# Understanding uncertainties when inferring mean transit times trough tracer based lumped parameter models in Andean tropical montane cloud forest catchments

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#### 13 Abstract

14 Weekly samples from surface waters, springs, soil water and rainfall were collected in a 76.9 km<sup>2</sup> mountain rain forest catchment and its tributaries in southern Ecuador. Time series 15 of the stable water isotopes  $\delta^{18}$ O and  $\delta^2$ H were used to calculate mean transit times (MTTs) 16 and the transit time distribution functions (TTDs) solving the convolution method for seven 17 18 lumped parameter models. For each model setup, the Generalized Likelihood Uncertainty 19 Estimation (GLUE) methodology was applied to find the best predictions, behavioral 20 solutions and parameter identifiability. For the study basin, TTDs based on model types such 21 as the Linear-Piston Flow for soil waters and the Exponential-Piston Flow for surface waters 22 and springs performed better than more versatile equations such as the Gamma and the Two 23 Parallel Linear Reservoirs. Notwithstanding both approaches yielded a better goodness of fit 24 for most sites, but with considerable larger uncertainty shown by GLUE. Among the tested 25 models, corresponding results were obtained for soil waters with short MTTs (ranging from 2 26 to 12 weeks). For waters with longer MTTs differences were found, suggesting that for those 27 cases the MTT should be based at least on an intercomparison of several models. Under 28 dominant baseflow conditions long MTTs for stream water  $\geq 2$  yr were detected, a 29 phenomenon also observed for shallow springs. Short MTTs for water in the top soil layer 30 indicate a rapid exchange of surface waters with deeper soil horizons. Differences in travel 31 times between soils suggest that there is evidence of a land use effect on flow generation.

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#### 33 **1** Introduction

34 The mean transit time (MTT) of waters provides a valuable primary description of the 35 hydrological (Fenicia et al., 2010) and biochemical systems (Wolock et al., 1997) of a 36 catchment and its sensitivity to anthropogenic factors (Landon et al., 2000; Turner et al., 37 2006; Tetzlaff et al., 2007; Darracq et al., 2010). Whereas the MTT describes the average 38 time it takes for any given water parcel to leave the catchment, the transit time distribution 39 function (TTD) describes the retention behavior of all those water parcels as a frequency function over time (McGuire and McDonnell, 2006). Together with the physical 40 characteristics of the catchment, the MTT and TTD (for the particular case of soil water, MTT 41 42 should be more properly understood as Mean Residence Time, and TTD as Residence Time Distribution function) allow inferring the recharge of aquifers (Rose et al., 1996), the bulk 43 44 water velocities through its compartments (Rinaldo et al., 2011), and the interpretation of the

water chemistry (Maher, 2011); all of which supports the design of prevention, control,
remediation and restoration techniques. Additionally, MTT and TTD data are useful to reduce
the uncertainty of results and improve input parameter identifiability for either hydrologic
modeling studies (Weiler et al., 2003; Vache and McDonnell, 2006; McGuire et al., 2007;
Capell et al., 2012) or solute movement analyses through soil and aquifers using mixing
models (Iorgulescu et al., 2007; Barthold et al., 2010).

The stable water isotopes  $\delta^{18}$ O and  $\delta^2$ H are commonly used as environmental tracers for a 51 52 preliminary assessment of the transport of water in watersheds with transit times less than 5 yr 53 (Soulsby et al., 2000; Rodgers et al., 2005; Viville et al., 2006; Soulsby et al., 2009). For 54 longer MTTs of up to 200 yr (Stewart et al., 2010), tritium radioisotopes are used to analyze 55 the storage and flow behavior in surface water and shallow groundwater systems (Kendall and 56 McDonnell, 1998), while, for example, carbon isotopes are employed for analyzing the 57 dynamics of deep groundwater with ages of hundreds to thousands of years (Leibundgut et al., 58 2009).

59 Since Barnes and Bonell (1996), researchers in tracer hydrology use quasi distributed and 60 conceptual models to encompass the non-linearity of the processes related to the transit states of the soil moisture dynamics (Botter et al., 2010; Fenicia et al., 2010). However, the use of 61 62 such modeling approaches is only advisable after basic inferences about the underlying mixing processes and the way water is routed through the system have been drawn. Insights 63 64 that can be provided by applying simpler lumped TTD functions as the models proposed by Maloszewski and Zuber (1982, 1993), which are based on quasi-linearity and steady state 65 66 conditions. These models include the exponential (EM), piston (PM), or linear (LM) models, in which the MTT of the tracer is the only unknown variable, and also combinations of 67 68 models such as the exponential-piston flow (EPM) and the linear-piston flow (LPM) models. 69 Among the two-parameter lumped models, the dispersion model (DM), that considers simplifications of the general advection-dispersion equation, has been applied in 70 71 environmental tracer studies (Maloszewski et al., 2006; Viville et al., 2006; Kabeya et al., 72 2006). Since almost one and a half decades ago, other lumped models are being exploited 73 such as the two parameter Gamma model (GM) proposed by Kirchner et al. (2000), which is a 74 more general and flexible version of the exponential model; and the Two Parallel Linear 75 Reservoirs model (TPLR), a three-parameter function that combines two parallel reservoirs, 76 each one represented by a single exponential distribution (Weiler et al., 2003). The use of 77 these models for estimating the MTT in the compartments of a catchment has become a 78 standard practice for the preliminary assessment of the catchment functioning. The advantage 79 of the latter functions relies on that they allow the representation of different mixing processes 80 in different system components, such as soil and groundwater. In contrast, simpler models 81 assume instantaneous and complete mixing over the entire model domain (Hrachowitz et al., 82 2013). Regarding to lumped parameter models, McGuire and McDonnell (2006) presented in 83 their study a compilation of the most frequently used models for deriving MTTs. Under the 84 condition that a particular model ought to be concordant with the physical characteristics of 85 the aquifer system, this condition hinders the applicability of lumped parameter models to 86 poor gauged catchments with scarce or no information on the physical characteristics of the 87 system. For these cases the authors believe that it is better to use an ensemble of models in 88 order to be certain that the results or the inferences point in the same direction, or if not, to 89 have a better idea of the uncertainties.

90 Particular for tropical zones the knowledge of hydrological functioning is still limited and 91 investigation of system descriptors such as TTD and MTT are keys to improve our 92 understanding of catchment responses (Murphy and Bowman, 2012; Brehm et al., 2008). This 93 is especially the case for tropical mountain rainforest systems. In this study we focus on the 94 San Francisco river basin, a mesoscale headwater catchment of the Amazon in Ecuador. 95 Notwithstanding the recent characterization of the climate (Bendix et al., 2006), soils (Wilcke 96 et al., 2002), water chemistry (Buecker et al., 2011) and hydrology (Plesca et al., 2012) of the 97 basin, we are still lacking a perceptual model that explains the observations of chemical, hydrometric and isotopic variables and related processes (Crespo et al., 2012). 98

99 To enhance the understanding of the hydrological functioning of the San Francisco basin, this 100 study focuses on the (i) estimation of the MTT in the different compartments of the 101 catchment; (ii) characterization of the dominant TTD functions; and (iii) evaluation of the 102 performance and uncertainty of the models used to derive the MTTs and TTDs. Translated 103 into hypotheses the study reported in this paper aimed to test if

- 104 1) the diversity of the sampling sites allows evaluating the spatial variability in
- 105 catchment hydrology, identifying the dominant processes, and screening the106 performance of the TTD models;
- 107 2) the multi-model approach and the identifiability of their parameters enable108 identification of the respective TTDs and MTTs.

109 The hypotheses are based in the following assumptions:

- 110 1) the used tracers are conservative, there are no stagnant flows in the system, and the 111 tracer mean transit time  $\tau$  represents the MTT of water (e.g. McGuire and McDonnell, 112 2006);
- stationary conditions are dominant in the basin and lumped equations based on linear
  or quasi-linear behaviors are applicable (Heidbüchel et al., 2012);
- 115 3) from insights derived of related studies (Soulsby et al., 2010; McGuire and
- 116 McDonnell, 2006; Rodgers et al., 2005), considering the drainage areas, the steepness
- 117 of the topography and the shallow depth of the soil layers, the transit times of the
- 118 sampling sites are less than 5 yr, making it possible to use  $\delta^2$ H and  $\delta^{18}$ O as tracers.
- 119 2

#### 2 MATERIALS AND METHODS

#### 120 **2.1 Study area**

The San Francisco tropical mountain cloud forest catchment (Fig. 1, Table 1), 76.9 km<sup>2</sup> in 121 122 size, is located in the foothills of the Andean cordillera in South Ecuador, between Loja and Zamora, and drains into the Amazonian river system. Hourly meteorological data recorded at 123 124 the Estación Científica San Francisco (ECSF, 1,957 m a.s.l.), El Tiro (2,825 m a.s.l.), Antenas (3,150 m a.s.l.) and TS1 (2,660 m a.s.l.) climate stations are available from the DFG funded 125 126 Research Unit FOR816 (www.tropicalmountainforest.org). Monthly averages of the main 127 meteorological parameters for the period 1998-2012 allow a description of their spatial and 128 interannual variation. Mean annual temperature ranges from 15°C in the lower part of the 129 study area (1,957 m a.s.l.) to 10°C on the ridge (3,150 m a.s.l.), with an altitude gradient of -0.57°C per 100 m, without marked monthly variability. The wind velocities of the prevailing 130 south-easterlies reach average maximum daily values of 10 m s<sup>-1</sup> between June and 131 132 September, while wind velocities in the middle and lower catchment areas are fairly constant, equal to 1 m s<sup>-1</sup>. The humid regime of the catchment is comparatively constant with the 133 134 relative humidity varying between 84.5% in the lower parts to 95.5% at the ridges. Among all 135 meteorological parameters, precipitation shows the largest spatial variability, with an average 136 gradient of 220 mm per 100 m (Bendix et al., 2008b). However, this gradient is not constant 137 throughout the catchment and shows substantial spatial variability (Breuer et al., 2013). 138 Recent estimation of horizontal rainfall revealed its significance, contributing 5 to 35% of 139 measured tipping bucket rainfall, respectively to the lower and ridge areas of the catchment

140 (Rollenbeck et al., 2011). Rainfall is marked by low rainfall intensities, generally less than 10 141 mm h<sup>-1</sup> and high spatial variability. Annual rainfall is uni-modal distributed with a peak in the 142 period April-June. Using the Thiessen method and considering horizontal rainfall, the 143 precipitation depth amounted 2,321 mm in the period August 2010-July 2011, and 2,505 mm 144 in the period August 2011-July 2012. A more detailed description of the weather and climate 145 of the study area is given in Bendix et al. (2008a).

In line with findings of Crespo et al. (2012) in the same area, baseflow accounts for 85% of the total runoff (Table 1), notwithstanding the rapid and marked response of flows to extreme rainfall events. In just a few hours peak discharges are several times higher than baseflows (Fig. 2a), carrying considerable amounts of sediment and accompanied by drastic changes in some of the cross sections.

151 Major soil types are Histosols associated with Stagnasols, Cambisols and Regosols, while Umbrisols and Leptosols are present to a lesser degree (Liess et al., 2009). The geology is 152 153 reasonable similar throughout the study area, consisting of sedimentary and metamorphic 154 Paleozoic rocks of the Chiguinda unit with contacts to the Zamora batholith (Beck et al., 155 2008). The topography is characterized by steep valleys with an average slope of 63%, 156 situated in the altitudinal range of 1,725 to 3,150 m a.s.l. (Table 1). Protected by the 157 Podocarpus National Park, the southern part of the catchment is covered by pristine primary forest and sub-páramo. In the northern part, particular during the last two decades, land is 158 159 being converted to grassland. Presently 68% of the catchment is covered by forest, 20% is sub-páramo, 6.5% is used as pasture and 3% is degraded grassland covered with shrubs 160 161 (Goettlicher et al., 2009; Plesca et al., 2012). Landslides are present in the catchment, especially along the paved road between the cities Loja and Zamora. 162

#### 163 **2.2 Catchment composition and discharge measurements**

The San Francisco catchment was subdivided into seven sub-catchments with areas ranging between 0.7 and 34.9 km<sup>2</sup>, characterized by different land uses varying from pristine forest and sub-páramo to pasture areas (Fig. 1 and Table 1). In order to define baseflow conditions, each sub-catchment was equipped with a water level sensor (mini-diver, Schlumberger Water Services, Delft, NL). Reference discharge measurement, using the salt dilution method, where made frequently during the time of sampling. However, due to the high variability of the river bed for the sites QP, QZ and QR, only continuous records for sub-catchments FH, QN, QM, QC, and for the main outlet PL were considered as reliable to calculate stage-discharge curves
and the hydrographs, as shown in Fig. 2a for PL. For the remaining sites, discharge measured

173 at the moment of sampling was used.

#### 174 **2.3** Isotope sampling and analyses

175 Weekly water samples for isotope analysis were collected manually in the main river (Fig. 176 2b), its tributaries, creeks and springs in the period August 2010 to mid-August 2012 and later for soil water starting in September/November 2010 (Table 2), using 2 mL amber glass 177 178 bottles. Soil water sampling was performed along two altitudinal transects covered by forest 179 and pasture (Table 2), in 6 sites (Fig. 1) and 3 depths (0.10, 0.25 and 0.40 m) using wick-180 samplers. Wick-samplers were designed and installed as described by Mertens et al. (2007). 181 Woven and braided 3/8 fiberglass wicks (Amatex Co. Norristown, PA, US) were unraveled 182 over a length of 0.75 m and spread over a 0.30 m  $\times$  0.30 m  $\times$  0.01 m square plastic plate. The 183 plate enveloped with fiberglass was covered with fine soil particles of the parent material and 184 then set in contact with the undisturbed soil, respectively at the bottom of the organic horizon 185 (0.10 m below surface), a transition horizon (0.25 m below surface) and a lower mineral 186 horizon (0.40 m below surface). The low constant tension in the wick-samplers guarantees 187 sampling of the mobile phase of soil water, avoiding isotope fractionation (Landon et al., 188 1999).

189 Along with the weekly sampling, event based rainfall samples for isotope analyses were 190 collected manually in 1 L bottles using a Ø 25 cm funnel at 1900 m a.s.l. (Fig. 1). After every 191 event, the sample bottles were covered with a lid and stored for analysis within a week in 2 192 mL amber glass bottles. Only sample volumes > 2 mL were suitable for permanent storage 193 and measurements. Events with a sample volume below 2 mL were discarded. The end of a 194 single rainfall event was marked by a time span of 30 min without rainfall, whereby a total of 946 samples were collected with an average duration of 3.2 h (varying from 0.25 to 19 h with 195 196 up to 11 events per day). Since the solving of the convolution equation needs a continuous 197 time step of input data (Maloszewski and Zuber, 1982), the time resolution of the input series 198 was set to 7 days (Fig. 2c). In this sense, weekly mean isotopic signatures for smaller rainfall 199 events during longer dry periods (only 5 among 104 weeks had no rainfall event > 2 mL 200 sampling volume) were interpolated using antecedent and precedent measurements.

201 The final isotope signature used for the models represents:

- 202 for rainfall water, the weighted mean of all events during each week (Sundays to
- Saturdays) using the rainfall data recorded at the nearby meteorological station (400 m toECSF),
- 205 for soil water samples, the weekly average isotope signal for each soil depth, and
- 206 for stream, creek and spring water samples, an instantaneous isotopic concentration in
- time. These samples were not flux-weighted. For stream waters, only isotope samples from
  designated baseflow conditions were later considered (see Section 2.5).

The stable isotopes signatures of  $\delta^{18}$ O and  $\delta^{2}$ H are reported in per mil relative to the Vienna Standard Mean Ocean Water (VSMOW) (Craig, 1961). The water isotopic analyzes were performed using a compact wavelength-scanned cavity ring down spectroscopy based isotope analyzer (WS-CRDS) with a precision of 0.1 per mil for  $\delta^{18}$ O and 0.5 for  $\delta^{2}$ H (Picarro L1102i, CA, US).

#### 214 **2.4** Isotopic gradient of rainfall

215 Throughout the catchment, the recorded rainfall time series from meteorological stations are correlated (r<sup>2</sup> was at least 0.6, based on weekly precipitation data). As the models in question 216 217 are only driven by the isotope signal and not by the actual amount of incoming precipitation 218 on site, a flux weighting based on a single station within the catchment (ECSF) was sufficient. 219 Given the large altitudinal gradient in the San Francisco basin, it is to be expected that the 220 input isotopic signal of rainfall for every sub-catchment varies according to its elevation 221 (Dansgaard, 1964). In this regard, Windhorst et al. (2013) estimated this variation for the main transect of the catchment: -0.22‰  $\delta^{18}$ O. -1.12‰  $\delta^{2}$ H and 0.6‰ deuterium excess per 222 100 m elevation gain. Applying this altitude gradient to the flux weighted isotope signal under 223 224 the assumption that the incoming rainfall signal is the sole source of water, thereby excluding 225 any unlikely source of water from outside the topographic catchment boundaries with a 226 different isotope signal, it was possible to derive the recharge elevation and localized input 227 signal in each sub-catchment. The derived recharge elevations were used to crosscheck that 228 they are inside the topographic boundaries of every sub-catchment and comparable to their 229 mean elevations.

The justification to adopt only the mentioned gradient to extrapolate the isotope signals, was based in previous studies on spatial and temporal variation of stable isotopes of rainfall in the same catchment, which revealed that, only the altitude effect is significant and that in this factor there is no influence of temperature, relative humidity and precipitation amount orintensity (Windhorst et al, 2013).

Since no marked fractionation was observed for all analyzed waters it is highly probable that similar estimations of MTT are derived using either  $\delta^{18}$ O or  $\delta^{2}$ H (Fig. 3). Therefore, in this study  $\delta^{18}$ O was selected for further analysis.

#### 238 **2.5** Mean Transit Time estimation and Transit Time Distribution

239 Mean transit times were calculated based on stationary conditions. In the case of stream water 240 this condition was fulfilled by considering only baseflow conditions (Heidbüchel et al., 2012), 241 which were dominant in the catchment during the 2 yr observation period (Figs. 2a and 2b 242 depict this characteristic for the main outlet), accounting for 85% of total runoff volume. 243 Baseflow separations for streamflow were obtained through parameter fitting to the slope of 244 the recessions in the observed hourly flows using the Water Engineering Time Series 245 PROcessing tool (WETSPRO), developed by Willems (2009). To account for samples taken at baseflow conditions in sites where hydrometric records were not available, the specific 246 247 discharges of the closer catchments with similar characteristics in terms of land use, size, and observed hydrologic behavior were used. In this sense, QZ, QR and QP were considered 248 249 similar to QN, QM and QC (Table 1). In contrast, all spring and creek water samples were 250 included in the analysis since their isotopic signatures were less influenced by particular rain 251 events (as inferred from the smooth shape of the observed isotope signal) in the San Francisco 252 catchment. In regard to soil water, we considered all samples, since each sample represents a 253 volume weighted weekly average signature (isotopic signatures of particular high rainfall 254 events are smoothed at a weekly time span).

For the calculation of MTTs, the authors used the lumped parameter approach. In this, the aquifer system is treated as an integral unit and the flow pattern is assumed to be constant as outlined in Maloszewski and Zuber (1982) for the special case of constant tracer concentration in time-invariant systems. In this case the transport of a tracer through a catchment is expressed mathematically by the convolution integral. The tracer output  $C_{out}(t)$ and input  $C_{in}(t)$  are related as function of time:

261 
$$C_{out}(t) = \int_{-\infty}^{t} C_{in}(t') \exp\left[-\lambda(t-t')\right] g(t-t') dt'$$
 (1)

In the convolution integral, the stream outflow composition  $C_{out}$  at a time *t* (time of exit) consists of a tracer  $C_{in}$  that falls uniformly on the catchment in a previous time step *t*' (time of entry),  $C_{in}$  becomes lagged according to its transit time distribution g(t-t'); the factor  $exp[-\lambda(t-t')]$  is used to correct for decay if a radioactive tracer is used ( $\lambda$  = tracer's radioactive decay constant). For stable tracers ( $\lambda = 0$ ), and considering that the time span *t-t*' is the tracer's transit time  $\tau$ , Eq. (1) can be simplified and re-expressed as:

268 
$$C_{out}(t) = \int_{0}^{\infty} C_{in}(t-\tau)g(\tau)d\tau$$
(2)

269 where the weighting function  $g(\tau)$  or tracer's transit time distribution (TTD), describes the 270 normalized distribution function of the tracer injected instantaneously over an entire area 271 (McGuire and McDonnell, 2006). As it is hard to obtain this function by experimental means, 272 the most common way to apply this lumped approach is to adopt a theoretical distribution 273 function that better fits to the studied system. In general meaning, any type of a weighting 274 function is understood as a model. In accordance, seven lumped parameter models to infer the 275 MTTs for diverse water storages (stream, springs, creeks and soil water) were applied in this 276 study. Results were evaluated on the basis of the best matches to a predefined objective function, their magnitude of uncertainty and the number of observations in the range of 277 278 behavioral solutions. The equations for each of the lumped parameter models used are shown 279 in Table 3. EM and LM reflect simpler transitions where the tracer's mean transit time  $\tau$  is the 280 only unknown variable. More flexible models consider a mixture of two different types of 281 distribution. EPM includes piston and exponential flows, while the LPM accounts for piston 282 and linear flows. In both cases the equations are integrated by the parameter  $\eta$  indicating the percentage contribution of each flow type distribution. The DM, derived from the general 283 284 equation of advection-dispersion, is also one of the common models used in hydrologic 285 systems (Maloszewski et al., 2006). In this model the fitting parameter  $D_p$  is related to the 286 transport process of the tracer (Kabeya et al., 2006). In the GM, the product of the two shape 287 parameters  $\alpha$  and  $\beta$  equals  $\tau$ . This method was successfully applied by Dunn et al. (2010) and Hrachowitz et al. (2010). The TPLR model (Weiler et al., 2003) is based on the parallel 288 289 combination of two single exponential reservoirs (despite of its name TPLR follows 290 exponential and not linear assumption), representing fast  $\tau_f$  and slow flows  $\tau_s$ , respectively. The flow partition between the two reservoirs is denoted by the parameter  $\phi$ . 291

#### 292 **2.6 Convolution equation resolution**

293 Due to the similarities between the seasonal isotopic fluctuations of the sampled effluents and 294 rainfall signal, a constant interannual recharge of the aquifers was assumed. For each 295 sampling site, the 2 yr isotopic data series were used as input for the models. To get stable 296 results between two consecutive periods, these input isotope time series were repeated 20 times in a loop; an approach similar to the methodology presented by Munoz-Villers and 297 298 McDonnell (2012) resulting in an artificial time series of 40 yr. It is common practice to 299 extend the time series artificially by duplicating it (Hrachowitz et al., 2010 and 2011). This 300 does not change the results; it rather gives the model more room to find stable results. Data of 301 the last loop were considered for statistical treatment and analysis. The repetition of the input 302 isotopic signal implies that the interannual variation is negligible; an acceptable assumption 303 for the San Francisco catchment considering the high degree of similarity between the same 304 months along the analyzed 2 yr period (Fig. 4). Comparable monthly isotopic seasonality of 305 rainfall has been described by Goller et al. (2005) for the same study area and for nearby 306 with similar climatic conditions, e.g., Amaluza **GNIP** station regions 307 (http://www.iaea.org/water).

Modelled output results are available for the weekly time span chosen for the input function (an average signal of rainfall was distributed for every week at Wednesdays 12:00). These results were interpolated in order to perform statistical comparisons with instantaneous observed data. For soil waters, direct comparisons were performed between predictions and observed data.

#### 313 **2.7 Evaluation of model performance**

The search for acceptable model parameters for each site was conducted through statistical comparisons of 10,000 simulations based on the Monte-Carlo method, considering a uniform random distribution of the variables involved in each model. For each site and model its performance was calculated using the Nash-Sutcliffe Efficiency (NSE). Quantification of errors and deviations from the observed data were respectively calculated by the root mean square error (RMSE) and the bias. MatLab version 7 was used for data handling and solving the convolution equation.

When looking for the optimum parameter range, we first set a wide range (maybe even unrealistic) to be sure to cover all possible solutions (Table 3). By checking the plots of these 323 preliminary results we were able to identify the convergence of model solutions (we used 324 NSE as the objective function for all model parameters), thereby making it possible, for a 325 second simulation, to narrow down the parameter range for each variable. Once the variation 326 ranges were identified and bounded, according to the largest solution peak for every site and 327 for every variable, all the solutions 5% below the top NSE efficiency were selected. For these 328 behavioral efficiencies, weighted quantiles between 0.05 and 0.95 (90% prediction limits) 329 were calculated in order to refine limits of behavioral solutions for every variable. Using these 330 limits, a final simulation for each site and model was performed (at this stage the 10,000 331 simulations were allowed to vary only for the corresponding final solution ranges). Results 332 are shown in Tables 4 and 5, as well as in Annexes 1 and 2.

333 The before mentioned approach is based on the Generalized Likelihood Uncertainty 334 Estimation (GLUE, Beven and Freer, 2001). The GLUE approach considers that several likely 335 solutions are valid as long as efficiency of a particular simulation is above a pre-set, but 336 subjective threshold. In this sense, considering the large number of sites and models used, no 337 specific lower limit was set to discriminate predictions, but (as explained earlier) a range that 338 depended on the top efficiency for each case. Only for the analysis of results and for 339 intercomparison between predictions, we considered that a prediction was poor for NSE <340 0.45.

The following three criteria were used to select the best solutions of MTTs and TTDs from the final model runs: 1) NSE; 2) magnitude of the uncertainty of the prediction, expressed as a percent of the predicted MTT value; and 3) percentage of observations covered by the range of behavioral solutions defined according to the second criteria.

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#### **3**46 **3 Results**

#### 347 **3.1 Soil water**

Of all predictions the best matches of the models, with respect to the NSE objective function, ranged between 0.64 and 0.91 (Fig. 5a). When only the best goodness of fit was considered, the GM and the EPM models performed best in most of the sampled sites (13 from 18), followed by the DM, LM and LPM models (Fig. 5b). Only these models were considered for further mutual comparison. Even when the derived MTT values were similar among the models that best fitted the objective function (Fig. 6a, Table 4 and Annex 1), the LPM model performed best taking into consideration additional selection criteria, as shown in Figs. 6b and
6c. Fig. 7 depicts, for the LPM model applied to site C2, the uncertainty and the range of
behavioral solutions for the two model parameters.

357 Considering results from the LPM model (Table 4), differences between observed and 358 predicted values described by the RMSE are up to 1.72‰ and the larger absolute bias 359 accounts for 0.181‰ (Table 4). Bearing in mind the ranges of behavioral solution, MTT 360 results were between 2.3 to 6.3 weeks for pastures soils and between 3.7 to 9.2 weeks for 361 forested soils, while parameterizations for  $\eta$  (ratio of the total volume to the volume in which 362 linear flow applies) ranged from 0.84 to 2.23 and from 0.76 to 1.61 respectively.

363 Regarding to the shapes of the distribution functions, Fig. 8 shows the best matching results for two representative and comparable sampling sites (C2 for pastures and E2 for forest) for 364 365 each lumped model (results for LM model are not included since best matching results for LPM were achieved with  $\eta \approx 1$ , see Table 4). These probability (PDF) and cumulative density 366 367 functions (CDF) depict how water is routed through the system. In this sense, pasture sites 368 generally show a faster and higher response of the tracer peak when compared to forest sites. 369 The CDF (Figs. 8b and d) of all models are quite similar for the major part of the flows, even including the linear function LPM that averages the shape of the peaks described by the other 370 371 models. Models based on exponential functions (EPM, DM, or GM in Figs. 8b and d) predict 372 a small portion of the flow with an exponentially delayed tail, which is larger for forested sites 373 than for pastures. Best distribution function results (based on highest NSEs) for all sampled 374 sites, according to the type of land cover, are shown in Figs. 9a and b for the LPM and GM 375 models applied to pasture sites, and in Figs. 9c and d for forest sites. Considering the range of 376 possible or behavioral solutions (e.g., shaded area represents range of solutions for C2 site in 377 Figs. 9a and b, and for E2 in Figs. 9c and d), distributions functions for each type of model 378 and land cover are very similar between each sampled site.

#### **379 3.2 River and tributaries**

Considering all sites and models the criteria NSE > 0.45 was exceeded in 41 of the 63 predictions (9 sites per 7 models, Fig. 5a). Among the analyzed sites the TPLR model yielded the best matches for PL, SF, FH, QZ, QN, QM and QC, while the EPM model for the QR and QP sites (Fig. 5b). The GM model reached closest efficiencies when compared to the best match for every site. Consequently only the TPLR, EPM and GM models were further 385 considered. Differences between MTT predictions for all sites are depicted in Fig. 10a and 386 results from retained models in Table 5 and Annex 2. Although MTT results according to the 387 best NSEs were reached using the TPLR model, compared to the GM or the EPM, these 388 predictions also showed the largest uncertainties (Fig. 10b) and at the same time depicted the 389 lowest number of observations inside the predicted range of behavioral solutions (Fig. 10c). 390 Considering these additional selection criteria, EPM performed better. For stream water at the 391 main outlet, Figs. 11-13 show the parameter uncertainties and behavioral solutions for the 392 TPLR, GM and EPM models, respectively.

- 393 Considering results from the EPM model (Table 5, Fig. 10a), the fitting efficiencies reached a 394 maximum NSE of 0.56 for the main stream, and NSEs between 0.48 and 0.58 for the main tributaries (Fig. 5a). The predicted MTT at catchment outlet was 2.0 yr with a  $\eta$  parameter of 395 396 1.84 (a similar value was estimated for the main river at the SF sampling site, MTT = 2.0 yr 397 and  $\eta = 1.85$ ) and varied from 2.0 (QM,  $\eta = 1.85$ ) to 3.9 yr (QC,  $\eta = 1.97$ ) for the main 398 tributaries. Uncertainties of MTT predictions between sites were similar with a maximum 399 range between 14.1% and 20.4% of the predicted MTT, as derived for the FH and QM sites 400 (Table 5). Similarly,  $\eta$  ranged from 1.61 (QZ) to 2.21 (QP), the average value of  $\eta = 1.85$ 401 implies a 54% of volume portion of exponential flow and a 46% volume of piston flow; the 402 uncertainty for the  $\eta$  parameter was 25% on average.
- 403 Figures 14a and 14b show the shape of the TTD for the main river outlet (PL), corresponding 404 to the highest NSEs for EPM, GM and TPLR models. The curve for EPM shows a delayed 405 peak that is not accounted in the GM or TPLR models (Fig. 14a), which in turn are very 406 similar between them (at least after a short initial time since GM tends to infinity for times 407 closes to cero). Besides, the latter models show a more delayed flow tail when compared to 408 EPM, which show in general a faster transit time (Fig. 14b). Differences between stream 409 water TTDs from the main sub-catchments considering EPM and GM models are shown in 410 Figs. 15a and b. For comparison of the degree of similarities between sites, these plots include the range of behavioral solutions for the main outlet (PL), thereby being clear that apart from 411 412 QC or QP, the remaining sites have similar (EPM or GM) transit time distribution functions.

#### 413 **3.3 Springs and creeks**

414 Of 35 predictions (7 models for 5 sites) the criterion NSE > 0.45 was fulfilled in 20 cases. 415 Sites with reduced isotope signal (small  $\sigma$ ) yielded lower efficiencies (Fig. 5a, Table 5 and

- 416 Annex 2). Apart from TP and QRS, in the remaining sites the criterion NSE > 0.45 was 417 reached at least by 5 models. TP, PLS and SFS sites were best described by using a TPLR 418 model (Fig. 5b). In this regard, GM and EPM were the second and third best models. Figure 419 10a shows the MTT results predicted by the three models, while detailed information is given 420 in Table 5 and Annex 2. As for stream waters, the EPM model performed best when looking 421 at the uncertainties and the number of observed data inside the range of behavioral solutions 422 (Figs. 10b and c).
- 423 Considering EPM, MTTs of 4.5 yr (NSE = 0.49,  $\eta = 1.74$ ) for TP and 2.1 yr (NSE = 0.65,  $\eta =$ 424 1.84) for Q3 were estimated; while for springs, 2.0 yr (NSE = 0.69,  $\eta = 1.85$ ) for PLS and 3.3 425 yr (NSE = 0.47,  $\eta = 1.42$ ) for SFS. Results for the QRS site showed poor reliability due to the 426 reduced amplitude of  $\delta^{18}$ O in the observed data (Table 5), the lowest among the observed sites 427 ( $\sigma = 0.17$ ). Estimations of MTTs for this site was larger than 5 yr, and therefore beyond the 428 level of applicability of the method for natural isotopic tracers.
- 429 Figures 14c and d show the TTD results of EPM, GM and TPLR models, for a representative 430 site with long MTT (creek TP). This site show a distinctive more delayed time to the peak (for 431 EPM model) and longer duration of flow tails compared to stream water (Figs. 14a and b). In 432 Figs. 15c and d, the TTDs for all spring and creek sampled sites are shown for the EPM and 433 GM models. In these figures, it is noticeable that the sites Q3 and PLS show the same patterns 434 described previously for most of the stream waters (Figs. 14a and b), while some differences 435 related to more delayed flow responses can be accounted for SFS, TP or QRS sites (Figs. 15c 436 and d), which are more similar to QP and QC stream waters.

#### 437 **4 Discussion**

438 For each soil water site, similar MTT results of a few weeks to months were obtained 439 regardless of the lumped parameter model used (Fig. 6a, Table 4 and Annex 1). Although the 440 LPM model did not vield predictions with the highest efficiencies (Fig. 5a), provided smaller 441 ranges of uncertainty (Fig. 6b) and a larger number of observations inside them (Fig. 6c), 442 advantages that could not be inferred by using only the best matches to NSE, for which GM 443 and EPM models performed better than others (Fig. 5b). Using a LPM model, suitable to 444 describe a partially confined aquifer with increasing thickness (Maloszewski and Zuber, 445 1982), we found MTTs varying from 2.3 to 6.3 weeks for pastures sites and from 3.7 to 9.2 446 weeks for forested soils. If we consider that only the top soil horizon was sampled (maximum 447 sampled depth was 0.4 meters), these results are comparable to values between 7.5 and 31

448 weeks found in 2.0 meter soil columns of typical Bavarian soil using the DM model 449 (Maloszewski et al., 2006). When analyzing the distribution function for soil waters, 450 similarities between model results are evident (Figs. 8 and 9). Considering the range of 451 possible solutions of each site (shaded areas in Figs. 9a-d), it is noticeable that the major part 452 of the flow's transit can be described similarly by all models, even using the simpler function (LPM). For these sites, when considering exponential models (EPM, GM or DP), a small 453 454 portion of the flow is depicted as having a delayed tail; however, compared to the magnitude 455 of the total volume, an LPM distribution could still be considered as a reliable method to 456 estimate MTTs.

457 Considering the LPM results for MTTs of soil water from pastures (4.3 weeks on average) 458 and forest sites (5.9 weeks on average) as independent data sets, a two tailed *p*-value of 459 0.0075 for a Student's t-test was calculated, meaning that the difference between the two 460 groups was statistically significant, although physical characteristics, like length, slope and 461 altitude and meteorological conditions of the respective hill slopes were more or less similar. 462 Land use effects, affecting soil hydraulic properties controlling the infiltration and flow of water, were detected in previous studies within the research area (Huwe et al., 2008). 463 464 Confirming findings in other tropical catchments were published by Zimmermann et al. (2006) and by Roa-Garcia and Weiler (2010), who stated that under grazing the hydraulic 465 466 conductivity decreased, overland and near surface flows increased, the storage capacity of the 467 soil matrix declined, with feedbacks on the MTT of soil water. Similar insights were found by 468 Tetzlaff et al. (2007) comparing two small catchments in Central Scotland Highlands of 469 different land use.

For larger MTTs (> 1 yr), as derived for sampled surface waters and shallow springs, there were differences when predicted results among models were compared (Fig. 10a, Table 5 and Annex 2), especially for sites with strong damped signals of measured  $\delta^{18}$ O (e.g. QRS and TP sites). When considering uncertainties, the EPM model performed significantly better when compared to the TPLR or GM models (Figs. 10b and c), although the latter two performed best for most of the sampled surface waters according to the NSE objective function (Figs. 5a and b).

When analyzing results from different models, dotty plots of model parameter uncertainty are
very useful to display not only the magnitude of uncertainty but also its tendency. Similarly,
the uncertainty bands of behavioral solutions can help to account for the sensitivity of the

parameter uncertainty on  $\delta^{18}$ O modeled results. For example, when predicted results for the 480 481 PL site are compared, larger parameter uncertainty and skewness are notorious for TPLR than 482 for EPM or GM models (Figs. 11a-c for TPLR; 12a-c for GM; 13a and b for EPM). At the 483 same time EPM shows the highest sensitivity in modeled results (Figs. 11d, 12d, 13c). In 484 order to contrast the signature of the effluent with younger waters such as rainfall, Figs. 11e, 12e, or 13d show the damped observed (and predicted)  $\delta^{18}$ O signatures at the main outlet; a 485 486 characteristic present in all analyzed surface waters. Considering the efficiencies reached by 487 the predictions, we should keep in mind that ranges of behavioral solutions derived from a 488 fixed 5% of the top NSE are generally smaller than a predefined lower limit for all waters, 489 e.g., a predefined lower efficiency limit of 0.30 and 0.45 were used by Speed et al. (2010) and 490 Capell et al., (2012), respectively.

491 For stream waters, as for springs and creeks, the main differences between EPM and GM (or 492 TPLR) results consisted first in a delayed response of the tracer signal in the outlet, modeled 493 by a parameter  $\eta > 1$  (Table 5), while for GM or TPLR the response of the flow occurred 494 instantaneously after the spread of the tracer along the catchment (Figs. 14 and 15, Annex 2); 495 and secondly by a comparatively smaller exponential flow tails, which also means that in 496 general the flow transport is faster considering EPM than GM or TPLR models. For these 497 cases, regardless of the degree of efficiencies or uncertainties, the decision on which TTD is 498 more reliable would depend on the conceptual knowledge of the functioning of the catchment. 499 For the San Francisco catchment this can be gained through additional field experiments in 500 selected sites or sub-catchments using either higher resolution samples from the effluents in 501 order to analyze non steady conditions (Botter et al., 2011) or considering different mixing 502 assumptions (Hrachowitz et al., 2013). Another approach could be to analyze longer time 503 series of stable isotopes, or even to include radioactive isotopes as tritium, which would help 504 to crosscheck results, as it has been claimed that, in some cases, the inferences of the 505 processes using solely stables isotopes, underestimate the delayed part of the flow (Stewart et al., 2010). 506

Regardless of the used model, efficiencies of MTT for stream waters were lower than for soil waters. This was somehow expected, since the dampening effect on a catchment to subcatchment scale generates a smoother signal filtering/averaging the heterogeneity observed at a single point along a precise transect. Since for most of the cases MTTs for soil waters showed an increasing trend according to increasing soil depth, longer MTTs corresponding to 512 deeper soil layers are to be expected. Soil water below 0.4 m was not monitored within this 513 study, given the shallow soil depth and the increasing fraction of rock material with depth, 514 preventing the use of wick samplers.

515 The similarities and differences between models for sites with MTTs > 1 yr, as for stream and 516 spring waters, gave insights about the importance to account for a proper TTD, defined 517 according to the conceptual knowledge of the catchment's functioning, before calculating 518 MTT. In this regard, the use of a multi-model approach and uncertainty analysis is believed 519 essential as to be able of defining which functions describes in a better way the parameter 520 identifiability and bounds of behavioral solutions. By considering best matches to NSE for 521 stream waters, best predictions were obtained with the TPLR, EPM and GM models; being 522 more flexible versions of a pure exponential distribution function (i.e. EM model), which help 523 to account for non-linearities of the system. The same distribution functions were identified as 524 good predictors of observed data in a related study by Weiler et al. (2003). When comparing 525 the TPLR to EPM or GM models, the latter two take the non-linearity of the flow without 526 splitting it in two reservoirs with different exponential behaviors into account, therefore 527 yielding more identifiable results. However, findings by Weiler et al. (2003) suggest that the 528 TPLR distribution function could achieve better predictions for runoff events generated by 529 mixed fast and slow flows. In related studies using multiple models, the EPM model yielded 530 the best predictions for surface and spring waters (Viville et al., 2006). Considering this 531 model, in the San Francisco catchment, the average  $\eta = 1.85$  value for surface waters (similar 532 values were found for creeks:  $\eta = 1.79$  and springs:  $\eta = 1.64$ ) implies that a significant portion 533 of old water (46%) is released previous to the new one (54%). The  $\eta$  value in this study is 534 larger than the  $\eta$  value found in studies for stream water in temperate small headwaters 535 catchments ( $\eta = 1.09$ , Kabeya et al., 2006;  $\eta = 1.28$ , McGuire et al., 2002;  $\eta = 1.37$ , Asano et 536 al., 2002), and close to results published by Katsuyama et al. (2009) for two riparian groundwater systems ( $\eta = 1.6$  and 1.7). 537

Regarding to the Gamma model, it was also identified as an applicable distribution function in headwater montane catchments with dominant baseflow in temperate climate (Hrachowitz et al., 2009a, 2010; Dunn et al., 2010). For our study area, a characteristic shape parameter  $\alpha < 1$ (e.g. Fig. 12b and Annex 2) was found in all stream and spring sites meaning that an initial peak or a significant part of the flow was quickly transported to the river. Similar results were found recently for mountain catchments of comparable size in Scotland by Kirchner et al. 544 (2010), who also stated the importance for accounting the best distribution shape, which is 545 usually assumed as purely exponential ( $\alpha = 1$ ). MTTs derived without the use of observed 546 data, using a purely exponential model, frequently led to an overestimation of  $\alpha$  and 547 consequently an underestimation of MTTs. The higher flexibility of the GM model permits to 548 account for the non-linearity in the behavior of a catchment system (Hrachowitz et al., 2010).

#### 549 **5 Conclusions**

550 The research revealed that looking for the best TTD and its derived MTT is not only matter of 551 accounting for the best fit to a predefined objective function, instead, it is recommended to (1) 552 include in the analysis several potential TTD models, (2) assess the uncertainty range of 553 predictions and (3) account for the parameter identifiability. Although the uncertainty range 554 increases for MTTs larger than 1 to 2 yr, using simpler models that still yield acceptable fits 555 to an objective function can help to reduce the uncertainty associated to the predictions. In 556 this sense, using the best predictions from models like LPM for soil waters and EPM for 557 surface and spring waters yielded a more reliable range of MTT inferences through lowering 558 the uncertainty associated in the predictions of certain models. Sites that showed substantial 559 differences in predictions between models (e.g. QRS or TP) were related to a strong reduction 560 of the isotopic signal yielding larger uncertainties and extended MTT predictions getting close 561 to the limitations of the used method. It is recommended to interpret these results with care, 562 even to not consider them until longer time series of isotopic data are available.

563 The diversity of sampling sites and uncertainty analysis, based on the best fits to the objective 564 function NSE and the identifiability of the parameters of the convolution equations of 7 565 conceptual models, allowed to define with adequate accuracy the ranges of variation of the 566 mean transit times and the proper distributions functions for the main hydrological 567 compartments of the San Francisco catchment. Pure exponential distributions (i.e. EM) 568 provided the poorest predictions in all sites, suggesting non-linearities of the processes, as 569 produced by preferential or bypass flow. On the other hand, models such as EPM or GM 570 which have a better performance in terms of considering the non-linearity, in most cases 571 yielded better fits to the observed data and at the same time better identifiability of its 572 variables ( $\tau$ ,  $\eta$  or  $\alpha$ ).

573 For baseflow conditions, which are annually dominant in the catchment area, stream water at 574 the main outlet (PL) and five tributaries (FH, QZ, QN, QR, QM) yielded similar MTT 575 estimations, ranging from 1.8 to 2.5 yr, including uncertainty ranges; while the MTT 576 estimation for two tributaries (QP and QC) were between 3.5 to 4.4 yr. Despite the similar 577 contribution areas, 2 small creeks described contrasting transit times, TP between 4.2 and 5.1 578 yr, and Q3 between 1.9 and 2.2 yr. Springs showed a longer variation range, from 2.0 yr for 579 PLS to larger than 5 yr for QRS. Considering the predominance of the stream water characteristics of the larger sub-catchments and the higher variability of smaller tributaries 580 581 (creeks and springs), there is a clear indication that the heterogeneity of the small scale 582 aquifers is averaged in large areas. In this sense, an in depth analysis on individual 583 functioning or intercomparison between analyzed sites, which was beyond the scope of this 584 paper, should be performed in selected areas using longer time series.

Two transects based on land cover characteristics showed differences in MTTs. Pastures have shorter ranges (2.3-6.3 weeks) than forested (3.7-9.2 weeks) areas. Considering the characteristics of the sampling sites (Table 1), results suggest a possible regulatory effect of land use on water movement. Although the representativeness of the sampled sites is low in comparison to the total catchment area, findings point out the potential of environmental tracer methods for estimating the effects of changes in vegetation, a task usually difficult to accomplish by conventional hydrometric methods.

592

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_		Outlet			Su	b-catchm	ent		
Parameter	Units	PL	FH	QZ	QN	QR	QP	QM	QC
Catchment physical of	characteristics								
Drainage area	[km <sup>2</sup> ]	76.9	34.9	11.2	9.8	4.7	3.4	1.3	0.7
Mean elevation	[m a.s.l.]	2,531	2,615	2,615	2,591	2,472	2,447	2,274	2,290
Altitude range	[m]	1,325	1,133	991	975	1,424	975	772	516
Mean slope	[%]	63	63	63	60	69	67	57	56
Hydrological parame	eters								
Discharge	[mm]	2,959	2,691	-	1,291	-	-	3,315	2,742
Baseflow	[mm]	2,520	2,152	-	1,044	-	-	2,118	2,268
	[%]	85.2	80.0	-	80.8	-	-	63.9	82.7
Land use									
Forest	[%]	68	67	72	65	80	63	90	22
Sub-páramo	[%]	21	29	15	17	18	10	9	10
Pasture/Bracken	[%]	9	3	12	16	2	26	1	67
Others	[%]	2	1	1	2	0	1	0	1
Soil type									
Histosols	[%]	74	74	70	71	70	62	57	54
Regosols	[%]	15	15	18	16	18	21	25	24
Cambisols	[%]	7	7	8	8	8	11	13	14
Stagnasols	[%]	4	4	4	5	4	6	5	8

### **Table 1.** Main characteristics of the San Francisco catchment and its tributaries.

Sample type	Collection method	Sampled since <sup>a</sup>	Site Name	Site code	Altitude m a.s.l.	Samples Number (Weeks)
Rainfall	Collector	ctor AUG 2010 Estación San Francisco		ECSF	1900	99
			Planta (outlet)	PL	1725	104
Main river	Manually	AUG 2010	San Francisco	SF	1825	104
			Francisco Head	FH	1917	98
			Zurita	QZ	2047	103
			Navidades	QN	2050	104
Tributaries	Manually	AUG 2010	Ramon	QR	1726	104
			Pastos	QP	1925	103
			Milagro	QM	1878	104
			Cruces	QR	1978	102
		DEC 2010	Pastos tributary	TP	1950	88
Creeks	Manually	DEC 2010	Q3	Q3	1907	88
			PL Spring	PLS	1731	98
Springs	Manually	AUG 2010	SF Spring	SFS	1826	100
			QR Spring	QRS	1900	100
			Pastos alto <sup>b</sup>	A1 / A2 / A3	2025	60 / 58 / 45
Pastures soil	Wick-sampler	NOV 2010	Pastos medio <sup>b</sup>	B1 / B2 / B3	1975	70 / 70 /63
water			Pastos bajo <sup>b</sup>	C1 / C2 / C3	1925	67 /71 / 55
			Bosque alto <sup>b</sup>	D1 / D2 / D3	2000	78 / 74 / 62
Forest soil water	Wick-sampler	SEP 2010	Bosque medio <sup>b</sup>	E1 / E2 / E3	1900	86 / 80 / 62
mater			Bosque bajo <sup>b</sup>	F1 / F2 / F3	1825	55 / 53 / 36

### **Table 2.** Applied sampling strategy in the San Francisco catchment.

<sup>a</sup> Sampling campaign was completed until mid-August 2012.

<sup>b</sup> There are three wick-samplers per site (i.e. A1=0.10 m, A2=0.25 m and A3=0.40 m below surface).

Model	Transit time distribution $g(\tau)$	Parameter(s) range
Exponential Model (EM)	$\frac{1}{\tau} \exp\left(\frac{-t}{\tau}\right)$	τ[1-400]
Linear Model (LM)	$\frac{1}{2\tau}  \text{for } t \le 2\tau$	τ [1-400]
	$0 \text{ for } t > 2\tau$	
Exponential Piston flow Model (EPM)	$\eta_{\text{evp}}\left(-\eta_{+},\eta_{-}\right)$	$\tau$ [1-400]
	$\frac{\tau}{\tau} \exp\left(-\frac{\tau}{\tau} + \eta - 1\right) \text{ for } t \ge \tau (1 - \eta^{-1})$	η [0.5-4]
	$0_{\text{for }} t < \tau(1 - \eta^{-1})$	
Linear Piston flow Model (LPM)	η	$\tau$ [1-400]
	$\overline{2\tau}$ for $\tau - \frac{\tau}{\eta} \le t \le \tau + \frac{\tau}{\eta}$	η [0.5-4]
	$0_{\text{for other}} t$	
Dispersion Model (DM)	$(4\pi D t)^{-1/2}$ $\left[ (t)^2 (\tau)^2 \right]$	$\tau$ [1-400]
	$\left(\frac{mD_{p^{t}}}{\tau}\right)  t^{-1}\exp\left[-\left(1-\frac{t}{\tau}\right)\left(\frac{t}{4D_{p}t}\right)\right]$	<i>D<sub>p</sub></i> [0.5-4]
Gamma Model (GM)	$\tau^{\alpha-1}$ , $\alpha$	α [0.0001-10]
	$\frac{1}{\beta^{\alpha}\Gamma(\alpha)}\exp^{-\tau/\beta}$	$\tau$ [1-400]
	$p + (\alpha)$	$\beta = lpha /  au$
Two Parallel Linear Reservoirs	$\phi$ $\begin{pmatrix} t \\ -t \end{pmatrix}$ $1-\phi$ $\begin{pmatrix} -t \\ -t \end{pmatrix}$	$\tau_{s}$ [1-400]
(TPLR)	$\frac{\psi}{\tau_f} \exp\left(-\frac{\iota}{\tau_f}\right) + \frac{1-\psi}{\tau_s} \exp\left(\frac{-\iota}{\tau_s}\right)$	$\tau_{f}$ [1-40]
		$\phi$ [0-1]

839  $\tau =$  tracer's mean transit time;  $\eta =$  parameter that indicates the percentage contribution of each flow type distribution;  $D_p =$ 840 fitting parameter;  $\alpha$  and  $\beta =$  shape parameters;  $\tau_s$ ,  $\tau_f =$  transit time of fast and slow flows,  $\phi =$  flow partition parameter 841 between fast and slow flow reservoirs. Units for parameters and their respective ranges are a-dimensional except for  $\tau$ , which 842 has units of time (for our case it is given in weeks).

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**Table 4.** Main statistical parameters of observed  $\delta^{18}$ O and predicted results for soil waters 846 using a LPM distribution function. Statistical parameters of modeled results: RMSE, bias, 847 mean and  $\sigma$  correspond to the best matching value of the objective function NSE. Uncertainty 848 bounds of modeled parameters ( $\tau$  and  $\eta$ ), calculated through Generalized Likelihood 849 Uncertainty Estimation (GLUE) are showed in parenthesis.

Sampling		Observed				Modeled $\delta^{18}$ O, ‰, VSMOW							
Site	depth	δ <sup>18</sup> O,	‰, VS	SMOW	Mean	σ	NSE	RMSE	Bias	τ	η		
	m	Mean	N	σ	%0	‰	-	‰	‰	weeks	-		
Pastu	res transect												
A1	0.10	-6.70	60	3.65	-6.80	3.06	0.87	1.32	-0.099	3.5 (2.8 - 4.4)	1.40 (0.93-2.23)		
A2	0.35	-6.79	58	3.33	-6.87	2.46	0.73	1.72	-0.084	5.3 (4.6 - 6.3)	0.99 (0.90-1.28)		
A3	0.60	-7.13	45	3.98	-7.31	3.18	0.86	1.46	-0.181	4.9 (3.6 - 5.3)	1.11 (0.88-1.37)		
B1	0.10	-6.84	70	3.71	-6.91	3.01	0.83	1.52	-0.069	4.7 (3.4 - 5.1)	1.10 (0.93-1.47)		
B2	0.35	-7.03	70	3.41	-7.02	2.71	0.78	1.57	0.007	4.3 (3.9 - 5.3)	0.98 (0.90-1.33)		
B3	0.60	-6.76	63	3.41	-6.77	2.97	0.79	1.54	-0.006	4.5 (3.4 - 5.2)	1.03 (0.89-1.45)		
C1	0.10	-6.65	67	3.66	-6.74	3.15	0.84	1.44	-0.090	3.3 (2.3 - 4.2)	0.96 (0.87-1.82)		
C2	0.35	-7.06	71	3.49	-7.10	3.11	0.87	1.27	-0.043	3.1 (2.7 - 4.4)	0.89 (0.84-1.55)		
C3	0.60	-6.52	55	3.07	-6.53	2.56	0.80	1.36	-0.015	5.4 (4.4 - 5.8)	1.09 (0.88-1.32)		
Fore	st transect				-								
D1	0.10	-7.38	78	3.12	-7.26	2.56	0.78	1.44	0.122	5.7 (4.8 - 6.4)	1.27 (0.97-1.60)		
D2	0.35	-7.06	74	2.59	-6.97	2.56	0.78	1.19	0.087	6.8 (5.5 - 9.2)	1.04 (0.86-1.19)		
D3	0.60	-6.80	62	2.75	-6.73	2.56	0.80	1.22	0.062	6.0 (4.8 - 6.7)	0.99 (0.86-1.28)		
E1	0.10	-6.65	86	3.14	-6.58	2.56	0.80	1.40	0.070	5.1 (4.8 - 6.3)	1.15 (0.93-1.61)		
E2	0.35	-6.63	78	2.94	-6.64	2.56	0.78	1.37	-0.016	6.4 (5.7 - 7.3)	1.01 (0.93-1.45)		
E3	0.60	-6.44	62	2.57	-6.48	2.56	0.76	1.24	-0.036	8.3 (7.2 - 9.2)	1.03 (0.88-1.18)		
F1	0.10	-6.75	55	3.16	-6.79	2.56	0.89	1.05	-0.039	4.3 (3.8 - 5.5)	0.96 (0.87-1.38)		
F2	0.35	-6.45	53	3.15	-6.54	2.56	0.89	1.03	-0.089	4.3 (3.7 - 5.5)	0.94 (0.83-1.58)		
F3	0.60	-8.09	36	2.56	-8.05	2.56	0.66	1.46	0.045	6.0 (6.0 - 7.8)	0.80 (0.76-0.94)		

N = number of samples,  $\sigma$  = standard deviation, RMSE = Root Mean Square Error, NSE = Nash-Sutcliffe Efficiency.

858 **Table 5.** Main statistical parameters of observed  $\delta^{18}$ O and predicted results for surface and 859 spring waters using an EPM distribution function. Statistical parameters of modeled results: 860 RMSE, Bias, Mean and  $\sigma$  correspond to the best matching value of the objective function 861 NSE. Uncertainty bounds of modeled parameters ( $\tau$  and  $\eta$ ), calculated through Generalized 862 Likelihood Uncertainty Estimation (GLUE) are showed in parenthesis.

	Drainage	Outlet	Recharge		Observ	ved	Modeled $\delta^{18}$ O, ‰, VSMOW						
Site	area	altitude	altitude	δ <sup>18</sup> O	, ‰, V	SMOW	Mean	σ	NSE	RMSE	Bias	τ	η
	km <sup>2</sup>	m a.s.l.	m a.s.l.	Mean	N	σ	‰	‰	-	‰	‰	yr	-
Strea	т												
PL	76.93	1,725	2,488	-8.25	97	0.54	-8.25	0.42	0.56	0.36	0.003	2.0(1.8 - 2.2)	1.84(1.73 - 1.98)
SF	65.09	1,825	2,437	-8.12	88	0.56	-8.11	0.43	0.55	0.37	0.001	2.0(1.9 - 2.2)	1.85(1.71 - 1.97)
Strea	mwater trik	outaries											
FH	34.92	1,917	2,492	-8.28	83	0.55	-8.28	0.42	0.48	0.39	0.000	2.1(2.0 - 2.3)	1.84(1.70 - 1.93)
QZ	11.25	2,047	2,565	-8.41	93	0.47	-8.42	0.36	0.55	0.32	-0.004	2.2(2.1 - 2.5)	1.72(1.61 - 1.82)
QN	9.79	2,050	2,503	-8.28	92	0.50	-8.28	0.40	0.57	0.33	-0.002	2.1(2.0 - 2.3)	1.78(1.67 - 1.90)
QR	4.66	1,726	2,350	-7.96	97	0.48	-7.96	0.16	0.56	0.32	0.000	2.2(2.0 - 2.4)	1.73(1.62 - 1.84)
QP	3.42	1,925	2,418	-8.07	98	0.34	-8.07	0.26	0.57	0.22	-0.001	3.7(3.5 - 4.1)	2.06(1.91 - 2.21)
QM	1.29	1,878	2,310	-7.81	90	0.59	-7.81	0.44	0.51	0.41	0.005	2.0(1.8 - 2.2)	1.85(1.73 - 1.98)
QC	0.70	1,978	2,197	-7.62	95	0.30	-7.62	0.24	0.58	0.19	0.000	3.9(3.8 - 4.4)	1.97(1.81 - 2.06)
Creek	ts.												
TP	0.14	1,950	2,213	-7.66	80	0.25	-7.66	0.20	0.49	0.17	0.000	4.5(4.2 - 5.1)	1.74(1.61 - 1.82)
Q3	0.10	1,907	2,165	-7.67	88	0.54	-7.67	0.45	0.65	0.32	-0.002	2.1(1.9 - 2.2)	1.84(1.72 - 2.01)
Sprin	gs												
PLS	-	1,731	2,377	-8.03	101	0.50	-8.04	0.43	0.69	0.28	-0.009	2.0(1.9 - 2.2)	1.85(1.70 - 1.94)
SFS	-	1,826	2,187	-7.61	101	0.29	-7.61	0.23	0.47	0.21	-0.002	3.3(3.0 - 3.6)	1.42(1.36 - 1.47)
QRS	-	1,900	2,285	-7.80	97	0.17	-7.79	0.09	0.28	0.14	0.005	9.6(8.8 - 10.1)	1.70(1.65 - 1.82)

863 N = number of samples,  $\sigma$ = standard deviation, RMSE = Root Mean Square Error, NSE = Nash-Sutcliffe Efficiency.

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Fig. 1. San Francisco catchment with sampling locations and delineation of drainage area.
Acronyms in bold are defined in Table 1. Framed image shows the zoomed area of the lower
part of the catchment.



<sup>871</sup> Date [m/d/yy] <sup>872</sup> **Fig. 2. (a)** Time series of rainfall for ECSF meteorological station, hourly discharge and <sup>873</sup> baseflows at the catchment outlet (PL); (b) weekly  $\delta^{18}$ O and  $\delta^{2}$ H of streamwater at PL for <sup>874</sup> baseflow and high flow conditions; and (c) weekly  $\delta^{18}$ O and  $\delta^{2}$ H at the ECSF rainfall <sup>875</sup> sampling collector; light blue bubbles indicate daily  $\delta^{18}$ O and relative volume of daily <sup>876</sup> rainfall.



Fig. 3. Shaded area depicts the expected variation range of the Local Meteorological Water
Line of rainfall (LMWL) considering the altitudinal range of the catchment (1,725-3,150 m
a.s.l.) and estimated d-excess gradient. Symbols in colors depict weekly values of some of the
catchment's waters. Acronyms are defined in Table 1.

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**Fig. 4.** Monthly isotopic  $\delta^{18}$ O signals between two consecutive years (2010-2012) at ECSF (1,900 m a.s.l.) and averaged monthly values (1992-1994) at Amaluza GNIP station (latitude -

886 2.61, longitude -78.57, altitude 2,378 m a.s.l.).





**Fig. 5. (a)** Best NSE for each of the seven lumped parameter models; **(b)** MTT estimation according the best NSE per site: symbols represent MTT corresponding to the best matching result among 7 models considering the NSE criteria showed in **(a)**, vertical line represents uncertainty bounds according the GLUE methodology for the selected model.



892

**Fig. 6.** Intercomparison of models for soil sites according to their: (a) estimated mean transit times; (b) uncertainty ranges expressed in percentage of its respective MTT estimation; and

895 (c) number of observations inside the range of behavioral solutions.



**Fig. 7.** Fitted results of the LPM model compared to observed data for soil water of a pastures site (C2). Sub-plots (**a**) and (**b**) show the uncertainty analysis of 10,000 simulations and the feasible range of behavioral solutions of model parameters as a 5% of the top best prediction. Black filled circles in sub-plot (**c**) represents the observed data; the black line and the shaded area represent the best possible solution and its range of variation according to the 5-95% confidence limits of the behavioral solutions shown in (**a**); and the gray dashed line with crosses represents the weekly rainfall variation as input function for the model.



Fig. 8. Comparative characteristic shapes of residence time distribution functions
corresponding to the best NSE using four lumped parameter models (DM, EPM, GM and
LPM): (a) and (b) for the soil site C2 located in a pastures land cover; (c) and (d) for the soil
site E2 located in a forest land cover.



Fig. 9. Comparative results between LPM and GM models of soil water residence time distributions functions corresponding to the best NSE for every sampling site: (a) pastures sites using LPM; (b) pastures sites using GM; (c) forest sites using LPM; (d) forest sites using GM. Gray shaded area in each plot corresponds to the range of possible shapes of the distribution function for one of the sampling sites: C2 in sub-plots (a) and (b), and E2 in sub-plots (c) and (d).



Fig. 10. Intercomparison of models for surface waters and springs according to their: (a)
estimated mean transit times; (b) uncertainty ranges expressed in percentage of its respective
MTT estimation; and (c) number of observations inside the range of behavioral solutions.



925

926 Fig. 11. Uncertainty ranges for outlet stream water (PL site) using a TPLR distribution 927 function. Sub-plots (a), (b) and (c) show the modeled parameter uncertainties of 10,000 928 random simulations and the feasible range of behavioral solutions taking a lower limit of 5% 929 from the best solution. Black filled circles in the sub-plots (d) and (e) represents the observed 930 data, the black line and shaded area depict the best possible solution and its range of variation 931 according to the 5-95% confidence limits of the behavioral solutions shown in sub-plot (b); 932 and the gray dashed line with crosses in sub-plot (e) represents the weekly rainfall variation as 933 input function for the model.



935 Fig. 12. Uncertainty ranges for outlet stream water (PL site) using a GM distribution function. 936 Sub-plots (a), (b) and (c) show the modeled parameters uncertainties of 10,000 simulations 937 and the feasible range of behavioral solutions taking a lower limit of 5% from the best 938 solution. Black filled circles in the sub-plots (d) and (e) represents the observed data, the 939 black line and the shaded area represent the best possible solution and its range of variation 940 according to the 5-95% confidence limits of the behavioral solutions shown in sub-plot (a); 941 and the gray dashed line with crosses in sub-plot (e) represents the weekly rainfall variation as 942 input function for the model.



944 Fig. 13. Uncertainty ranges for outlet stream water (PL site) using an EPM distribution 945 function. Sub-plots (a) and (b) show the modeled parameters uncertainties of 10,000 946 simulations and the feasible range of behavioral solutions taking a lower limit of 5% from the 947 best solution. Black filled circles in the sub-plots (c) and (d) represent the observed data, the 948 black line and the shaded area represent the best possible solution and its range of variation 949 according the 5-95% confidence limits of the behavioral solutions shown in sub-plot (a); and 950 the gray dashed line with crosses in sub-plot (d) represents the weekly rainfall variation as 951 input function for the model.



Fig. 14. Comparative characteristic shapes of the transit time distribution functions corresponding to the best NSE using three lumped parameter models (EPM, GM and TPLR):
(a) and (b) for the stream water sampled at the main outlet PL; (c) and (d) for the small creek TP.



960

Transit time [years]

961 Fig. 15. Comparative results between EPM and GM models of soil water transit time distribution functions corresponding to the best NSE for every sampling site: (a) stream water 962 of main outlet and sub-catchments using EPM, and (b) using GM; (c) spring waters and 963 creeks using LPM, and (d) using GM. Gray shaded area in each plot corresponds to the range 964 965 of possible shapes of the distribution function for one of the sampling sites: the main outlet 966 (PL) in sub-plots (a) and (b) and TP creek in sub-plots (c) and (d).

# Annex 1. Predicted results of soil waters for the lumped models: Gamma, Exponential-Piston Flow, Dispersion and Linear.

- **Table 1.** Best predicted results for the Gamma model parameters ( $\tau$ ,  $\alpha$ ) and corresponding
- 973 uncertainty ranges.

	Mean	σ	NSE	RMSE	Bias	τ	α
Site	<sup>0</sup> / <sub>00</sub>	<sup>0</sup> / <sub>00</sub>	-	<sup>0</sup> / <sub>00</sub>	<sup>0</sup> / <sub>00</sub>	weeks	-
Pastur	es transec	et					
A1	-6.74	3.06	0.87	1.33	-0.04	3.6(2.9-4.4)	3.6(2.0-13.4)
A2	-6.72	2.46	0.73	1.72	0.07	5.5(4.5-6.7)	1.8(1.2-3.4)
A3	-7.17	3.18	0.85	1.54	-0.04	4.4(3.5-5.5)	2.0(1.4-8.3)
B1	-6.58	3.01	0.83	1.53	0.27	4.4(3.6-5.3)	2.0(1.4-7.0)
B2	-6.88	2.71	0.80	1.53	0.15	5.0(4.1-6.1)	1.7(1.2-3.5)
B3	-6.72	2.97	0.80	1.51	0.04	4.4(3.6-5.4)	2.1(1.3-5.1)
C1	-6.68	3.15	0.86	1.36	-0.04	3.5(2.7-4.2)	2.4(1.6-9.0)
C2	-7.19	3.11	0.88	1.19	-0.14	3.7(2.9-4.6)	2.1(1.2-5.4)
C3	-6.53	2.56	0.80	1.35	-0.01	5.3(4.5-6.4)	1.9(1.3-3.8)
Forest	transect						
D1	-7.26	2.79	0.81	1.35	0.12	6.1(5.1-7.5)	2.4(1.5-4.9)
D2	-7.03	2.35	0.82	1.08	0.03	7.6(6.6-9.2)	1.9(1.3-3.2)
D3	-6.82	2.40	0.82	1.16	-0.02	6.7(5.8-7.9)	1.8(1.2-3.6)
E1	-6.54	2.79	0.82	1.34	0.10	5.9(5.1-6.8)	2.9(1.8-7.1)
E2	-6.52	2.44	0.78	1.37	0.11	7.3(6.4-8.2)	2.7(1.8-5.6)
E3	-6.43	1.97	0.79	1.16	0.02	9.4(8.2-10.7)	2.5(1.8-4.0)
F1	-6.81	2.72	0.90	0.99	-0.06	5.0(4.2-6.1)	1.9(1.3-4.7)
F2	-6.74	2.79	0.90	0.97	-0.29	4.7(3.8-5.7)	2.4(1.4-6.4)
F3	-8.50	1.87	0.69	1.41	-0.41	10.2(8.7-12.5)	1.6(1.2-2.2)

 $\sigma$ = standard deviation, NSE = Nash-Sutcliffe Efficiency, RMSE = Root Mean Square Error

Sito	Mean	σ	NSE	RMSE	Bias	τ	η
Sile	<sup>0</sup> / <sub>00</sub>	<sup>0</sup> / <sub>00</sub>	-	<sup>0</sup> / <sub>00</sub>	<sup>0</sup> / <sub>00</sub>	weeks	-
Pastur	es transec	t					
A1	-6.88	3.00	0.86	1.38	-0.18	3.7(2.9-4.8)	1.40(1.28-1.59)
A2	-6.91	2.53	0.73	1.71	-0.12	5.7(4.7-7.2)	1.26(1.18-1.34)
A3	-7.31	3.23	0.84	1.57	-0.18	4.5(3.5-5.7)	1.33(1.21-1.48)
B1	-6.99	3.11	0.84	1.49	-0.14	5.1(4.0-6.3)	1.33(1.24-1.43)
B2	-7.14	2.82	0.80	1.51	-0.10	5.5(4.4-6.9)	1.28(1.20-1.36)
B3	-6.82	2.94	0.80	1.52	-0.05	4.7(3.8-6.0)	1.30(1.21-1.40)
C1	-6.75	3.15	0.86	1.38	-0.10	3.7(2.9-4.7)	1.40(1.29-1.57)
C2	-7.15	3.09	0.88	1.18	-0.09	3.8(3.0-5.0)	1.36(1.25-1.51)
C3	-6.59	2.54	0.80	1.36	-0.08	5.5(4.5-6.9)	1.25(1.17-1.33)
Forest	transect						
D1	-7.40	2.79	0.83	1.28	-0.02	7.0(5.6-8.6)	1.44(1.33-1.56)
D2	-7.06	2.36	0.82	1.11	0.00	8.5(7.2-10.2)	1.32(1.26-1.39)
D3	-6.84	2.36	0.81	1.19	-0.05	7.2(6.0-8.9)	1.18(1.12-1.23)
E1	-6.67	2.75	0.82	1.34	-0.03	6.6(5.5-8.1)	1.47(1.37-1.63)
E2	-6.69	2.38	0.77	1.40	-0.07	8.2(6.9-9.8)	1.37(1.29-1.46)
E3	-6.54	1.99	0.78	1.21	-0.09	10.3(8.9-12.1)	1.45(1.32-1.58)
F1	-6.88	2.73	0.90	0.97	-0.13	5.2(4.2-6.6)	1.27(1.19-1.36)
F2	-6.61	2.65	0.91	0.95	-0.16	4.8(3.8-6.1)	1.25(1.16-1.37)
F3	-8.14	2.02	0.74	1.30	-0.05	9.6(8.4-11.7)	1.37(1.22-1.47)

978 **Table 2.** Best predicted results for the Exponential Piston flow model parameters  $(\tau, \eta)$  and 979 corresponding uncertainty ranges. \_

 $\sigma$ = standard deviation, NSE = Nash-Sutcliffe Efficiency, RMSE = Root Mean Square Error

0:4-	Mean	σ	NSE	RMSE	Bias	τ	D <sub>n</sub>
Sile	<sup>0</sup> / <sub>00</sub>	<sup>0</sup> / <sub>00</sub>	-	<sup>0</sup> / <sub>00</sub>	<sup>0</sup> / <sub>00</sub>	weeks	-
Pastur	es transec	t					
A1	-6.77	3.10	0.86	1.33	-0.07	3.6(3.1-4.7)	0.13(0.07-0.53)
A2	-6.63	2.45	0.72	1.76	0.16	5.7(4.7-7.8)	0.33(0.22-0.99)
A3	-7.15	3.23	0.84	1.59	-0.02	4.5(3.6-6.1)	0.22(0.11-0.97)
B1	-6.56	3.08	0.82	1.55	0.29	4.6(3.8-5.8)	0.21(0.11-0.78)
B2	-6.79	2.77	0.79	1.57	0.24	5.1(4.3-7.2)	0.31(0.21-1.06)
B3	-6.64	2.94	0.80	1.52	0.12	4.5(3.8-6.5)	0.28(0.17-0.87)
C1	-6.61	3.17	0.86	1.37	0.03	3.5(2.9-5.1)	0.19(0.10-0.85)
C2	-7.00	3.06	0.88	1.19	0.06	3.7(3.2-5.8)	0.29(0.17-0.97)
C3	-6.46	2.53	0.79	1.38	0.06	5.5(4.7-7.5)	0.32(0.20-0.84)
Forest	transect						
D1	-7.24	2.68	0.83	1.28	0.14	6.7(5.7-9.2)	0.31(0.18-0.64)
D2	-6.99	2.33	0.82	1.08	0.07	8.4(7.2-11.7)	0.34(0.23-0.76)
D3	-6.77	2.40	0.81	1.19	0.03	7.2(6.2-10.0)	0.32(0.19-0.82)
E1	-6.55	2.75	0.82	1.33	0.10	6.3(5.4-7.8)	0.21(0.12-0.46)
E2	-6.51	2.45	0.77	1.39	0.11	7.6(6.8-9.4)	0.20(0.13-0.43)
E3	-6.41	2.00	0.78	1.19	0.03	9.8(8.7-11.8)	0.22(0.15-0.39)
F1	-6.72	2.72	0.90	1.00	0.04	5.2(4.3-7.1)	0.29(0.18-0.83)
F2	-6.66	2.73	0.91	0.95	-0.21	4.8(3.9-6.7)	0.29(0.15-0.73)
F3	-8.49	1.90	0.70	1.39	-0.40	11.6(9.8-14.6)	0.41(0.29-0.75)

**Table 3.** Best predicted results for the Dispersion model parameters  $(\tau, D_p)$  and 983 corresponding uncertainty ranges.

 $\begin{array}{ll} 985 & \sigma = \mbox{ standard deviation, NSE = Nash-Sutcliffe Efficiency, RMSE = Root Mean Square Error} \\ 986 & \end{array}$ 

0:4-	Mean	σ	NSE	RMSE	Bias	τ
Site	<sup>0</sup> / <sub>00</sub>	<sup>0</sup> / <sub>00</sub>	-	<sup>0</sup> / <sub>00</sub>	<sup>0</sup> / <sub>00</sub>	weeks
Pastur	es transec	rt				
A1	-6.85	3.06	0.86	1.37	-0.15	3.5(2.8-4.5)
A2	-6.87	2.63	0.73	1.72	-0.08	5.4(4.5-6.2)
A3	-7.32	3.30	0.86	1.46	-0.19	4.4(3.5-5.2)
B1	-6.89	3.19	0.83	1.52	-0.04	4.3(3.3-4.9)
B2	-7.03	3.02	0.78	1.57	0.00	4.4(3.8-5.2)
B3	-6.77	3.03	0.79	1.54	0.00	4.4(3.4-4.9)
C1	-6.72	3.17	0.84	1.44	-0.07	3.5(2.5-4.1)
C2	-7.10	3.16	0.87	1.27	-0.04	3.5(2.9-4.5)
C3	-6.54	2.71	0.80	1.36	-0.02	4.9(4.4-5.9)
Forest	transect					
D1	-7.31	2.91	0.76	1.50	0.07	5.4(4.8-6.2)
D2	-6.97	2.56	0.78	1.19	0.09	6.6(5.9-7.1)
D3	-6.74	2.61	0.80	1.22	0.05	6.0(4.9-6.6)
E1	-6.65	2.84	0.80	1.41	0.00	5.4(4.8-6.1)
E2	-6.64	2.55	0.78	1.37	-0.01	6.4(5.8-7.1)
E3	-6.48	2.14	0.76	1.24	-0.04	8.1(7.3-9.2)
F1	-6.79	2.90	0.89	1.05	-0.03	4.5(4.0-5.5)
F2	-6.52	2.79	0.89	1.03	-0.08	4.6(3.9-5.6)
F3	-8.42	2.37	0.64	1.51	-0.33	7.2(7.1-8.2)

**Table 4.** Best predicted results for the Linear Model parameter  $(\tau)$  and corresponding uncertainty ranges.

 $\sigma$ = standard deviation, NSE = Nash-Sutcliffe Efficiency, RMSE = Root Mean Square Error

# Annex 2. Predicted results of stream, creek and spring waters for the lumped models Gamma and Two Parallel Linear Reservoirs.

**Table 1.** Best predicted results for the Gamma model parameters  $(\tau, \alpha)$  and corresponding 998 uncertainty ranges.

Mean	σ	NSE	RMSE	Bias	τ	α
<sup>0</sup> / <sub>00</sub>	<sup>0</sup> / <sub>00</sub>	-	<sup>0</sup> / <sub>00</sub>	<sup>0</sup> / <sub>00</sub>	yr	-
-8.16	0.42	0.61	0.34	0.0909	2.2(1.6-3.2)	0.62(0.55-0.71)
-8.03	0.43	0.62	0.34	0.0836	2.0(1.5-3.1)	0.63(0.56-0.72)
er tributa	ries					
-8.21	0.42	0.58	0.36	0.0765	1.8(1.5-2.9)	0.71(0.60-0.78)
-8.35	0.36	0.58	0.31	0.0596	2.7(2.0-3.9)	0.63(0.57-0.72)
-8.21	0.40	0.64	0.30	0.0681	2.1(1.6-3.2)	0.66(0.58-0.75)
-7.86	0.16	0.45	0.35	0.0915	3.5(2.6-4.4)	0.60(0.56-0.67)
-8.04	0.26	0.54	0.23	0.0240	4.3(3.3-5.4)	0.65(0.62-0.73)
-7.74	0.44	0.60	0.37	0.0706	2.5(1.8-3.7)	0.57(0.51-0.64)
-7.57	0.24	0.53	0.21	0.0508	4.5(3.7-5.4)	0.68(0.64-0.74)
-7.63	0.20	0.45	0.18	0.0249	5.5(4.8-5.9)	0.68(0.64-0.73)
-7.66	0.45	0.68	0.30	0.0126	1.7(1.3-2.8)	0.65(0.55-0.74)
-7.94	0.43	0.69	0.28	0.0945	2.6(1.9-3.7)	0.58(0.53-0.66)
-7.57	0.23	0.56	0.19	0.0432	3.9(3.0-4.9)	0.74(0.68-0.81)
-7.78	0.09	0.25	0.14	0.0146	6.0(5.3-6.5)	0.94(0.91-1.00)
	Mean <sup>0</sup> / <sub>00</sub> -8.16 -8.03 <u>er tributa</u> -8.21 -8.35 -8.21 -7.86 -8.04 -7.74 -7.57 -7.63 -7.66 -7.94 -7.57 -7.78	Mean $\sigma$ $0/_{00}$ $0/_{00}$ -8.16         0.42           -8.03         0.43           er tributaries	Mean $\sigma$ NSE $0/_{00}$ $0/_{00}$ -           -8.16         0.42         0.61           -8.03         0.43         0.62           er tributaries         -           -8.21         0.42         0.58           -8.35         0.36         0.58           -8.21         0.40         0.64           -7.86         0.16         0.45           -8.04         0.26         0.54           -7.74         0.44         0.60           -7.57         0.24         0.53           -7.66         0.45         0.68           -7.94         0.43         0.69           -7.57         0.23         0.56           -7.78         0.09         0.25	Mean $\sigma$ NSE         RMSE $0_{/00}$ $0_{/00}$ - $0_{/00}$ - $0_{/00}$ - $0_{/00}$ - $0_{/00}$ - $0_{/00}$ - $0_{/00}$ - $0_{/00}$ - $0_{/00}$ - $0_{/00}$ - $0_{/00}$ - $0_{/00}$ - $0_{/00}$ - $0_{/00}$ - $0_{/00}$ 0.61 $0.34$ - $0.42$ $0.58$ $0.34$ - $0.42$ $0.58$ $0.31$ - $0.40$ $0.64$ $0.30$ - $0.40$ $0.64$ $0.33$ - $0.40$ $0.64$ $0.23$ - $0.24$ $0.53$ $0.21$ - $-         -         -           -         0.43 0.69 0.28           -         0.56 0.19 -           -         0.78 0.0$	Mean $\sigma$ NSE         RMSE         Bias $0_{00}$ $0_{00}$ $ 0_{00}$ $0_{00}$ - $0_{00}$ $ 0_{00}$ $0_{00}$ - $0_{00}$ $ 0_{00}$ $0_{00}$ - $0_{00}$ $ 0_{00}$ $0_{00}$ - $0_{00}$ $ 0_{00}$ $0_{00}$ - $0.42$ $0.61$ $0.34$ $0.0909$ - $0.43$ $0.62$ $0.34$ $0.0836$ er tributaries         -         -         -         -           -8.21 $0.42$ $0.58$ $0.31$ $0.0596$ -8.21 $0.40$ $0.64$ $0.30$ $0.0681$ -7.86 $0.16$ $0.45$ $0.35$ $0.0915$ -8.04 $0.26$ $0.54$ $0.23$ $0.0240$ -7.57 $0.24$ $0.53$ $0.21$ $0.0508$ -         -         -         -         -         -	Mean $\sigma$ NSE         RMSE         Bias $\tau$ $0/_{00}$ $0/_{00}$ $0/_{00}$ $0/_{00}$ $yr$ -8.16         0.42         0.61         0.34         0.0909         2.2(1.6-3.2)           -8.03         0.43         0.62         0.34         0.0836         2.0(1.5-3.1)           er         rtibutaries

 $\sigma$ = standard deviation, NSE = Nash-Sutcliffe Efficiency, RMSE = Root Mean Square Error

**Table 2.** Best predicted results for the Two Parallel Reservoir model parameters ( $\tau_s$ ,  $\varphi$ ) and corresponding uncertainty ranges. A fixed range from 4 to 4.5 weeks was maintained for  $\tau_f$  in

all cases.

C:4-	Mean	σ	NSE	RMSE	Bias	τ <sub>s</sub>	φ
Site	<sup>0</sup> / <sub>00</sub>	<sup>0</sup> / <sub>00</sub>	-	<sup>0</sup> / <sub>00</sub>	<sup>0</sup> / <sub>00</sub>	yr	-
Stream							
PL	-8.24	0.44	0.66	0.32	0.0176	2.5(1.9-5.6)	0.622(0.554-0.706)
SF	-8.10	0.44	0.64	0.33	0.0117	2.1(1.6-4.3)	0.631(0.555-0.721)
Streamw	ater tribu	taries					
FH	-8.24	0.43	0.60	0.34	0.0383	2.0(1.5-3.1)	0.708(0.605-0.782)
QZ	-8.41	0.37	0.60	0.30	0.0000	2.5(1.9-4.7)	0.632(0.570-0.717)
QN	-8.27	0.41	0.67	0.29	0.0141	2.2(1.6-3.6)	0.660(0.582-0.749)
QR	-7.93	0.23	0.52	0.33	0.0280	4.6(3.1-7.0)	0.603(0.562-0.672)
QP	-8.09	0.24	0.54	0.23	-0.0207	3.6(2.8-6.5)	0.653(0.620-0.728)
QM	-7.84	0.48	0.63	0.36	-0.0307	2.7(2.1-8.3)	0.565(0.506-0.636)
QC	-7.60	0.23	0.59	0.19	0.0183	5.2(3.8-6.8)	0.685(0.642-0.741)
Creeks							
TP	-7.65	0.17	0.51	0.17	0.0054	7.0(5.7-7.8)	0.680(0.642-0.726)
Q3	-7.71	0.43	0.67	0.31	-0.0428	1.7(1.3-2.7)	0.648(0.554-0.742)
Springs							
PLS	-8.04	0.44	0.78	0.24	-0.0045	4.0(2.6-8.0)	0.581(0.526-0.659)
SFS	-7.58	0.23	0.59	0.19	0.0255	3.6(2.8-5.2)	0.735(0.684-0.813)
QRS	-7.79	0.09	0.25	0.14	0.0119	6.1(5.3-6.6)	0.945(0.911-0.997)

 $\sigma$ = standard deviation, NSE = Nash-Sutcliffe Efficiency, RMSE = Root Mean Square Error