the whole data set and flavoured and sparkling waters are symmetrical. However, for the whole data set and sparkling waters a small hump can be detected at the right part at the higher d-excess values (Fig. 5a). In the whole data set, this hump can be explained by the presence of natural sparkling waters. All sparkling groups show irregular behaviour with a polymodal shape. The artificial sparkling water group shows two peaks at approximately 7.5 ‰ and 12.5 ‰. Slightly different peaks are observed in natural sparkling waters where at the same time peak at an approximate value of 17.5 ‰ is identical to the hump of the whole data set. The latter indicates those waters originating from the Rogaška Slatina mineral water province. An asymmetry of data is also reflected in the cumulative mode diagram on the probability scale (Fig. 5b). Except in the lower tail shapes of the flavoured and still water groups, distributions are almost identical. Natural sparkling waters are positioned below the whole data set, indicating the irregular shape of their EDF. A similar irregularity is also detected in the group of artificial sparkling waters, showing a different shape of the upper tail.

The kernel densities shown in Figures 5a and 5b can be treated as an indicator of their probability density functions. Owing to the relatively low number of data estimates of the artificial sparkling water group and natural sparkling water group, these must be treated with caution. However, we believe that they indicate the complicated isotopic fractionation processes of the sparkling water group. Similarly, the flavoured and still water groups can be interpreted as the still water representing the parent water for the flavoured water.

It has been illustrated that in the δ^2H and $\delta^{18}O$ diagram the regression lines for each group of water are significantly different (BRENCIC & VRECA, 2006). Surprisingly, the ANOVA of d-excess for the same groups shows no significant differences. Tukey's post-hoc test confirms that the differences among the groups are very small.

Table 3. Deuterium excess values in flavoured waters

Bottled by	Origin	Brand	Flavour	d-excess (‰)
Vino Brežice	Slovenia	Active™	Elder lemon	9.9
Vino Brežice	Slovenia	Active™ (B)	Elder lemon	9.7
Vino Brežice	Slovenia	Active™	Fitness	10.0
Vino Brežice	Slovenia	Active™	Guava lime	6.4
Vino Brežice	Slovenia	Bistra™	Apple	11.6
Vino Brežice	Slovenia	Bistra™	Lemon	8.1
Vino Brežice	Slovenia	Mercator™	Lemon	10.6
Vino Brežice	Slovenia	Mercator™ (B)	Lemon	8.9
Vino Brežice	Slovenia	Spar Active™	Fitness	8.8
Vino Brežice	Slovenia	Spar Active™	Apple	11.9
Vino Brežice	Slovenia	Spar Active™	Orange	9.0
Dana	Slovenia	Dana™	Apple	9.8
Dana	Slovenia	Dana™ (S)	Apple	11.6
Dana	Slovenia	Dana™	Mango	11.4
Dana	Slovenia	Dana™	Lime	9.3
Dana	Slovenia	Spar™	Apple	10.6
Dana	Slovenia	Spar™	Lime	9.4
Dana	Slovenia	Spar™ (B)	Lime	9.8
Union Brewery	Slovenia	Za™	Lemon	11.2
Union Brewery	Slovenia	Za™ (B)	Lemon	10.1
Union Brewery	Slovenia	Za Life™	Apple	10.4
Radenska	Slovenia	Izvir™	Peach	8.5
Radenska	Slovenia	Izvir™	Guava	10.0
Radenska	Slovenia	Izvir™	Strawberry	9.5
Radenska	Slovenia	Izvir™ (B)	Strawberry	9.9
Radenska	Slovenia	Izvir™	Lemon balm	9.7
Jamnica	Croatia	Jana™	Strawberry guava	14.6
Jamnica	Croatia	Jana™	Lemon lime	14.0
Perne	Slovenia	Juliana™	Lemon	11.8
S.M.A.	Slovenia	Har Di™	Lemon	11.5
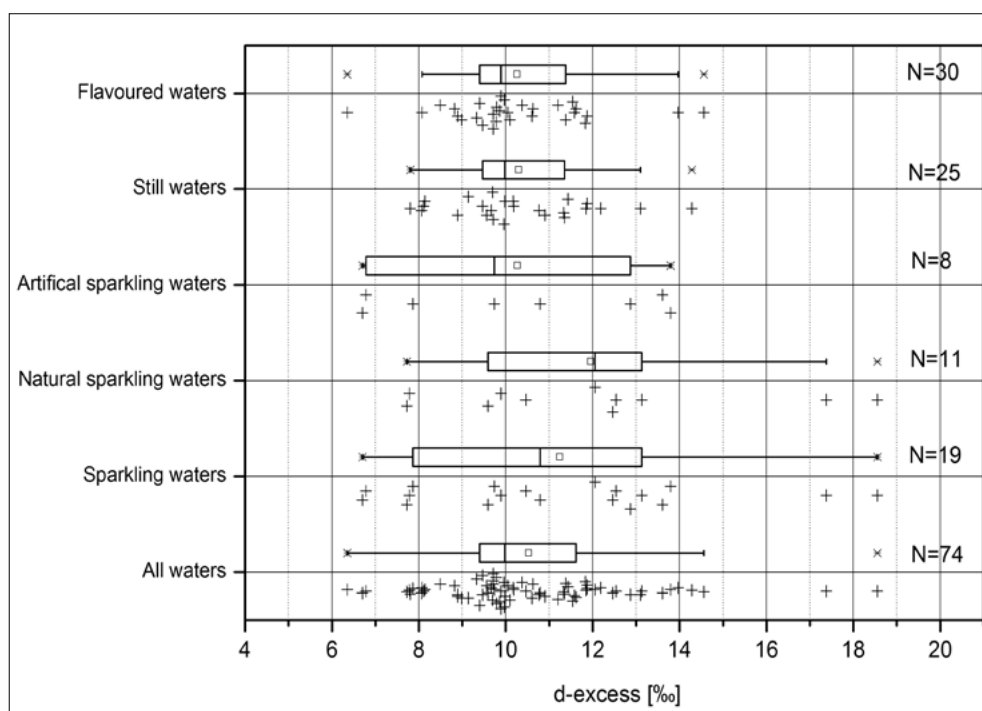
Fig. 3. Box plots of d-excess values with data point values for different groups of bottled waters.
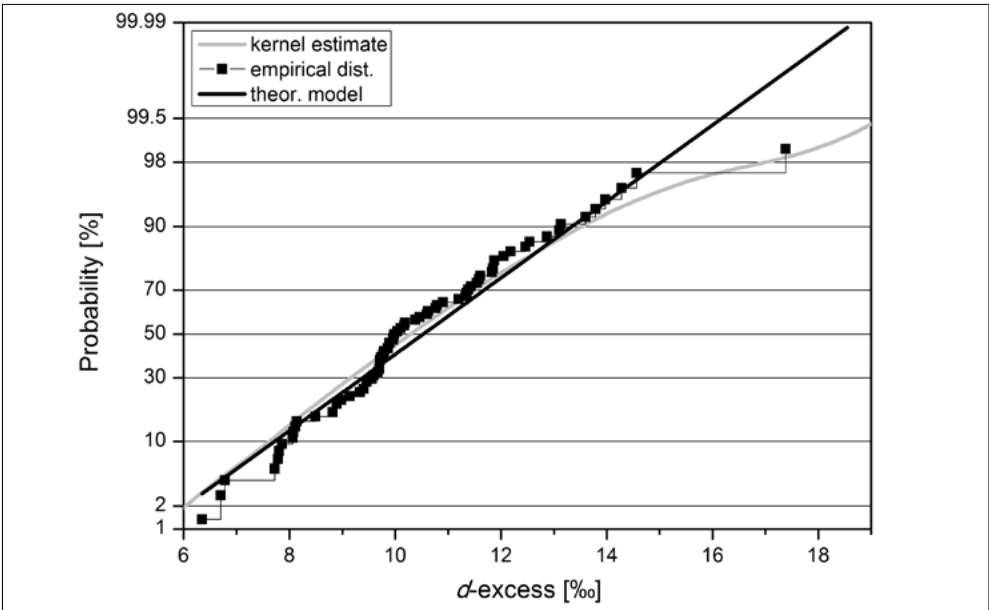
Fig. 4. Cumulative density diagram of the probability scale representing the empirical distribution, normal probability model and cumulative kernel density estimate for the whole set of bottled water
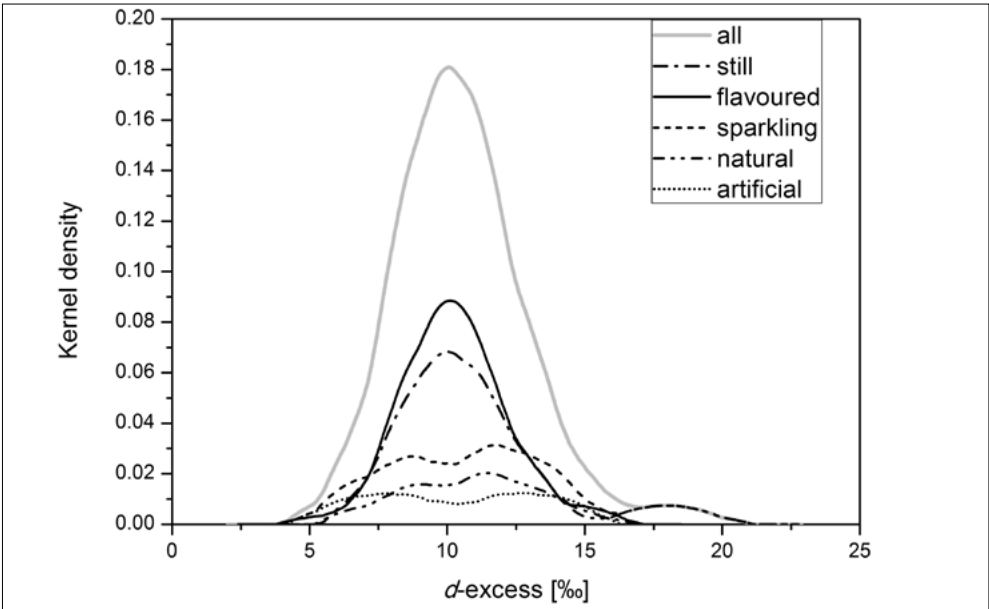

Fig. 5a. Probability density function estimates with kernel densities for different groups of bottled water.
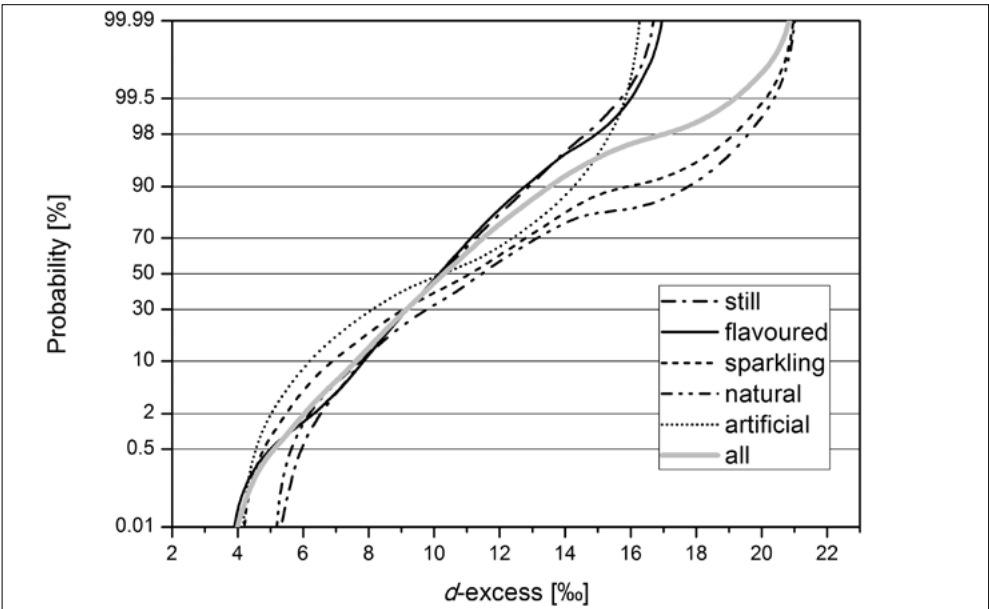

Fig. 5b. Cumulative density function estimates with kernel densities for different groups of bottled water on the probability scale diagram.

Table 4. Descriptive statistics of d-excess (‰) values for different types of bottled waters

	Average	Median	Std. dev.	Minimum	Maximum	Range	N
All waters	10.5	10.0	2.2	6.4	18.6	12.2	74
Sparkling waters	11.2	10.8	3.3	6.7	18.6	11.9	19
Natural sparkling waters	12.0	12.1	3.5	7.7	18.6	10.8	11
Artificial sparkling waters	10.3	10.3	3.0	6.7	13.8	7.1	8
Still waters	10.3	10.0	1.6	7.8	14.3	6.5	25
Flavoured *waters*	10.3	9.9	1.6	6.4	14.6	8.2	30

Table 5. Results of Anderson-Darling A^2 statistics and significaNce level of null hypothesis

	A^2	p
All	1.054	0.01
Flavoured	0.673	0.08
Still	0.303	0.43
Sparkling	0.374	0.24
Natural	0.440	0.16
Artificial	0.413	0.19

There is an apparent discrepancy between the results of the Anderson–Darling test and the kernel density estimates for both groups of sparkling waters. The test confirms the zero hypothesis that the EDF for all groups can be modelled with a normal probability model. However, the kernel densities show that the sparkling water groups are not distributed according to the expected bell-shaped curve of the normal probability model. These discrepancies are connected with the power and robustness of the statistical test and the power of the applied kernel method to properly represent the shape of the probability density curve with a low number of data. The question remains open for further investigation.

d-excess in relation to bottlers

If d-excess is considered in relation to the phases of the bottled water life cycle, analysis at a bottler level must also be performed. It is expected that production conditions as well as the condition in the parent water body are relatively homogenous. In the available data set, there are seven bottlers with several samples that can be used to analyse bottler-related influences on the isotopic fingerprint. According to the source water aquifers, these bottlers can be subdivided into two groups (Brenčič et al., 2010).

In the first group are bottlers exploiting deeper aquifers with natural source of CO_2. This group is represented by Kolinska ($n=6$) and Radenska ($n=15$), the biggest and oldest bottled water bottlers in the country. In this group, Jamnica ($n=5$) from Croatia should also be mentioned. These bottlers offer large ranges of products, including still waters, flavoured waters, and sparkling waters. In Slovenia, highly mineralised bottled water originates from two specific mineral water provinces (Fig. 2) with different geochemical characteristics and high natural CO_2 concentrations. In both cases,

the bottled water is a mixture of shallow and deeper groundwater. It is supposed that deeper groundwater has a relatively long retention time. Pezdič (1997) reported for the Rogaška Slatina mineral province that waters represent a mixture of older waters with ages of more than 8,000 years and of several younger waters with different recharge areas no older than 35 years. According to the authors' best knowledge, the exact age of the water from the Radenska mineral water province has never previously been thoroughly investigated and no precise dating of water has been published until now. Žižek (1982) reported only ^{14}C ages in the interval of 12,500 and 40,000 years, which because of the high concentration of CO_2 in the aquifer (Pezdič, 1991) is too long estimate.

In the available data set for the Kolinska bottler, sparkling water predominates, and there is only one sample of still water (Tiha™) with a d-excess value of 10.9 ‰. This value is similar to values in the Ljubljana precipitation and no peculiarities can be reported. In sparkling waters, d-excess values are in the range 12.5–18.6 ‰, with upper two values representing outliers in the whole data set (Donat-Mg™). For Tempel™ and Edina™, slightly higher d-excess values than the average d-excess values of the precipitation at Ljubljana (Vreča et al., 2008) and Zagreb stations (Barešić et al., 2006) have been observed. Values from bottled waters can be compared with the d-excess values calculated from the values of δ^2H and $\delta^{18}O$ published by Pezdič (1997). These values are in the range of –4.9 ‰ to 10.7 ‰ and are lower than the values from our data set. A close inspection of this published data shows that these values are all distributed along the line with a slope of 5.9, clearly indicating that samples were probably exposed to secondary evaporation from sampling containers (Rozanski & Chmura, 2008). Based on only two samples it is difficult to interpret the reason for the relatively high d-excess values in Donat-Mg™. Pezdič (1997) argued that no water–rock interaction is present in the aquifer and that the isotopic composition is the consequence of water infiltration in the distant past with climatic regime different then the present one. These d-excess high values of Donat-Mg™ can be also a consequence of the aquifer processes and the presence of high CO_2 concentrations in the aquifer. The exact interpretation of these values remains open until further more detailed field investigations will be performed. The d-excess values of other water samples from Kolinska could be the consequence of mixing between shallow

end members such as Tiha™ and deeper water end members such as Donat-Mg™.

The Radenska bottler is represented by three subgroups. In the first subgroup are sparkling waters with a range of d-excess values between 7.7 ‰ and 12.0 ‰, in the second subgroup are still waters with a range of d-excess values between 7.8 ‰ and 10.0 ‰, and in the third subgroup are flavoured waters with a range of d-excess values between 8.5 ‰ and 10.0 ‰. The average d-excess of all samples originating from Radenska is 9.5 ‰. These values can also be compared with the d-excess values calculated from the results of more than 60 boreholes from the Radenska mineral water province (PEZDIČ, 1991) ranging from 5.5 ‰ to 17.7 ‰ with an average value of 11.2 ‰. More than half of these reported data are in the range of 7.7 ‰ and 12.0 ‰, the range also defined for the Radenska bottled water. We conclude that based only on d-excess values it is not possible to assign isotopic changes to production processes or influences of storage conditions in the data set.

Jamnica (Croatia) should also be mentioned when interpreting bottler's d-excess values for waters originating from aquifers with higher concentrations of dissolved solids. According to its geological origin, the parent water is mineral water with a high CO_2 concentration. Jamnica sparkling water has d-excess values 6.7 ‰ and 6.8 ‰. Still water, which probably originates from shallow water, has a d-excess value of 10.8 ‰, which is close to the expected values in the precipitation in Zagreb (BAREŠIĆ et al., 2006). Flavoured water samples have higher d-excess values of 14.0 ‰ and 14.6 ‰, respectively. It is assumed that these differences are the consequence of production processes with water aeration and gas removal/reinjection as well as different types of parent aquifers.

The second group of bottlers exploiting shallow aquifers is represented by Union Brewery (n=5), Plastenka (n=5), Dana (n=8), and Vino Brežice (n=12). These businesses use relatively shallow groundwater with a recharge area between 200 and 300 m above sea level (BRENCIC & VRECA, 2006). The residence times of the groundwater in this group of bottlers are supposed to be relatively short, no longer than several years. According to the authors' best knowledge, the exact age of this water has not previously been investigated and no dating of this water has been published until now.

The average d-excess value of Union Brewery products is 10.6 ‰ and the range is between 10.0 ‰ and 11.4 ‰, which is similar to that reported (TRČEK, 2006) in the parent aquifer. The average d-excess value of Dana products is 10.3 ‰ and the range is between 9.3 ‰ and 11.6 ‰. This range agrees with precipitation data for Ljubljana (VREČA et al., 2008). The same is valid for Plastenka, which has a range of d-excess values for still waters between 9.1 ‰ and 11.4 ‰ with an average of 10.0 ‰.

Vino Brežice offers numerous flavoured waters and one still water brand. The average d-excess value of all its products is 9.5 ‰ and the range is between 6.4 ‰ and 11.9 ‰. This range is the consequence of the variation in flavoured waters. From the isotopic data it follows that nearly all samples of flavoured waters are positioned in the left part of the δ^2H and $\delta^{18}O$ diagram below the still water sample, which represents the parent water (BRENCIC & VRECA, 2006). The distribution of these samples probably indicates the influence of production processes in relation to low pH. However, the d-excess values do not show any trends that clearly confirm this indication.

Bottled water life cycle

When interpreting geochemical and isotopic characteristics it must be recognised that bottled water is a food product with its own life cycle, which does not only depend on the natural processes from where it originates but also on various production processes and storage conditions (BRENČIČ et al., 2010). These processes can considerably change the isotopic image of the bottled water. To interpret the d-excess values of bottled water three main life cycle phases must be considered: i) processes in the atmosphere before the interaction with the parent water body; ii) processes in the parent water body, and iii) production and storage processes. Therefore, it is necessary to recognise that all waters in the data set (BRENCIC & VRECA, 2006) originate from the underground water bodies, namely aquifers from temperate and humid climates.

In general, in temperate and humid climates the stable isotopic composition of the groundwater closely matches that of the precipitation in the recharge areas (GAT, 2010). Relatively large fluctuations in stable isotopic characteristics in the precipitation are smoothed out in the groundwater, and fluctuations are reflected in values along the GMWL. Therefore, groundwater represents a homogenised sample of the isotopic composition of the precipitation in the recharge areas. Deviations in groundwater isotope characteristics from the present day overall precipitation characteristics in the recharge areas of the aquifers can be a result of evaporation processes in the surface water bodies or in the unsaturated zone of the aquifers– or water aquifers–rock interaction and, consequently, the exchange between the water and aquifer matrix. Deviations from the present day GMWL can be a consequence of the long-term residence times of water in the aquifers, indicating that water was infiltrated underground during a different climatic regime in the past.

In Slovenia, the isotopic composition of precipitation has been investigated at Ljubljana since 1981 (VREČA et al., 2008) and the station is central to all considered bottler locations (Fig. 2). Between 1981 and 2006 the d-excess values fluctuated on the monthly basis in the range

between –19.9 ‰ and 19.4 ‰, with an average value and median of 9.3 ‰ and standard deviation of 3.8. In the SW part of Slovenia, the isotopic composition of precipitation was systematically monitored at the Portorož and Kozina stations for the period 2001–2003 (VREČA et al., 2006). The d-excess values fluctuated in the monthly samples at Portorož between 2.4 ‰ and 18.9 ‰ with an average of 9.2 ‰, median of 8.5 ‰, and standard deviation of 4.8, whereas at Kozina the values varied between 3.7 ‰ and 23.7 ‰ with an average of 11.6 ‰, median of 10.8 ‰, and standard deviation of 3.7. Daily observations showed even larger fluctuations (VREČA et al., 2007). In the analyses of d-excess in Slovenian bottled waters, foreign precipitation stations near the state borders must also be considered. In Austria, the mean d-excess value for the period 1973–1994 at Villacher Alpen was 9.6 ‰ (FROEHLICH et al., 2008) and at Graz for the period 1973–2002 it was 8.8 ‰ (IAEA, 2010). In Croatia, the d-excess value for the period 1976–1996 at Zagreb was 7.8 ‰ and daily fluctuations were between –9 ‰ and 18 ‰ (BAREŠIĆ et al., 2006). For the period 2001–2003 a mean value of 9 ‰ was reported (VREČA et al. 2006).

In all bottled water groups, the average d-excess values (Table 4) were slightly higher than those reported in the precipitation data. The only exceptions are natural sparkling waters. From the available hydrogeological information in Slovenia, water rock interaction and water sediment interaction and the interaction with deeply originating CO_2 are possible only in the case of natural sparkling waters originating from the Radenska and Rogaška Slatina mineral water provinces (Fig. 2). These deviations are reflected also in the d-excess values of considered bottled water originating from these provinces.

In all other parent aquifers of Slovenian bottled water, deviations in d-excess from local precipitation characteristics are not expected. In fact, the literature data confirm this hypothesis. OGRINC et al. (2008) reported that in the Sava basin, which represents the largest river basin in the country and is central to all considered bottlers locations, d-excess in the porous aquifers of the basin is 10.4 ‰ and the water in the river is close to 10.0 ‰. For the aquifer of Ljubljansko barje and the western part of Ljubljansko polje in the central Slovenia area, TRČEK (2006) reported a range of d-excess values between 10.6 ‰ and 12.6 ‰. Groundwater d-excess values from Slovenia are slightly higher than those reported in Ljubljana precipitation.

During the production of bottled water, several processes can influence the d-excess values of bottled water. Three subphases important for isotopic composition understanding must be considered: i) water pumping from the parent water body and the storage of water in buffer tanks; ii) the production and filling processes; and iii) storage in bottlers' facilities and sellers' locations.

During pumping from the aquifer water is usually transferred from a relatively closed thermodynamical system (e.g. confined aquifer) to an open system. During this process water is aerated and redox conditions drastically change towards a more oxidised environment. Water originating from aquifers with higher gas partial pressures is degassed. To avoid fluctuations of discharges from the well and to use energy more efficiently, in nearly all production facilities water is pumped into large buffer tanks from where it flows into the filling equipment. These tanks represent an open system where water is at least part of the time under a turbulent regime. In some cases, water is stored in tanks for several days before bottles are filled. During these processes the water temperature slightly rises compared with that of the parent water body. In the case of mineral and thermomineral water the temperature drops. In both cases, the water chemical equilibrium can be substantially changed. The exact changes in isotopic composition caused by production processes depend on the onsite conditions and were not studied in detail.

Large equilibrium changes are also present in the filling process during which bottlers often change the pH and concentrations of some dissolved species. One well-known example is the change of the $CaCO_3$ – CO_2 system equilibrium with the shift in pH and partial pressure of CO_2 (BECK et al., 2005). CO_2 degassing is a frequent production process that is allowed under mineral water legislation (EU, 1980). The aeration of water and consequent CO_2 degassing process is stimulated artificially to remove dissolved iron and manganese species. After the iron and manganese removal, CO_2 gas is reintroduced during the filling process. As illustrated in Figure 1, all these processes can potentially shift the isotopic composition of water from the parent body. However, precise analyses and interpretation of these processes can be given only based on more detailed information from the production process which at present are not available.

Substantial changes in the chemical equilibrium and subsequent isotopic fingerprint changes can also appear during the preparation of flavoured and functional water. Several flavours, sugars, organic acid-based and conservation chemicals are added. During these processes pH changes are substantial and, consequently, a relatively low pH was determined in some waters (BRENCIC & VRECA, 2007).

Finally, it is also well known that plastic packing materials are water soluble and porous. The solubility of plastic material can cause time-dependent changes of bottled water and, consequently, higher porosity and gas permeability. It is expected that the transport of gases through the walls of the bottle influences its chemical and isotopic composition. In some cases, where a higher concentration of dissolved calcite

and dolomite are present in the water, precipitate can appear in the case of the diffusion of CO_2 from the bottle. If CO_2 is present the diffusion of other gases and evaporation is also possible. All these processes can be simply detected with the time-dependent change of plastic bottle hardness. Over time bottles become more and more deformed and soft. The aging of plastic material and gas diffusion processes lead to lower d-excess values in the parent water, as also reported for sample containers (STEWART, 1981; ROZANSKI & RZEPKA, 1991; ROZANSKI & CHMURA, 2008). The influence of bacteria and their time-dependent activities on the water's isotopic composition is also possible and can cause changes in chemical equilibrium.

Conclusions

Based on the available data set of δ^2H and $\delta^{18}O$ values from bottled waters on the Slovenian market, d-excess values were calculated and analysed. Basic descriptive statistics were performed, different groups of bottled waters were compared, and their EDF were investigated. Following the well-known principles of water isotopic geochemistry possible changes in the isotope footprint reflected in the d-excess values were interpreted.

The descriptive statistical analyses and one-way ANOVA demonstrated that there are no significant differences in d-excess values among the groups. Explicit differences among groups were detected with kernel densities estimates in the shapes of their empirical distributions. Still and flavoured waters have similar shapes of empirical distribution. Vivid differences are present among the shapes of sparkling waters and other waters. Sparkling waters also differ among each other; artificial sparkling waters have a different shape of EDF to natural sparkling water. Empirical distributions of different bottled water groups of sole δ^2H and $\delta^{18}O$ variables are symmetrical, contrary to the empirical distributions of d-excess values in sparkling bottled waters. These differences indicate the complicated processes that govern the isotopic composition of sparkling water in their parent aquifers and possibly also during production processes.

In the data set two distinctive groups of bottlers are present. The first group is represented by bottlers exploring waters originating from the natural aquifers rich in highly mineralised groundwater and relatively high concentrations of CO_2 gas. These produce a large range of products with waters originating from different aquifers with diverse recharge conditions. Consequently, their d-excess values have a larger range. In the second group are bottlers that use only groundwater from relatively shallow aquifers for the production of still and flavoured waters. This bottled water has similar d-excess values to the local precipitation and their empirical distributions are unimodal and symmetrical.

The considered data set represents only a single sampling from the whole national market performed during a relatively short time period. The data set presents a general overview of the isotopic characteristics of bottled water on the market. No significant differences among identical bottled water products and the same bottler can be observed with such sampling and consequently no detailed interpretation of the process in the source and production can be given. Based on the applied interpretation and theoretical considerations we conclude that the d-excess values can be an additional tool to δ^2H and $\delta^{18}O$ analyses in the interpretation of the bottled water life cycle and their authentication. However, for a better interpretation more frequent sampling of the same water brand is needed. A better knowledge of how the particular production phases influence the isotopic characteristics is also required. Usually information about particular production processes are not available, therefore additional experimental work is required to detect process that can influence the isotope footprint of bottled water. This knowledge can help to improve the bottled waters' authentication process.

Author's note: Any uses of trade, product, or company names in this article are for descriptive purposes only and do not imply endorsement by the authors or their employers.

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