An isotope mass balance model for the correlation of freshwater bivalve shell (Unio pictorum) carbonate $\delta^{18}O$ to climatic conditions and water $\delta^{18}O$ in Lake Balaton (Hungary)

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ABSTRACT

The oxygen isotope composition of bivalve shells ($\delta^{18}O_{shell}$) can potentially record environmental variability of shallow lakes and therefore it has been extensively used as a proxy in the reconstruction of past climate and environmental conditions. As $\delta^{18}O_{shell}$ reflects - besides the water temperature - the oxygen isotope composition of lake water ($\delta^{18}O_L$), it is required to interpret the quality and impact of parameters influencing the $\delta^{18}O_L$. Using the isotope mass balance model, I tested the hypothesis that Balaton lake water $\delta^{18}O$ variability can be described as a result of the combined effects of three main climatic parameters such as river runoff, precipitation and evaporation. I calculated $\delta^{18}O_L$ time series for the period 1999-2008 for the whole water body at Sófok (eastern part of Lake Balaton, Hungary) based on measured precipitation, inflow and evaporation amount and measured inflow, precipitation $\delta^{18}O$ and calculated vapour $\delta^{18}O$ data. The comparison of the modelled $\delta^{18}O_L$ time series to measured surface $\delta^{18}O_L$ data revealed that $\delta^{18}O$ of Balaton water is sensitive for variation of climatic parameters. This variability is most striking at the surface, while according to the results of the model, the whole water body itself is less sensitive. Monthly differences suggest that generally during summer the whole water body is mixed up, while moderate isotope stratification (0.3-0.7‰ difference between surface and whole water body) can be assumed in early spring and autumn. Predictions of shell $\delta^{18}O$ values were made using the measured surface water $\delta^{18}O$ data and the modelled $\delta^{18}O$ values for the whole water body. High-resolution sampling was conducted on two Unio pictorum shells covering the period of 2001-2008, and both predictions were compared to measured shell $\delta^{18}O$ records. The results showed that the prediction for the whole water body gives a better fit to the measured shell $\delta^{18}O$, suggesting that the whole water body better describes the isotope variability of shell carbonate. As a practical application of the isotope mass balance model was used to present the effect of precipitation and evaporation on $\delta^{18}O_{shell}$. The relationship between intra-shell $\delta^{18}O$-variability and precipitation amount (precipitation/evaporation ratio) were determined, which allows the quantified prediction the impact of meteorological parameters affecting the oxygen isotope composition of shell carbonate.

Key words: shallow lake, stable oxygen isotope, biogenic carbonate, isotope stratification, intra-shell amplitude, seasonal change

1. INTRODUCTION

Oxygen isotope composition of shell carbonates has been extensively used to evaluate recent (Dettman et al. 1999; Kaandorp et al. 2003) and past (Wurster & Patterson 2001) climatic and environmental conditions, and can be related to variability of summer air temperature (Schöne et al. 2004) or even river discharge conditions (Versteegh et al. 2009).

Unionid bivalves precipitate their shells in oxygen isotopic equilibrium with the host water. Therefore the stable oxygen isotope composition of shell carbonate reflects the water temperature and the oxygen isotope variability of the water ($\delta^{18}O_L$) (Dettman et al. 1999; Versteegh et al. 2009). Oxygen isotopes of lake waters are used in the interpretation of hydrological dynamics in lakes (Perini et al. 2009) and the isotope mass balance model has been successfully applied to estimate water balance components (Dinçer 1968; Hermann et al. 1986), especially lake throughflow, residence time (Gibson et al. 2002) and water loss by evaporation (Gibson et al. 2001).

Unio pictorum shells are common in Lake Balaton (Hungary), which is the largest shallow lake in Central Europe (Fig. 1). Due to its shallow depth (mean depth 3 m) this lake is sensitive to variations in climatic factors, such as evaporation and precipitation directly or through inflowing rivers and creeks. Because of the sensitivity of lake water $\delta^{18}O$, the detailed investigation of various factors influencing the $\delta^{18}O_L$ is required for the interpretation of isotope signals of shell carbonate.

The aim of this study was to investigate the impact of climatic parameters on $\delta^{18}O_L$ in order to better understand the climatic signals detected in the $\delta^{18}O_{shell}$ Record. For that purpose, the $\delta^{18}O_L$ variation was calculated using the isotope mass balance equation based on hydrological and meteorological parameters such as precipitation, river inflow and evaporation. To demonstrate the applicability of isotope mass balance model in Lake Balaton, firstly modelled $\delta^{18}O_L$ values were compared to measured surface $\delta^{18}O_L$ data, secondly calculated $\delta^{18}O_{shell}$ values based on the modelled $\delta^{18}O_L$ data and on measured surface $\delta^{18}O_L$ were compared to measured $\delta^{18}O_{shell}$ values.
Based on the model hypothetical δ18O shell profiles can be calculated under different conditions to interpret seasonal extremities and quantify the effects of parameters such as precipitation and evaporation.

1.1. Hydrological background

Lake Balaton is situated in the Transdanubian Region of Hungary (Fig. 1). Although there are many surface inflows (51 rivers flow into the Lake Balaton through the catchment area (5775 km²); 20 have permanent runoff), Zala River (at the southwestern part of the Lake) is the largest one providing 52% of the total runoff (the Western Belt Canal the second largest with 10.1%). Inflow reaches its maximum in March and its minimum during summer.

The second largest contribution to water influx is the precipitation over the lake surface, which fluctuated between 449 (1971) and 888 (1965) mm per year during the period of 1951-2009 with a mean value of 607.5 mm. According to the 58-year dataset, the wettest months are June (71 mm), July (66 mm) and August (65 mm). The driest season is winter with a mean rainfall amount of 34 mm (in January) and 33 mm (in February). The spatial distribution of precipitation shows a remarkable difference in precipitation amount (30 year average of 140 mm) between the western (Keszthely) and eastern (Balatonalmádi) parts of the lake (Virág 1998). Beside inflows, Lake Balaton is canalized by the partly artificial Sió-channel at the end of the eastern side of the lake, through which the water is drained during high water level periods (Fig. 1).

As Lake Balaton is a large shallow lake, evaporation plays an important role in its hydrologic balance. The amount of evaporation ranges from 13.6 mm (January) to 156.2 mm (July). The evaporation rate shows a seasonal pattern following temperature variability.

According to the previous studies a wind of 4 m s⁻¹ can cause the full mixis of the lake, and therefore the lake has no permanent thermal stratification (Entz & Sebestyén 1940). Most stratification events are short-lived, while longer stratification (more than a day or even a week) can occur during calm situations (Vörös et al. 2010). Although the lake is mixed up in early spring, a possible thermal stratification (2-3 °C) occurs during wind-free periods between the water surface and the bottom (Entz 1981), and even larger differences (as much as 4.4 °C) are expected between the surface and the mud, especially during summer (Entz & Sebestyén 1940).

Isotope and thermal stratification of Lake Balaton was studied in 3 m water depth once in August 2005 (Barna & Fórizs 2006). The difference in δ18O values at the surface and bottom was 0.1-0.2‰ (coupled with temperature offset less than 2 °C).

2. METHODS

2.1. Sampling

Water samples were collected every two weeks from the lake at Siófok from January 2006 to December 2008. Approximately 20 mL of water samples were taken from the surface (20 cm) and kept refrigerated until measurements were performed. Additionally, precipitation water was also studied. Each precipitation event was sampled and amount-weighted monthly averages were obtained from Balatonszemes and Keszthely between January 2008 and December 2009 (Fig. 2a). Two living U. pictorum shells were collected in September 2004 from 2.5 m water depth (SUP_04) and in December 2008 from ~3 m water depth (SUP_08) at Siófok, as close as possible to the water sampling. The outer organic layer (periostracum) was removed by a
treatment with sodium hypochlorite (Gaffey & Bronnimann 1993). Holes for carbonate (CaCO₃) samples were drilled near equidistantly from the maximum width of the shell surface (highest growth rate) with a 0.6 mm tip dental drill in order to sample the growth increments at high resolution. In total, 109 samples were taken for stable isotope analysis.

2.2. Stable isotope analyses

The oxygen isotope composition of water samples was determined by means of the conventional CO₂-H₂O equilibration method (Epstein & Mayeda 1953). One mL of water sample was equilibrated with CO₂ at 32 °C for 18 hours. Stable carbon and oxygen isotope compositions of approximately 150-200 µg carbonate samples were determined applying the carbonate - orthophosphoric acid reaction at 72 °C and using automated GSBENCH II equipment attached to a mass spectrometer (Spötl & Vennemann 2003). $^{18}O/^{16}O$ and $^{13}C/^{12}C$ ratios were measured using a Thermo Finnigan Delta Plus XP mass spectrometer at the Institute for Geochemical Research, Hungarian Academy of Sciences, Budapest, Hungary. The stable isotope compositions are expressed as $\delta^{13}C$ and $\delta^{18}O$ values in ‰ relative to international standards, where $\delta = (R_{sample}/R_{standard} - 1)1000$, $R$ is the $^{18}O/^{16}O$ or $^{13}C/^{12}C$ ratio.

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**Fig. 2.** a: Monthly average of precipitation (measured $\delta^{18}Op$ from Balatonszemes and Keszthely 2008-2009) and $\delta^{18}Op$ from Vienna (1964-2001) Source: IAEA (2006) Isotope Hydrology Information System. The ISOHIS Database. http://iaea.org/water) b: Monthly river runoff (mm) 1999-2008 and $\delta^{18}O_i$ (Zala River, Western Belt Canal and the weighted average) calculated after Craig & Gordon (1965). Source of the river runoff, precipitation and evaporation amount data: Central-Transdanubian Environmental and Water Authority (Székesfehérvár).
2.4. The growth of the shell

The growth of the shell can be described by the following equation:

\[ D_2 = D_1 + P - E \]  

(McKinney et al. 1950), and the standard is V-SMOW (Vienna Standard Mean Ocean Water) for water and V-PDB (Vienna Pee Dee Belemnite) for carbonates (Coplen 1996). The analytical reproducibility for water analyses is ±0.1‰, whereas the standard long-term reproducibility for carbonate analyses is better than 0.15‰, based on multiple measurements of international standards (NBS-19; NBS-18), in-house reference materials and samples.

2.3. Hydrological data and statistical analyses

Water temperature, precipitation, evaporation and inflow amount and chlorophyll-α concentration data were obtained from the database of Central-Transdanubian Environmental and Water Authority (available at http://www.kdtvizig.hu) and from the Middle-Transdanubian Environment Inspectorate, Székesfehérvár (http://www.kvvm.hu/balaton).

For the period 1999-2005, unpublished water δ¹⁸O data (Csúnyi, pers. comm.) were used for the determination of monthly averages. Since no continuous δ¹⁸O record is available for precipitation and river inflow, monthly averages of values were determined based on precipitation δ¹⁸O data from period 2008-2009 and river inflow δ¹⁸O data from the periods 1999-2001 and 2007-2009 (Fig. 2b).

For statistical analyses monthly averages were used. Due to the non-parametric data distribution, the predicted and measured monthly shell δ¹⁸O mean values were analysed by the non-parametric Mann-Whitney U test. The probabilities of significant differences are listed in tabular form (Tab. 1). One-way ANOVA was used to analyse the effects of input parameters. In case of significant factor effect, Tukey HSD post hoc test was used for pairwise comparisons. The long-term trends in δ¹⁸Osh data were tested by a linear regression (ANOVA). The statistical analyses were carried out with the Past software (Hammer et al. 2001) and R (version 2.12.0) a free software program for statistical computing (R Development Core Team 2011).

2.4. The growth of the shell Unio pictorum

Shell growth pattern is visible to the naked eye and even intra-annual growth ring can be identified using an optical microscope (Veinott & Cornett 1996). The growth cessations of shell specimens were determined using a binocular microscope. In riverine environments, the growth of Unio pictorum shells stops when water temperature falls below 13.5 °C (Versteegh et al. 2010). As there are no available data on temperature limits for Lake Balaton, the 13.5 °C limit has been used to select the period of growth (from May to October).

The growth rate is not assumed to be perfectly constant, intra-annual growth mainly depends on water temperature (Jones & Quinmeyer 1996) and food availability. In the Rhine River, shells from Unionidae mainly grow during summer (Ricken et al. 2003), but can grow five times faster during early summer, when chlorophyll-α concentration is increases (Versteegh et al. 2010).

In the Siófok basin of Lake Balaton the chlorophyll-α concentration is more balanced (compared to the riverine environment mentioned by Versteegh et al. 2010) and characterized by a slight increase during autumn. On the other hand, during summer the higher water temperature (26-28 °C) can cause the cessation of growth due to heat induced hypoxic conditions (McManus & Bogan 2001) which can easily occur in Lake Balaton because of elevated water temperature during summer. Considering the above, a more balanced growth can be assumed than in river systems and therefore a linear growth model was used similarly to some previous studies (Dettman et al. 1999; Kaandorp et al. 2003).

For interpretation, monthly means of measured data were calculated (Fig. 3) on the basis of the following principles 1) the cessation bands detected by optical microscopy were taken as signs of winters, 2) the growth period from May to October was chosen when water temperature is above 13.5 °C, 3) measured δ¹⁸Osh data for each growth period were divided into six months on the basis of "equal intervals" assuming equal intra-annual growth.

2.5. The application of isotope mass balance model for calculating δ¹⁸Osh

Consistently to many lakes, the natural water mass balance equation according to Gat & Levy (1978) can be described by the following equation:

\[ D_2 = D_1 + P - E \]  

Tab. 1. The statistical analyses of calculated (based on measured δ¹⁸Osh) - measured δ¹⁸Osh and model - measured δ¹⁸Osh. Significant differences are in bold.

<table>
<thead>
<tr>
<th>Year</th>
<th>Model-measured Differences</th>
<th>p value</th>
<th>Calculated-measured Differences</th>
<th>p value</th>
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</thead>
<tbody>
<tr>
<td>2001</td>
<td>-0.23</td>
<td>0.69</td>
<td>0.53</td>
<td>0.23</td>
</tr>
<tr>
<td>2002</td>
<td>0.33</td>
<td>0.09</td>
<td>1.08</td>
<td>0.07</td>
</tr>
<tr>
<td>2003</td>
<td>-0.57</td>
<td>0.29</td>
<td>-1.12</td>
<td>0.05</td>
</tr>
<tr>
<td>2004</td>
<td>0.79</td>
<td>0.09</td>
<td>1.26</td>
<td>0.05</td>
</tr>
<tr>
<td>2005</td>
<td>0.82</td>
<td>0.03</td>
<td>1.21</td>
<td>0.04</td>
</tr>
<tr>
<td>2006</td>
<td>0.96</td>
<td>0.09</td>
<td>no available δ¹⁸O data</td>
<td></td>
</tr>
<tr>
<td>2007</td>
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<td>0.17</td>
<td>1.38</td>
<td>0.19</td>
</tr>
<tr>
<td>2008</td>
<td>0.57</td>
<td>0.23</td>
<td>1.29</td>
<td>0.01</td>
</tr>
</tbody>
</table>
where D is the water depth ($D_1 = \text{initial}, D_2 = \text{final}$), P is precipitation amount (in the similar terms of water depth) and E is the evaporation.

The corresponding isotope mass balance is given as follows:

$$\delta_2 = [D_1 \delta_1 + P \delta_P + I \delta_I - E \delta_E]/D_2 \quad (2)$$

Where and $\delta_1$, $\delta_2$, $\delta_P$, $\delta_I$ and $\delta_E$ are the isotope compositions of lake (1 = initial and 2 = final), precipitation, inflow and evaporated vapour. Precipitation (P) and river inflow (I) are the input fluxes, E is the evaporation flux. Since Lake Balaton has an outflow (O) through the Sió-channel, the equation 2 has to be completed as:

$$\delta_2 = [D_1 \delta_1 + P \delta_P + I \delta_I - E \delta_E - O \delta_O]/D_2 \quad (3)$$

where $\delta_O$ is the isotopic composition of outflow, which is similarly to that of lake water.

During evaporation, the water molecules with the lighter ($^{16}\text{O}$) isotopes are preferentially enriched in the formed vapour, while the heavier isotopes ($^{18}\text{O}$) remain in liquid phase and cause a positive shift of the $\delta^{18}\text{O}$ (Hoefs 1997). The oxygen isotope composition of evaporating lightest ($^{16}\text{O}$) isotopes are preferentially enriched in the liquid phase and cause a positive shift of the $\delta^{18}\text{O}$, where $\alpha$ is the fractionation factor.

$$\delta^{18}\text{O}_L = \delta^{18}\text{O}_V/L$$

where $\delta^{18}\text{O}_V$ is the isotopic composition of water vapour over the lake ($\delta^{18}\text{O}_L$) cannot be measured directly, and therefore has to be calculated from Craig & Gordon model (1965) used by Gat et al. (2001) in this form:

$$\delta^{18}\text{O}_E = (\alpha_{\text{V/L}} \delta_L - h_N \delta_A + \epsilon_{\text{diff}} + \epsilon_{\text{evap}})/(1 - h_N - \epsilon_{\text{diff}}) \quad (4)$$

where $\alpha_{\text{V/L}}$ is the equilibrium isotope fractionation factor between water vapour (V) and liquid water (L), $\epsilon_{\text{V/L}} = \alpha_{\text{V/L}} - 1 (<0)$, the fractionation factor $\alpha_{\text{V/L}}$ can be calculated using the equation of Majoube (1971):

$$\ln \alpha_{\text{V/L}}(^{18}\text{O}) = - \ln \alpha_{\text{V/L}} = 2.0667(10^{-3}) + 0.4156/T - 1.137(10^{-2}T^2) \quad (5)$$

where $T$ is the water temperature expressed in degrees Celsius.

$\delta_L$ is the isotopic composition of lake water (for the model 10-year monthly averages were used); $h_N$ is the relative humidity of the atmosphere over the lake, normalized to the lake surface temperature:

$$h_N = h \frac{P_{\text{SAT (air)}}}{P_{\text{SAT (water)}}} \quad (6)$$

where $h$ is the relative humidity, $P_{\text{SAT (air)}}$ and $P_{\text{SAT (water)}}$ (the saturation vapour pressures with respect to air and water temperature) can be calculated from the empirical equation of $P_{\text{SAT}} = \exp[(16.78T - 116.9)/(T + 237.3)]$ [kPa] (Ward & Elliot 1995) ($T$ is the temperature expressed in degrees Celsius valid from 0 to 50 °C).

The isotopic composition of the free atmosphere water vapour over the lake ($\delta_\Lambda$) can be estimated from available isotope data for local precipitation (or derived from evaporation pan data). The rationale of the equation is that the isotopic composition of monthly precipitation is assumed to be in isotopic equilibrium with atmospheric moisture at a given temperature (Schoch-Fisher et al. 1984; Jacob & Sonntag 1991):

$$\delta_\Lambda = \alpha_{\text{V/L}} \delta_P + \epsilon_{\text{V/L}} \approx \delta_P + \epsilon_{\text{V/L}} \quad (7)$$

where $\epsilon_{\text{V/L}} = \alpha_{\text{V/L}} - 1 (<0)$.

$\epsilon_{\text{diff}}$ transport (kinetic) fractionation can be calculated (Gat 1996) as:

$$\epsilon_{\text{diff}} = C_k \theta (1 - h_N) \quad (8)$$

where $C_k$ is an empirical coefficient, a value close to 14.3% (Gonfiantini 1986), which is widely used to describe evaporation from open water bodies; (1 - h) is the humidity deficit; $\theta$ is the turbulence parameter that has been shown to have a value of 0.88 for natural systems such as the Great Lakes region (Gat 1994).

Since the amount and isotopic composition of all parameters are known for the period 1999-2008, the quantitative and isotopic changes using a two component mixing model for each parameter can be described. The effects of the river inflow ($\delta^{18}\text{O}_{\text{infl}}$) precipitation ($\delta^{18}\text{O}_{\text{prec}}$) and evaporation ($\delta^{18}\text{O}_{\text{evap}}$) on $\delta^{18}\text{O}_L$ in given n month (in %) are expressed as:

$$\delta^{18}\text{O}_{\text{infl}} = [(D_e - 1)\delta^{18}\text{O}_{\text{infl}} + 10^{\delta^{18}\text{O}_{\text{infl}}}]D_e - \delta^{18}\text{O}_{\text{infl}} \quad (9)$$

$$\delta^{18}\text{O}_{\text{prec}} = [(D_e - P)\delta^{18}\text{O}_{\text{infl}} + P\delta^{18}\text{O}_{\text{prec}}]/D_e - \delta^{18}\text{O}_{\text{infl}} \quad (10)$$

$$\delta^{18}\text{O}_{\text{evap}} = [(D_e + E)\delta^{18}\text{O}_{\text{infl}} - E\delta^{18}\text{O}_{\text{prec}}]/D_e - \delta^{18}\text{O}_{\text{infl}} \quad (11)$$
Oxygen isotope variations in bivalve shells in Lake Balaton

where $D_n$ is the water column in mm, I, P and E are the river inflow, the precipitation and evaporation amounts in mm. $\delta^{18}O_{L(n)}$ is the $\delta^{18}O$ in given n month, $\delta^{18}O_{L(n-1)}$ is the $\delta^{18}O$ in previous (n - 1) month. For comparison of water $\delta^{18}O$ records, calculations were made for a mean 3 m water column according to the mean water depth of the lake, sampling depth was considered to model shell $\delta^{18}O$. For the initial isotopic composition of lake, a 10-year December average (-2‰) was used.

Since the shells were from the eastern part of the Lake (Siófok) and Zala River flows into the lake at the western part, the residence time of the river water is required to model the eastern part (Siófok). Since water moves from Fenékpuszta (inflow) to Sió (outflow) (Fig. 1), the effect of evaporation can be detected as a difference in $\delta^{18}O_L$ along a southwestern-northeastern axis, which can reach as much +2.4‰ (Barna & Fórizs 2007).

The lake can be divided into four sub-basins: Keszthely, Szigliget, Szemes and Siófok (Fig. 1). Based on tritium measurements, the 10-100% of lake water moves from Keszthely basin into the Szigliget-Basin, 5-35% flows further into the Szemes basin, from which 2-15% come to Siófok basin (Baranyi 1975). The maxima can be calculated for spring, while minima represent the summer water flow. With increasing distance for the river inflow, the two-component mixing has to be calculated for each basin, considering the ratio of the mixing and the evaporation (Fig. 4a).

As the effect of each parameter was calculated, the resulting changes for each month can be described as the sum of effects ($\delta^{18}O_{SUM(n)} = \delta^{18}O_{L(I)} + \delta^{18}O_{L(p)} + \delta^{18}O_{L(E)}$) (Fig. 4b).

The modelled $\delta^{18}O_I$ was calculated based on the equation 3 but also can be determined using the summed monthly effects of parameters with the relationship of $\delta^{18}O_{L(n)} = \delta^{18}O_{L(n-1)} + \delta^{18}O_{SUM(n)}$.

2.6. Prediction of $\delta^{18}O_{shell}$

The oxygen isotope composition of shell depends on the water temperature and lake water $\delta^{18}O$ according to the equation by Dettman et al. (1999) for freshwater unionid shells:

$$1000 \ln (\alpha) = 2.559 (10^6 T^2) + 0.715$$

where $T$ is temperature in degrees Kelvin, $\alpha$ is the fractionation factor between water and aragonite according to the equation:

$$\alpha_{CaCO3-water} = (1000 + \delta^{18}OCaCO3) / (1000 + \delta^{18}O_{water})$$

Based on both, measured surface and modelled $\delta^{18}O_L$, monthly shell $\delta^{18}O$ averages were calculated, and the results were compared to the monthly measured shell $\delta^{18}O$ precipitated at Siófok.

Using the model, hypothetical $\delta^{18}O_{shell}$ profiles were determined for average, dry and wet years to interpret the extremities. For this calculation, the 10-year average precipitation, evaporation and river runoff data were used for "average" year. To demonstrate a "dry" year, precipitation and river runoff minima for 10 years were coupled with maximal evaporation data. The calculation for a hypothetical "wet" year was based on the 10-year maximal precipitation and river runoff data with the smallest evaporation rate.

In addition, for quantifying the effect of the main parameters: precipitation and evaporation, theoretical intra-shell amplitudes were calculated for different precipitation amounts and precipitation-evaporation ratios (P/E). Evaporation amounts were determined using the 50-year monthly evaporation-precipitation relationships.

3. RESULTS

3.1. Oxygen isotope composition of water balance components

The measured isotope composition of precipitation ($\delta^{18}O_p$) is between -13.8 and -3.0‰ with an average value of -7.7 ± 3.1‰. The $\delta^{18}O_p$ follows the variation of temperature showing a seasonal pattern in which winter precipitation is generally more depleted in the heavy isotope ($^{18}O$) than summer precipitation. The precipitation mainly comes with the north-westerly rainstorm.

Fig. 4. a: The effect of the main inflow on the four basins (Keszthely, Szigliget, Szemes, Siófok) b: The modelled effects of the precipitation, inflow and evaporation on $\delta^{18}O$ of lake water in Siófok basin for each month between 1999 and 2008 in 3 m water depth.
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fronts (Baranyi 1980), which explains why the $\delta^{18}O_p$ values plot close to the $\delta^{18}O_p$ values for Vienna (Fig. 2a). The weighted average monthly mean oxygen isotope compositions of inflow ($\delta^{18}O_I$) range between -9.1 $\pm$ 0.3 and 4.5 $\pm$ 0.6‰ (Fig. 2b). Based on the Craig-Gordon model, the calculated monthly mean has an average $\delta^{18}O_E$ value of -7.9 $\pm$ 5.8‰ typically depleted in heavy oxygen isotopes relative to $\delta^{18}O_L$ (Fig. 2c).

3.2. The measured and modelled $\delta^{18}O_L$

The measured surface $\delta^{18}O_L$ for the period 1999-2008 ranges from -4.0 to -0.3‰ and has an average value of -1.74 $\pm$ 0.9‰.

The summed effects ($\delta^{18}O_{SUM} = \delta^{18}O_{LO}(p) + \delta^{18}O_{LO}(I) + \delta^{18}O_{LO}(E)$) based on the isotope mass balance model varies from -0.17 to +0.19‰ (Fig. 4b). According to the statistical analyses a significant effect was revealed on the input variable factors (F(3,476) = 402.1, $p <0.001$). During summer and autumn the evaporation seems to have the largest effect on $\delta^{18}O_L$ ($p <0.001$), while during winter and spring the precipitation has a greatest impact on $\delta^{18}O_L$ ($p <0.001$). The effect of the inflows in the Siófok basin is not remarkable.

The modelled $\delta^{18}O_L$ time series show a seasonal pattern and fewer variables than those from measured and range from -2.3 to -1.3‰ with an average value of -1.8 $\pm$ 0.2‰ (Fig. 5a).

The average difference between modelled and measured $\delta^{18}O_L$ data show a seasonal pattern, the best correspondence ($<0.25‰$) occurred during winter, May and June, while during early spring the modelled $\delta^{18}O_L$ values are 0.5-0.6‰ greater in average, than the measured surface $\delta^{18}O_L$ values and the opposite phenomena can be observed during late summer and autumn, when the modelled $\delta^{18}O_L$ values are generally more negative, than the measured surface $\delta^{18}O_L$ with the difference of 0.3-0.7‰ (Fig. 5b).

According to the linear regression there is a positive increase in $\delta^{18}O_L$ in time (F(1,206) = 82.18, $p <0.001$) both in the modelled and measured $\delta^{18}O$ record. The $\delta^{18}O$ increases in the measured and modelled data by 0.014 ($\pm 0.0021$) and 0.0045 ($\pm 0.0004$), respectively.

3.3. Measured, calculated and modelled $\delta^{18}O_{shell}$

The measured $\delta^{18}O_{shell}$ values in shell SUp_04 and SUp_08 range from -2.9 to 0.3‰ and from -4.8 to -0.3‰ with the average values of -1.5 $\pm$ 0.7 and -2.3 $\pm$ 0.8, respectively. The isotope profiles show seasonal cycles with negative values during the spring and summer, and enriched values in autumn (Fig. 3).

The calculated $\delta^{18}O_{shell}$ based on the surface $\delta^{18}O_L$ and surface temperature data range between -3.3 and 1.0‰ with an average value of -1 $\pm$ 1.0‰ (Fig. 6a).

Using the modelled $\delta^{18}O_L$, $\delta^{18}O_{shell}$ values were calculated (modelled $\delta^{18}O_{shell}$). The modelled $\delta^{18}O_{shell}$ data range between -2.8 and 0.3‰ with an average value of -1.6 $\pm$ 0.8‰. Month to month comparisons showed that the modelled $\delta^{18}O_{shell}$ values agree with the measured data (Fig. 6a, Tab. 1). Only 2005 showed significant differences ($p <0.05$) between measured and modelled $\delta^{18}O_{shell}$ values.

Comparing the calculated and measured $\delta^{18}O_{shell}$ data, significant differences for the study period except 2001 and 2007 have been found (Fig. 6a, Tab. 1).

The modelled-measured and calculated-measured $\delta^{18}O_{shell}$ differences have positive values and similar pattern. Best correspondence ($<0.25‰$) occurs in summer (modelled-measured) and in spring and early summer (calculated-measured), while larger offsets were detected in September and October with the mean difference of 0.8-0.9‰ and 1.3-1.4‰ (Fig. 6b).

3.4. The effect of precipitation

The calculation of $\delta^{18}O_{shell}$ under different conditions (average, dry and wet) shows systematic variability. The amplitudes (i.e., the deviation from the fixed May 0 values) of $\delta^{18}O_{shell}$ in average, dry and wet years are -2.3, -2.0 and -2.7‰, respectively (Fig. 7a). The results showed that a 50 mm increase in monthly precipitation

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**Fig. 5. a:** the modelled $\delta^{18}O_L$ (black circles) and measured surface $\delta^{18}O_L$ (grey circles) for the period 2001-2008. **b:** monthly differences between modelled and measured $\delta^{18}O$ (open squares), with the average values (black squares).
resulted in 0.1-0.25‰ decrease in annual δ¹⁸O-amplitude (Fig. 7b) and the relationship of intra-shell amplitude vs P and vs P/E ratio can be determined (see discussion).

4. DISCUSSION

Balaton as a dynamic shallow lake system is sensitive to variability of climatic parameters (i.e., precipitation, river inflow and evaporation). Since the oxygen isotope compositions of these parameters significantly differ from that of the lake water, these effects can be detected. Precipitation and river runoff are more depleted in heavy isotopes (¹⁸O) (Figs 2a and b) shifting the δ¹⁸O towards more negative values, while evaporation causes an enrichment of lake water in ¹⁸O. The seasonal variations of δ¹⁸O reflect the countering effects of these parameters (Figs 4b and 5a). The role of evaporation is minor in the winter/spring period and therefore the δ¹⁸O values become more negative due to increasing river runoff and precipitation amount. During summer, the increased evaporation rate overwhelms the effect of precipitation and river runoff, the δ¹⁸O values become more positive. Although, the amount of precipitation increases during summer, the δ¹⁸OP is not as much depleted as during winter (Fig. 2a), and therefore the effect is not remarkable (Fig. 4b).

The variability of the modelled δ¹⁸O data series is not as much remarkable as the measured surface-δ¹⁸O data have greater amplitude could be linked to the sensitivity of the epilimnion to evaporation and precipitation, in contrast to the model δ¹⁸O for whole water body, which is more constant.

The differences between modelled and measured δ¹⁸O is less than 0.25‰ from May to July in average suggesting that generally the whole water body is mixed.
up during early summer. The model δ values for whole water body are higher in early spring compared to measured surface δ values, while lower during the period from August to October. Despite the great deviations observed in differences during the period 2001-2008 (Fig. 5b), a possible stratification can be assumed during early spring (similarly to Entz & Sebestyén 1940), when the precipitation and/or meltwater input can cause the upper epilimnion becoming more negative compared to the modelled δ18O. On the other hand, the increased amount of evaporation can cause the enrichment of epilimnion in 18O, resulting in an offset of 0.3-0.7‰ in average, compared to the whole water body (Fig. 5b).

The modelled δ18Oshell (calculated based on model δ18O; values are generally similar to the measured δ18Oshell variations and give a slightly better correspondence than that of calculated δ18Oshell data (based on measured surface δ18O) (Fig. 6a, Tab. 1).

According to the averages of monthly differences (Fig. 6b), the best correspondence between modelled and measured δ18Oshell occur during summer, when presumably the whole water body is mixed up similarly to the assumption based on δ18O. The larger discrepancies between the model and measured δ18Oshell detected in May and September-October can be explained by a possible thermal stratification. The possible difference in temperature between surface and bottom can occur in spring when the sunlight warms the surface layer, but the bottom of the lake remains cold and warms only gradually. A similar setting is suggested in autumn, when the decreased air temperature causes cooling from surface to bottom. However, this thermal stratification is not supposed to be constant, a 2-3 °C difference during wind-free periods can be assumed.

According to the equation of Dettman et al. (1999), a 0.5‰ offset (in May) and 0.8-0.9‰ in δ18Oshell values can be caused by a 2.5 and 4-4.5 °C difference in water temperature, respectively. Although 2.5 °C difference between surface and the whole water due to the thermal stratification is possible, it is unlikely that this difference could constantly reach as much as 4-4.5 °C. The more likely explanation for the discrepancy in autumn can be that beside the offset in water temperature, the δ18O also differs between the whole water body and the bottom/mud.

The stable oxygen isotope composition of shell carbonate is controlled by the δ18O of water temperature. Variations in water temperature cause 0.2‰ variance in shell δ18O per °C (Dettman et al. 1999). In Lake Balaton, the seasonal variation in surface water δ18O reaches 0.7-1.7‰ and 0.1-0.5‰, based on the model for the whole water body during the growth periods. When seasonal variations in δ18O do not overwhelm the water temperature effect (i.e., temperature dominated environments with variable δ18O; according to Dettman & Lohmann 1993), the interrelation of these parameters determines the variation in δ18Oshell. Besides increased temperature, a negative shift in δ18Oshell can be related to the increased amount of precipitation, while a positive shift suggests increased evaporation rates coupled with decreased precipitation amounts. This can be shown in calculated shell isotope values under different (average, dry and wet) conditions (Fig. 7a). The deficit of precipitation, coupled with increased amount of evaporation resulting in a depressed δ18Oshell curve when environmental variability of δ18O_L dampens the effect of temperature by the antagonistic effect of evaporation. Wet conditions cause the increase of annual amplitude of δ18Oshell (2.7‰), overwhelming the effect of temperature (Fig. 7a).

The δ18O is affected by the interrelated effects of precipitation (and river runoff), and evaporation. The δ18Oshell reflects the variation in precipitation and evaporation. The relationship of intra-shell amplitude vs precipitation amount and amplitude vs P/E ratio were determined (Fig. 7b), and are given as follows:

Amplitude (‰) = −0.0039Precipitation(mm)−2.0167 (14
Amplitude (‰) = 0.004(P/E)−2.12(P/E)−2.04 (15

Increasing precipitation/evaporation ratio increases the annual amplitude, and 50 mm increase in monthly precipitation amount causes a 0.1-0.25‰ decrease in δ18O minima (Fig. 7b).

5. CONCLUSIONS

The results showed that an isotope mass balance model can be used for Lake Balaton and the isotopic variability of lake water for whole water body can be calculated. Comparisons of modelled δ18O_L and measured surface δ18O suggest that the whole water body is mixed during summer, while moderate isotope stratification can be suggested during spring and autumn between the whole water body and epilimnion.

According to the comparisons of the model-measured and the calculated-measured δ18Oshell data, the model data (based on the lake water isotope mass balance model) gives better estimates for the δ18O of precipitated shell carbonate than the ones calculated based on surface δ18O. The results suggest that differences in water temperatures between the surface and bottom can occur in spring and especially in autumn, which are caused by the sensitivity of the epilimnion, and should be taken into account during the interpretation of shell δ18O records.

As the isotope mass balance model can be used for the lake, this basis allows the precise quantification of climate parameters affecting δ18O_L and δ18Oshell. According to the results, dry and wet years can be detected in shell amplitude as a deviation from the water temperature effect. Theoretical intra-shell amplitudes were calculated under different precipitation amounts, and the relationship between amplitude and precipita-
tion amount and precipitation/evaporation ratio was determined.

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