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Determination of groundwater discharge rates and water residence time of groundwater-fed lakes by stable isotopes of water (¹⁸O, ²H) and radon (²²²Rn) mass balances

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Abstract: Lacustrine groundwater discharge (LGD) and the related water residence time are crucial parameters for quantifying lake matter budgets and assessing its vulnerability to contaminant input. Our approach utilizes the stable isotopes of water ($\delta^{18}O, \delta^{2}H$) and the radioisotope radon (²²²Rn) for determining long-term average and short-term snapshots in LGD. We conducted isotope balances for the 0.5 km² Lake Ammelshainer See (Germany) based on measurements of lake isotope inventories and groundwater composition accompanied by good quality and comprehensive long-term meteorological and isotopic data (precipitation) from nearby monitoring stations. The results from the steady-state annual isotope balances that rely on only two sampling campaigns are consistent for both δ^{18} O and δ^{2} H and suggested an overall long-term average LGD rate which was used to infer the water residence time of the lake. These findings were supported by the good agreement of the simulated LGD driven annual cycles of δ^{18} O and δ^{2} H lake inventories with the observed lake isotope inventories. However, radon mass balances revealed lower values which might be the result of seasonal LGD variability. For obtaining further insights into possible seasonal variability of groundwater-lake interaction, stable water isotope and radon mass balances could be conducted more frequently (e.g., monthly) in order to use the derived groundwater discharge rates as input for time-variant isotope balances.

Key words: groundwater discharge, isotope balance, stable isotopes of water, radon, groundwater-lake interaction, water residence time, water balance

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1. Introduction

Lakes provide a wide range of ecosystem services such as a habitat for freshwater species, climate change mitigation, sediment and nutrient retention and processing as well as hydrological regulation (Schallenberg et al., 2013). Hence, lakes represent valuable aquatic ecosystems, which are exposed to various anthropogenic pressures related to human demands such as recreation, fisheries or water abstraction. The lakes ecosystem health and the fulfilment of user's demands are highly dependent on its water quality, which is directly linked to the quality of discharging waters and the water residence time within the lake. Groundwater discharge into lakes or lacustrine groundwater discharge (LGD) is often neglected in lake water balances due to difficulties in its determination. However, several authors have shown that LGD may dominate the water balance both for lakes with (e.g., Rosenberry and Winter, 2009; Kidmose et al., 2013) and without (e.g., Stets et al., 2010; Zhou et al., 2013) surface water inlets or outlets. Consequently, LGD may also play a crucial role in the lakes geochemical budgets, e.g., due to the input of nutrients (Nakayama and Watanabe, 2008) or of sulphate and iron into post-mining lakes ('acid mine drainage' (Knöller and Strauch, 2002; Knöller et al., 2004)), both of which represent a serious problem for lake water quality. Another key factor for lake water quality is its residence time. This parameter is a determinant of ecological health since water residence time governs the exposure time to chemical substances introduced into the lake. For instance, longer water residence times may favor the growth of harmful cyanobacteria (Romo et al., 2013).

Several methods for determining LGD exist including watershed-scale studies, lake-water budgets, combined lake-water and chemical budgets, well and flow-net analysis, groundwater flow modelling, tracer studies, thermal methods, seepage meters and biological indicators (Rosenberry *et al.*, 2015). Several authors calculated discharge rates from hydraulic gradients between lake and groundwater and hydraulic properties of the aquifer and lake bed sediments (Kishel and Gerla, 2002; Rudnick *et al.*, 2015). A major difficulty of this approach is that the results depend on small differences of hydraulic heads and small-scale variations of the hydraulic conductivity which may fall in the range of measurement uncertainty. Numerical groundwater flow modelling (Wollschläger *et al.*, 2007) requires high quality a priori information that might not be available in many cases. The only approach for direct measurement of LGD are seepage meters (Rosenberry *et al.*, 2008). While providing precise point-scale information a general drawback of seepage meters is that they may not be spatially representative since LGD is known to be highly heterogeneous in many lakes. Whereas, direct measurements are limited to specific areas or lakeshore sections, mapping of geochemical tracers allow obtaining an integrated signal of the entire water body.

Stable isotopes of water (Krabbenhoft *et al.*, 1990; Knöller and Strauch, 2002; Knöller *et al.*, 2004; Hofmann *et al.*, 2008; Gibson *et al.*, 2016a; Gibson *et al.*, 2016b) and the radioisotope radon (Corbett *et al.*, 1997; Schmidt *et al.*, 2008; Dimova and Burnett, 2011) or a combination of both (Schmidt *et al.*, 2009; Arnoux *et al.*, 2017a; 2017b) are well-established in groundwater-lake interaction studies. For instance, Luo *et al.* (2016) and Dimova and Burnett (2011) reported on significant temporal variation of LGD on a multi-day timescale based on radon for a Chinese desert lakes and small lakes in central Florida (United States), respectively. Kluge *et al.* (2012) and Dimova *et al.* (2013) demonstrated LGD variability also on a sea-

sonal time-scale. Arnoux *et al.* (2017a), applied both radon and stable isotopes to determine intra-annual LGD variability into a small glacial lake in Quebec (Canada).

Stable isotope based LGD estimates are highly dependent on the relative air humidity and the isotopic composition of the atmospheric vapour and the evaporate (Knöller and Strauch, 2002; Hofmann *et al.*, 2008; Arnoux *et al.*, 2017a). Radon based estimates depend mainly on the radon concentration of the groundwater end-member as well as on the quantification of atmospheric radon losses and diffusive radon inputs (Dimova and Burnett, 2011; Arnoux *et al.*, 2017a). All of these parameters are prone to error. However, simultaneous use of stable water isotopes and radon decreases the uncertainty of LGD rate estimates as well as of the corresponding water residence time. We want to emphasize that both methods indicate LGD rates at different time scales. While the mean stable water isotope inventory reflects the average conditions during the entire water residence time (usually months to several years), radon based approaches rather reflect a snapshot of LGD rate representing a period of maximum of 20 days (five ²²²Rn half-lives, $t_{1/2}=3.8$ d).

In the presented study we determined LGD and derived water residence times for the 0.5 km² groundwater-fed Lake Ammelshainer See (Germany) based on field observations of the stable water isotopes (¹⁸O, ²H) and the radionuclide radon (²²²Rn). Both approaches utilize gradients of these tracers between groundwater and lake water and rely on additional climatic and isotopic information. This study demonstrates the potential of combined $\delta^{18}O / \delta^{2}H$ and Rn mass balances to study LGD at different time-scales. The key issue of this study is to demonstrate the power of stable isotope techniques for estimating the long-term mean LGD rate and the corresponding water residence time of groundwater-fed lakes based on a relatively small amount of field data (lake isotope inventories and groundwater isotope composition) accompanied by good quality and comprehensive long-term meteorological and isotopic data (precipitation) from nearby monitoring stations. This approach requires the determination of the mean stable water isotope inventory of the lake as well as the estimation of the stable isotope signature of the evaporate using the stable isotope signatures of lake, groundwater and precipitation. The combination of the estimated LGD rate with the meteorological and isotopic data allows the simulation of the annual cycle of the lakes stable water isotope inventory which can subsequently be compared to the observations of the lake inventory at specific dates, The additional application of a radon mass balance illustrates the potential for determining LGD rates at temporal snapshots which supports the study of temporal LGD variability.

2. Material and methods

2.1 Theoretical background

2.1.1 Water balance of groundwater-fed lakes

Groundwater-fed lakes (or "through-flow" lakes) gain water, aside from direct precipitation on the lake, by continous discharge of groundwater into the lake, which is balanced by a combination of evaporation and water exfiltration, i.e. outflow into the aquifer (Gibson *et al.*, 2002). In absence of noteworthy surficial in- and outflows the hydrological balance can be written as

$$\frac{\partial V}{\partial t} = P + G_i - E - G_o \tag{Eq. 1}$$

where V is the volume of the lake, t is time, P is precipitation, G_i is LGD, E is evaporation and G_0 is groundwater outflow.

2.1.2 Water residence time of lakes

We recognised some confusion regarding the definition of residence time in the literature, which inhibits direct comparability of residence time estimates and is, thus, impeding the vulnerability assessment. Some authors use the water discharge rate (Knöller and Strauch, 2002; Gibson *et al.*, 2016a) or the groundwater outflow rate plus evaporation for residence time calculation; other authors use the water outflow while excluding evaporation (Hofmann *et al.*, 2008). As pointed out by Quinn (1992) evaporation is indeed an outflow term regarding water molecules but it does not remove conservative dissolved substances from a lake. Whereas the first approach for calculating the residence time refers to a parcel of water, the latter refers to a conservative substance. In this study, we follow the latter definition since it presents the more conservative approach in terms of vulnerability assessment. The mean residence time of water (τ) can be calculated from eq. 2 assuming a well-mixed lake.

$$\tau = \frac{V}{c_o}$$
(Eq. 2)

2.1.3 Stable isotope mass balance

The use of δ^{18} O and δ^{2} H for determining LGD, groundwater outflow and lake water residence time is based on an isotope mass balance (IMB). For that purpose, the isotope compositions of all components of the lakes water balance are required with δ_L , δ_P , δ_{Gi} , δ_{Go} and δ_E being the isotope composition of the lake, the precipitation, the discharging groundwater, the exfiltrating water and the evaporation, respectively.

The annual IMB (Eq. 3) follows Eq. 1 under the assumption of constant lake volume over time.

$$P\delta_p + G_i\delta_{G_i} = E\delta_E + G_o\delta_{G_o}$$
(Eq. 3)

While assuming the IMB in inter-annual steady state, seasonal fluctuations of δ_L as a result of temporal variable LGD and groundwater outflow rates and their respective isotope composition are considered (Eq. 4). Following Eq. 4 the dynamic IMB for a well-mixed lake can be written as

$$\delta_{L_{t+1}} = \delta_{L_t} + \frac{[P_t \delta_{P_t} + G_i \delta_{G_i} - E_t \delta_{E_t} - G_o \delta_{G_o}]}{V}$$
(Eq. 4)

By assuming a quasi-steady state, i.e. a constant seasonal cycle, eq. 4 can be re-arranged and solved for G_i or G_0 . While δ_L , δ_P and δ_{Gi} can be directly measured, δ_{Go} is usually assumed to equal δ_L . In contrast δ_E cannot be easily measured. However, since evaporation is the process that dominates the evolution of isotope composition of a lake its accurate estimation is crucial for the precision of water balances. δ_E is calculated (Eq. 5) using the linear resistance model of Craig and Gordon (1965) which describes δ_E as a function of relative humidity, air temperature, the isotopic compositions of the lakes surface (δ_{Ls}) and the atmospheric moisture

 (δ_A) . The isotopic composition of δ_{Ls} was parameterized semi-quantitatively by assuming an annual cycle with maximum isotopic enrichment at the end of the evaporation season in September and minimum enrichment in winter (Supplementary data S1). For parameterization we utilized the observations of lake surface water in June and September assuming roughly linear enrichment rates during July and August. The isotopic signature at the lake surface for the remaining months October to May were estimated loosely based on the observed annual amplitudes for lakes in the investigated region with most negative values during winter (Knöller and Strauch, 2002; Hofmann *et al.*, 2008; Seebach *et al.*, 2008).

$$\delta_E = \frac{\frac{\delta_{L_S} - \varepsilon^+}{\alpha^+} - h \,\delta_A - \varepsilon_K}{1 - h + 10^{-3} \varepsilon_K} \tag{Eq. 5}$$

The variables in Eq. 5 are the equilibrium isotopic separation ε^+ (temperature dependent), the equilibrium isotopic fraction factor α^+ (temperature dependent), the kinetic isotopic separation ε_K (humidity dependent) and the relative humidity h [-]. A detailed description of all calculations required for the IMB can be found elsewhere (e.g., Gibson *et al.*, 2016a).

 δ_A can either be measured or estimated from δ_P and air temperature. Gibson *et al.* (2016a) introduced the seasonality factor k [-], which compensates for the effect of seasonality on isotopic fractionation during the evaporation process. This compensation is required since δ_A is usually not in equilibrium with δ_P throughout the year in seasonal climates. The seasonality factor k ranges from 0.5 for highly seasonal climates to 1 for non-seasonal climates and is estimated by dual analysis of $\delta^2 H$ and $\delta^{18} O$. For that purpose, the mean annual evaporation flux weighted δ_A is adjusted (by optimizing k) to fit δ_E (Eq. 6) to the local evaporation line (Gat, 2000).

$$\delta_A = \frac{\delta_P - k \,\varepsilon^+}{1 + 10^{-3} \,k \,\varepsilon^+} \tag{Eq. 6}$$

2.1.4 Radon mass balance

Radon mass balances (RMB) assume equilibrium over time between radon (222 Rn) inputs and Rn losses and are a common approach for determining LGD rates to surface water bodies such as lakes, rivers or the sea (Burnett and Dulaiova, 2003; Schmidt *et al.*, 2008; Dimova and Burnett, 2011; Gilfedder *et al.*, 2015). After accounting for all radon sources and sinks within the considered system the residual Rn flux [Bq m⁻² d⁻¹] that is required for mass balancing is attributed to LGD. Finally, for conversion of Rn flux to water discharge [m³ d⁻¹] the resulting groundwater-borne Rn flux (F_{GWi}) is divided by the Rn concentration of groundwater [Bq m⁻³]. Our RMB is defined as follows:

$$F_{GW_i}[Bq \ m^{-2}d^{-1}] = F_{dec} + F_{atm} - F_{dif} - F_{prod}$$
(Eq. 7)

Rn decay flux (F_{dec}) solely depends on the Rn inventory of the lake and the Rn decay constant ($\lambda_{Rn} = 2.098 * 10^{-6} \text{ s}^{-1}$). The atmospheric Rn Flux (F_{atm} , eq. 8) or Rn evasion [Bq m⁻³] is driven by the Rn concentration gradient between lake surface water (Rn_s) and air (Rn_{air}) and the wind speed [m s⁻¹], which acts as a proxy for the turbulence in the surface layer. In Eq. 8 the term a [-] refers to the Rn partitioning coefficient between water and air (Schubert *et al.*, 2012) and K [m d⁻¹] is the Rn transfer velocity (MacIntyre *et al.*, 1995).

$$F_{atm_t} \left[Bq \ m^{-2}d^{-1} \right] = (Rn_s - a * Rn_{air}) * K$$
 (Eq. 8)

As a consequence of wind speed variability F_{atm_t} [Bq m⁻² d⁻¹] is temporally highly dynamic. Moreover, the effect of Rn degassing on the Rn inventory of a water body is not only a result of the wind speed intensity during sampling but also during the days prior to sampling. This is the result of the systems 'memory effect' regarding Rn degassing. If Rn is removed from a water body after an intense storm event, several days with 'normal' wind conditions are required to build up the pre-storm inventory. To account for this 'memory effect' we considered not only the wind speed on the day of measurement but also during the days prior to measurement. Therefore we calculated F_{atm} (Eqs. 8 and 9) for a period of 10 d prior to sampling by introducing a weighting factor w_t that reflects the effect of an evasion event prior to sampling on the observed Rn inventory.

$$w_t \left[-\right] = e^{-\lambda_{Rn} * t} \tag{Eq. 9}$$

$$F_{atm} \left[Bq \ m^{-2} d^{-1} \right] = \frac{\sum_{t=0}^{t_{max}} \left[w_t * F_{atmt} \right]}{\sum_{t=0}^{t_{max}} w_t}$$
(Eq. 10)

The weighting factor was parameterized utilizing the Rn decay rate, which is expected to be the primary driver of the systems 'memory effect'. Since MacIntyre *et al.* (1995) stated a coefficient of determination of 0.66 for their gas flux model, we derived an uncertainty of 34 % for F_{atm} calculations.

The diffusive Rn flux (F_{dif} , eq. 11) is governed by the Rn concentration gradient between lake bottom water (Rn_L) and bottom sediment pore water (Rn_{PW}). F_{dif} was calculated from a depth-independent model introduced by Martens *et al.* (1980) where n [-] is porosity and D [m² s⁻¹] is the diffusion coefficient of Rn in water.

$$F_{dif} [Bq \ m^{-2}d^{-1}] = \sqrt{n * D * \lambda_{Rn}} * (Rn_{PW} - Rn_L) * 86400 \text{ s}$$
(Eq. 11)

After solving the RMB, GW_i [m d⁻¹] is derived by dividing F_{GWi} [Bq m⁻² d⁻¹] by the representative Rn concentration in groundwater (radon end-member) [Bq m⁻³].

2.2 Study site

Lake Ammelshainer See (51.296692 °N, 12.608284 °E) was chosen as a study site because of the absence of any surface water inflow or outflow. Due to its proximity to Leipzig (Saxony, Germany) (Fig. 1A) where continuous monitoring of stable isotope composition in precipitation is conducted these data can be assumed as representative for the precipitation falling on the lake. Therefore, additional measurements of stable isotopes in precipitation are not required.

Lake Ammelshainer See is an artificial lake (former gravel pit) with an area of 0.54 km² that is located 20 km east of Leipzig. The lake is situated in a lowland landscape characterized by Tertiary and Quaternary sand and gravel sediments. Lake Ammelshainer See has a mean depth of 12 m and maximum depth of 28 m resulting in a volume of 6.7×10^6 m³. The regional groundwater flow direction is not uniform in the vicinity of the lake according to groundwater contour analysis (Fig. 1B). LGD is expected at the northern and eastern shore.

Schmidt *et al.* (2008) described the lake as dimictic with a well-mixed water body in spring and autumn and thermal stratification during summer and winter. Groundwater wells in a 5 km radius around Lake Ammelshainer See (Saxonian State Office for the Environment, Agriculture and Geology, 2016) reveal a typical seasonal cycle of groundwater level fluctuations with lowest groundwater levels between September and November and highest groundwater levels from March to April with an average annual amplitude of ~ 40 cm.

The lake is hydraulically well-connected to a phreatic aquifer with a thickness of 20 m. The mean annual air temperature is 10.0 ± 0.7 °C (reference period 2000 - 2015), annual precipitation is 617 ± 98 mm (reference period 2000 - 2015) and annual potential evaporation is 682 ± 35 mm (reference period 2001-2010) with \pm indicating the interannual variability (1 standard deviation).

Figure 1

2.3 Sampling design

Sampling campaigns were conducted on 3 June 2015, 9 June 2016 and 22 September 2016. In June 2015 the Rn concentration distribution at the lake surface was mapped, Rn depth profiles were measured and stable isotope sampling at the lake surface was conducted at multiple locations. In June 2016 and September 2016 sampling focused on two depth profiles of stable water isotopes. In September 2016 two Rn depth profiles were additionally measured at the same locations. Groundwater was sampled from a well tapping the uppermost unconfined aquifer which is located less than 100 m south of the lake in the up-gradient area. The well is filtered from a depth of 7.8 m; the groundwater level was 3.4 m below the surface during sampling.

2.4 Analytical techniques

2.4.1 Stable water isotopes

Samples for the analysis of oxygen and hydrogen in water were filtered through a 0.2 μ m syringe filter and filled into gas-tight 1.5 mL glass vials. Stable isotope analyses of ¹⁸O and ²H were carried out using laser cavity ring-down spectroscopy (Picarro L2120-i, Santa Clara, USA) without further treatment of the water samples. The isotope ratios of ¹⁸O/¹⁶O and ²H/¹H are conventionally expressed in delta notations of their relative abundances as deviations in per mil (‰) from the Vienna Standard Mean Ocean Water (VSMOW). Samples were normalized to the VSMOW scale using replicate analysis of internal standards calibrated to VSMOW and SLAP certified reference materials. The analytical uncertainty of the δ^{18} O measurement is ± 0.1 ‰, for hydrogen isotope analyses, an analytical error of ± 0.8 ‰ has to be considered.

2.4.2 Radon

The Rn concentration of lake water was measured employing two on-site mobile Rn-in-air monitors AlphaGuard PQ 2000 (Saphymo) which were operated in parallel following Schubert *et al.* (2006) while the Rn concentration of groundwater samples was measured using the mobile Rn-in-air monitor RAD 7 (Durridge Company). The Rn mapping on lake was executed by boat cruises. For both, lake water and groundwater, Rn was measured from a

permanent water pump stream (water flow rate of 2 1 min⁻¹) which was connected to a Rn extraction unit (MiniModule® by Membrana GmbH, Germany) where Rn equilibrates between water pump stream and a closed air loop as a consequence of temperature dependent Rn partitioning between water and air (Schubert *et al.*, 2012). Each sample of the depth profile was measured for 30-40 min after water-air equilibration to obtain at least three replicate measurements at each depth (counting cycle 10 min). Groundwater samples were measured for 30-40 min (counting cycle 5 min) after water-air equilibration to obtain at least six replicate measurements. Equilibration times were ~ 10 min for the AlphaGuard and ~ 40 min for the RAD7.

2.5 Climate, groundwater and isotope data

Data of air temperature, precipitation and relative humidity (German Weather Service, 2016) was derived from for nearby stations Leipzig-Holzhausen (10 km west) and Oschatz (35 km east). Relative humidity, precipitation rate and air temperature for Lake Ammelshainer See was derived from the arithmetic mean of the monthly means of both stations for the reference period 2000-2015. Monthly averages of relative humidity range from 0.68 (April to July) to 0.85 (November to December), monthly air temperatures range from 0.9 °C (January) to 19.5 °C (July) and precipitation rates range from 31 mm (February and April) to 86 mm (July). Potential evaporation was calculated by the Turc-Wendling method by Saxonian State Office for the Environment (2016). Data were derived for the period 2001-2010. Equivalently, potential evaporation from Lake Ammelshainer See was calculated as arithmetic mean of stations Leipzig-Holzhausen and Oschatz. Potential evaporation peaks in July (114 mm) and is lowest in December (11 mm).

Stable isotope signatures of water in precipitation are measured continuously at the Helmholtz Centre for Environmental research (UFZ) in Leipzig. Data of monthly means were available for the period from 2012 to 2014. The isotopic composition has a clear seasonal pattern with a range from -11.1 ‰ (January) to -5.2 ‰ (June) and -78.2 ‰ (January) to -35.1 ‰ (August) for δ^{18} O and δ^{2} H, respectively. The amount weighted mean annual composition of precipitation for this period was -8.4 ‰ for δ^{18} O and -58.7 ‰ for δ^{2} H.

3. Results

3.1 Water depth profiles

Depth profiles of Rn, δ^{18} O and δ^{2} H were measured to determine the isotope inventories of the lake. In addition, temperature was measured and deuterium excess, as an indicator for evaporation (Gat, 2000), was calculated. Temperature data indicate higher temperatures in the upper part of the lake for June 2016 (17.5 °C) and September 2016 (18.8 °C). Temperatures in deep lake waters were virtually the same in September and June (~8.5 °C) and reflect roughly the mean annual air and groundwater temperature. Rn data were measured in June 2015 and June 2016, i.e. at the same seasonal stage of the year. The mean Rn concentration at the lake surface was 31 Bq m⁻³ in both years. Highest Rn concentrations were observed for the deepest samples for both sampling periods. Due to low concentrations and the small number of replicate measurements analytical uncertainty is comparably high. However, a tendency of

higher Rn concentrations with increasing water depth is suggested for both sampling periods. Data on δ^{18} O and δ^{2} H reveal similar patterns for both sampling periods: an enrichment of heavier isotopes in the upper layer (down to 4-5 m in June 2016 and to 7-8 m in September 2016) and a relatively constant isotopic composition below that layer. The depth of the isotopic boundary layer correlates well with the thermocline depth. Below a depth of 8 m isotopic values were found to be -3.7 ‰ to -3.6 ‰ for δ^{18} O and ~ -35.5 ‰ for δ^{2} H without significant variation with depth. In the upper layer a clear difference between June and September was recognized for both isotopes. The values were -3.4 ‰ (June) / -2.8 ‰ (September) and – 34.5 ‰ (June) / - 32.0 ‰ (September) for δ^{18} O and δ^{2} H, respectively. The more pronounced deuterium excess (D excess [‰] = δ^{2} H – 8 * δ^{18} O) in the surface layer underpins the causal relationship between isotopic enrichment and evaporation (Gat, 2000).

Figure 2

3.2 Lake isotope inventory

In order to obtain representative lake isotope inventories, the isotope depth profiles were weighted according to the lake bathymetry. In a first step, a non-linear asymptotic regression model was fitted to Rn data and a non-linear regression model which was adopted from membrane separation techniques was fitted to stable water isotope data (Fig. 2). These models provided continuous isotope-depth relationships for all locations. The resulting non-linear regression models for Rn data (Eq. 12) and for stable water isotopes (Eq. 13) had the variable z [m], representing the water depth, and the coefficients a, b, c and d which were fitted to the observed data.

Rn = a + b *
$$e^{c*z}$$
 (Eq. 12)
 δ^{18} 0; δ^{2} H = $[a + b * 10^{(c+d*z)}]/[1 + 10^{(c+d*z)}]$ (Eq. 13)

Subsequently, isotope values were calculated for each water depth of Lake Ammelshainer See. Then, bathymetry was analyzed using ArcGIS to obtain the volumetric contribution to lake water of each water depth layer (1 m resolution). For example, the water layer ranging from 0 to 1 m depth comprises 8.2 % of the lakes water, the layer from 1 to 2 m depth 7.6 %, the layer form 27 to 28 m < 0.1 % etc.. By linking isotope depth profiles with bathymetric analysis we were able to compute the depth weighted isotope inventory of the lake. Following this procedure the lake inventories were calculated with -3.59 ‰ and -3.23 ‰ for δ^{18} O as well as -35.0 ‰ and -33.9 ‰ for δ^{2} H in June 2016 and September 2016, respectively. Mean Rn concentration were 33.6 Bq m⁻³ in June 2015 and 28.9 Bq m⁻³ in September 2016 (Tab. I) which results in lake inventories of 395 and 340 Bq m⁻² for June 2015 and September 2016, respectively.

3.3 Isotope composition in groundwater

The mean composition of δ^{18} O and δ^{2} H (n=4) in groundwater was -8.25 ± 0.1 ‰ and -59.4 ± 1.0 ‰, respectively. Radon concentration was 18,900 ± 500 Bq m⁻³ (n=2). Variations of both stable water isotopes and Rn were within the analytical uncertainty.

3.4 δ^{18} O and δ^{2} H of the evaporate

The isotopic composition of lake evaporate was estimated by accounting for the δ^{18} O and δ^{2} H composition of lake water, groundwater and precipitation (Fig. 3A). The groundwater samples plot close to the Local Meteoric Water Line (LMWL), which indicates that the groundwater is recharged by the local precipitation. In contrast to precipitation and groundwater, lake water samples deviate significantly from the LMWL as a consequence of isotopic enrichment of lake water due to evaporation. The linear regression model fitted to lake water samples and the sources of lake water (groundwater and amount-weighted annual precipitation) defines the Local Evaporation Line (LEL), which is $\delta^2 H = 5.07(\pm 0.08) * \delta^{18}O - 17.10(\pm 0.38)$ (n = 25, R² = 0.99, p < 0.0001). As proposed by Gibson *et al.* (2016a) the seasonality factor k (2.1.3) was adjusted (eq. 6) aiming at fitting the evaporation flux-weighted annual mean δ_E (eq.5) to the LEL. In the case of Lake Ammelshainer See k ranges from 0.73 to 0.78 under consideration of the LEL confidence interval ($\pm 1 \sigma$). Accordingly, the evaporation flux-weighted annual mean δ_E ranges from -21.1 ‰ to -22.8 ‰ and from -122 ‰ to -135 ‰ for δ^{18} O and δ^{2} H, respectively.

3.5 δ^{18} O and δ^{2} H mass balance

The input parameters for the isotope mass balance are given in Table II. The sum of precipitation falling on the lake surface is ~ 333,000 m³ a⁻¹ and the sum of evaporation from the lake surface is ~ 368,000 m³ a⁻¹. The isotopic composition of the lake in June ($\delta^{18}O_L = -3.59 \%$ and $\delta^2 H_L = -35.0 \%$) was used as initial value for δ_L and for δ_{GWout} for the dynamic isotope mass balance model. This value was iteratively adjusted to best fit the modelled annual isotope cycle to the observed inventories of $\delta^{18}O$ and $\delta^2 H$ in June and September. Accordingly, the optimized value for annual mean δ_L and δ_{GWout} were -3.5 ‰ and -34.8 ‰ for $\delta^{18}O$ and $\delta^2 H$, respectively.

Tab. 2

Assuming a hydrologic and isotopic interannual steady state, the annual LGD was calculated following eq. 3. The calculated LGD ranged from 1,084,000 m³ a⁻¹ to 1,193,000 m³ a⁻¹ for δ^{18} O and 1,027,000 m³ a⁻¹ to 1,224,000 m³ a⁻¹ for δ^{2} H. Converted to a mean daily flux the range of LGD equals 2,800 m³ d⁻¹ to 3,350 m³ d⁻¹ for the wider, more conservative error range of δ^{2} H. Accordingly, the mean groundwater outflow rates ranges from 2,700 m³ d⁻¹ to 3,250 m³ d⁻¹. The determined range of groundwater outflow rates were further used to calculate water residence time in the lake (Eq. 3) which ranges from 5.4 to 6.6 a.

For validating the estimated LGD and outflow rates the annual δ^{18} O and δ^{2} H cycles were simulated with a time-step width of one month and compared to the measured isotope inventories in June and September 2016 (Fig. 4). Therefore we used the monthly values presented

in Tab. 1 under assumption of constant LGD over time, which ranges from 3,050 to 3,250 m³ d⁻¹ and from 2,800 to 3,350 m³ d⁻¹ for δ^{18} O and δ^{2} H balance, respectively. Water balances are assumed to be at steady-state on a monthly basis, i.e. groundwater outflow rates were calculated to balance LGD, evaporation and precipitation rates.

Figure 4

The simulated annual cycle is characterized by the most negative isotope values at the end of the non-evaporation season in March and the most positive isotope values at the end of the evaporation season in September. This behavior is a consequence of the cumulative character of the lakes isotope inventory (eq.4), i.e. during the evaporation season the lakes isotope inventory is successively enriched in heavier isotopes until the monthly isotope balances are becoming negative in October. In contrast to that, the lakes isotope inventory is constantly depleted in heavier isotopes during the non-evaporation season until the monthly isotope mass balances are becoming positive again in April.

For both isotopes, the modelled seasonal ranges (assuming k values of 0.73 to 0.78) fit well with the observed stable water isotope inventories, although, modelled and observed data are in better agreement for δ^{18} O than for δ^{2} H. For δ^{18} O, both observations are within the uncertainty range of the model. For δ^{2} H, the model slightly underestimates the isotope inventory for June and slightly overestimates the isotope inventory for September compared to the observed values.

3.6 Radon mass balance

The Rn decay losses for the measured lake inventories (3.2) were calculated to be 71.6 Bq m⁻² d⁻¹ and 61.6 Bq m⁻² d⁻¹ for June 2015 and June 2016, respectively. Evasion rates were calculated based on wind speed data for a 10 day period prior to the sampling campaigns from the closest weather station (Leipzig-Holzhausen). Wind speed data were available in hourly resolution and are characterized by a median of 2.5 m s⁻¹ (range 0.5 to 5.8 m s⁻¹) for June 2015 and a median of 1.5 m s⁻¹ for September 2016 (range 0.3 to 4.0 m s⁻¹). Additional input data for Rn degassing rate calculation are the Rn concentration in surface water, which was 31 Bq m⁻³ for both campaigns, the measured water temperature at the lake surface (18° C in June 2015; 19° C in September 2016), salinity of 0.1 and the Rn concentration in air in the vicinity of the lake of 5 Bq m⁻³, which is based on previous experience (Schmidt *et al.*, 2008). The weighted Rn degassing rates were 14.5 ± 4.9 Bq m⁻² d⁻¹ for June 2015 and 8.3 ± 2.8 Bq m⁻² d⁻¹ for September 2016 which basically reflects the differences in wind speed during the days prior to both sampling campaigns.

The required parameters for the calculation of Rn input via diffusion are Rn in sediment porewater, Rn in lake bottom water, porosity and the Rn diffusion coefficient in water. Rn in sediment porewater underlying the lake was assumed to equal the Rn in groundwater concentration (18,900 \pm 500 Bq m⁻³). Rn concentration in lake bottom water was calculated by the non-linear regression models discussed in Sect. 3.1 with ~ 70 Bq m⁻³. The Rn diffusion coefficient for the observed temperatures in lake bottom water of 8.5 °C for freshwater is ~ 7.8 * 10⁻¹⁰ m² s⁻¹ (Schubert and Paschke, 2015). Porosity was assumed to be 0.35 which is typically for sand and gravel sediments. Finally, the Rn diffusion from the lake bottom sediment porewater into the overlying water column was calculated with 38.9 \pm 1.0 Bq m⁻² d⁻¹. The

required Rn flux to equilibrate the Rn mass balance was 47.4 ± 5.1 Bq m⁻² d⁻¹ for June 2015 and 30.9 ± 3.0 Bq m⁻² d⁻¹ for September 2016. This residual Rn flux was attributed to LGD. For a Rn concentration in groundwater of $18,900 \pm 500$ Bq m⁻³, the median LGD velocity averaged over the entire lake area was 2.5 ± 0.3 mm d⁻¹ for June 2015 and 1.6 ± 0.2 mm d⁻¹ for September 2016. Multiplication with the lake surface area of 540,000 m² results in volumetric LGD rates of $1,350 \pm 150$ m³ d⁻¹ for June 2015 and 900 ± 100 m³ d⁻¹ for September 2016 (Fig.5).

Figure 5

4. Discussion

The resulting LGD (2,800 to 3,350 m³ d⁻¹) and groundwater outflow rates (2,700 to 3,250 m³ d⁻¹) of Lake Ammelshainer See derived from the steady-state isotopic mass balances are in a similar range for δ^{18} O and δ^{2} H (Fig. 5). The difference between discharge and outflow is a consequence of exceedance of evaporation over precipitation with an interannual mean of ~ 100 m³ d⁻¹ under the assumption of constant lake volume. The LGD rates indicated by δ^{18} O and δ^{2} H reflect the long-term (interannual) mean conditions, i.e. they represent an integrated value over the entire residence time of water in the lake.

In contrast to that, results from the radon mass balance (RMB) indicated LGD rates of 1,350 \pm 150 m³ d⁻¹ and 900 \pm 100 m³ d⁻¹ for snapshots in June 2015 and September 2016. These results represent conditions during a few days prior to the sampling campaign basically due to radioactive decay and the evasion intensity of radon (Fig. 5). Both processes govern the persistence of a memory effect regarding the Rn concentration in the water body. Consequently, the offset between the stable isotope and the radon based LGD rates does not necessarily reflect a significant disagreement. Rather, the results from the RMB in June and September may reflect lower LGD rates due to seasonality effects. This hypothesis is supported by the observation of seasonal groundwater level fluctuations with lowest levels measured from late summer to mid-autumn. The groundwater level is the key driver of the hydraulic gradient between groundwater and lake water, which in turn governs LGD rates. However, if stable isotope and Rn based results are both correct June and September would represent periods with below average LGD rates. This implies that other periods of the year, such as late-winter to late-spring, do likely represent periods with above-average LGD rates to close the stable isotope and water mass balance. Late-winter to early spring typically has higher groundwater levels, which supports this assertion. Still, the hypothesis of temporal varying groundwater discharge rates needs to be validated by additional field campaigns which were beyond the scope of this study. In addition, the radon groundwater end-member relies on one sampled well only which introduces considerable uncertainty. Therefore, the LGD rates inferred from the RMB should be interpreted with care. The accuracy of the radon in groundwater endmember determination needs to be validated in future investigations.

Despite of the given uncertainty in LGD estimation, the dominating role of groundwater in the lakes water balance becomes clear by comparing LGD to precipitation (~900 m³ d⁻¹) and evaporation (~1000 m³ d⁻¹). Thus, LGD rate is a factor of 1 to 3.5 higher than the precipitation rate for Rn and stable isotope based estimates.

Our approach for calculating the isotopic composition of the lake evaporate utilizes the slope of the local evaporation line (LEL) and its uncertainty in a quantitative manner. The observed source water to the lake (i.e. groundwater discharge plus precipitation) is removed either by evaporation, a process that is isotopically fractionating causing enrichment, or by outflow, which is non-fractionating. Weighted inflow, including contributions from groundwater discharge and precipitation on the lake surface, and mean lake water define a straight line in δ^{18} O- δ^{2} H space (LEL) as a consequence of isotopic fractionation processes, with overall enrichment of lake water determined by conservation of mass. Hofmann et al. (2008), who investigated a lake in a similar climatic setting only 80 km northeast of Lake Ammelshainer See calculated monthly δ^{18} O values of the evaporate based on measurements of monthly δ^{18} O in precipitation and a vapour-precipitation equilibrium approach without considering evaporation seasonality. As a consequence, the isotopic values used in their study showed a much wider spread throughout the year ranging from -30.1 (August) to 56.6 % (November) compared to our study, in which the values ranged from -26.0 to -27.4 (August) up to -2.4 to -6.0 (January) (Tab. 2). The values estimated by Hofmann et al. (2008) are on average slightly more negative during the evaporation season from April to September (~ 2 ‰) and dramatically more positive (up to > 60 %) during the low-evaporation season compared to our study, although the explanation for the latter observation is unclear. In fact, these very high values calculated by Hofmann et al. (2008) resulted in a relatively heavy mean weighted δ^{18} O of the evaporate of -15.4 ‰ compared to our calculation of -21.1 to -22.8 ‰. While our use of a seasonality factor for calculating the isotopic composition of the evaporate remains to be further tested and compared in the study area, it has been applied previously in northern Canada (Gibson et al., 2016a) and appears to offer a first-approximation approach consistent with the mass balance between inflow terms (groundwater and precipitation), lake water and evaporate. The simulated annual cycle of δ^{18} O and δ^{2} H of lake inventories matches well with the observations in June and September. However, the simulations fit better for δ^{18} O than for δ^2 H, which requires further assessment. Further, a higher number of monitoring wells along the lake shore as well as depth-differentiated sampling would be favorable to decrease the uncertainty of the stable isotope groundwater end-member which would in turn further increase the validity of the determined LGD rates. The stable isotope composition of groundwater may be spatially heterogenouos and may deviate from the mean weighted local precipitation for several reasons. For instance, if a considerable share of the catchment area is covered by lakes, evaporation from these lakes could generate an evaporation signal in stable water isotopes of lake water entering the aquifer. Consequently, the groundwater entering the lake of interest may already show an evaporation signal.

A radon mass balance (RMB) for Lake Ammelshainer See was previously conducted by Schmidt *et al.* (2008). The authors of this study report similar Rn inventories and Rn fluxes attributed to groundwater. However, the LGD rates they derived are 23 to 41 times higher than our estimates. This discrepancy is mainly a result of the definition of the Rn groundwater end-member. Schmidt *et al.* (2008) derived the Rn end-member concentrations from sed-

iment batch experiments with ~ 300 Bq m^{-3} while we found Rn concentration in groundwater of ~ 19.000 Bq m^{-3} in a monitoring well close to the lake (as described above) and assumed those as representative for the composition of the discharging groundwater. This tremendous offset cannot be readily explained by spatial or temporal variability. The differences also highlight the inherent sensitivity of the approach to the definition of the end-member concentrations, an issue also raised by Arnoux et al. (2017a); (2017b). We considered the actual measurement of Rn in groundwater as more representative for the Rn groundwater endmember since the thickness of the lake bottom sediment layer is only a few centimeters in the littoral zone (Schmidt et al., 2008) where the majority of LGD is expected to occur. Under consideration of the groundwater flow velocity of 22-29 cm d⁻¹ in the vicinity of the lake given by Schmidt et al. (2008) a groundwater residence time of less than one day within these potentially low Rn sediments would not be sufficient to significantly alter the Rn concentration in groundwater. Our assumption regarding end-member definition is further supported by the reasonable agreement of the Rn and $\delta^{18}O/\delta^2H$ based estimates in this study. However, due to the large sensitivity of the RMB derived water fluxes to the Rn end-member concentration and the fact that Rn concentration in groundwater is known to be highly variable in space, further measurements of Rn in groundwater at different locations (if available and accessible) are suggested to determine its variability (spatially and temporally). These groundwater samples should be located upstream of the lake and close to the lake shoreline to best capture the actual composition of the discharging fluid. The poor data basis regarding Rn in groundwater samples introduce a high uncertainty of the Rn groundwater end-member which limits the reliability of the radon based LGD estimate. Further, the validity of the radon depth profiles which are required for estimating the radon inventory of the lake need to be improved in future investigations. For this purpose, the analysis of Rn in the home lab using liquid scintillation counting (Schubert et al., 2014) represents a time efficient alternative for achieving a higher accuracy.

The water residence time of 5.4 to 6.6 years derived from the stable isotope mass balance refers to the residence time of conservative substances (see section 2.1.2). In addition, we would like to mention the water residence of a parcel of water itself is 4.2 to 4.8 years, for better comparability with other studies, which was calculated by inclusion of evaporation as a loss term. The offset between residence times depending on how it is defined emphasizes the need for a clear definition of the term "residence time" to allow the regional application of this indicator in vulnerability assessments.

The present approach relies on several assumptions. The reliability and accuracy of the results can be further improved by testing and/or replacing these assumptions with field-based measurements. In our dynamic stable isotope mass balance, assumptions such as constant LGD rate and the constant lake volume may be decisive oversimplifications. In our model groundwater outflow rates are adjusted to balance seasonally varying evaporation to precipitation ratios to keep the lake volume constant. However, we expect that LGD rates vary over time as a consequence of seasonally varying hydraulic gradients between groundwater and the lake. As a next step, radon and stable isotope mass balances could be conducted at higher temporal resolution (e.g., monthly) for obtaining insight into their seasonal variability. These time-variant LGD rates could be used as input data for time variant mass balances of $\delta^{18}O$ and $\delta^{2}H$ in combination with lake water level monitoring. This combined approach would help to quantify temporal dynamics and to validate annual averages of LGD rates into lakes. Further, the delineation of the subsurface catchment of the lake determined by a groundwater flow model would be a great advantage, e.g. for sampling design as well as for evaluating the effect of other lakes in the catchment on stable water isotope composition of groundwater. Moreover, in the case of a significant vertical isotopic variability within the aquifer information on depth-dependent discharge rates are of interest for defining the flux-weighted groundwater end-member. Although, in most cases LGD is focused to the near-shore (e.g. McBride and Pfannkuch, 1975), fine sediment sealing the lake bottom may differentiate this picture.

The presented approach contributes to validation of numerical groundwater flow models for evaluating matter fluxes of e.g., sulphate, acidity or nutrients into lakes. Further, the introduced procedure can be applied for a comprehensive investigation of LGD and water residence time of groundwater-fed lakes in regions with a dense meteorological and isotopic monitoring network requiring only limited collection of field data.

5. Conclusion

In this study we present an approach for determining LGD rates into groundwater-fed lakes and for deriving the respective water residence times. The study shows the benefits and limitations of combining $\delta^{18}O/\delta^2H$ and Rn isotope mass balances for quantification of groundwater connectivity of lakes based on a relatively small amount of field data (lake isotope inventories and groundwater isotope composition) accompanied by good quality and comprehensive long-term meteorological and isotopic data (precipitation) from nearby monitoring stations. The combination of stable isotopes of water and radon offers the opportunity to simultaneously study long-term average conditions and short-term fluctuations of LGD rates. Despite the discussed limitations and uncertainties, the results from both approaches are reasonable and not contradicting. With a greater effort on sampling (e.g., monthly stable isotope and Rn inventories of the lake) further insight into seasonal variability will expectedly be achieved and uncertainty will be reduced.

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Table I: Isotope inventories for sampling campaigns in 2015 and 2016.

Date	δ ¹⁸ Ο [‰]	δ ² Η [‰]	Rn [Bq m ⁻²]
Jun 2015	_ ^a	- ^a	395
Jun 2016	-3.59	-35.0	-
Sep 2016	-3.23	-33.9	340

^a only measurements at the lake surface

Acc

Table II: Climate and isotopic data used as input for stable isotope mass balance and resulting LGD and outflow rates. Relative humidity, air temperature and precipitation refers to the period 2000-2015, evaporation refers to the period 2001-2010.

	Rel. humidity	Air temperature	P	recipitatio	on		Evaporatio	on		LGD		Groundwater outflow
Month	[-]	[°C]	Rate	δ ¹⁸ Ο	δ ² H	Rate	δ ¹⁸ Ο [‰]	δ ² Η [‰]	Rate	δ ¹⁸ O	δ ² H	Rate [m ³ /d]
			[mm]	[‰]	[‰]	[mm]			[m³/d]	[‰]	[‰]	
Jan	0.84	0.9	47.5	-11.1	-78.2	13.3	-2.4 to	-35 to	2,800 to	-8.2	-59.4	3,415 to 3,965
							-6.0	-63	3,350			
Feb	0.81	1.7	30.8	-10.3	-71.7	20.5	-11.1 to	-81 to	2,800 to	-8.2	-59.4	2,985 to 3,535
	0 - 4		10.4	10.0			-13.9	-103	3,350		7 0 4	
Mrc	0.76	5.0	40.6	-10.3	-74.2	41.2	-15.1 to	-83 to	2,800 to	-8.2	-59.4	2,790 to 3,340
	0.60	10.0	20.0	0 7	<0 -	72.2	-17.1	-98	3,350	0.0	7 0 (2 0 2 2 4 0 4 0 2
Apr	0.69	10.0	30.8	-8.7	-60.5	72.2	-21.3 to	-115 to	2,800 to	-8.2	-59.4	2,055 to 2,605
	0.70	14.0	(2.2	0.2	50 1	05.0	-22.7	-126	3,350	0.0	50.4	2 210 / 2 7 60
May	0.70	14.2	62.3	-8.3	-58.1	95.0	-21.5 to	-114 to	2,800 to	-8.2	-59.4	2,210 to 2,760
T	0.00	17.2	55 0	50	25.0	102 0	22.8	-124	3,350	0.0	50 4	1.040 += 2.400
Jun	0.69	17.3	55.2	-5.2	-35.9	102.9	-2/.7 to	-154 to	2,800 to	-8.2	-59.4	1,940 to 2,490
T1	0.60	10.4	95.0	5.6	26.0	110.0	-29.0	-104	3,350	0.7	50.4	2 250 to 2 000
JUI	0.09	19.4	83.9	-3.0	-30.9	110.9	-23.9 to	-145 to	2,800 to	-0.2	-39.4	2,330 10 2,900
Ang	0.70	18 0	71.6	53	35.1	05.6	-27.2	-133	$\frac{3,350}{2,800}$ to	87	50 /	2 365 to 2 920
Aug	0.70	10.7	/1.0	-5.5	-35.1	95.0	-20.0 to	-14910 -	2,800 10	-0.2	-39.4	2,303 10 2,920
Sen	0.77	14 5	563	-6.6	-44 7	63.2	-27.4	-137 to	2 800 to	-8.2	-594	2 675 to 3 225
Sep	0.77	14.5	50.5	0.0	/	03.2	-23.3	-152	3 350	0.2	57.7	2,075 10 5,225
Oct	0.82	10.0	38.0	-10.2	-70.4	37.9	-4.9 to	-47 to	2.800 to	-8.2	-59.4	2.805 to 3.355
	0.02	1010	2010	10.2	,	5117	-7.8	-68	3.350	0.2	0,711	2,000 10 0,000
Nov	0.85	5.7	53.4	-9.4	-70.6	17.8	-6.3 to	-40 to	2,800 to	-8.2	-59.4	3,440 to 3,990
							-10.1	-69	3,350			
Dec	0.85	2.1	44.3	-9.9	-68.4	11.8	-6.8 to	-66 to	2,800 to	-8.2	-59.4	3,385 to 3,935
							-10.6	-95	3,350			
Sum			617			682						
Mean	0.77	10.0		-8.0	-55.5		-21.1 to	-122 to	2,800 to	-8.2	-59.4	2,700 to 3,250
							-22.8	-135	3,350			