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Estimation of evaporative loss based on the stable isotope composition of water using *Hydrocalculator*

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SUMMARY

Accurate quantification of evaporative losses to the atmosphere from surface water bodies is essential for calibration and validation of hydrological models, particularly in remote arid and semi-arid regions, where intermittent rivers are generally minimally gauged. Analyses of the stable hydrogen and oxygen isotope composition of water can be used to estimate evaporative losses from individual pools in such regions in the absence of instrumental data but calculations can be complex, especially in highly variable systems. In this study, we reviewed and combined the most recent equations required for estimation of evaporative losses based on the revised Craig–Gordon model. The updated procedure is presented step-by-step, increasing ease of replication of all calculations. The main constraints and sources of uncertainties in the model were also evaluated. Based on this procedure we have designed a new software, *Hydrocalculator*, that allows quick and robust estimation of evaporative losses based on isotopic composition of water. The software was validated against measures of field pan evaporation under arid conditions in northwest Australia as well as published data from other regions. We found that the major factor contributing to the overall uncertainty in evaporative loss calculations using this method is uncertainty in estimation of the isotope composition of ambient air moisture.

1. Introduction

While transpiration is generally considered the largest contributor to continental water flux (Lawrence et al., 2007; Jasechko et al., 2013), evaporative losses from surface water bodies and subsequent water level fluctuations in rivers, lakes and wetlands are important elements of the terrestrial hydrological cycle (Gammons et al., 2006; Hamilton et al., 2005). This is particularly true of arid and semi-arid regions where vegetation cover is often sparse. For example, potential evaporation can exceed precipitation several-fold in northwest Australia, thus constraining groundwater recharge (Dogramaci et al., 2012). At more local scales, the degree of evaporative losses from individual pools and reaches of intermittent rivers also determines the concentration of organic carbon, nutrients and oxygen in water, thus also strongly influencing aquatic ecosystem functioning (Fellman et al., 2011). While clearly important in hydrologic studies, determination of evaporation losses and overall estimation of water budgets, particularly in highly dynamic systems, can be challenging due to uncertainties in monitoring of water flow and volume measurements of water bodies. Many hydrologic studies, particularly at the catchment scale, have traditionally required extensive field programs and relied on measured parameters or comprehensive meteorological and hydrological coverage. Such approaches are generally impractical, time-consuming and costly in remote areas that lack appropriate infrastructure. On the other hand, hydrochemical methods using, for example, conservative ions concentrations (e.g., Cl), can be an alternative approach for assessing evaporative losses. However, a major disadvantage of Cl-base methods is an assumption that an increase in salt concentration results from evaporation loss only. This is not necessarily true in

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areas where a significant portion of salt can be recycled during subsequent wetting and drying cycles and also where transpiration losses are significant (Dogramaci et al., 2015).

Alternatively, the evaporative loss from a pool or a lake over a fixed period of time can be calculated relatively easily if the transient stable hydrogen and oxygen isotope compositions of water are known or if the stable isotope composition of inflowing and outflowing water is known (Craig and Gordon, 1965). This method is inexpensive as the calculation requires the stable isotope analysis of just two water samples (assuming there are no additional new water sources during the study period), basic weather data, and estimation of the stable isotope composition of ambient air moisture. Consequently, this approach has been applied in numerous hydrological studies around the world and at multiple scales (Lawrence et al., 2007; Gammons et al., 2006; Mayr et al., 2007; Tweed et al. 2009; Gibson and Reid, 2010; Strauch et al., 2006). However, the complexity of the mathematical formulation can be both challenging and time-consuming for users unfamiliar with the theory underpinning isotopic fractionation processes associated with water, thus constraining application by water managers more generally. Here, we present a user-friendly software (*Hydrocalculator*) that allows quick calculation of both the estimated evaporative loss (f) in a non-steady-state condition when the water body volume changes over time, and the estimated evaporation over inflow ratio (E/I) in the steady state condition, based on the stable isotopic composition of inflowing and outflowing water (Supplementary data 1, 2, 3). Our study includes: (1) an overview and update on the Craig–Gordon model; (2) development of the *Hydrocalculator* software concept; and (3) field experimental verification of the software calculations. This verification was also used to assess how well the modified Craig–Gordon model applies to field conditions in arid climates. We assessed the potential influence of uncertainty in air temperature and humidity measurements and of ambient air stable isotope composition estimations and variations on the computed f and E/I values, which also demonstrates how this approach might be applied to other climatic conditions.

2. Theory

2.1. Overview

The principles of evaporative losses calculation are founded on the so-called Craig–Gordon (C–G) model (Craig and Gordon, 1965), which explains how the stable isotope compositions of liquid water and vapour change during progressive evaporation in response to conditions during the evaporation process. This theoretical model was revised by Horita et al. (Horita and Wesolowski, 1994, Horita et al., 2008). A simplified version of the original C–G model was used initially by Gonfiantini (1986) and subsequently by Gat (1995) for calculation of the progress of evaporation from lakes. The model equations used by Gonfiantini and Gat were also recently verified and applied by Gibson and Reid (2014), Gibson (2002), and Bennett et al. (2008). In their study, Bennett et al. (2008) proposed also an adjusting factor (x) for better estimation of the stable isotope composition of ambient air moisture (δ_A), based on the stable isotope signature of local precipitation and the Local Evaporation Line (LEL). The *Hydrocalculator* proposed here is based on the revised mathematical reformulation of the equations listed in the above original publications (see details in Section 2.2.). However, the algorithm used by *Hydrocalculator* to estimate evaporation losses did not include several minor local parameters that can be used in a revised C–G model (Horita et al., 2008). In particular, changes in ambient air moisture and its stable isotope composition at different heights over the evaporating water body may vary due to wind, direct sunlight, surrounding topography and the size and depth of a water body. All these factors have the potential to influence the uncertainty of the final results of the computations. A more detailed analysis of these local factors, while feasible under laboratory conditions, is not practical during field studies. Moreover, the uncertainty resulting from the use of mean values for temperature, relative humidity and the procedure for measurement or estimation of likely δ_A may introduce higher computational error with their inclusion in the C–G model. An important assumption of the C–G model is that there are no other sources of water in the study system (i.e., no additional surface or groundwater inflow or rain for the study period). Any new water sources will thus lead to higher uncertainty in the calculations and need to be carefully considered. Similarly, water stable isotope signatures used for calculations should be verified or adjusted using a water isotope mixing mass balance. Infiltration or transpiration while possibly changing water levels will not strongly influence the stable isotope composition of water (Dogramaci et al., 2015).

2.2. Main variables and equations

2.2.1. Stable isotope composition of water

The calculation of evaporative losses fraction (f) over a period of time requires at least two analyses of the water stable isotope composition (non-steady state model) of a water body (Table 1). The first analysis is to determine an initial δ-value for water (sampling #1, δ_P); evaporation will be estimated assuming that this value is a starting point (any evaporation prior the sampling #1 will not be taken into account). The second analysis is the final δ-value of water, sampled after some period of time #2 (δ_L) and assuming that there no supplementary water inflows. The δ-values of water

Table 1
The list of variables used for calculation of evaporative losses based on the Craig–Gordon model (Craig and Gordon, 1965) following equations after Gonfiantini (1986), Gat (1995), Gibson (2002) and Gibson and Reid (2014).

Variable	Description	
T	Temperature (°C), mean between sampling #1 and #2	Measured or assumed
h	Relative humidity (fraction), mean between sampling #1 and #2	
δ_{Rain}	Precipitation, mean between sampling #1 and #2 (for δ_A calc only)	
δ_P	Pool water initial value[a] or inflow[b] (‰), sampling #1	
δ_L	Pool water final value[a] or outflow[b] (‰), sampling #2	
LEL	Slope of Local Evaporation Line	
δ_A	Air ambient moisture (‰), mean between sampling #1 and #2	
ε_k	Kinetic isotope fractionation factor (‰) (h dependent)	Calculated from the model
ε^+	Equilibrium isotope fractionation factor (‰) (T dependent)	
ε	Total isotope fractionation (‰)	
C_k	The kinetic fractionation constant (‰)	
α^+	Equilibrium isotope fractionation factor (‰) (T dependent)	
δ^*	Limiting isotopic composition (‰)	
m	Calculation factor $(h - \varepsilon/1000)/(1-h+\varepsilon_k/1000)$	
E/I	Result for steady-state model: evaporation over Inflow ratio	Results
f	Result for non-steady-state model: evaporated fraction of the volume	

[a] Non steady state model, f calculation.
[b] Steady state model, E/I calculation.

from sampling #2 will be higher (more enriched in the heavier isotope) than the value of water collected at sampling #1 ($\delta_L > \delta_P$), reflecting the progressive evaporation of water (and loss of the lighter isotope) under local conditions assuming that there is not additional water inflow. A time series of analyses can be performed, allowing evaluation of the progress of evaporation. It is also possible to estimate evaporative losses of inflowing water in through-flow pools in a stream (E/I). In this type of calculation the stable isotope composition of the inflowing water (δ_P) and the outflowing water (δ_L) is required (steady-state model).

The δ_L values from several subsequent samplings of a water body at the same location ideally should make a robust regression line for the relationship between δ^2H and δ^{18}O. The intercept of the regression line will depend on the initial value of the stable composition of water in the studied water bodies; however, the slope will depend on local environmental and climatic conditions. Thus, the slope should be similar to those for the Local Evaporation Line (LEL). A significant deviation from this regression line may result from additional water sources, such as rainfall events, surface run-off, and groundwater inputs between sample times. While useful for identifying these events (Fellman et al., 2011), these deviations may also introduce uncertainty in the calculation of evaporative losses depending on the volume of water added to the water bodies.

2.2.2. Air temperature and relative humidity

Air temperature (T) and relative humidity (h) during evaporation influence the stable isotope composition of the remaining water in water bodies (Table 1). The most accurate option is to record the mean air temperature and humidity directly at the point of water sampling, which is easily done with small in situ data loggers. The use of a T and h data set from a more distant regional weather station may introduce additional uncertainty, the level of which depends on the scale of temperature differences between a weather station and a sampling point. These differences may arise from the local patterns of temperature distribution in the landscape due to topography, vegetation cover, and the presence of the water body itself. The calculation of evaporative losses requires the mean air temperature for the time period between water samplings #1 and #2, in Celsius degrees. The mean air relative humidity (h) used in all presented equations is expressed as a fraction (not a percentage).

2.2.3. Stable isotope composition of moisture in ambient air

The last parameter required for the calculation of evaporative loss is the stable isotope composition of the moisture in the ambient air (δ_A) (Table 1). Direct measurement of this parameter in the field can be challenging. However, δ_A can be determined in three different ways depending on the data available and the adopted approach: (1) direct on-site measurements; (2) a calculation based only on the known local precipitation stable isotope composition; or (3) a calculation based on the known local precipitation stable isotope composition but corrected using known local LEL.

Option #1. Direct measurement of δ^2H and δ^{18}O of ambient air is the most accurate way of determining δ_A. However, such measurements remain challenging in terms of logistics and required resources, if conducted in remote areas. Direct measurements are now possible using relatively mobile, laser-based isotope analysers for constant monitoring, allowing calculation of the mean δ_A for the relevant period (e.g., Picarro, Picarro Ltd., Sunnyvale, CA, USA; or Los Gatos, Los Gatos Research, Mountain View, California). The other alternative for direct measurement is a sampling device that allows condensation of moisture and subsequent analyses of the obtained liquid water, which reflects the stable isotope composition of the ambient air moisture (Mayr et al., 2007). The third alternative is frequent subsampling of air into specially prepared bottles or bags followed by measurement of the moisture of stable isotope composition (Johnson et al., 2011). However, air needs to be sampled frequently to fully reflect mean moisture isotope composition during study period; therefore, all of these options require running instrumentation at a field station or frequent atmospheric moisture sampling.

Option #2. Given the difficulties of directly measuring δ_A in the field, δ_A is frequently estimated from the stable isotope composition of local precipitation. In this scenario, isotopic equilibrium between δ_{rain} and δ_A is assumed. The mean δ_{rain} at the sampling location needs to be known or estimated for the observation period. The optimal approach using this option would be to make frequent analyses of the stable isotope composition of precipitation over few seasons. Alternatively, the mean monthly weighed averages from a local GNIP station can be used (http://www-naweb.iaea.org/napc/ih/IHS_resources_isohis.html). However, the distance between the GNIP station and the sampling location needs to be considered, along with differences in elevation and distance to the coast. If these data are not available, the precipitation can be roughly estimated using a global algorithm for the estimation of stable isotope composition of precipitation, at given location and altitude (e.g., http://waterisotopes.org Bowen and Revenaugh, 2003). Following the simplified classical approach the δ_A value based on the stable isotope signature of precipitation can be defined as follows (Gat, 1995; Gibson and Reid, 2014):

$$\delta_A = (\delta_{rain} - \varepsilon^+)/\alpha^+ \tag{1}$$

where ε^+ is the temperature dependent equilibrium isotope fractionation factor defined as $\varepsilon^+ = (\alpha^+ - 1) \times 1000$ and α^+ as by Horita and Wesolowski (1994) given in Eqs. (2a and 2b):for hydrogen

$$\begin{aligned} 103 \times \ln(\alpha^+) = {} & 1158.8 \times T^3 10^{-9} - 1620.1 \times T^2 \times 10^{-6} \\ & + 794.84 \times T \times 10^{-3} - 161.04 + 2.9992 \times 10^9 \times T^{-3} \end{aligned} \tag{2a}$$

for oxygen

$$\begin{aligned} 10^3 \times \ln(\alpha^+) = {} & -7.685 + 6.7123 \times 10^3 \times T^{-1} - 1.6664 \\ & \times 10^6 \times T^{-2} + 0.35041 \times 10^9 \times T^{-3} \end{aligned} \tag{2b}$$

where temperature (T) is given in Kelvin degrees. In our *Hydrocalculator*, α^+ has been used as was determined experimentally by Horita and Wesolowski (1994).

Option #3. The δ_A may also be estimated from local records of precipitation stable isotope composition (δ_{rain}), corrected using the LEL. The slope of the LEL used for correction of δ_A is derived from pan evaporation experiments or multiple measurements of the changes in stable isotope composition of water of a few pools or lakes in the study area. The δ_A value is calculated based on δ_{rain} as follows (Gibson and Reid, 2014):

$$\delta_A = (\delta_{rain} - x \times \varepsilon^+)_{rain}/(1 + x \times \varepsilon^+ \times 10^{-3}) \tag{3}$$

where δ_{rain} is the stable hydrogen and oxygen isotope composition of precipitation and ε^+ is the equilibrium isotope fractionation factor, which depends only on temperature (Horita and Wesolowski, 1994). Initially, Eq. (3) was solved using $x = 1.0$ and then the slope of LEL was calculated from Eq. (4):

$$Slope_{LEL} = \frac{\left[\frac{h\cdot(10^{-3}\cdot\delta^2H_A - 10^{-3}\cdot\delta^2H_{Rain}) + (1+10^{-3}\cdot\delta^2H_{Rain})\cdot 10^{-3}\cdot\varepsilon}{h - 10^{-3}\cdot\varepsilon}\right]_H}{\left[\frac{h\cdot(10^{-3}\delta^{18}O_A - 10^{-3}\cdot\delta^{18}O_{Rain}) + (1+10^{-3}\cdot\delta^{18}O_{Rain})\cdot 10^{-3}\cdot\varepsilon}{h - 10^{-3}\cdot\varepsilon}\right]_O} \tag{4}$$

where h is air relative humidity (given as a fraction) ε is the total fractionation factor and equals the sum of the equilibrium isotope fractionation factor ε^+, as given above plus the kinetic isotope fractionation factor ε_K (Gibson and Reid, 2010):

$$\varepsilon = \varepsilon^{+}/\alpha^{+} + \varepsilon_{\mathrm{K}} \tag{5}$$

The kinetic fractionation ε_{K} is defined as (Gat 1995):

$$\varepsilon_{\mathrm{k}} = (1 - h) \times C_{\mathrm{k}} \tag{6}$$

where C_{k} is the kinetic fractionation constant: 12.5‰ for δ^{2}H and 14.2‰ for δ^{18}O (Gonfiantini, 1986; Araguas-Araguas et al., 2000).

The calculation was then repeated number of times using x between 1.0 and 0.6, and so on. The final x adjusting parameter was chosen based on subsequent iteration, when the difference between the calculated slope of LEL (Eq. (4)) and the actually observed slope of LEL based on field studies was the lowest (or x reached the boundary values, 0.6 or 1.0). The slope of LEL for finding x can be calculated (Eq. (4)) based on the adjusted moisture in the ambient air $\delta^{2}\mathrm{H}_{\mathrm{A}}$ and $\delta^{18}\mathrm{O}_{\mathrm{A}}$ and mean precipitation $\delta^{2}\mathrm{H}_{\mathrm{Rain}}$ and $\delta^{18}\mathrm{O}_{\mathrm{Rain}}$ (Gibson et al., 2008). However, the moisture in the ambient air and mean precipitation need to be in isotopic equilibrium; what is not always the case, particularly in arid climates or climates characterised by highly seasonal and often episodic precipitation. For large lakes, influencing regionally δ_{A} in air ambient moisture or small pools but located in narrow gorges or caves with limited ventilations δ of the lake or pool water could be used for δ_{A} determination, instead of δ_{Rain}.

2.2.4. Limiting isotope composition enrichment

The progressive enrichment of stable hydrogen and oxygen isotope compositions of surface water bodies during evaporation is limited by physical conditions and the rate and extent depends on the local meteorological conditions (Gat and Levy, 1978; Gat, 1981). When the threshold of the limiting isotope composition (δ^{*}) is reached, further evaporation no longer results in isotope enrichment of the remaining water (Table 1). The limiting threshold can be experimentally tested in the field; however, evaporation of large quantities of water under local conditions can be time consuming and requires several samplings and analyses. Therefore, δ^{*} is usually calculated using air humidity (h), the isotope composition of moisture in ambient air (δ_{A}) and a total enrichment factor (ε) (Gat and Levy, 1978; Gat, 1981):

$$\delta^{*} = \frac{h \times \delta_{\mathrm{A}} + \varepsilon}{h - \frac{\varepsilon}{1000}} \tag{7}$$

2.3. Non-steady-state model

An pool of water isolated from groundwater table is generally considered to be in a non-steady-state, e.g., when no water inflow or outflow occurs to/from the pool and the volume of the water in the pool decreases only due to evaporation progresses. Therefore, the stable isotope composition of water only changes due to isotope fractionation during the evaporation process. In this scenario, the evaporative loss fraction of the pool volume (f) can be calculated using the original equation (Gonfiantini, 1986) reformulated to include isotope mass balance as presented (Eq. (8)) (e.g., Hamilton et al., 2005):

$$f = 1 - \left[\frac{(\delta_{\mathrm{L}} - \delta^{*})}{(\delta_{\mathrm{P}} - \delta^{*})}\right]^{\frac{1}{m}} \tag{8}$$

where δ_{P} is the initial value of water in the pool (sampling #1), δ_{L} is the final value of water in the pool, δ^{*} is the limiting isotope enrichment factor as given above (Eq. (7)) and m is the enrichment slope as defined previously (Welhan and Fritz, 1977; Allison and Leaney, 1982):

$$m = \frac{h - \frac{\varepsilon}{1000}}{1 - h + \frac{\varepsilon_{k}}{1000}} \tag{9}$$

where h is air humidity given as a fraction, ε_{K} is the kinetic fractionation (Eq. (6)) and ε is the total fractionation factor (Eq. (5)).

2.4. Steady-state model

Under steady-state condition, a water body is constantly replenished by inflowing water and the water level remains constant as the evaporative losses from the pool are compensated by inflow that equals or exceeds evaporation. A typical example would be a lake supplied by one river and discharged by another river. Evaporation from the lake surface occurs relative to the local conditions and surface area; however, the evaporated lake water is constantly mixing with inflowing input proportionally to the lake volume and the volume of inflowing water. In this scenario, where the volume of the inflowing water and the volume of the pool are not known, the ratio of evaporation over inflow (E/I) can be calculated using following reformulated equation (e.g. as by Mayr et al. (2007), Allison and Leaney (1982)). E/I is the fraction of inflowing water evaporated from a lake:

$$E/I = \left[\frac{(\delta_{\mathrm{L}} - \delta_{\mathrm{P}})}{(\delta^{*} - \delta_{\mathrm{L}}) \times m}\right] \tag{10}$$

where δ_{P} represents inflowing water and δ_{L} represents water discharged from the lake, δ^{*} is the limiting isotope enrichment factor as given above (Eq. (7)) and m is a factor defined by Eq. (9). A low value of E/I suggests that the evaporation is relatively low compared to the water inflow. For instance, E/I of 0.05 indicates that the volume of inflowing water is twenty-fold greater than the evaporative loss at the sampling point at outflow; therefore, the water retention time is short. In contrast, high values (e.g., E/I of 0.30) suggest high evaporation compared to inflow and therefore, a slow water inflow and a long retention time, as 30% of the inflowing water is evaporating. If E/I equals 1.0, this means that the evaporation equals inflow and there is no outflow from the lake, as all the inflowing water evaporates. The E/I values >1.0 suggest that evaporation is greater than inflow and that the volume of the lake decreases along with the water level; this is not a steady-state condition in a strict sense and the steady state model can be inadequate to represent the mass balance.

3. Methods

3.1. Pan evaporation experiments

Two pan evaporation experiments were designed to assess the accuracy of the C–G model in arid conditions and validate the *Hydrocalculator* calculations. For the first experiment, a normalised evaporation pan of 1.2 m diameter and surface of 1.13 m^{2} (following the Australian Bureau of Meteorology standard), was located in the northern part of Western Australia (22.6°S 117.3°E, altitude 550 m) at an automatic weather station that recorded air temperature, relative humidity, precipitation, wind speed and solar radiation. The weather station featured a Vaisala HMP45A temperature and humidity probe, a Middleton EQ08-E Solar Radiation probe, and a Rimco 8020 Tipping Bucket rain gauge. Both the pan and weather station were located at the same altitude, on an alluvial plain.

The pan evaporation experiment was replicated at different location (23.0°S 119.1°E, altitude 700 m) and at different dates (11 months after the first pan experiment). We used exactly the same procedure as during the first experiment; however, the initial volume of water was 225 L (comparing to 119 L during the first experiment) and the water level was measured in three places in each pan in order to improve precision. These results were averaged and used for calculation of volume changes. In this experiment, three pans were used, where pans A and B were exposed to sun and pan C was in shade.

The daily change in the stable isotope composition of water in the pans, along with recorded air temperature and humidity and the isotope signatures of the last substantial rainfall, were used for computation of evaporative losses between the start of the experiment and each subsequent sampling. Option #3 (see Section 2.2.3) was used to calculate the ambient air moisture using the stable isotope composition of rainfall and the slope of LEL. The δ^2H and δ^{18}O of the rain were adjusted to LEL following Eq. (3), while the adjusting parameter *x* varied between 0.83 and 0.99 for different days of the experiment.

3.2. Laboratory stable isotope analyses

The stable isotope analyses of water samples were performed using an Isotopic Liquid Water Analyser Picarro L1115-i with V1102-I vaporiser (Picarro, Santa Clara, California, USA) in West Australian Geochemistry Centre at The University of Western Australia. Each sample was analysed six times and then the first three results were discarded in order to minimize any instrument memory effect. The δ^2H and δ^{18}O raw values of samples were normalised to the VSMOW (Vienna Standard Mean Ocean Water) scale, based on three laboratory standards, each replicated twice and reported in per mil (‰) following the principles of the three-point normalisation (Skrzypek, 2013). All laboratory standards were calibrated against international reference materials that determine the VSMOW-SLAP scale (Coplen, 1996), provided by the International Atomic Energy Agency (for VSMOW2 δ^2H and δ^{18}O of equal 0‰ and for SLAP equal $\delta^2\mathrm{H} = -428.0$‰ and $\delta^{18}\mathrm{O} = -55.50$‰). The long-term analytical uncertainty (one standard deviation) was determined as 0.8‰ for δ^2H and 0.06‰ for δ^{18}O (Skrzypek and Ford 2014).

4. The *Hydrocalculator*

4.1. Description

The *Hydrocalculator* was designed based on the equations described in the Methods. *Hydrocalculator* has been produced in two forms: (1) an online web based calculator available on http://hydrocalculator.gskrzypek.com (also in Supplementary data 3); and (2) a downloadable software package for PC/Windows computers, hydrocalculator.exe file (Supplementary data 1). *Hydrocalculator* requires the user to enter data in three steps, and results are then displayed in the fourth step. The steps are:

Step 1: Selection of the hydrological regime of the studied water body: (a) non-steady-state (no inflow or outflow to the pool, the water level decreases due to progressive evaporation only) or (b) steady-state model (inflow *I* equals evaporation *E* plus outflow). The decision about the selection in this step will determine which equation (Eqs. (8) or (10)) will be used and for which model the results will be calculated (as *f* or *E*/*I*).

Step 2: Selection of the option for δ_A value determination: (1) known δ_A value based on field measurements; (2) δ_A calculated from the stable isotope composition of precipitation (δ_{Rain}) for the studied location and season; (3) δ_A calculated from δ_{Rain} and the slope of the LEL. The selection in this step will determine what data need to be used in Step 3.

Step 3: Entering analysed stable isotope composition of water (as Table 1): δ_P –initial value for water in the pool (for non-steady state) or value for water inflowing to the pool (for steady state); δ_L – final value for water in the pool (for non-steady state) or a value of outflowing water (for steady state) and measured parameters: *T* – temperature; *h* – relative humidity of air (as fraction); δ_A – the stable isotope composition of moisture in ambient air (if known); δ_{Rain} –the stable isotope composition of precipitation (if δ_A is not known); LEL – if known for the study area.

Step 4: After entering all required variables and pressing "calculate", results will be displayed as a fraction of the evaporated volume *f*, or as fraction evaporation over inflow *E*/*I*, depending on the selected model. Along with results, the intermediate parameters, calculated based on entered variables, will be listed: kinetic isotope fractionation constant – C_k; kinetic isotope fractionation factor – ε_k; equilibrium isotope fractionation factor – ε^*, total isotope fractionation – ε, fractionation factor – α, limiting isotopic composition – δ^* and parameter *m* (Table 1).

The off line version of the *Hydrocalculator* (Supplementary data 1) also allows recalculation of large data sets using batch processing.

Table 2

The calculation examples as described in Sections 4.2 and 5.2. The calculation example of *E*/*I* based on data from Canada (Bennett et al., 2008), randomly selected sample BM10 (Example B) and NE5 (Example C) and from Patagonia (Mayr et al. 2007) random sample Laguna Azul from 2002 (Example D). All δ-values given as permil ‰ in relation to VSMOW scale.

Symbol	Example A		Example B	Example C	Example D	
	Option #3 – ambient air moisture δ_A based on δ_{Rain} and adjusted versus LEL $x = 0.6957$		Option #1 – known ambient air moisture δ_A	Option #1 – known ambient air moisture δ_A	Option #1 – known ambient air moisture δ_A	
	δ^2H	δ^{18}O	δ^{18}O	δ^{18}O	δ^{18}O	
T	25.00		11.97	12.37	7.58	Measured or assumed
h	0.50		0.68	0.67	0.63	
δ_{Rain}	−21.00	−5.10	–	–	–	
δ_P	−51.60	−8.05	−18.69	−18.25	−13.40	
δ_L	−40.90	−6.41	−8.59	−11.09	−4.17	
LEL	4.59		–	–	–	
δ_A	−71.85	−11.53	−23.67	−23.47	−19.30	
ε_k	6.25	7.10	4.54	4.69	5.25	Calculated from the model
ε^+	78.75	9.35	10.53	10.49	10.98	
ε	79.25	16.36	14.97	15.07	16.11	
C_k	12.50	14.20	14.20	14.20	14.2	
α^+	1.0787	1.0093	1.01	1.01	1.01	
δ^*	102.97	21.91	−1.70	−1.00	6.44	
m	0.83	0.95	2.05	1.96	1.64	
Result	$f = 0.0827$	$f = 0.0573$	$E/I = 0.715$	$E/I = 0.363$	$E/I = 0.532$	

The input data file is prepared following the template provided (inputdata.csv included in Supplementary data 1) and all variables listed above in the steps 1, 2 and 3 need to be provided in the appropriate columns. The batch conversion will proceed after pressing opening input data file. The input file will be saved on the computer after selecting folder and file name. Please see the electronic version of this paper to download the Supplementary electronic attachment Supplementary data 1 from the publisher's website http://dx.doi.org/10.1016/j.jhydrol.2015.02.010 or from http://hydrocalculator.gskrzypek.com. The mathematical algorithm of calculation that is in-built in the binary file can be followed in MS Excel file, where all formulas and links between the variables are displayed (Supplementary data 2). The batch conversion option can be also used for assessment of an uncertainty in calculations (as presented in Section 4.2) by adding multiple scenarios covering all range of replicated analyses, variability in data using maximum and minimum values.

4.2. Example calculations of evaporation loss using Hydrocalculator

The calculator computations and user's own calculations can be tested using the equations listed above (Section 2.2.) and following the example shown in Table 2, Example A. In this example, a small water pool was sampled twice and evaporative loss was calculated for the period between sampling #1 (δ_P) and #2 (δ_L). The local weather station recorded mean air temperature (T, °C) and relative humidity (h) for the period between sampling #1 and #2. The pool is in non-steady-state conditions and there was no inflow of water to the pool from other sources. The δ_A-value of the ambient air moisture was calculated based on the stable isotope composition of local precipitation and then δ^2H and δ^{18}O were adjusted to match the established during the experiment LEL. The correction factor x was calculated by *Hydrocalculator* (method described in Section 2.2.3, option #3) following the algorithm proposed by Gibson et al. (2008) and modified by Gibson and Reid (2014). The calculated evaporative losses were equal to 8.27% based on δ^2H and 5.73% based on δ^{18}O (Table 2, Example A). This calculation example is also available as a Microsoft Excel file (Supplementary data 2) and an example inputdta.csv prepared for batch conversion calculations using the off line version (Supplementary data 1) and it is in-build in the online version of the software (Supplementary data 3). All these files are available for download as Supplementary electronic materials from the publisher's web site (http://dx.doi.org/10.1016/j.jhydrol.2015.02.010).

5. Validation and uncertainty in estimates of evaporative loss

5.1. Uncertainty in input data

The uncertainty in the calculated percent evaporative loss depends mainly on uncertainty associated with different variables used in the model (analytical uncertainty in measurement of the stable isotope composition, temperature, humidity and others). First, the stable isotope composition of water is usually analysed in a laboratory with an uncertainty of ~0.1‰ in δ^{18}O and ~1‰ δ^2H. This range of uncertainty may result in an increased difference between the values of δ_P and δ_L by up to 0.2‰ for δ^{18}O and by up to 2.0‰ for δ^2H, when the respective values for #1 and #2 sampling differ from the true values by maximum analytical uncertainty (±0.1‰ and ± 1‰). Taking into account the maximum expected uncertainty of measured δ-value, the final calculations, as for the example A given in Table 2 (option #3), will differ by up to a maximum of 0.8% (E/I) for δ^{18}O and 1.7% (E/I) for δ^2H and 0.7% (f) for δ^{18}O and 1.4% (f) for δ^2H. However, this difference depends on the relative change in δ-values resulting from evaporation and will be lower for more evaporated samples.

Table 3
The first field based pan evaporation experiment conducted in the northern part of Western Australia (22.6°S 117.3°E, altitude 550 m). For δ^2H_A calculations was used δ^2H_{Rain} = −57.95‰ and $\delta^{18}O_{Rain}$ = −9.19‰ as mean weighted stable isotope composition of the most recent cyclone Lua (precipitation 80.8 mm on 17/03/2012) and LEL 4.673 as from pan evaporation (Fig. 1A), x in the range 0.65–1.00. Calculated volumes are averages from volumes calculated using δ^2H and δ^{18}O.

Date/time	δ^{18}O (‰ VSMOW)	δ^2H (‰ VSMOW)	Water level (mm)	Water volume in pan (dm^3)	Field measured water volume loss from start (%)	T_{air} (°C), mean from start	RH (%), mean from start	Solar radiation, mean from start (W/m^2)	Calculated water volume evaporated from start, Option #3 (%)	Difference between field measurement and calculated loss. Option #3 (%)	Calculated matching moisture δ^2H_A (‰ VSMOW)	Calculated matching moisture $\delta^{18}O_A$ (‰ VSMOW)
1/5/12 08.00 start	−6.87	−50.6	105	119	0.0	–	–	–	–	–	–	–
3/5/12 06.40	−3.52	−38.8	92[a]	104	12.4	25.47	25.9	12.4	14.3	−1.9	−88	−7.6
4/5/12 07.10	−1.71	−33.3	80	90	23.8	25.31	25.9	14.5	21.0	2.8	−160	−25.1
5/5/12 06.50	−0.01	−25.6	74	84	29.5	25.28	26.2	13.7	28.0	1.5	−135	−22.4
6/5/12 06.40	1.05	−21.5	67	76	36.2	25.16	27.5	12.5	31.4	4.8	−150	−26.6
7/5/12 06.40	2.62	−13.5	63	71	40.0	24.88	31.2	11.8	36.5	3.5	−123	−21.3
8/5/12 06.45	4.33	−5.2	56	63	46.7	24.70	31.9	11.8	42.5	4.2	−120	−21.8
9/5/12 06.40	6.04	2.9	50	57	52.4	24.40	32.1	11.8	48.2	4.2	−118	−21.8
10/5/12 07.20	8.24	12.7	44	50	58.1	24.42	32.1	11.6	54.8	3.3	−113	−20.7
11/5/12 06.30	11.29	26.4	36	41	65.7	24.59	31.5	11.6	63.1	2.6	−109	−20.2
12/5/12 06.25	15.14	43.2	30	34	71.4	24.65	30.5	11.8	72.0	−0.6	−96	−17.4
13/5/12 06.00	19.46	61.9	23	26	78.1	24.68	29.5	11.9	80.0	−1.9	−92	−16.3
14/5/12 06.00	22.98	81.6	17	19	83.8	24.73	29.2	11.9	85.8	−2.0	−88	−16.8
15/5/12 06.00	26.76	100.7	13	15	87.6	24.76	29.1	11.8	90.4	−2.8	−80	−15.3
16/5/12 06.00	31.15	123.1	6	7	94.3	24.72	28.8	11.7	94.3	0.0	−100	−19.7
17/5/12 06.40	–	–	Empty	–	–	–	–	–	–	–	–	–

[a] Change over two days.

The model used in the *Hydrocalculator* is less sensitive to uncertainty in climatic variables. A difference of 1 °C in temperature (T) will result only in a difference in the calculated results of <0.1% based on both $\delta^{18}O$ and $\delta^{2}H$ (f and E/I). Even a difference of 5 °C will result in a calculation difference of ~0.4% ($\delta^{2}H$) and ~0.1% ($\delta^{18}O$) in the example given in Table 2 (Example A). A similar range of uncertainty will introduce uncertainty in h. A difference of 0.1 (RH 10%) will result in a difference in the final outcome of ~1.3% when $\delta^{2}H$ is used for calculations and ~0.4% when $\delta^{18}O$ is used.

Much higher uncertainty is associated with ambient air moisture (δ_A) or the stable isotope composition of precipitation (δ_{Rain}) used for estimation of δ_A (Gibson et al., 1993). This difference can be substantial, depending on what data are available on the climatic conditions for the study area. In extreme conditions (e.g., prolonged drought, variable air mass circulation or variable air temperature) the error may be high. An error in $\delta^{2}H_A$ estimation of 10‰, for example, will result in a difference in final calculations of a maximum of 1.4% (E/I) and 1.1% (f), respectively. On the other hand, an error in $\delta^{18}O_A$ estimation of 1.0‰, for example, will result in a difference in the final calculations of a maximum of 0.3% (E/I) and 0.2% (f), respectively (Table 2, data from example A but with option #1: change in $\delta^{2}H_A$ from −99.90 to −109.90‰ and $\delta^{18}O_A$ from −13.05 to −14.05‰).

5.2. Comparison of results computed using Hydrocalculator with pan evaporation experiments and published data

We assessed the accuracy of the C–G model in arid conditions and validated the *Hydrocalculator* calculations comparing them with field observations by two pan evaporation experiments conducted during two different seasons at two different locations (see Section 3). During the first pan experiment, the pan was filled with groundwater (TDS = 350 mg/L) that was pumped from a nearby groundwater borehole. The initial water level was measured (105 mm) and the initial volume was calculated (119 L). The water level (±0.5 mm) was measured and water samples for analyses of the stable isotope composition (2 mL each) were collected daily over 16 days until dryness (1-17/5/12; Table 3). Water evaporative losses were calculated from the observed volume change and compared with results of calculations using *Hydrocalculator*. Mean air temperature, humidity and solar radiation for the period from the start of experiment and time of the sampling were calculated based on data from the local weather station. The stable isotope composition of ambient air moisture was not measured on site, but was estimated based on the most recent large volume rainfall as a result of a cyclone occurring 45 days prior the pan evaporation experiment (Cyclone Lua 17/03/2012). The mean weighted stable isotope composition of precipitation during Cyclone Lua was $\delta^{2}H = -57.95‰$ and $\delta^{18}O = -9.19‰$ (collected rainwater sample representing whole precipitation event). The experiment was conducted in very dry conditions (RH 26–32%). The last rain had occurred 24 days prior the start of the experiment (2.4 mm on 6/04/2012). The last substantial rain had occurred in March (cyclone Lua 80.60 mm). Between Lua and the experiment, only eight scattered showers were observed for a total rainfall of 17.2 mm. However, these were very small events and the water evaporated completely shortly after rainfall; the largest rainfall was 6.2 mm and the smallest was 0.2 mm.

Pan water level decreased by 4–12 mm per day. On day nine, the water level lowered from initial 105 mm to 50 mm; i.e., 52.4% of the water volume evaporated. The pan was dry on day 17. A robust correlation was observed between $\delta^{2}H$ and $\delta^{18}O$, allowing the establishment of a new LEL for the time and place of the experiment (slope 4.67, Fig. 1A). This slope is similar to the regional slope of LEL established based on whole year data set from 189 observations of various pools in the region (slope

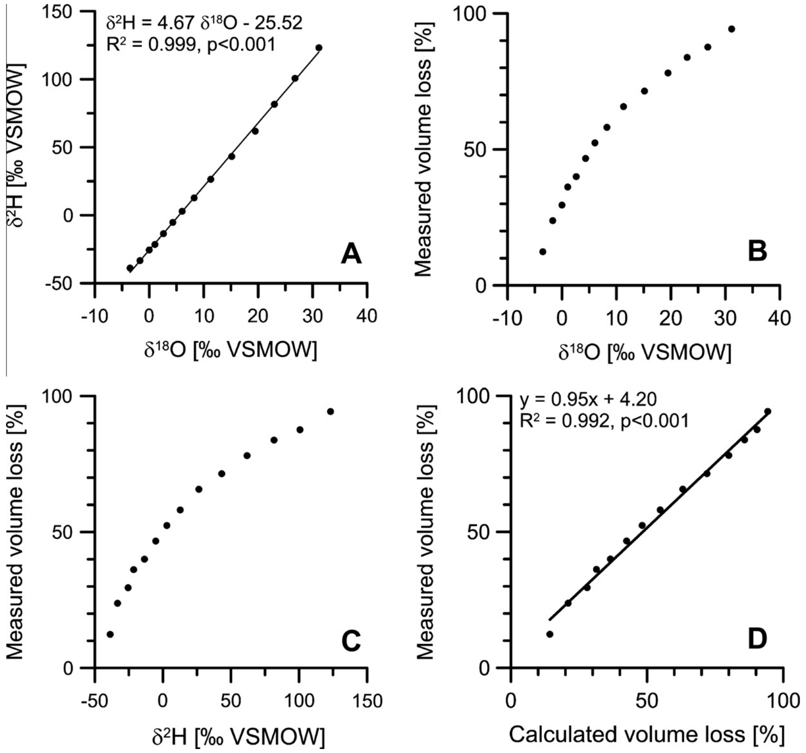

Fig. 1. Results of the first pan evaporation experiment conducted in Western Australia (22.6°S 117.3°E, altitude 550 m), mean daily temperature 24.7 °C and relative humidity 28.8%. (A) Local Evaporation Line (LEL) for pan experiment; (B and C) progressive increase in $\delta^{18}O$ and $\delta^{2}H$ following progressive evaporation; (D) correlation between field measured and calculated using *Hydrocalculator* volume losses.

5.16; Dogramaci et al., 2012). The stable isotope composition of water became subsequently more positive as the evaporation progressed (Fig. 1B and C).

We compared the volume losses observed in the field based on the water level changes with results calculated using *Hydrocalculator* (Table 3). The mean evaporative loss based on changes in the water stable isotope composition (mean change calculated from δ^2H and δ^{18}O) and the observed volume change are in good agreement with calculations based on water level observations ($R^2 = 0.992$, $p < 0.001$, Fig. 1D). For computation option #3 (Section 2.2.3.), the differences between calculated and observed evaporative loss were between 0.0% and 4.8%, and 1.3% on average.

As discussed above, the estimation of δ_A is the largest source of potential uncertainty in the calculations. In our calculation, just one average δ_A value was used for calculation for all sampling days over two weeks. However, in reality, δ_A may vary daily. According to our onsite weather monitoring, the mean temperature between samplings was quite constant, at between 24.8 °C and 25.5 °C, but the relative humidity varied from 25.9% and 29.4%. Therefore, we may also expect some variations in δ_A. Using calculation option #1, we reversely calculated the δ_A value required in order to match the calculated evaporative losses with those observed in the field (Table 3). These results show that δ_A may have wide range of δ^2H_A values, from −80 to −160‰ and $\delta^{18}O_A$ from −7.6 to −26.6‰. The most negative δ_A value was calculated for and after days with the highest solar radiation. However, more detailed studies are required to explain the mechanism causing these changes.

The pan evaporation experiment was replicated at different location 11 months after first pan experiment following the same principles and calculation algorithm; Table 4). The maximum difference between observed and calculated evaporative losses was 3.1% (Table 4). The difference in calculated evaporative loss between the two pans exposed to sun (A and B) was not larger than 2.3%. The experiment was stopped after evaporation of half of water volume. At the end of the experiment the water volume in the shaded pan was 0.6% and 1.6% less evaporated compared to the pans exposed to direct sunlight. The smaller difference between observed and calculated evaporative loss (<3.1%) during this second experiment reflects the more precise measurements of water levels in pans (mean level based on measurements in three places on each pan).

The pan evaporation experiments allowed verification of the performance of the *Hydrocalculator* for calculation of *f* only (non-steady state conditions). To verify the uncertainty in the calculation of *E*/*I* (steady state conditions) we thus sought to use published data to verify the calculation of *E*/*I*. We used the data set for Canadian lakes (Bennett et al. 2008) for validation of *Hydrocalculator* estimates of *E*/*I*, as this study is one of the few that provided all the required parameters required for replication of calculations. The results of our calculations along with the input data from Bennett et al. (2008) are presented in Table 2 (Example B and C) and compared with their

Table 4

The second field based pan evaporation experiment conducted in the northern part of Western Australia (23.0°S 119.1°E, altitude 700 m), pan parameters as in first experiment. For δ^2H_A calculations was used $\delta^2H_{Rain} = -54.4‰$ and $\delta^{18}O_{Rain} = -9.15‰$ as mean weighted stable isotope composition of the precipitation in January 2012 (cyclone Heidi, total precipitation 221 mm) and LEL 4.0967 as from the pan evaporation A, $x = 1$. Calculated volumes are averages from volumes calculated using δ^2H and δ^{18}O.

	Apr 2013	Time	δ^{18}O [‰ VSMOW]	δ^2H [‰ VSMOW]	Field measured water volume loss – from start (%)	T_{air} (°C) mean from start	RH (%) mean from start	Calculated water volume loss, Option #3 (%)	Difference measurement and calculated loss (%)
Pan A – in sun	15	12:00	−8.44	−56.1	0.0	29.76	19.32	–	–
	16	7:15	−7.18	−51.9	3.8	30.04	19.15	5.5	−1.7
	17	7:15	−6.04	−47.1	10.2	30.00	19.59	10.8	−0.6
	18	7:15	−4.70	−42.4	15.0	29.98	20.42	16.2	−1.2
	19	7:15	−3.79	−39.4	20.3	29.77	21.96	19.6	0.7
	20	7:15	−2.50	−33.4	25.1	29.64	22.66	25.2	−0.1
	21	7:15	−1.47	−29.0	30.5	29.42	23.34	29.3	1.2
	22	7:15	−0.05	−24.6	34.8	29.08	23.55	33.8	1.0
	23	7:15	1.02	−18.4	40.4	28.92	23.35	38.2	2.2
	24	7:15	2.95	−11.6	45.7	28.74	23.35	44.0	1.7
	25	7:45	4.68	−3.1	50.8	28.56	23.96	49.8	1.0
	26	6:45	6.41	3.6	56.1	28.22	25.87	54.9	1.2
Pan B – in sun	15	12:00	−8.46	−55.1	0.0	29.76	19.32	–	–
	16	7:15	−7.22	−51.8	4.3	30.04	19.15	4.9	−0.6
	17	7:15	−5.96	−48.1	10.3	30.00	19.59	9.8	0.5
	18	7:15	−5.24	−43.7	13.3	29.98	20.42	13.9	−0.6
	19	7:15	−4.07	−39.4	19.6	29.77	21.96	18.6	1.0
	20	7:15	−2.83	−33.9	24.6	29.64	22.66	23.9	0.7
	21	7:15	−1.68	−30.0	29.6	29.42	23.34	28.0	1.6
	22	7:15	−0.47	−24.4	34.2	29.08	23.55	32.7	1.5
	23	7:15	1.19	−18.1	39.7	28.92	23.35	38.3	1.4
	24	7:15	2.71	−13.5	45.2	28.74	23.35	42.5	2.7
	25	7:45	4.39	−4.1	51.8	28.56	23.96	48.7	3.1
	26	6:45	6.12	2.9	55.3	28.22	25.87	54.0	1.3
Pan C – in shade	15	12:00	−8.23	−56.8	0.0	29.76	19.32	–	–
	16	7:15	−7.14	−52.0	5.0	30.04	19.15	5.5	−0.5
	17	7:15	−5.96	−47.3	9.0	30.00	19.59	10.8	−1.8
	18	7:15	−5.29	−43.5	13.8	29.98	20.42	14.4	−0.6
	19	7:15	−4.12	−39.9	18.8	29.77	21.96	18.7	0.1
	20	7:15	−3.22	−35.8	22.5	29.64	22.66	22.6	−0.1
	21	7:15	−1.87	−31.0	27.5	29.42	23.34	27.6	0.0
	22	7:15	−0.89	−25.5	32.5	29.08	23.55	31.9	0.6
	23	7:15	0.92	−19.0	37.5	28.92	23.35	37.8	−0.3
	24	7:15	2.04	−14.2	43.0	28.74	23.35	41.5	1.5
	25	7:45	4.03	−6.4	47.5	28.56	23.96	47.6	−0.1
	26	6:45	5.39	0.7	52.8	28.22	25.87	52.4	0.4

results as presented in their original paper). We found no significant difference between the calculated *E/I* of 71.5% (using option #1 in our calculator) and reported by Bennett et al. (2008) evaporative loss of 70.9% for the randomly selected sample BM10. Similarly the *E/I* value for the sample NE5 was calculated as 36.3% comparing to 36.0% reported by Bennett et al. (2008). We also did not observe significant difference comparing our calculation result (53.2%) using original input data from Patagonia (sample Laguna Azul 2002) with original calculations by Mayr et al., 2007 (53.0%). While small differences likely arise from mathematical rounding and small differences in calculation algorithm, the agreement between approaches in the estimates of evaporative loss indicate that *Hydrocalculator* estimates are robust at least under these study conditions. Additional validation of the *Hydrocalculator* across a broader range of conditions would require verification of the Craig–Gordon model under different climate scenarios. Unfortunately, there is a dearth of studies that have reported all the parameters required for replication of calculations. Ideally, several pan experiments should be to conducted under different climatic conditions and then this experimental result compared with the theoretically calculated values using *Hydrocalculator*.

6. Conclusions

Hydrocalculator provides a robust tool to estimate evaporative loss and it is a very useful in providing a quick and cost-effective insight into the water balance of surface water pools. The algorithm used returned results for evaporative loss in the range of calculated analytical uncertainty when compared to measured data, confirming the validity of our approach and the correctness of the used mathematical algorithm. Results computed using our *Hydrocalculator* are also in good agreement with results from field-based pan evaporation experiments and other published data (Bennett et al., 2008). The use of δ^{18}O in the model returns more accurate data than does the use of δ^{2}H. The major source of uncertainty in water loss calculations is the estimation of the stable isotope composition of the moisture in ambient air; therefore, this parameter should be directly measured in the field. Alternatively (and probably more practically) the isotope composition of precipitation should be monitored and a local evaporation line established.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhydrol.2015.02.010.

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