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Discussions

The physics behind groundwater recession and hydrologically passive mixing volumes.

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Abstract: Transit time and water age characteristics are fundamental descriptors of catchment response, and their determination is vital for the implementation of sustainable strategies for managing nutrients and other contaminants in water environments – especially for groundwater where the deeper stores take decades to flush the dissolved solutes. The deterministic transit time models can be broadly categorized into 2 sorts – lumped models based on conceptual parameters and distributed models based on physical and quantifiable hydrodynamic parameters. Due to their simplicity, applicability and flexibility, lumped conceptual models are thus far widely and successfully used in modelling the groundwater flow, transport, and transit time of solutes. Usually, a bunch of parallel hydrological response units work in harmony to model the desired hydrological and solute concentration time-series. But sole reliance on calibration, non-scalability, leveraging on hydrologically passive mixing volumes, lack of forward modelling potential and ineffective scrutiny of the physical basis of the parameters of these conceptual models often generate skepticism in the research community. To address this issue, we devised a technique to determine the physical basis of these conceptual reservoirs, and to establish a mathematical connection between physical hydrodynamic parameters and lumped conceptual parameters. A lumped groundwater nitrate transit time model composed of two parallel stores (slow and fast) was previously calibrated (using GLUE) to generate the time series of baseflow and nitrate concentration time series in a groundwater dominated agricultural catchment in France. In this study, we generated synthetic 2D Dupuit-Forchheimer unconfined aquifers using a standard finite element code (FEFLOW 7.5) to replicate outputs of the lumped model. Furthermore, sensitivity tests were performed on these synthetic catchments and overall, a clear mathematical connection between physical and conceptual parameters was demonstrated. It was further observed that the difference between fast and slow stores can be explained using dual porosity – with drainable porosity affecting recession, and immobile porosity affecting the size of hydrologically passive mixing volumes. The spatial mean of the age distributions, the mean transit time and the half nitrate recovery time agreed with each other for both stores. Further sensitivity tests showed that lumped conceptual stores individually cannot acknowledge dispersivity – the difference in attenuation of different stores, in unison, produce a pseudo-dispersive behavior. Also, being purely depth-based, there is a scale issue in lumped models – an

erroneous input of catchment dimension can yield the identical results for a completely different set of hydrodynamic parameters leading to equifinality. Therefore, transit times should always be normalized by catchment scale while cross-comparing catchments using lumped models. These finding can help reduce calibration reliance of lumped models, providing options to investigate parameter effectiveness, and offers these models a forward modelling potential which can be used to calculate the flow and transport behavior of catchments that lack long term observed time series but have proper measurements of hydrodynamic properties.

1. Introduction:

Transit time distributions give us insights on the overall age structure of a hydrological system, and for conservative solutes, the chemical composition of specific pools of water (Hrachowitz et al., 2016). Transit time estimation has thus become a common tool of process representation in flow and transport models in recent times, and a strong test of model output realism (Benettin et al., 2022). But certain aspects of transit time theory still come under the "unsolved problems" in hydrology (Blochl et al., 2019). Subsurface water is an important medium for transporting geochemical constituents on a global scale. But unlike surface water, subsurface water is not easy to access and quantify, and water and solute fluxes through subsurface systems are very difficult to measure (Phillips and Castro, 2003). However, intensification of agriculture and the resultant increment in application of nitrate rich products in agricultural catchments for the past few decades has dramatically increased the legacy nitrate concentration in both vadose zone and groundwater along with nitrate loading in streams (Galloway et al., 2004; Seitzinger et al., 2010; Howden et al., 2011; Worrall et al., 2012; Dunn et al., 2012; Ehrhardt et al., 2019) leading to global issues like the nitrate time-bomb problem (Wang et al., 2013), and exceedance of the planetary boundary by the nitrogen cycle (Rockstorm et al., 2009). The attenuated response of legacy nitrogen stored in deeper groundwater compartments often causes catchments to take several decades to flush out existing nitrates (Martinec, 1975; Ruiz et al., 2002; Tomer and Burkart, 2003; Basu et al., 2010; Meals et al., 2010; Stewart et al., 2010; Aquilina et al., 2012; Basu et al., 2022) resulting in a very long timescales to reflect managerial measures on stream nitrate concentration. It is thus necessary to estimate the solute release rate of catchments by modelling groundwater and solute transit time, and it has been thus prevalent in hydrology for a very long time (Maloszewski and Zuber,1982; Goode,1996; Etcheverry and Perrochet, 1999; Kirchner et al, 2000; Duffy, 2010; Gilmore et al., 2016; Bhaduri et al., 2022a). Therefore, a lot of advances have been made in catchment scale flow and transport modelling in the last couple decades (McGuire and McDonnell, 2006; Hrachowitz et al., 2016; Benettin et al., 2022). Amongst these, physics-driven distributed hydrological models like MODFLOW-MT3D (McDonald and Harbaugh, 2003; Zheng et al., 2012), PARFLOW (Kollet and Maxwell, 2006), FEFLOW (Diersch, 2013) etc can most accurately simulate catchment flow and transport processes whilst being able to account for the process complexity and heterogeneity. But such models have a large computational expense, and they still deal with ill-posedness in inverse problem definition (Hrachowitz et al., 2016; Bhaduri et al., 2022b). Consequently, reliance in parsimonious lumped conceptual models was reaffirmed in recent times (Birkel et al., 2014; Fovet et al., 2015) primarily due to adaptability and computational simplicity, despite having issues like lack of physical basis, non-scalability and inability to forward model (Hrachowitz et al., 2016; Bhaduri et al., 2022b). But the question of whether these models will be able to imitate realistic catchment processes and in turn accurately determine the transit times and produce "right answers for the right reasons" still remains (Kirchner, 2006; Hrachowitz et al, 2013). Furthermore, there is a very big challenge of limitation of long-term time series measurements of groundwater and solutes (Li et al., 2021) which are essential to calibrate lumped models – so there are new avenues to explore about the linkage of the lumped conceptual parameters to field measurements giving hydrologists some recipes of forward modelling using lumped models.

There are multiple ways to improve the transit time predictive performance of lumped conceptual models. In terms of data, enabling the model to use long-term discharge and concentration time series of the streams, as well as long term groundwater storage and chemical or tracer information will help the model better constrain itself and yield better results (Seibert and McDonnell, 2002; Gupta et al., 2008; Fovet et al., 2015; Bhaduri et al., 2022a). In terms of process representation, using different static and dynamic mixing coefficients that represent different fractions of input water mixing with resident water (Dunn et al., 2007, Fenicia et al., 2010; McMillan et al., 2012; Soulsby et al., 2015; Birkel et al., 2015) has been quite beneficial, which eventually led to the development of piecewise linear SAS functions (Benettin et al., 2022). One step forward could be an attempt to generate the physical equivalent synthetic box catchments resembling the conceptual stores optimized by a lumped model and analyze those synthetic domains to comprehend what the conceptual stores are trying to convey about the emergent properties of the catchment. This might reduce the calibration dependency of lumped models and provide opportunities to inspect effectiveness of conceptual parameters. Savenije (2018) mathematically connected Darcy law of groundwater flow to linear reservoir theory (connecting field scale to laboratory scale). But according to him that was an "opinion paper" that did not provide a "proof of concept". He further mentioned that predicting solute transport in such systems is "much less straightforward requiring assumption of dual porosities". We explore here the possibility of validating Savenije's opinion on groundwater recession through synthetic modelling. We investigate possible presence of such mathematical connections between catchment hydrodynamic parameters and hydrologically passive conceptual mixing volumes used in lumped models to aid solute dilution. Such mathematical connections can generate a forward modelling potential for both flow and transport in lumped models, which would be beneficial for pristine catchments with no long-term time series measurements.

A lumped conceptual nitrate transport model ETNA (Ruiz et al., 2002) was developed based on two completely mixed disjoint reservoirs (fast and slow stores) which acted in harmony to convert leached nitrogen time series to stream concentration time-series of nitrate. The configuration of the stores was - linear reservoir with certain recession coefficients representing pressure diffusion of water, attached to immobile volumes with zero hydraulic pressure aiding for additional dilution of solutes. This model was adapted by Fovet et al. (2015) for modelling a small agricultural groundwater fed French headwater catchment using measured long term stream discharge and nitrate concentration time series in order to determine the nitrate transit time of the catchment. As an extension, in this study, we construct synthetic homogeneous aquifers and we model using FEFLOW

7.5 their responses for matching the optimized stores of the calibrated conceptual model from xxx. With obtained synthetic results, we try to analyze those to get deeper insights into what exactly these lumped conceptual stores are trying to say. Our main objectives are:

1. To explore the box catchment configurations exactly representing the different conceptual stores of ETNA, and to check if an unambiguous mathematical relationship can be formed between empirical lumped parameters and measurable physical hydrodynamic aquifer properties.
2. To check the correlation between the half nitrate recovery time obtained from ETNA and the mean transit time and groundwater age distributions obtained from FEFLOW 7.5.
3. To check the sensitivity of breakthrough concentration and groundwater age at the outlet to variation of physical properties (both geometric and hydrodynamic).

Our primary goal is to check what the conceptual stores of a lumped model used to explain the hydrology and transport of a groundwater dominated agricultural catchment are trying to convey in terms of the physics of the catchment, and how reliable and physically accurate these widely used models are in terms of what they are conveying. Our broader goal is to establish a clear relationship between lumped and conceptual model parameters so that lumped models can also be used for forward modelling for regions where hydrological and concentration time series are not long enough for inverse modelling.

2. Materials and Methods:

2.1 Study site and data:

Kerrien (Figure 1), a 10.5 ha agriculture dominated headwater catchment located in the Kerbernez site of South-Western French Brittany (47°35′ N; 117°52′ E) belongs to the AgrHys Critical Zone Observatory (Fovet et al., 2018; https://www6.inra.fr/ore_agrhys_eng/). For the detailed description of topography, climate, soil, data monitoring and surveys please refer to Fovet et al., 2015.

The forcings are the same time series that has been used by Fovet et al., 2015 – the N available for leaching, the meteorological data (PET and precipitation) and the soil properties (depth and water holding capacity) were fed to Burns model (Burns, 1975) to get the recharge and leachate time series which was then used as the loading in our analysis. For spinning up the output nitrate concentration time series, a historical triangular N input trend was used.

Below, we will briefly in 4 steps describe the method we have adopted for our analysis.

2.2. Step 1: Geometry of synthetic homogeneous FEFLOW catchments:

The main target is to use FEFLOW 7.5 to generate synthetic homogeneous box catchments hydrologically equivalent to ETNA stores which will produce nitrate concentration time series that exactly match those stores. To do this, we must first look at the dimensions and physical properties of the actual catchment. In Figure 1, we show that the diagonal of the catchment Kerrien (which looks like a rhombus) along the probable mean direction of overall groundwater movement, according to the topography and piezometry, is about 385m long (distance of outlet E3 from ridge). We thus decided the dimensions of the rectangular 2D box catchments that we produce will be 400m*270m to match the area of the catchment. The width (W) of 270m does not matter as we took the left and right boundaries to be no-flux (for both fluid and mass) boundaries making the domain behave like an 1d Dupuit-Forchheimer aquifer as shown in Figure 1. The aquifer was taken to be unconfined because both stores of ETNA receive Burns recharge from top (Fovet et al., 2015). The length we have taken is 15 m more than the chief diagonal because (L=385m) the observation point representing the outlet of the catchment should be taken slightly inwards to avoid the boundary effect. To explain the dimensionality in simple terms to a non-FEFLOW user, a triangular discretization (meshing) was done in the X-Y plane, but due to no-flux boundaries on left and right, and zero transverse dispersivity, both flow and transport was forced along the X-direction (along parallel streamlines). The parabolic head distribution along X from upper to lower boundary is just a Hydraulic Grade Line (HGL) and not Z-dimension. and flow and transport are non-existent along Z, but the HGL height can be considered as the unconfined aquifer thickness that aids dilution/mixing. The Upper and the Lower boundaries are thus just representative of x=0 and x=400 m respectively. Dirichlet boundary conditions for hydraulic head at the upper and lower boundaries are calibrated in accordance to past studies. The Dirichlet boundary conditions for mass is 0 mg/l concentration at both upper and lower boundaries, with a minimum mass flow constraint of 0 mg/l at lower boundary.

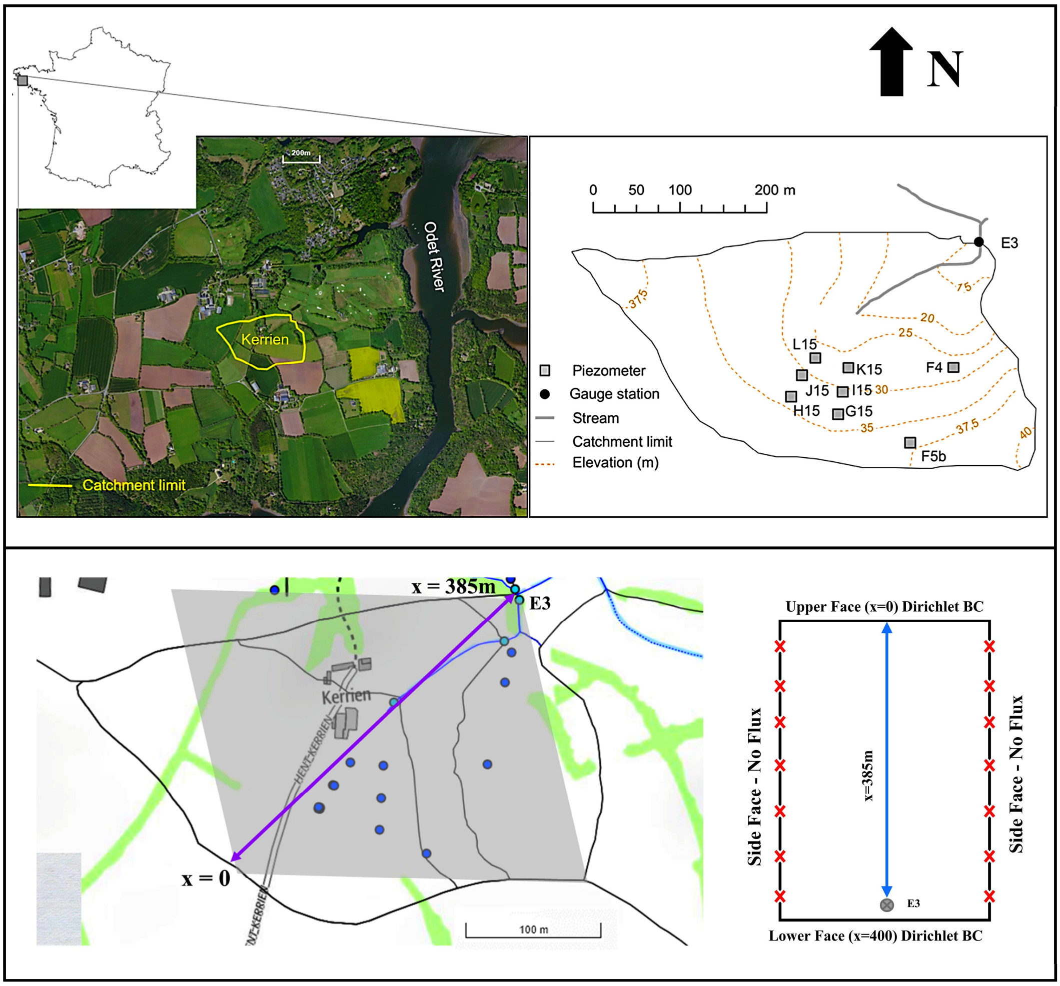

Figure 1: (a) A map of Kerrien catchment (AgrHys Critical Zone Observatory) highlighting important observation locations, stream, catchment limits and elevation contour lines (https://geosas.fr/agrhys/) (b) Outline of the diagonal (since Kerrien looks like a rhombus) representing a hypothetical linear stream tube from ridge to outlet E3 along which all the groundwater flow is hypothesized to be taking place. (c) Line-drawing of the basic 2D box aquifer blueprint which is optimized to mimic different ETNA stores.

2.3. Step 2: Parameter initialization:

Next step is to decide the primary hydrodynamic parameterization of the synthetic box catchments. In the homogeneous representation of Kerrien by Martin et al., 2006, the hydraulic conductivity (K) was taken to be 7×10^{-6} m/s (=0.605m/d). We use this as a starting value. The topographic gradient varied from 14% in the upslope region to 5% in the downslope region, so we took mean hydraulic gradient (i) of 10% as the value to begin with. The initial value of longitudinal hydrodynamic dispersivity (D) was taken to be 10m (Martin et al., 2006) based on Gelhar's charts (Gelhar et al., 1992). The initial total porosity (η) and drainable porosity (η_f) was taken to be 60% and 5% based on RMS measurements (Martin et al., 2006).

2.4. Step 3: Parameter calibration:

We perform a sensitivity study – we first check the degree of variation of the area under the output nitrate breakthrough of the synthetic 2D box aquifer to increase or decrease in 3 main hydrodynamic parameters - hydraulic gradient (K), hydraulic conductivity (i) and longitudinal hydrodynamic dispersivity (D) by one order of magnitude from their initial values. The height of the hydraulic grade line, as mentioned in section 2.2, can be considered as a virtual thickness, that depends on the chosen Dirichlet BCs on the Upper and Lower boundary, and the total porosity. This thickness depends on the choice of the boundary heads. For example, a variation of boundary heads from 100m to 50m will produce a different thickness than boundary heads varying from 50m to 0m because of difference in volume available for mixing (all other parameters being constant), causing different levels of dilution. So apart from the gradient, the Dirichlet boundary conditions applied to reproduce the gradient also matters in dilution. Here for the sensitivity study, we made the Dirichlet head BCs vary from 20m at upper boundary to 0 at lower boundary.

With the knowledge of this sensitivity, we then adjust the parameters to match the hydrological recession and the nitrate breakthrough concentration time series of the optimized fast and the slow stores of ETNA by Fovet et al., 2015. All simulations were run from 1965 to 2014 (with a time step of 1 day) using FEFLOW 7.5. We use trial and error to settle for the final set of parameters because a) FEFLOW 7.5 parameter estimation program (FEPEST) is highly time consuming and buggy, and b) Dirichlet BCs are variables and cannot be optimized as parameters using FEPEST.

FEFLOW 7.5 produces a hydraulic head field but does not explicitly display discharge. Although it shows nodal and elemental Darcy flux, it does not provide a time series of Darcy discharge across individual elements, so we cannot add up Darcy flux across elements to get a net discharge time series. Furthermore, whether the net discharge will match the discharge of ETNA will largely depend on the method used to calculate the discharge. Thus, the only way to compare the water release rates of the fast and the slow stores of ETNA and FEFLOW is to compare their discharge recessions. The discharge recession will be different from groundwater head recessions, the estimation technique of which is demonstrated below.

We took 16 equispaced observation points (Figure 3) along the catchment at 25 m intervals, with point 1 and point 16 at 12.5m distance from the boundaries as shown in Figure 3. We simulated the head distribution profiles at those 16 points, and calculated their daily leakages during recessions over the entire simulation period using the following formula:

$$q_L = \frac{\eta_f\,(h_{t-1} - h_t)}{t\,(=1\,\mathrm{d})} \qquad \mathrm{Eq}(1)$$

Where q_L is the daily leakage in m/d and h is the head in m. The sum of these leakage time series at all 16 locations, when fit using an exponential decay, will give us a decay constant which is our recession constant. We optimized our value of K, i and η_f in such a way that the mean of such recession constants (i.e., parameters a_{fast} and a_{slow}) over the entire simulation period match that of ETNA.

We tried to choose the DBCs and the η of our representative box aquifers in a way that not only produce the required i, but also the hydrodynamic thickness and the immobile porosity $(\eta - \eta_f)$ rationally best represents the immobile mixing volumes associated with the fast and the slow stores of ETNA and produce desired dilution in breakthrough concentration.

2.5. Step 4: Mean residence time calculation:

To determine the nitrate transit time using ETNA, unit pulses of nitrate were sent on 1st August 1968, 1974 and 1980 representative of dry, average and wet climatic sequences, for the entire behavioral parameter set obtained from GLUE (Fovet et al., 2015) and the time required to recover half the input nitrate was calculated as Half Nitrate Recovery Time (HNRT) which is supposed to be slightly lower than Mean Transit Time (MTT) for long tailed distributions.

But in ETNA the nitrate pulse was a lumped concentration pulse. In FEFLOW we can load a dirac delta mass pulse and the centroid of the output concentration breakthrough provides an estimate of MTT. We sent 1g/m^2/d impulse loading on 1st August 1968, 1974 and 1980 for all the finalized box aquifers and calculated the MTT by determining the centroid in time. For this, the rainfall time series from 2020-2070 was generated just by repeating the time series of 1970-2020.

We also calculated the age distribution of the optimized box aquifers. The formula of the mean age is also a centroid calculation formula, and the mean transit time is just the mean age at the outlet. Direct simulation of groundwater age (Goode, 1995) can be done using FEFLOW 7.5 using the following equations:

$$A = \frac{\int_0^\infty tC\,dt}{\int_0^\infty C\,dt} \qquad \mathrm{Eq}(2)$$

$$q\nabla A - \nabla(D\nabla A) = \eta \qquad \mathrm{Eq}(3)$$

Equation 3 is derived by substituting Equation 2 in advection-dispersion equation for porous media. q = (Ki) is the Darcy velocity and C is the concentration. The boundary condition for age is very simple – the age is 0 at the inflow boundary (upper boundary).

Alteration of the hydraulic conductivity and hydraulic gradient do affect the age distributions to a small degree, but these 2 parameters/variables primarily determine the behavior of mobile water flowing with a certain velocity, i.e., they affect the recession. The immobile volumes primarily influencing solute transit times are conceptual representations of some physical parameter that aids dilution – it can apparently be dispersivity, 2D hydraulic thickness of unconfined aquifer and immobile porosity. Therefore, the sensitivity of changes in age distribution with changes in the above 3 parameters has been explored.

In order to compare this sensitivity of age distribution calculated by FEFLOW and the sensitivity of residence times in the conceptual model, the sensitivity of HNRT it simulates has also been performed. Every conceptual reservoir has only 2 parameters that decide the transit time: recession (a) and immobile volume (V). Starting with a = 0.05 and V = 5000mm, the values of these 2 parameters have been altered to check their impact on the response of a unit pulse of nitrate sent on 1st August 1968. The above 2 analyses were then compared to check the equivalences/dissimilarities in the two transit time estimation procedures.

3. Results and Discussions:

3.1. Findings from Sensitivity Study:

We saw that the area under the breakthrough is most sensitive to change in hydraulic gradient. On average, we obtained a 45.34 folds change in area under breakthrough curve for one order of magnitude change in hydraulic gradient from the initial value 0.1. This area is least sensitive to change in hydrodynamic dispersivity. On average a 1.12 folds change in area under breakthrough curve was observed for one order of magnitude change in hydrodynamic dispersivity from the initial value 10m. Sensitivity to hydraulic conductivity falls in the middle with on average a 5.64 folds change in area under breakthrough curve for one order of magnitude change in hydraulic conductivity from the initial value 0.6m/d. The graphs (Figure 2) give us an idea which hydrodynamic parameters should we focus on adjusting to get the physical equivalent of the conceptual stores in terms of breakthrough concentration. Adjusting dispersivity apparently is not very fruitful because sensitivity is low and dispersivity can only go up to a maximum of 385m (because dispersivity can never exceed maximum length dimension of catchment). In addition, the increase in dispersivity acts as almost equivalent to increase in mixing volume in terms of solute dilution, which can be done by changing the DBCs and η, provided the recession behavior is reproduced correctly. Transverse dispersivity, as mentioned earlier in section 2.2, is taken as 0 as we force the flow to be linear and not braided.

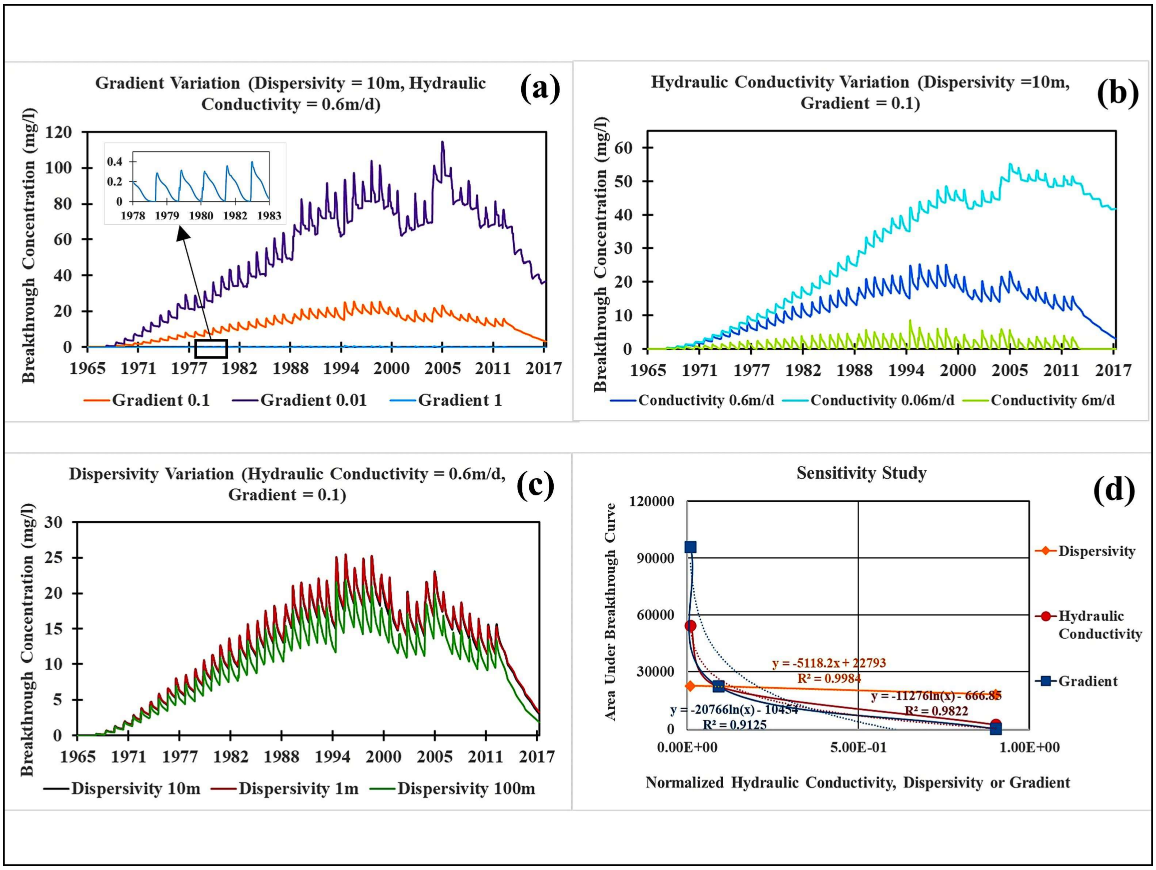

Figure 2: Illustration of how output breakthrough concentrations change with change in hydraulic gradient (a), hydraulic conductivity (b) and dispersivity (c); and graph showing how sensitive are the areas under those breakthrough curves when the parameters change over orders of magnitude.

3.2. Parameter Optimization and implications of storages:

3.2.1. Parameter values: After a significant amount of trial and error we figured that there is not any equifinality in the physical parameters that logically and exactly reproduce the fast and slow conceptual stores. Optimal parameters for the most probable realization are shown in Table 1.

Table 1: Set of optimal physical parameters, namely hydraulic gradient (i), Dirichlet Boundary Conditions of fixed hydraulic heads in the upper and lower boundaries (DBC), hydraulic conductivity (K), total porosity (η), drainable/fillable porosity (η_f), longitudinal hydrodynamic dispersivity (D), length (L) and width (W), that are reproducing concentration breakthroughs equivalent to the calibrated ETNA stores.

Store	i(%)	DBC	K (m/d)	η	η_f	D (m)	L (m)
Fast	5	Up = 40m Down= 20m	0.202	0.092	0.022	10	385
Slow	5	Up = 40m Down= 20m	0.202	0.565	0.065	10	385

3.2.2. Analysis of parameter significance:

3.2.2.1. Hydrological equivalence:

The hydraulic gradient of 5% is a constant approximation – it changes along the Dupuit-Forchheimer parabola, getting gradually steeper from upper towards lower boundary (if no mound formation happens). Length of both stores was equal to the length of the chief diagonal, which can be visualized as a stream-tube carrying all the groundwater.

After performing the hydrological analysis mentioned in section 2.4, we settled for the K and η_f mentioned in Table 1 to get the mean recession values of 0.023 (varying between 0.022 and 0.024) for fast store and 0.0077 (varying between 0.007 and 0.009) for slow store. We have shown a sample of the analysis technique for the year 2009 in Figure 3 (b). We have also shown the reproduced groundwater heads at all 16 points of either optimized store for a period of 2000-2010 in Figure 3 (c). The calibrated mean ETNA recession of fast store was $a_{fast}=0.0252\pm11.22\%$ and slow store was $a_{slow}=0.0079\pm13.42\%$ in Fovet et al., 2015. As can be seen, mean recessions for the slow store and the fast store for our optimized synthetic box aquifers fall within the bounds prescribed by Fovet et al., 2015. This part, as mentioned in the introduction, can be explained by the linkage of Darcy flow to linear reservoir theory (Savenije, 2018). If we want to mathematically represent recession in terms of conventional groundwater parameters, it will be:

$$a = \frac{K}{L\eta_f} \qquad \text{Eq(4)}$$

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Which comes out to be 0.0238 for fast store and 0.008 for slow store, agreeing with both the calibrated conceptual stores and FEFLOW aquifers. This, in a way, substantiates the opinion of Savenije, 2018 on equivalence of Darcy equation to linear reservoir equation.

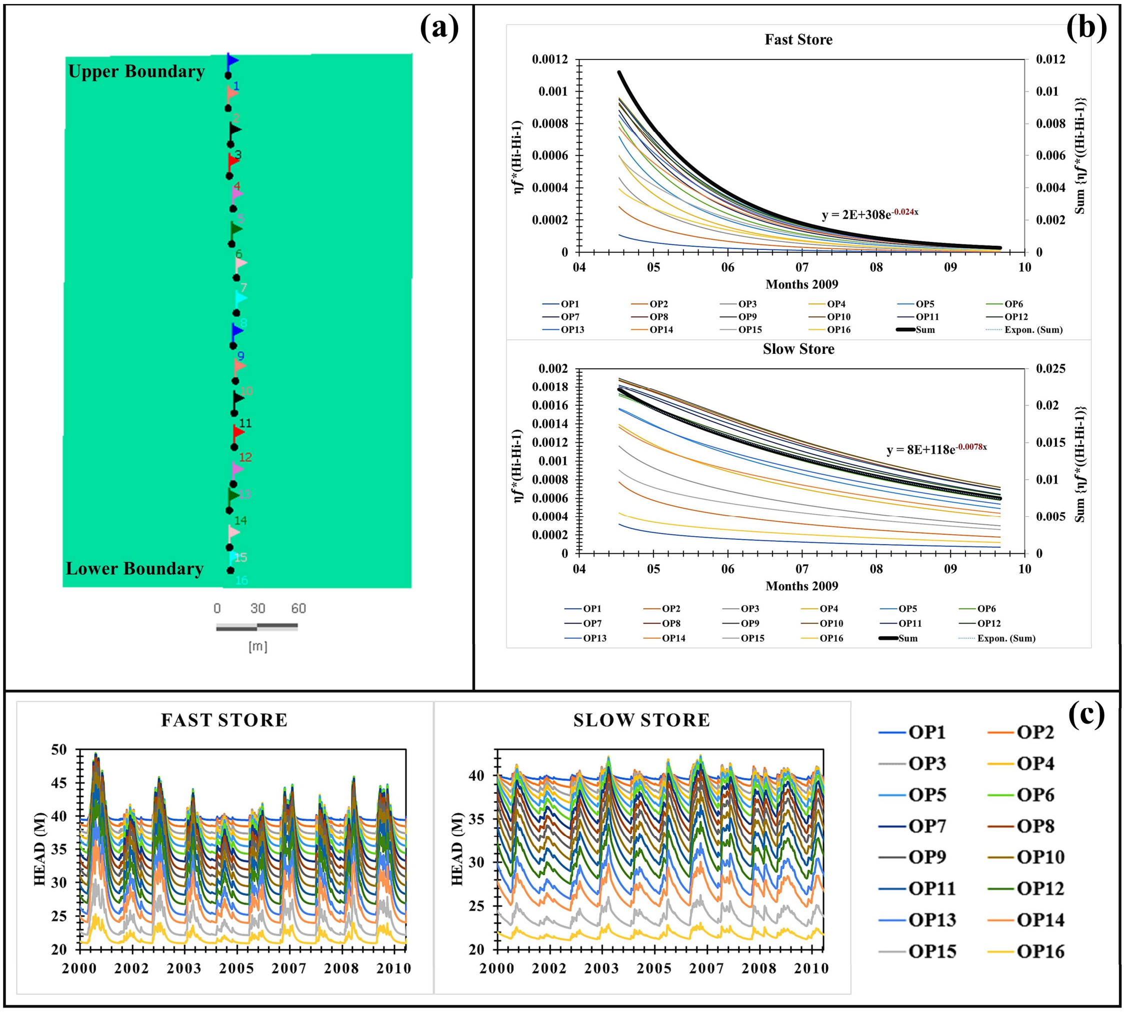

Figure 3: (a) The box catchment with the location of 16 observation points. (b) Illustration of sample recession calculation technique for fast and slow FEFLOW stores for 2009 (April to September). (c) Hydraulic heads at all 16 observation points of both stores for the period 2000-2010.

3.2.2.2. Equivalence in solute transport:

The Dirichlet BCs at upper and lower boundary and the immobile porosity is optimized in such a way that concur with the calibrated immobile volumes in ETNA reservoirs. The 3D view of 2D Dupuit-Forchheimer aquifer with hydraulic head isolines are shown in Figure 4.

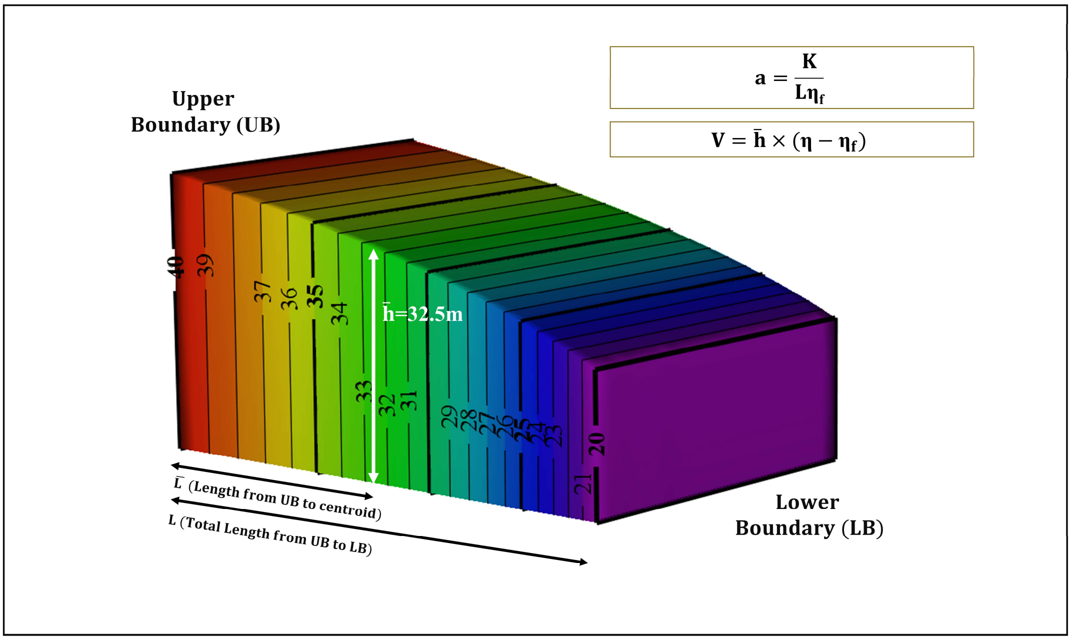

Figure 4: 3D view of optimized 2D synthetic Dupuit-Forchheimer box aquifer showing hydraulic head (m) isoline distribution under steady state, and featuring the dimensional parameters required for a and V calculation.

The geometric centroid of a semi-parabola is at 3/8th distance from the semi-minor axis. In the case of a Dupuit-Forchheimer parabola, one has to count 3/8th of the total number of isolines from the upper boundary, and the head at that corresponding location will be the central head which is demarcated as $\bar{h}$ in Figure 4. For both stores, as shown in Figure 4, a 5% slope is reproduced by a hydraulic head varying from 40m (up) to 20m (down). There are 20 isolines between 40m and 20m DBC heads, so at 7.5 isolines away from 40m DBC we have the isolinear centroid where $\bar{h}$=32.5m.

For the fast store, since the immobile porosity (η- η_f) is 0.07, 2.275m is the immobile volume available for mixing which falls within the range of 2354mm±11.01% (Fovet et al., 2015). For the slow store, since the immobile porosity (η- η_f) is 0.5, 16.25m is the immobile volume available for mixing which falls within the range of 16032mm±7.22% (Fovet et al., 2015). So we have an overall low porosity (both mobile and immobile) fast store and high porosity slow store.

For both realizations for all stores, dispersivity was kept constant at 10m. Increase in dispersivity was showing reduction in breakthrough concentration, but the seasonality was not agreeing with the breakthroughs from individual conceptual stores, indicating that D is not generating an equivalence with whatever process is causing dilution in conceptual stores.

So apparently, it looks so that the static storage at the isolinear centroids is representative of the immobile or passive mixing volume used in lumped models.

$$V = \bar{h}(\eta - \eta_f) \qquad \text{Eq(5)}$$

Figure 5 shows that the output concentration breakthroughs of FEFLOW storages are in well agreement with the originally calibrated conceptual storages. The concentration isoline distributions of the FEFLOW stores for different years across the period of simulation are also shown in Figure 5.

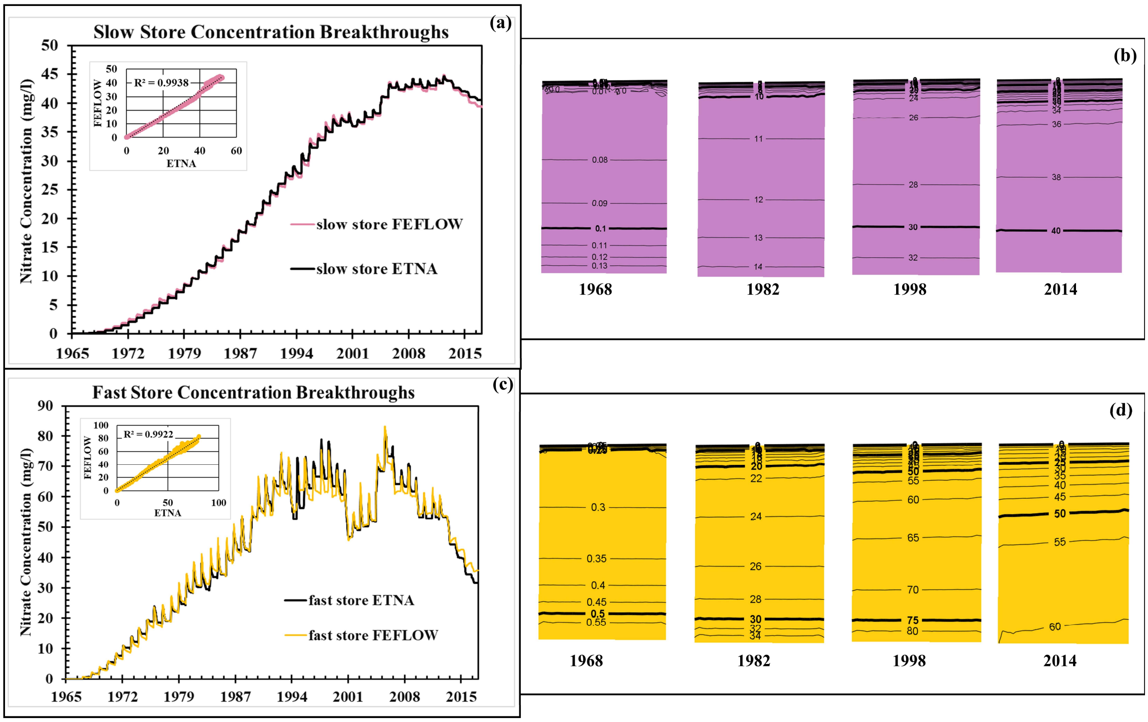

Figure 5: Simulated concentration breakthroughs of slow store (a) and fast store (c) vs corresponding ETNA concentration breakthroughs; concentration isolines in mg/l of slow store (b) and fast store (d) for different intermediate years of the simulation period.

The values of parameters lie within the broader ranges prescribed from field studies (Martin et al, 2006), but are not quite in agreement with the degree of heterogeneity that has been observed in the catchment. However, as mentioned before, our goal is not to check which configuration of hydrodynamic parameters best represents the catchment, but rather to utilize the parameters of lumped stores once calibrated to reproduce the catchment behavior in terms of nitrate concentrations to determine their relationship with conventional groundwater flow parameters.

3.3. Transit time and Age:

Table 2 shows the HNRT calculated using ETNA, the MTT using FEFLOW, and mean age the for fast and slow stores. Mean age has been calculated as the same way as mean head – the age at age-isolinear centroid (i.e., the age at the location of 3/8th of total number of age isolines from the upper boundary) is the mean age. Figure 6 shows the age distribution profiles for different stores (in days).

MTT for slow store is slightly on the higher side, because the distribution is long tailed.

Table 2: Transit times calculated using different methods:

Stores	HNRT (ETNA)	MTT (FEFLOW)	Mean age (from Figure 6 charts)
Fast Store	3.22 years	3.15 years	3.08 years
Slow Store	18.44 years	19.3 years	19.17 years

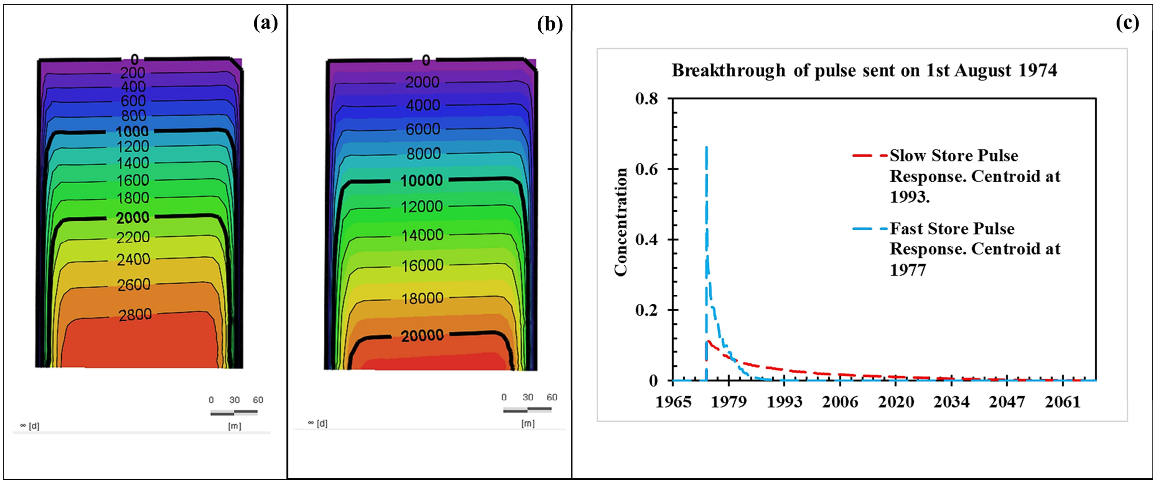

Figure 6: Diagrams showing age distribution in the form of age isolines in days of (a) slow store (b) fast store. (c) Shows responses of unit mass pulses sent on 1st August 1974 (targeting average climatic sequence) for both stores.

The results of the age sensitivity analysis performed are illustrated in Figure 7. It is seen that with the increase in hydraulic thickness, concentration breakthroughs become more dilute, but the age remains nearly constant; with the increase in dispersivity, concentration breakthroughs become more dilute, and the mean age reduces; with the increase in immobile porosity, concentration breakthroughs become more dilute, and the mean age increases.

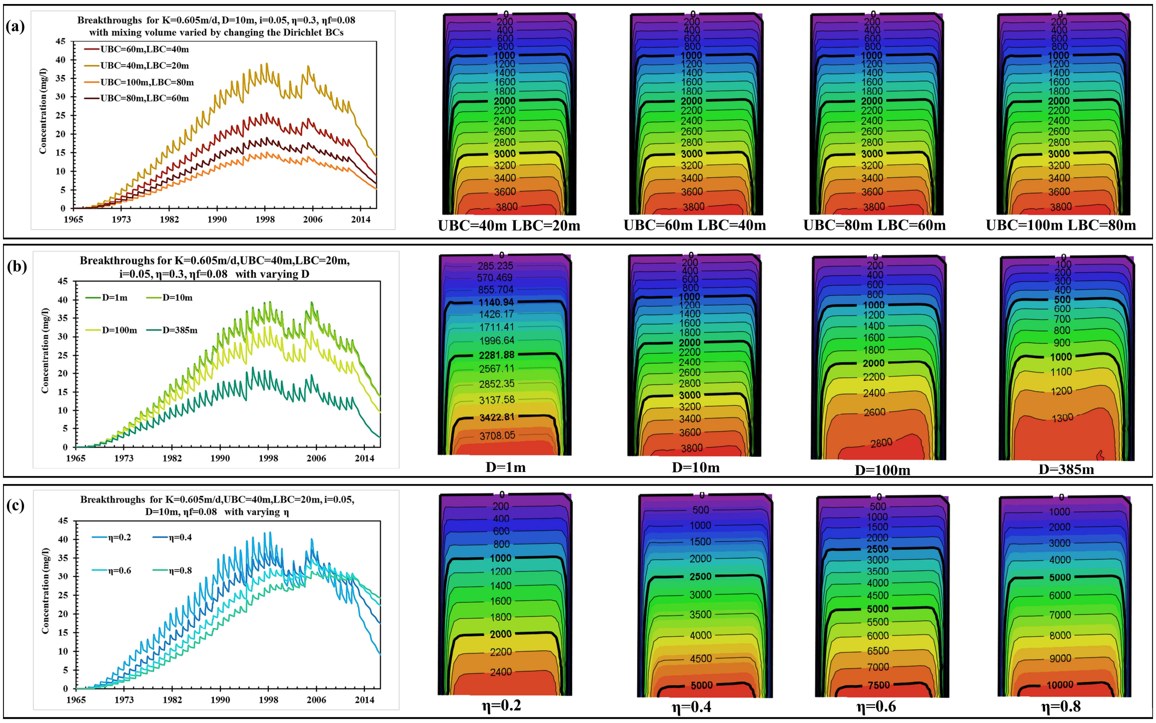

Figure 7: Sensitivity analysis showing changes in concentration breakthroughs in mg/l and age isolines in days with changes in (a) Dirichlet BCs of hydraulic heads, (b) hydrodynamic dispersivity and (c) total porosity keeping the hydraulic gradient, hydraulic conductivity and effective porosity constant.

The results of the HNRT sensitivity analysis performed are illustrated in Figure 8. It is seen that the time taken for the response concentration to reach 50% of steady state concentration is not sensitive to a, but very sensitive to V. Also increase in V reduces the breakthrough concentration – which means transit time in ETNA is proportional to the dilution.

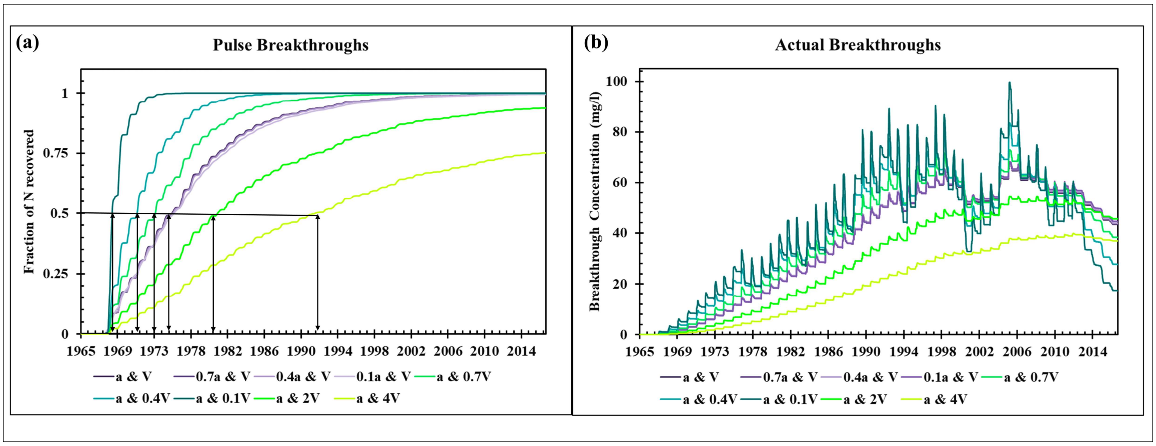

Figure 8: Graphs showing (a) Sensitivity of HNRT (i.e., time taken to recover 50% concentration of a pulse sent on 1st August 1968) and (b) sensitivity of breakthrough concentration with Burns recharge and leachate as loading - with changes in recession and immobile volume (a and V) of one conceptual ETNA box.

The above sensitivity analyses support that:

i) The difference of total and drainable porosity (η- η_f) is primarily playing the role of immobile volume in lumped models.

ii) Lumped models with parallel stores like ETNA do not understand dispersivity. The phase lag between the responses of the stores arises from different levels of attenuations, and when they are aggregated in their respective proportions, they apparently display a pseudo-dispersion in the concentration breakthrough.

In Table 3, we provide a mathematical equivalence of the 2 primary lumped store parameters - recession (a, in day^{-1}) and immobile volume (V, in mm). The respective fractions (f) at which they mix is a tricky parameter. For simplicity, in a 2-store lumped model, the parameter f:

i) Creates a hydrological balance between the faster store which dominates storage accretion and slower store which dominates recession. ii) Creates a pseudo-dispersion by combining the concentration breakthrough of less attenuated faster store and more attenuated slower store. This combination, in their respective optimized weights, enabling the lumped model to produce a concentration breakthrough that mimics the real breakthrough which is produced by some degree of dispersivity in the system. So, f is purely conceptual, and it is not possible to mathematically connect f to any measurable conventional parameters. In fact, it is not even essential to use 2 stores to model long term groundwater flow (Hrachowitz et al., 2016). Rather, the solute dispersion that is being caused by a dual porosity system (Section 3.2.2.2) is being handled by f. Globally, in a lot of catchments we can see that a "thin veneer" of faster flowing water is disproportionately feeding the stream (Berghuijs and Kirchner, 2017) creating a bias towards shorter transit times of solutes. In ETNA, f (=86.5%) being the contribution of the fast store to the stream nitrate breakthrough, is creating this bias.

Table 3: Mathematically connecting lumped store parameters a,V with measurable parameters K, L, $\bar{h}$, η, η_f,

Lumped Store Parameter	The Distributed Equivalent	Source of Evidence
Recession (a)	$\frac{K}{L\eta_f}$ K=Hydraulic conductivity η_f=Fillable porosity L=Length of flow path	Mentioned by Savenije, 2018. Validated in this study. (Section 3.2.2.1, Eq (4))
Immobile Volume (V)	$\bar{h} \times (\eta - \eta_f)$ η=Total porosity $\bar{h}$ = Average hydraulic thickness at 3/8th isolinear distance (defined as isolinear centroid of Dupuit-Forchheimer parabola) from the upper boundary.	(Section 3.2.2.2, Eq (5)) Figure 4.

Our results show that the lumped parameters of each individual storages are combinations of actual physical parameters, even if these combinations are not obvious. For a field hydrologist who would like to start forward modelling a pristine catchment using lumped model, at first, he/she needs to look at the boundary heads and up to what depth flow is significant. This can be inferred from geophysical explorations. Then, even analytically, the Dupuit-Forchheimer aquifer can be constructed and the depth at isolinear centroid can be determined. From such a model it would be easy to determine a and V from Table 3 once the K, η, η_f is determined. Based on the heterogeneity, multiple stores can be considered, and their fractions can be adjusted. For 2 stores, we advise to begin with a value of f=0.5 – more dilution will be mimicked by increasing the contribution from the slower store. Apart from knowledge of fundamental hydrodynamic parameters, it is very important to know the length scale of the catchment to avoid equifinality.

4. Conclusion:

The main conclusions of this study are:

1. The fast and slow stores of lumped conceptual groundwater flow and transport models have proper physical basis. After detailed analysis it was observed that the fundamental and measurable catchment properties (apart from scale) that affect the hydrologic recession are K and η_f, and the ones that affect mixing (dilution) of solutes are immobile porosity (η-η_f) and mean aquifer thickness (Table 3). Also, we found that the three proxies of residence time distributions we could estimate from the different modelling approaches - the spatial mean of the age distributions, the mean transit time and the half nitrate recovery

time agreed with each other for all stores (Table 2). We found the store with overall lower porosity (mobile and immobile) is the faster store and with overall higher porosity is the slower store (Table 1) - which makes sense because lower porosity means steeper recession and less mixing. This also reminds us that the idea of such dual store conceptual representation of groundwater fundamentally came from the proposition of treating aquifers as dual-porosity systems.

2. Scale is a big issue - all physical representations of lumped parameters are in some way dependent on the catchment dimensions. Lumped conceptual models only operate on dimensions of depth of water column. It is therefore possible for the lumped models to yield the same results for a different set of hydrodynamic parameters for a catchment having different dimensions. Like, for example - transit time of a bigger catchment with low porosity might be same as a smaller catchment with high porosity. It is thus important to a) be extra attentive in deciding the catchment dimensions before using lumped models as forward models and b) to normalize the transit times with catchment dimensions whilst using lumped models for comparative study between catchment response rates.

3. The hydrodynamic dispersion is not accounted for by individual stores of the lumped models. It is quite evident from the age distribution profiles (Figure 7) that increase in dispersivity makes the concentration breakthroughs more dilute but at the same time reduces the groundwater age. This is expected based on the age transport equation (Equation 3). The opposite happens for lumped models where solute transit times are primarily dependent on mixing volumes, and an increase in the mixing volume increases both the dilution and detention time. Dilution is thus a process quite different from hydrodynamic dispersion. The phase lag between the responses of the parallel stores (representing different porosities), when assimilated in their respective proportions (f), apparently displays a synthetic dispersion in the concentration breakthrough due to differences in their respective attenuations. A negligible dispersivity 10m obtained from Gelhar's charts, which shows no difference in breakthrough behavior from 1m dispersivity (Figure 2) was thus maintained across all realizations.

Overall, this study has established that lumped conceptual models have a genuine physical basis and clear mathematical correlation with conventional hydrological parameters. Adaptation of these approaches reduces calibration reliance of lumped models and provides possibilities to scrutinize the effectiveness of obtained parameters. It also indirectly creates a lumped forward modelling potential that can be used to model the flow and transport behavior and solute transit times of catchments that have proper measurements of hydrodynamic properties, but the hydrologic and the breakthrough concentration time series are not long enough to inverse model.

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Code/Data availability:

All data sets are publicly available in the agrhys repository of INRAE, France.

Link to data: [Grapheur de VIDAE (agrhys.fr)](agrhys.fr)

Link to code and user instructions provided in supplement.

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