- 1 Title: Using stable isotopes to estimate young water fractions in a heavily-
- 2 regulated, tropical lowland river basin
- 3 Short Title: Young water fraction in tropical lowland basin

## 4 Keywords:

5 Day River, Vietnam, discharge sensitivity, water isotopes, sine wave fitting

## 6 **Authors:**

- 7 Trinh Anh Duc<sup>1\*</sup>, Do Thu Nga<sup>1,2</sup>, Virginia N Panizzo<sup>3</sup>, Suzanne McGowan<sup>3</sup>, Melanie J Leng<sup>4</sup>
- 8 <sup>1</sup>Nuclear Training Center, Vietnam Atomic Energy Institute, 140 Nguyen Tuan, Thanh Xuan,
- 9 Hanoi, Vietnam
- 10 <sup>2</sup>Graduate University of Science and Technology, Vietnam Academy of Science and Technology
- <sup>3</sup>Centre for Environmental Geochemistry, School of Geography, University of Nottingham,
- 12 University Park, Nottingham, NG7 2RD, UK.
- 13 <sup>4</sup>Centre for Environmental Geochemistry, British Geological Survey, Nicker Hill, Keyworth,
- 14 Nottingham, NG12 5GG, UK and School of Biosciences, University of Nottingham,
- 15 Loughborough, UK

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# **Key findings:**

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- 26 + Fyw is on average more than 0.5, implying more than a half of rainwater reaches the river
- 27 mainstream within the first 3 months, faster than global average.
- 28 + Unweighted and flow-weighted *Fyw* are indifferent.
- 29 + Fyw is insensitive to river discharge and rainfall, resulting from severely anthropogenic
- 30 activities.
- 31 + Urbanization appears to reduce Fyw.

## 32 **Data Availability Statement:**

- 33 The data that support the findings of this study are available from the corresponding author
- 34 upon reasonable request

## Abstract

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37 The young water fraction of streamflow (Fyw), an important hydrological variable, has been 38 calculated for the first time, for a monsoon-fed coastal catchment in northern Vietnam. Oxygen 39 stable isotopes ( $\delta^{18}$ O) from 6 river sites in the Day River Basin (DRB) were analysed monthly, 40 between January 2015 and December 2018. River  $\delta^{18}$ O signatures showed sine wave variability, reflecting the amount effect and tropical (dry-rainy) seasonality of the region. The  $\delta^{18}$ O 41 42 composition of precipitation ranged from -12.67 to +1.68%, with a mean value of -5.14%, and 43 in-streamflow signatures ranged from -11.63 to -1.37% with a mean of -5.02%. Fractions of young water (*Fyw*) were calculated from the unweighted and flow-weighted  $\delta^{18}$ O composition 44 45 of samples. Unweighted Fyw ranged between 29±8% and 82±21% with a mean value of 46 51±19%, and was not significantly different from flow-weighted Fyw (range between 33±25% 47 and 92±73%, mean 52±36%). Both unweighted and flow-weighted Fyw were highest in the middle of stream and lowest in downstream sites, capturing the impacts of landuse changes, 48 49 hydrology, and human activities in the catchment. Our calculations imply that more than a half 50 of rainwater reaches the DRB river mainstream within the first 3 months. The Fyw is much 51 higher than the global average (of one third) and insensitive to discharge due to the 52 combination of a humid catchment with high rainfall, low storage capacity, flat landscape and 53 an intensive drainage system in the DRB. Also the low discharge sensitivity of Fyw in the DRB implies that the regional hydrology is severely altered by humans. 54

## 1. Introduction

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Lowland catchments in the tropics such as the Day River Basin (DRB) in Vietnam are populous and concentrated with human activities such as agriculture, aquaculture, urbanization and industrialization. Water resources are extensively used for an array of purposes and therefore are heavily modified compared with their once pristine state. Simultaneously, climate change has profoundly altered the hydrological regimes in these areas (Smajgl et al., 2015; Dang et al., 2016). According to Chadwick et al. (2016), precipitation over tropical land areas (30°S to 30°N) has increased over the last decade reversing the drying trend that occurred from the mid-1970s to mid1990s. Safeguarding the livelihoods of communities living in lowland river catchments requires effective characterization of catchment/basin hydrologies, including knowledge of water transit time and flow paths. The time taken for water to travel from precipitation, through a catchment and to its outlet, is an important descriptor of the catchment's susceptibility to pollutant contamination and hydrological functioning. Such measurements are challenging in heavily modified basins with complex hydrology. Within a catchment, water derived from precipitation will take both slow and fast flow paths towards the outlet, where it becomes defined as streamwater (Tsuboyama et al., 1994). Slow flow paths include saturated and unsaturated flow through the soil matrix (Gannon et al., 2017), while fast flow paths include preferential flow (Wiekenkamp et al., 2016) and overland flow (Miyata et al., 2009). However, in a flat plain where irrigation-drainage networks (e.g. dykes, weirs, and pumps) are dense, the natural hydrological characteristics (flow rate, flow paths, transit/retention time) have been anthropogenically altered. As such, both the fast and slow flows cannot be easily estimated with the use of conventional hydrological approaches. To

77 overcome this, there should be a reliable and simple alternative approach to characterize the 78 essence of catchment hydrology. 79 The stable isotopes of water ( $\delta^{18}$ O and  $\delta^{2}$ H) are widely applied in the study of catchment flow 80 paths and transit times of precipitation through a catchment (McGuire & McDonnell, 2006). 81 Recently, one method that utilizes the stable isotopes of water for investigating fast flow paths 82 - the fraction of young water (Fyw) - was developed and evaluated (Kirchner 2016a; 2016b). 83 This method estimates Fyw, as the streamflow fraction that is roughly younger than three 84 months after entering the catchment as meteoric water (e.g. precipitation). This is done by 85 comparing the amplitudes of sine waves, fitted to the seasonally-varying isotope tracer signal in 86 precipitation and streamflow. The isotope signal (e.g.  $\delta^{18}$ O) in precipitation in tropical regions is 87 typically higher in dry seasons and lower during rainy periods (Dansgaard, 1964). As rain water passes through a catchment to reach the outlet, its  $\delta^{18}$ O signature is attenuated and shifted in 88 89 time, leading to a much smoother but still seasonally-varying isotope signal in the streamflow. 90 The ratio of the fitted streamflow sine wave's amplitude ( $A_s$ ), divided by the fitted precipitation 91 sine wave's amplitude  $(A_P)$  can be used to estimate the percentage of water in streamflow 92 which is younger than three months. Kirchner (2016a; 2016b) showed that Fyw calculations 93 were robust against spatial catchment heterogeneities (aggregation bias error), where previous 94 methods of transit time estimation by sine wave fitting produced highly uncertain results. To 95 date, this method has only been applied to theoretical data sets and smaller catchments in 96 temperate areas (Kirchner, 2016a; 2016b; von Freyberg et al., 2018; Stockinger et al., 2019). It 97 remains to be tested if Fyw can also be estimated in monsoon-impacted river basins.

This paper represents the first application of the Fyw estimation for the DRB, a tropical lowland catchment, which has undergone intensive human alteration. The objectives of this paper are to estimate the DRB's Fyw based on  $\delta^{18}$ O compositions from an extensive four year river dataset, and assess the (Fyw) spatio-temporal variability as function of the catchment's meteohydrological and landuse conditions. The broader aim is that the use of Fyw will help inform stakeholders and policy makers in better water resource management practices. The outcomes of this study are applicable within and beyond the DRB, and provide a potentially low-cost method for understanding other highly impacted, tropical lowland catchments around the world.

## 2. Materials and methods

## Description of the Day River Basin (DRB)

The DRB covers 7,665 km² (MONRE, 2006) with a total population of approximately 11.7 million (GSO, 2016). Located on the Red River Delta, the study area lies in a longitudinal direction. From West to East, the topography of the study area can be divided into the mountainous and delta areas respectively. The mountainous area in the west and southwest of the basin accounts for about 30% of the area and is mostly low mountain ranges (average elevation of 400 - 600 m) composed of terrigenous, carbonate sedimentary rocks. The whole DRB can be sub-divided in to 5 catchments named after the rivers Bui, Boi, Nhue, and Chau-Sat, and sub-basin estuary area (Luu et al., 2010).

The upstream reaches of the river system are meandering, winding, narrow and sloping, with many rapids and fast flowing waters, which trigger the risk of erosion and flash floods.

However, the middle and lower river channels are wide, with slow river flow, and poor drainage which leads to flooding during high rainfall events. The delta area accounts for about 60% of the DRB, the terrain of which is quite flat with elevations <20 m, descending from the Northwest to the Southeast. The plains are composed mainly of alluvial soils, clay and sand mixed with fine sand layers. From top down, the delta consists of (1) a 2 - 16 m layer of mixed clay and clay with sand; (2) a 1.3 - 6 m (10 m) layer of organic mud sediment and (3) a 50 - 90 m layer of sandy gravel and gravel. The plain surface is divided by intermittent river and canal systems. Agriculture is a vital activity in this basin, with approximately 50% of land in the DRB being used for farming and animal production. Rice paddies occupy 2,414 km<sup>2</sup>, while planted and natural forests are developed mostly in hilly areas and cover c. 1,264 km<sup>2</sup> (16% of the basin). Urbanized and industrial areas have expanded over recent decades to more than 1,000 km<sup>2</sup> (about 14%) of the basin, while open water including lakes, reservoirs, and waterways covers c. 400 km<sup>2</sup> (5.3%) of the basin. At present, the DRB river system is under considerable pressure from socioeconomic developmental activities and urbanization, and the basin is experiencing an annual population increase of about 5% (MONRE, 2006). However, the region's infrastructure (irrigation, drainage, traffic systems and urban planning) has not expanded at the same rate as population increase and so is unable to cope with such rapid development (Do & Nishida, 2014). Given the existing infrastructure resources, water regimes in upstream part of Day River, are largely controlled by a system of sluice gates and pumping stations, to allocate and redirect water for different purposes (e.g. irrigation and drainage or preventing urbanized areas from seasonal inundation).

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# Sampling and analysis

143 Water isotope sampling locations between January 2015 and December 2018 are shown in

144 Table 1.

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145 Table 1: Sampling sites in the DRB. Note that the sites are in strategic locations; upstream and

downstream of confluences between the main river flow and tributaries.

Station	River reach	Longitude	Latitude	Altitude	Distance to the
name		(°E)	(°N)	(m)	next downstream
		***************************************		***************************************	point
Ba Tha (D1)	Confluence between	105.70722	20.80583	10	25 km to D2
	Bui River and Day				
	River				
Te Tieu (D2)	Downstream Bui	105.74710	20.68646	9	35 km to D3
	River's confluence	NA 11 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1			
Que (D3)	Upstream Nhue	105.87263	20.57451	8	9 km to D4
	River's confluence	10.1388111111111111111111111111111111111		111111111111111111111111111111111111111	
Do (D4)	Downstream Nhue	105.91151	20.51578	7	20 km to D5
	River's confluence	TO MARKOTTO AND THE COLUMN TO	110 00000000000000000000000000000000000	1111300011111113000111111300011111	
Doan Vi (D5)	Upstream Boi River's	105.92081	20.36240	3	20 km to D6

	confluence				
Non Nuoc	Downstream Boi	105.98071	20.26526	3	60 km to the Sea
(D6)	River's confluence and				
	upstream Chau-Sat				
	River's confluence				

River waters were sampled monthly at a distance of approximately 10 m from riverbanks. They were filtered immediately with Sartorius technical filter papers (8 μm pore size) and collected in 30 ml HDPE plastic bottles. They were then kept at 20°C before being sent to the Isotope Hydrology Laboratory of the International Atomic Energy Agency (IAEA), Vienna, Austria for analysis. All samples were pipetted into 2 mL laser vials, and high-precision measurement using a Los Gatos Research liquid water isotope analyzer model 912-0032 (Los Gatos Research (www.lgrinc.com), California, USA). The method consisted of 9 injections per vial, excluding the first 4, with data processing procedures correcting for between-sample memory and instrumental drift, and normalization to the VSMOW-SLAP scale using LIMS for Lasers 2015 as fully described elsewhere (Wassenaar et al., 2014; Coplen & Wassenaar, 2015). A 2-point normalization used IAEA laboratory standards W-34 (low standard) and W-39 (high standard) to bracket the isotopic composition of the samples. IAEA laboratory standards were calibrated using VSMOW2 and SLAP2 primary reference materials with their assigned of values of 0±0.3, 0±0.02‰ and -427.5±0.3‰, -55.5±0.02‰ for δ²H and δ¹8O, respectively. The assigned values for the laboratory calibration standards W-39, W-34 and control W-31 were +25.4±0.8‰ and

 $+3.634\pm0.04\%$ ;  $-189.5\pm0.9\%$  and  $-24.778\pm0.02\%$ ;  $-61.04\pm0.6\%$  and  $-8.6\pm0.09\%$  for  $\delta^2 H$  and  $\delta^{18} O$  relative to VSMOW, respectively. The control W-31 long-term (1-yr running average) analytical reproducibility ( $\pm SD$ ) was  $\pm0.11\%$  and  $\pm0.7\%$  for  $\delta^{18} O$  and  $\delta^2 H$ , respectively. It should be noted that in this paper, only  $\delta^{18} O$  was used for the calculation of *Fyw*, as required by the method.

#### Supplementary data collection

Supplementary information from this catchment, including  $\delta^{18}$ O and  $\delta^{2}$ H compositions of rainwater and groundwater was taken from the IAEA archive (IAEA, 2016). Monthly rainwater stable isotope data from Hanoi's GNIP station (21.045347°N, 105.798668°E) during 2015-2018 was obtained from the IAEA's NUCLEAUS information resources. Groundwater isotope data were collected earlier in the 2004-2007 period. Hydrological data was collected daily between 2015 and 2018, at the main gauging stations of Ba Tha and Phu Ly in Day River (Fig. 1), and was acquired from the Vietnam National Hydro-Meteorological Station network. Landuse and elevation data of 2015 was acquired from the Ministry of Natural Resources and Environment. The GIS software ArcGIS 10.3 was used to generate DEM for catchment and subcatchment calculations (Do et al., 2019). Five groups of landuse with distinctive characteristics are categorized here: (1) Open water (soil submerged with water all around); (2) Urban and built-up (concrete and sewer networks); (3) Rice paddy (half of the time submerged with water, water well drained and irrigated); (4) Forest (sloping and untouched soil covered with trees); and (5) Grass+orchard+crop: vegetable planting (soil regularly kept from submerged with water).

# Estimation method of fraction of young water (Fyw)

184 Fyw was calculated by fitting a sine wave to both the seasonal-varying precipitation and

streamflow  $\delta^{18}$ O isotope signals. These are calculated, respectively, as:

186 
$$C_P(t) = A_P \sin(2\pi f t - \varphi_P) + k_P$$
 [1]

187 
$$C_S(t) = A_S \sin(2\pi f t - \varphi_S) + k_S$$
 [2]

where  $C_P(t)$  is simulated precipitation and  $C_S(t)$  is streamflow,  $\delta^{18}O$  isotope values of time t (decimal years), A is the amplitude (‰),  $\phi$  is the phase of the seasonal cycle (in radians, with  $2\pi$  rad equaling 1 year), f is the frequency (yr<sup>-1</sup>), and k (‰) is a constant describing the vertical offset of the isotope signal. After fitting these multiple regression equations, the Fyw can be calculated as:

$$F_{yw} = \frac{A_S}{A_B}$$
 [3]

For the flow-weighted *Fyw* computation, von Freyberg et al. (2018) considered flow as an independent variable weighing the cycle amplitude. They simplified that the seasonal cycle amplitude of the stable water isotope signal in stream water ( $A_s$ ) varies linearly with discharge (Q) (As = ns + ms\*Q), but the corresponding cycle amplitude in precipitation ( $A_P$ ) does not, such that Fyw varies with Q. However, in tropical coastal areas, precipitation water isotopes are known to be a function of precipitation amount (P) – "amount effect" and should not be neglected, especially for the uncertainty due to discharge/precipitation variability. Therefore, in this study, different to von Freyberg et al. (2018), we assess the Fyw as function of both  $A_s(Q)$  and  $A_P(P)$ .

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$$F_{yw} = \frac{n_S + m_S Q}{n_P + m_P P}$$
 [4]

 $n_P$ ,  $m_P$ ,  $n_P$ ,  $n_P$ ,  $m_P$  are determined via multi variable regression analysis of the 2 equations

205 
$$C_P(t) = (n_P + m_P P) \sin(2\pi f t - \varphi_P) + k_P$$
 [5]

206 
$$C_S(t) = (n_S + m_S Q) \sin(2\pi f t - \varphi_S) + k_S$$
 [6]

- 207 Each equation has 2 independent variables (time and flow), 1 dependent variable (isotopic
- 208 values), 4 coefficients  $(n, m, \varphi \text{ and } k)$
- The OriginPro 2019 software providing the user defined function/model was used for this
- regression analysis to obtain the coefficients A,  $\varphi$ ,  $k_p$ , n and m in Eq. 1, 2, 5, and 6. The
- 211 Levenberg-Marquardt algorithm was used to solve this generic curve-fitting problem.
- 212 Single sine wave fitting for the whole 2015-2018 period versus individual sine wave fitting for 1-
- 213 year time window was applied. We used a moving one-year time window which was moved in 1
- 214 month steps to calculate 37 Fyw estimates over the 2015-2018 time series. A minimum time
- 215 window length of one year was chosen to fully capture the annual isotope signal (Stockinger et
- 216 al., 2019).
- 217 Uncertainties in the calculated unweighted and flow-weighted *Fyw* are expressed as standard
- 218 errors (SEs) and are estimated using Gaussian error propagation.
- 219 Theoretically, the stream flow amplitude (A<sub>S</sub>) should be smaller than the precipitation
- amplitude  $(A_P)$ , resulting a Fyw in the range of 0 and 1. In which, 0 (1) is equivalent to 0%
- 221 (100%) of water in streamflow younger than three months after entering the catchment as
- meteoric water. Further description of the method can be found in von Freyberg et al. (2018).

Correlation analysis was used to assess the impact of land use changes on the *Fyw* over the monitoring sites. Land use data included percentage cover of open water, urbanization and built-up areas, rice paddy, grass land+orchard+crop, and forest. The DEM separates the DRB into 27 sub-catchments and land use at each site was classed as the sum of all sub-catchment land use that contributes water to that site. Forward selection was used to assess the significance of correlations between individual land use classes and the *Fyw* data which were analysed as separate years. The analysis was performed using OriginPro 2019 (9.65).

#### 3. Results

## Isotopic and hydrometric data

Between January 2015 and December 2018, minimum, maximum, and mean of precipitation recorded in Ha Noi was 4.2, 534.5, and 138.3 (mm month<sup>-1</sup>) respectively (Fig. 2a). The corresponding values of discharge measured at Ba Tha and Phu Ly were respectively 14, 374, 113 and 14, 364, 122 (mm month<sup>-1</sup>) (Fig. 2a). Low (high) precipitation was in January-March (July-September). Low (high) discharge occurs around the same period as (or occasionally 1 month later than) precipitation (Fig. 2a). The precipitation  $\delta^{18}$ O values ranged from -12.67 to +1.68‰, spanning a range of 14.65‰ (Fig .2b). By comparison, over the same period, streamflow  $\delta^{18}$ O values ranged from -11.63 to -1.37‰ with a range of 10.26‰ or about 72% of the precipitation values (Fig. 2b). In general, isotope profiles were sinusoidal, with maximum  $\delta^{18}$ O values occurring between January-May (the regional dry season) and minimum  $\delta^{18}$ O values between July –October (the regional rainy season). Peaks of river water  $\delta^{18}$ O isotope profiles occurred 1-2 months after the rainwater profile (Fig. 2b).

<Fig. 2 close to here>

<Fig. 3 close to here>

Precipitation  $\delta^{18}$ O composition was negatively correlated with the amount of monthly precipitation (r =-0.77, p < 0.0001). There were also similar tendencies between the river water  $\delta^{18}$ O and river discharge, with more negative  $\delta^{18}$ O during strong flow periods (Fig. 3).

## Sine wave fitting and fraction of young water estimation

The single sine waves for the whole study period fitted the 48 precipitation and 288 streamflow  $\delta^{18}$ O values well (Prob>|t| << 0.05). The precipitation amplitude ( $A_P$ ) was 4.37±0.42% and the streamflow amplitude ( $A_S$ ) was in the range of 2.15±0.24 (Non Nuoc Site) and 2.61±0.26% (Que Site), which results in an unweighted *Fyw* ranging between 49.3±7.3 and 59.7±8.2%. The corresponding values of flow-weighted *Fyw* were 50.0±16.9 (Non Nuoc Site) and 60.3±18.7% (Que Site). The sine wave profile of unweighted  $\delta^{18}$ O precipitation data fitted better (worse) than the flow-weighted  $\delta^{18}$ O precipitation data as assessed by the smaller error of fit (chisquare values) (Table 2 and Fig. 4-5).

<Fig. 4 close to here>

The individually-fitted sine waves for a period of 12 consecutive months showed some interannual variability in amplitude and phase shifts, leading to small deviations from the single sine wave fitted to the whole time series (Fig. 4). Overall, the mean of the individually-fitted sine waves was similar to the value of the single sine wave fitting. The amplitudes of  $\delta^{18}$ O in precipitation ranged between 3.22±0.52‰ and 5.84±0.97‰, with a mean value of 4.59±0.78‰ (Fig. 4), while streamflow amplitudes ranged between 1.44±0.28‰ and 3.18±0.80‰ with a

mean value of 2.34±0.54‰ (data not shown). The mean of all streamflow amplitudes was closer to the single sine wave amplitude (2.34±0.54‰ vs. 2.34±0.26‰) than the precipitation amplitudes (4.59±0.78% vs. 4.37±0.42%). Thus, using the average of the individually-fitted sine wave amplitudes to calculate Fyw, gives a result of 51.0% compared with 53.7% for the single sine wave. The range of unweighted Fyw obtained from individual sine wave fitting in the period 2015-2018 at our 6 study sites was 0.29±0.08 to 0.82±0.21, with a mean value of 0.51±0.19. In comparison, the range of volume(flow)-weighted Fyw resulting from the individual sine wave fittings was 0.33±0.24 to 0.92±0.73 with mean value of 0.52±0.36. As shown in Fig. 5, both unweighted and weighted Fyw values are very similar, reaching higher (lower) values at Que Site (Non Nuoc site). The weighted values have a larger error resulting from flow coefficient ( $m_s$ and  $m_p$ ) estimating uncertainty, and river discharge variability. Chi-square values of unweighted fitting is always higher than volume-weighted fitting, showing that volume-weighted fitting mimics better the isotopic profiles than unweighted fitting. Single sine wave fitting led to a discharge sensitivity (DS) range of 0.053±0.024 (Te Tieu Site) and 0.072±0.026 (Que Site) (d mm<sup>-1</sup>). Individual, DS values are small and positive. Taking into account their large uncertainty, we conclude that Fyw is insignificantly influenced by discharge. That is also explained by the fact that unweighted and weighted *Fyw* are relatively similar. Error propagated from river discharge uncertainty accumulates to the error of *Fyw* and DS.

285 <Fig. 7 close to here>

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Pearson correlation calculation revealed that single sine wave fitted *Fyw* and DS did not significantly correlate with any dominant landuse along the main stream (all *p*-values are higher than 0.05). On the other hand, mean±standard deviation of correlation coefficients between individual sine wave fitted *Fyw* (and its DS) and landuse (Fig. 8) shows a consistently weak but positive correlation between *Fyw* and Grass+orchard+crops and negative correlations between *Fyw* and Area (and Urban and built-up).

<Fig. 8 close to here>

Overall, correlation analysis indicated that *Fyw* was consistently - insignificantly, positively correlated with the proportion of Grass + orchard + crop in the catchment, and negatively correlated with the catchment area, the urban and built-up area (Fig. 8). Thus, *Fyw* tends to increase if a catchment is dominated by grass+orchard+crop and decrease downstream or if a catchment is dominated by urban areas. In addition, the rice paddy and forest landscapes appear (insignificantly and inconsistently) to decrease *Fyw*.

The analysis shows no correlation between DS and any landuse activities or catchment characteristics in the DRB.

## 4. Discussion

Water isotopes (rainwater, groundwater, and surface water isotopes) in the DRB  $\delta^{18}$ O isotopes and monthly rainfall were negatively correlated (Fig. 3), indicating that the amount effect dominates in this tropical precipitation regime (Trinh et al., 2017). Dansgaard (1964) defined the amount effect as a low latitude anticorrelation between the isotopic compositions and the amount of rain (based on monthly means). Since the tropical climate here

is characterized with a two season pattern (rainy and dry) this anticorrelation helps to create a sine wave seasonality of precipitation and river water  $\delta^{18}$ O. Approximately six monthly intervals between min and max isotopic values ensure the rate of increase equals the rate of decrease (Fig. 2). We assume that open water and paddy fields accounted for about half of the delta plain create a massive water buffering area, helping to smooth the variability in river flow and isotopic values. Differences between the mean and median of the isotopic data (in both rain and river water) are less than 10% of their absolute values. This bimodal seasonal pattern permits the successful application of the stream flow fraction estimation method, based on water  $\delta^{18}$ O isotope data (Kirchner, 2016a). Previous studies on  $\delta^{18}$ O signatures in the Red River Delta, which includes the DRB, report a mean, minimum, and maximum groundwater  $\delta^{18}$ O of -7.60%, -10.21%, and -3.8% (Trinh, et al., 2017). Based on the current isotope dataset, we infer that groundwater is recharged locally from precipitation because the long-term  $\delta^{18}$ O of precipitation (ca. -7.75‰) is close to the quasi-constant  $\delta^{18}$ O of groundwater reported in Trinh et al. (2017) (-7.60% ± 1.28%). On the other hand, streamflow was substantially enriched with the heavier isotope, with a mean value equal to or higher than -6.51%, implying strong evapotranspiration in the DRB which increases in the lowland delta where there are many standing waters including ponds, lakes, wetlands, and paddy fields (susceptible to strong evaporation under this tropical climate). Trinh et al. (2017) came to the same conclusion using hydrograph separation/and d-excess computation for the same catchment. This relative comparison between ground, river, and precipitation water  $\delta^{18}$ O isotopes also implies that the contribution of groundwater to river water is minimal.

Because the groundwater (subsurface) discharge to stream flow is slow, a large contribution of

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surface runoff as a fast flow path, (i.e. a high *Fyw*) to streamwater would be expected in the DRB.

# Fraction of young water

Young water fractions are estimated from the amplitude ratio of the seasonal cycles in stable water  $\delta^{18}$ O isotope signatures of precipitation and streamwater. These amplitudes can be estimated directly from the isotope measurements themselves, or by volume-weighting these measurements by the corresponding precipitation or discharge rates. While precipitation  $\delta^{18}$ O isotopes should generally be volume-weighted to prevent the influence of short-lived precipitation events from creating anomalous isotope values, streamwater  $\delta^{18}$ O isotope values can be flow-weighted (using stream discharges as weights) or unweighted. Here, the use of monthly data, instead of daily or hourly data, decreases the influence of anomalous events, but may miss capturing some important hydrological characteristics of the catchment. So, comparisons between unweighted and weighted *Fyw* are useful for assessing the suitability of the approaches.

Table 2: Fraction of young water (*Fyw*) and its discharge sensitivity (DS) (exclusively for flow-weighted calculation) at the different sites over the 2015-2018 period (Mean±SE)

Sine	Individual			Single		
wave						
fitted						
	Weighted	DS (d mm <sup>-1</sup> )	Unweighted	Weighted	DS (d mm <sup>-1</sup> )	Unweighted

Ba Tha	0.55±0.36	0.045±0.054	0.53±0.15	0.55±0.18	0.061±0.025	0.55±0.08
Te Tieu	0.49±0.34	0.039±0.056	0.48±0.14	0.52±0.17	0.053±0.024	0.52±0.08
Que	0.57±0.38	0.060±0.057	0.57±0.15	0.60±0.19	0.072±0.026	0.60±0.08
Do	0.50±0.37	0.053±0.059	0.49±0.15	0.53±0.18	0.060±0.025	0.53±0.08
Doan Vi	0.51±0.37	0.065±0.063	0.50±0.15	0.54±0.18	0.063±0.025	0.53±0.08
Non	0.48±0.35	0.058±0.056	0.47±0.14	0.50±0.17	0.063±0.025	0.49±0.07
Nuoc						

Weighted *Fyw* values are generally higher than the unweighted *Fyw* values, but differences between them are not significant (Table 2 and Fig. 5, 6). This is not surprising, since the effect of flow-weighting on *Fyw* is large at sites with relatively large variation of daily discharge (von Freyberg et al., 2018). In the DRB, daily discharge in the mainstream does not vary too much because it drains an area of 7665 km² and is located in a humid climate. In addition, our monthly sampling does not capture daily variability well. Therefore, our calculation for the DRB shows no significant difference between unweighted and weighted *Fyw*. Based on our *Fyw* calculations, more than a half of the rainwater reaches the DRB river mainstream within the first 3 months (Fig. 6, 7). This is much higher than other published studies (von Freyberg et al., 2018; Stockinger et al., 2019) (Table 2), and an analysis of 254 catchments which found that young streamflow accounts for about a third of river discharge globally (Jasechko et al., 2016). Of more relevance to the DRB, this large-scale analysis surprisingly concluded that steeper catchments tend to have smaller *Fyw* (Jasechko et al., 2016). In other word, catchments with

flat landscapes tend to have higher Fyw. It appears to be true in the DRB since it is composed of more than 80% of flat and submerged land, with limited capacity to retain water within the catchment, and therefore can transmit water and its associated solutes (e.g. dissolved contaminants) into streams at a much faster rate than the global average. For hundreds of years, hydrology in the DRB has been strictly regulated for agricultural and urban purposes (Luu et al., 2010; Do et al., 2019). Half of delta plain is open water and paddy fields which are constantly submerged in the rainy season. Water during and after intense rainfall events is pumped and/or drained from alluvial plains to the river to avoid unexpected inundation. In combination, the natural climate of the region (i.e. high humidity and intense precipitation (von Freyberg et al., 2018)), flat landscape, and the high level of human modification has led to high Fyw in the DRB. There is no straightforward gradient of *Fyw* between upstream and downstream areas. Instead, Fyw was highest at Que (a middle section site) and lowest at Non Nuoc (the most downstream site) (Table 2). The correlation analysis shows an insignificantly but consistently negative correlation between Fyw and Area (Fig. 8) which means the overall tendency of decreasing Fyw downstream (downstream sites represent the larger catchment area). Physically, recording the lowest Fyw at the most downstream site could be explained by several factors. First, further downstream a greater proportion of water is derived from the upstream reaches of the river, which has a dilution effect on the young water proportion of the DRB streamwater. This is reinforced by the elongated shape of the DRB (Fig. 1). Secondly, the downstream reaches of the DRB are influenced by tidal effects, which can slow down flow and increase water stagnation in some downstream areas. Finally, there is a greater proportion of

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groundwater exchange and interaction with streamwaters in the downstream (delta) reaches of the DRB, than in the more upland upstream reaches (Bui et al., 2011). Trinh et al. (2017) further support this account of groundwater levels being sufficiently high that they occasionally discharge into the stream during the dry period, when water level in the main river channels is low.

#### Topography, land use, hydro-climatic characteristics and Fyw

Relationships among *Fyw,* topography, land use and hydro-climatic characteristics (e.g. rainfall and discharge) can help to identify the dominant controls on the hydrological behavior of a basin. In this section, we examine how *Fyw* varies relative to changes in stream discharge and precipitation on annual timescales, as well as to changes in topography and land use among different sampling sites.

On an individual catchment basis, the sensitivity of Fyw (and thus seasonal  $\delta^{18}O$  isotope cycles) to annual variability in precipitation and river discharge has important hydrological implications (von Freyberg et al. 2018). Low discharge sensitivities imply greater persistence in the proportion of fast and slow runoff flow paths, as catchment wetness changes. Conversely, high discharge sensitivities imply that different dominant fast flow paths become activated during precipitation events, such as when the subsurface water table rises into more permeable layers and/or the river network expands further into the landscape (Godsey & Kirchner, 2014). A full assessment of the Fyw - discharge relationship should be based not only on hydro-climate and catchment characteristics, but also on different sampling periods and sampling strategies of the studies (Lutz et al., 2018).

As shown in Fig. 7c,d, DS is generally positive, indicating an activation of fast flow paths during high discharge. Nevertheless, due to its large standard errors (especially for individual fitted; Table 2), we conclude that Fyw in the DRB is characterized as having low and positive DS. According to von Freyberg et al. (2018), catchments with low DS of Fyw are characterized by dense river networks and/or generally humid conditions (e.g. large proportion of paddy fields and open water). These catchment properties are generally associated with predominantly shallow runoff flow paths during both large and small precipitation events, when Fyw remains relatively high under widely varying flow regimes. In contrast, in catchments characterized by lower drainage density and less humid conditions, larger or higher-intensity storms are likely to strongly alter the proportions of different dominant flow paths, leading to larger variations in Fyw (i.e. higher DS). For example, the dynamic extension of the stream network (e.g. Godsey and Kirchner, 2014; Jensen et al., 2017) and/or the increase in hydrological connectivity between the stream network and the surrounding landscape (e.g. Detty and McGuire, 2010; von Freyberg et al., 2015) should more strongly influence the relative proportion of young streamflow in catchments where drainage density is not already high. Likewise, the activation of shallow flow paths during larger storm events will have a bigger influence on Fyw in drier catchments than in wetter ones, where shallow flow paths are likely to be activated during both large and small events. The low DS therefore arises in the DRB definitely because it is characterized by dense river networks, located in a tropical climate (high humidity) and the intensive agricultural practices and urbanization have made shallow runoff flow paths predominant during both large and small precipitation events. In addition, an array of robust dams, dikes, and complex drainage networks in the DRB maintain the surface/fast flow paths

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and prevent them from expanding by changing their courses into the lanscape (Trinh et al., 2017).

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Correlation analysis confirmed that Fyw in the DRB has low DS (Fig. 7, 8) with no significant correlations (p-value < 0.05) between Fyw (its DS) and precipitation (discharge) – hydro-climatic forcing, or and landuse variability. The most likely explanations for the lack of correlation are the catchment characteristics described above (humid lowland with concentrated river drainage/irrigation networks) where there is low dependence catchment wetness conditions or hydro-climatic forcing. As the DS is low its error accumulates with the monthly isotopic - daily discharge uncertainty, it is not surprising that DS is not a function of particular forcing factors. In addition, anthropogenic activities such as agricultural practices and urban expansion (nearly 20% in the central section of the catchment), which function independently from natural and climate conditions lower the DS in the DRB. Low and non-significant (p-value > 0.05) correlations between Fyw (DS) and other catchment characteristics (Fig. 7, 8) implies that linking Fyw to catchment wetness conditions and hydro-climatic forcing may be difficult in catchments with streamflow regimes are discontinuous or strongly affected by water management (e.g. groundwater pumping, artificial groundwater recharge, irrigation, or water diversion) or land-use change (e.g. urban development, soil degradation, or forest clear cutting) (von Freyberg et al., 2018). Based on the correlation analysis, we found that Fyw varies positively in areas more dominated

by grass+orchard+crops (Fig. 8). The explanation is that usually, this landuse type should be kept dry. During storms or extreme rainfall, the agricultural practice in those areas is to drain water as fast as possible. Therefore, in this landuse, there are few persistent fast and slow flow

paths. The relative proportions of the fast and slow flow path vary greatly between dry and wet seasons, with an increase (decrease) in *Fyw* during wet (dry) periods. Combined with the fact that the DRB is located in a tropical monsoon region, *Fyw* in grass+crop+orchard areas is high and sensitive to (precipitation) discharge. This contrasts with urban and built up areas which have lower *Fyw*. For the flow paths going through urban and built up areas, we did expect some fast flows (high *Fyw*) because of the need for rapid rainwater drainage, but instead we observed that *Fyw* is lower in the urban and built up proportions of the DRB. This may be because domestic water used in the DRB is pumped mostly from groundwater, and so the isotopic signatures of water flow from urban and built up area are blended with old water signals.

## 5. Conclusion

This study presents the first calculation of *Fyw* for the DRB which represents, to our knowledge, its first application in a tropical, lowland catchment. Our study focuses on the spatio-temporal variability of *Fyw* in the DRB. The fraction of young waters obtained from either unweighted or volume-weighted, fitted over 12 month windows or for the whole dataset were quite similar, indicating the credibility of the approach. Compared with the global mean of one-third, the *Fyw* proportion in the DRB is higher (more than a half), reflecting a catchment that is predominantly wet and where water is quickly drained during intense rainfall events to alleviate inundation in its large lowland areas. This study supports the application of *Fyw* to assess the flushing of solute contaminants in lowland, plain catchments which are highly controlled by dikes and dams, and where hydrological models therefore fail to best capture flow patterns and processes.

Based on our analysis, we applied a generalized conceptual description that relates *Fyw* and its DS to dominant streamflow generation mechanisms (von Freyberg et al., 2018) for analyzing the effects of future climate change on catchment hydrological behavior. The DRB belongs to the category of a humid catchment, with frequent precipitation, low storage capacity, and dense river networks. This catchment is characterized with high *Fyw* and low DS, of which both variables are insensitive to landscape and hydro-climate forcing factors. Anthropogenic activities such as dams, dikes, and drainage networks have decoupled the relationship between discharge and *Fyw* (low DS) and suggest that overall the hydrology in DRB will not be strongly impacted by climate change, due to the overwhelming influence of human modifications.

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## References

- Bui, D. D. et al., 2011. Identification of aquifer system in the whole Red River Delta, Vietnam.
- 481 *Geosciences Journal*, 15(3), pp. 323-338.
- 482 Chadwick, R., Good, P., Martin, G. & Rowell, D. P., 2016. Large rainfall changes consistently
- projected over substantial areas of tropical land. *Nature Climate Change,* Volume 6, p. 177–181.
- 484 Coplen, T. B. & Wassenaar, L. I., 2015. LIMS for Lasers 2015 for achieving long-term accuracy
- and precision of  $\delta 2H$ ,  $\delta 17O$ , and  $\delta 18O$  of waters using laser absorption spectrometry. *Rapid*
- 486 Communications in Mass Spectrometry, Volume 29, pp. 2122-2130.
- Dang, D., Cochrane, A., Arias, E. & Van, P. D. T. D.-V. T., 2016. Hydrological alterations from
- water infrastructure development in the Mekong floodplains.. *Hydrological Processes*, 30(21),
- 489 pp. 3824-3838.
- 490 Dansgaard, W., 1964. Stable isotopes in precipitation. *Tellus A*, Volume 16, p. 436–468.
- 491 Detty, J. M. & McGuire, K. J., 2010. Topographic controls on shallow groundwater dynamics:
- 492 implications of hydrologic connectivity between hillslopes and riparian zones in a till mantled
- 493 catchment. *Hydrological Processes*, Volume 24, p. 2222–2236.
- 494 Do, T. N. & Nishida, K., 2014. A nitrogen cycle model in paddy fields to improve material flow
- analysis: the Day-Nhue River Basin case study. Nutrient Cycling in Agroecosystems, Volume 100,
- 496 pp. 215-226.

- 497 Do, T. N., Tran, B. V., Trinh, A. D. & Kei, K. N., 2019. Quantification of nitrogen load in a
- 498 regulated river system in Vietnam by material flow analysis. Journal of Material Cycles and
- 499 *Waste Management,* 21(4), p. 974–98.
- 500 Gannon, J. P. et al., 2017. Lateral water flux in the unsaturated zone: A mechanism for the
- formation of spatial soil heterogeneity in a headwater catchment. *Hydrological process*, 31(20),
- 502 pp. 3568-3579.
- 503 Godsey, S. E. & Kirchner, J. W., 2014. Dynamic, discontinuous stream networks: hydrologically
- driven variations in active drainage density, flowing channels, and stream order. *Hydrological*
- 505 *Processes* , 28(23), p. 5791–5803.
- 506 GSO, 2016. Report on the census of rural, agriculture and aquaculture, Hanoi, Vietnam: Vietnam
- 507 General Statistics Office.
- 508 IAEA, 2016. Water Isotope System for data analysis, visualization and Electronic Retrieval.
- 509 [Online]
- 510 Available at: https://nucleus.iaea.org/wiser/
- 511 [Accessed 30 April 2016].
- Jasechko, S., Kirchner, J. W., Welker, J. M. & McDonnell, J., 2016. Substantial proportion of
- 513 global streamflow less than three months old. *Nature Geoscience*, 9(2), pp. 126-129.
- Jensen, C. K., McGuire, K. J. & Prince, P. S., 2017. Headwater stream length dynamics across
- four physiographic provinces of the Appalachian Highlands. *Hydrological Processes*, Volume 31,
- 516 pp. 3350-3363.

- 517 Kirchner, J. W., 2016a. Aggregation in environmental systems Part 1: Seasonal tracer cycles
- 518 quantify young water fractions, but not mean transit times, in spatially heterogeneous
- catchments. *Hydrology and Earth System Sciences*, 20(1), pp. 279-297.
- 520 Kirchner, J. W., 2016b. Aggregation in environmental systems Part 2: Catchment mean transit
- 521 times and young water fractions under hydrologic nonstationarity. *Hydrology and Earth System*
- 522 *Sciences*, 20(1), p. 299–328.
- Lutz, S. R. et al., 2018. Spatial patterns of water age: Using young water fractions to improve the
- 524 characterization of transit times in contrasting catchments. Water Resources Research, 54(7),
- 525 pp. 4767-4784.
- 526 Luu, T. N. M. et al., 2010. Hydrological regime and water budget of the Red River Delta
- 527 (Northern Vietnam). Journal of Asian Earth Sciences, 37(3), pp. 219-228.
- 528 McGuire, K. J. & McDonnell, J. J., 2006. A review and evaluation of catchment transit time
- 529 modeling. *Journal of hydrology*, 330(3–4), p. 543–563.
- Miyata, S., Kosugi, K., Gomi, T. & Mizuyama, T., 2009. Effects of forest floor coverage on
- overland flow and soil erosion on hillslopes in Japanese cypress plantation forests. Water
- *resources research,* 45(6), p. doi.org/10.1029/2008WR007270.
- MONRE, 2006. State of Environment in Vietnam, Hanoi, Vietnam: Ministry of Natural Resources
- and Environment.
- 535 Smajgl, A. et al., 2015. Responding to rising sea-levels in Vietnam's Mekong Delta. *Nature*
- 536 *Climate Change*, Volume 5, pp. 167 174).

- 537 Stockinger, M. P. et al., 2019. Time-variability of the fraction of young water in a small
- headwater catchment. *Hydrology and Earth System Sciences*, pp. Discuss.,
- 539 https://doi.org/10.5194/hess-2018-604.
- Trinh, A. D., Luu, T. N. M. & Le, T. P. Q., 2017. . Use of stable isotopes to understand run-off
- generation processes in the Red River Delta. *Hydrological Processes*, Volume 31, pp. 3827-3843.
- Tsuboyama, Y., Sidle, R. C., Noguchi, S. & Hosoda, I., 1994. Flow and solute transport through
- the soil matrix and macropores of a hillslope segment. water resources research, 30(4), pp. 879-
- 544 890.
- von Freyberg, J. et al., 2018. Sensitivity of young water fractions to hydro-climatic forcing and
- landscape properties across 22 Swiss catchments. hydrology and earth system sciences, Volume
- 547 22, p. 3841–3861.
- von Freyberg, J., Rao, P. S. C., Radny, D. & Schirmer, M., 2015. The impact of hillslope
- 549 groundwater dynamics and landscape functioning in event-flow generation: a field study in the
- 550 Rietholzbach catchment, Switzerland. *Hydrogeological Journal*, Volume 23, pp. 935-948.
- Wassenaar, L., Coplen, I. & Aggarwal, P. K., 2014. Approaches for Achieving Long-Term Accuracy
- and Precision of  $\delta$ 180 and  $\delta$ 2H for Waters Analyzed using Laser Absorption Spectrometers.
- *Environmental Science and Technology,* Volume 48, pp. 1123-1131.
- Wiekenkamp, I. et al., 2016. Spatial and temporal occurrence of preferential flow in a forested
- headwater catchment. *Journal of Hydrology,* Volume 534, pp. 139-149.

## Figure captions

- Fig. 1: Topography and land use map of the Day River Basin
- Fig. 2: (a) precipitation and discharge and (b)  $\delta^{18}$ O in rain- and river-water in DRB.
- Fig. 3: (a) Monthly rain  $\delta^{18}$ O signatures vs rainfall (mm) and (b) river  $\delta^{18}$ O signatures vs river
- water discharge (m³ s⁻¹) at the Do site (D4), the most central site in DRB. Data cover the period
- of January 2015 to December 2018.
- Fig. 4: Phase shift and amplitude of the 12 month sine waves of the rain water  $\delta^{18}$ O isotope
- signatures (straight lines are vertical phase shifts and amplitudes of single sine wave fitting for
- the whole period January 2015 to December 2018); error bars are SEs
- 566 Fig. 5: Fraction of young water (*Fyw*) results from individual sine wave fitting at different
- sampling sites over 12 consecutive months starting from January to December 2015 to January
- to December 2018; error bars are SEs
- Fig. 6: (a) Flow-weighted Fyw vs Unweighted Fyw and (b) discharge sensitivity (DS) vs flow-
- weighted *Fyw*; error bars are SEs
- Fig. 7: (a) Flow-weighted fraction of young water (weighted Fyw) versus precipitation, (b)
- weighted Fyw versus discharge, (c) discharge sensitivity (DS) versus precipitation, and (d) DS
- versus discharge; error bars are SEs
- Fig. 8: Correlation analysis; (a) correlation coefficient (r) between Fyw and the landuse and
- catchment characteristics and (b) correlation coefficient (r) between DS and the landuse and
- 576 catchment characteristics; error bars are SDs from mean values