4.2.1 Model concept

A simple daily rainfall-runoff model, the Catchment Isotope Model (CIM), was developed to examine the effect of incorporating tracers and to assess associated errors and uncertainties in the data (Fig. 3). The model is based on the linear storage-runoff relationship $Q = S*k$ (linear scaling parameter k (s^{-1}), storage volume S (m^3) and discharge Q (m^3s^{-1})). The storage volume is equivalent to a depth of water multiplied by the catchment area. Two cascading reservoirs (the upper and lower active storage $activeS_{up}$ (m^3) and $activeS_l$ (m^3)) are connected via a recharge flux calculated with parameter R (s^{-1}) to model discharge from both reservoirs applying an upper (k_1 (s^{-1})) and a lower (k_2 (s^{-1})) scaling parameter. These water fluxes are used to route any conservative tracer through the catchment (Hooper et al., 1988) assuming that solutes fully mix within each of the two storage compartments. For each modelled water flux, the associated deuterium tracer flux *Dflux* (‰) is defined according to the following equation (Eq. 4), which mathematically expresses the link of water and tracer fluxes in the applied mixing cell approach (Herzer and Kinzelbach, 1987):

$$Dflux = \frac{DS \times flow \times \Delta t}{S} \tag{4}$$

with S being the storage volume (m^3), *flow* the water flux (m^3s^{-1}), DS the deuterium content of the storage (‰), and Δt is the time step (s). This form of equation applies to the fluxes from both storages after precipitation P and the observed tracer signature N is added to the upper active storage $activeS_{up}$ (m^3). This reservoir is not restricted to a lower limit; sub-zero values indicate that the active storage is emptied by evapotranspiration and does not generate any lateral flow, and in this case the associated tracer loss is depleted from the passive storage. This allows threshold-type behaviour to be captured by the model (Fenicia et al., 2008b). Due to the high turn over of storage in the flow model, two tracer parameters $passiveS_{up}$ (upper mixing volume (m^3)), $passiveS_l$ (lower mixing volume (m^3)) are introduced into the active storage routine $activeS_{up}$ and $activeS_l$ (Barnes and Bonell, 1996) to account for an additional mixing volume (passive water) in the catchment system (Fig. 3) resulting in a **5-parameter** version of the CIM model.

The unclosed nature of the water balance in the Wemyss catchment raises the question of leakage from the superficial catchment to the deeper sub-surface, which we acknowledge by an additional loss parameter *GWloss* (m^3s^{-1}) (Eq. 5) to account for a regional groundwater recharge *regGW* (m^3s^{-1}) (**6-parameter** model). The value of a parameter c (s^{-1}) to conceptualize a direct runoff generation component $Q_{direct}(t)$ (m^3s^{-1}) (Leaney et al., 1993) was also explored (**7-parameter** model). This mechanism allows direct mixing of rain with stream water, even when the upper active storage is not activated, representing a type of infiltration excess runoff mechanism. A water balance is calculated at each time step for both the upper and the lower storage of the CIM model:

$$\Delta S_{up(t)} = activeS_{up(t-1)} + passiveS_{up(t-1)} + ((P_{(t)} - ET_{(t-1)}) \times area - R_{(t-1)} - Q_{up(t-1)} - regGW_{(t-1)}) \times \Delta t$$

$$\Delta S_{l(t)} = activeS_{l(t-1)} + passiveS_{l(t-1)} + (R_{(t)} - Q_{l(t-1)}) \times \Delta t \qquad (5)$$

with ΔS_{up} (m^3) and ΔS_l (m^3) being the total upper and lower storage at time t (s), precipitation P (ms^{-1}), *area* (m^2), recharge R (m^3s^{-1}) to the lower storage and actual evapotranspiration ET (ms^{-1}). Total discharge Q_{total} (m^3s^{-1}) is the sum of the discharge of both upper Q_{up} and lower storage Q_l, and the direct runoff Q_{direct}, whereas the simulated tracer signature in the stream DQ (‰) is calculated via a weighted mean of tracer (DQ_{direct}, DQ_{up}, DQ_l) and water (Q_{direct}, Q_{up}, Q_l) fluxes:

$$DQ = \left[\left(DQ_{direct} \times Q_{direct}\right) + \left(DQ_{up} \times Q_{up}\right) + \left(DQ_{l} \times Q_{l}\right)\right] \div Q_{total} \tag{6}$$

Input time series are looped over 5 years to establish initial conditions and to verify the internal water balance.